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**ROLE OF LOCAL MODES IN NONRADIATIVE PROCESSES
TAKING PLACE IN IMPURITY DOPED LASER CRYSTALS**

by

DANA MANUELA CALISTRU

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor in Philosophy, The City University of New York

1997

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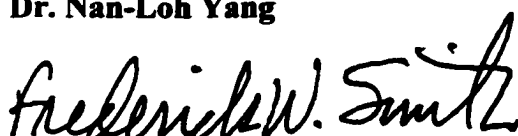

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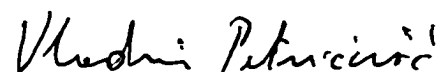
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Abstract

ROLE OF LOCAL MODES IN NONRADIATIVE PROCESSES TAKING PLACE IN IMPURITY DOPED LASER CRYSTALS

by

Dana Manuela Calistru

Adviser : Robert R. Alfano, Distinguished Professor of Science and Engineering

This thesis presents the identification and characterization in terms of energy and symmetry of Cr^{4+} local modes in the $\text{Cr:Mg}_2\text{SiO}_4$ tunable solid state laser, as well as their role and dynamics during nonradiative processes, using steady state and time resolved resonance Raman measurements.

The main feature which makes $\text{Cr:Mg}_2\text{SiO}_4$ suitable for studying the role of a laser ion's (Cr^{4+}) local modes during nonradiative relaxation is that the room temperature quantum efficiency for this laser crystal is $\sim 10\%$ due to strong nonradiative processes. The local modes of Cr^{4+} were identified in terms of energy and symmetry using polarized steady state resonance Raman scattering. Seven (out of the expected nine) Cr^{4+} local modes were identified in room temperature resonance Raman spectra having the following energy and symmetry (the symmetry for each mode is given in both the site C_s and the undistorted T_d (in

parenthesis) symmetries) : 765 cm^{-1} - $A'(A_1)$, 740 cm^{-1} - $A''(T_2)$, 690 cm^{-1} - $A'(T_2)$, 498 cm^{-1} - $A'(E)$, 480 cm^{-1} - $A''(E)$, 290 cm^{-1} - $A'(T_2)$, 253 cm^{-1} - $A'(T_2)$. Force constant calculations show a decrease of 13 - 19% in the intratetrahedral force constants for a CrO_4 molecule if compared to a SiO_4 molecule.

Low temperature resonance Raman spectra which offer improved resonance conditions reveal an anomalous number of 15 local modes, i.e. an increased number of decay channels for nonradiative processes, which was attributed to second neighbor interactions. This is the first report of second neighbor interactions observed using resonance Raman scattering.

Time resolved resonance Raman measurements performed with 500 fs pulses probed the dynamics of Cr^{4+} local modes following the ${}^3B_2({}^3T_1) - {}^1E$ bottleneck crossing. It was shown that during the nonradiative relaxation the energy from the nonequilibrium local mode population created following the bottleneck transition is transferred into a select number of daughter phonon modes. The daughter phonons decay due to anharmonic interactions with the phonon bath and the system returns to thermal equilibrium. The following parameters characterizing the nonradiative decay were estimated from time-resolved measurements : bottleneck transition time ~ 2.8 ps, local mode lifetime ~ 5.1 ps, phonon mode lifetime ~ 5 ps. This is the first report on the dynamics of a laser ion's local modes during the nonradiative relaxation in an impurity-doped laser crystal.

To my parents Eugenia (Foca) and Vasile (Bucă)

Pentru credință și pentru tăgadă
Te caut dîrz și fără de folos,
Ești visul meu din toate mai frumos,
Și nu-ndrăznesc să te dobor din cer grămadă.

Psalm - Tudor Arghezi

Am auzit că și la București
E ceață mare cînd mi-e dor de tine.
Te rog frumos să te obișnuiești
Că ne vedem în era care vine.

N-o să ma prindă iarna la New York.
N-am stare în furtuna ce m-apasă.
Și într-o zi oricum am să mă-ntorc
S-ajung să mor, printre nămeți, Acasă.

După Iarna la Paris - Adrian Păunescu

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Chapter 1

Introduction

1.1 Nonradiative processes in tunable solid state lasers

The overall properties of tunable solid-state lasers are affected by nonradiative relaxation processes which are considered to be the main loss channel in such materials. The first impurity doped tunable solid state lasers, which all had as active centers transition metal ions ($\text{Ni}^{2+}:\text{MgF}_2$ [1] and later Ni^{2+} , Co^{2+} and V^{2+} in different host crystals [2 - 4]) could not operate at room temperature due to strong nonradiative processes which destroyed laser action, and had to be cooled at cryogenic temperatures. These extreme operational conditions made impurity doped lasers undesirable and explained the shift of interest towards tunable dye lasers.

The major breakthrough in the field of tunable solid state lasers occurred in 1979 with the room temperature, broad band tunable laser operation in alexandrite [5, 6] ($\text{Cr}^{3+}:\text{BeAl}_2\text{O}_4$) shortly followed by emerald [7, 8] ($\text{Cr}^{3+}:\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$). Continuous research carried on over the past fifteen years has added to the family of transition-metal-based tunable solid state lasers two new active ions : Ti^{3+} [9, 10] and Cr^{4+} [11, 12, 13, 14]. The interest of the scientific community in impurity-doped solid state lasers is motivated by their broad tuning range, portability and compactness which makes them suitable for spaceborn remote sensing, optical communications, medical, industrial and basic scientific applications.

Nevertheless, the problem of nonradiative processes has not been completely solved, neither from the theoretical nor from the experimental point of view and the role of different subsystems of an impurity-doped crystal, such as

phonon modes, local modes, etc., in the nonradiative relaxation is not entirely understood. To date there are no consistent criteria predicting which host (lattice) and impurity ions should be considered for obtaining efficient laser systems and which are the most important physical characteristics accounting for improved laser efficiency. For example, although there several are Cr^{4+} -based tunable lasers operating at room temperature ($\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ [11, 12], $\text{Cr}^{4+}:\text{YAG}$ [13] and $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$ [14]), laser action can not be obtained for the same active ion in other hosts (e.g. $\text{Cr}^{4+}:\text{Y}_2\text{SiO}_5$, $\text{Cr}^{4+}:\text{LiNbGeO}_5$ [15, 16]) above cryogenic temperatures due to strong nonradiative processes.

The occurrence of nonradiative processes can be described as follows. After being photoexcited, an impurity (laser) ion is in a nonequilibrium (“hot”) state where besides the corresponding electronic state, several local mode levels (impurity associated) are populated (see Chapter 7). Nonradiative processes occur by a step-wise movement of the ion downward the electronic manifold. This decay is equivalent to a decrease in the occupation number of local modes and the release of energy into the lattice. It was shown that for a short period of time ($\sim$ ps) a select number of phonons take over the energy released during the nonradiative relaxation [17, 18]. Finally, these phonons transfer the energy into the phonon bath which brings the system back to thermal equilibrium.

As of this writing, the role and dynamics of local modes in nonradiative processes taking place in impurity-doped laser crystals had not been investigated. The present research focuses on the identification and characterization of Cr^{4+} local modes in chromium doped forsterite ($\text{Cr}:\text{Mg}_2\text{SiO}_4$), the first Cr^{4+} -based tunable solid state laser operating in the near-infrared region [11, 12]. The first study of the dynamics of a laser ion’s local modes during the nonradiative relaxation is presented, providing detailed information and a deeper insight into the mechanism of nonradiative decay. The results describing the dynamics of nonradiative processes allowed the individual characterization of the contribution

of the electronic, local mode and phonon mode subsystems at different steps during the nonradiative relaxation.

1.2 Thesis statement

The focus of this thesis is to identify and study the role and dynamics of local modes in nonradiative processes taking place in impurity-doped laser crystals using steady state and time resolved resonance Raman spectroscopy. The material of choice for this task was $\text{Cr:Mg}_2\text{SiO}_4$, the first Cr^{4+} -based tunable laser crystal which has a quantum efficiency of $\sim 10\%$ due to strong nonradiative relaxation [11]. The relative high strength of nonradiative processes in this material made it a good candidate for studying the role of local modes and the relevance of different criteria (total number of local modes, second neighbor interactions, electron-phonon interactions, local-phonon mode resonances, etc.) to the nonradiative decay.

The following main objectives were accomplished by this research :

- (1) Identification and characterization of Cr^{4+} local modes in terms of energy and symmetry (both molecular - T_d and site - C_5 due to lattice distortions) using room temperature steady state resonance Raman scattering;
- (2) Estimation of local changes induced by the impurity ion (change in intra-tetrahedral force constants for a CrO_4 molecule if compared to a SiO_4 molecule);
- (3) Demonstration of the failure of first neighbor interaction approximation for Cr^{4+} ions, leading to an anomalous number of first order resonance enhanced local modes in the low temperature resonance Raman spectrum. The increased number of local modes acting as decay channels supports the relative high strength of nonradiative processes.

This was the first report on the presence of second neighbor interactions detected using resonance Raman scattering;

- (4) Estimation of anharmonic constants for the 742 and 765 cm^{-1} Cr^{4+} local modes from up to fourth order resonance enhanced Raman spectra and the conclusion based on the small values of the anharmonic constants and a long observed overtone progression that electron-phonon interactions are sizable for these two local modes. This observation supports the strength of nonradiative processes and suggests that these modes in particular enable the energy transfer from the electronic to the vibrational system during nonradiative relaxation ;
- (5) Investigation of the dynamics of the 765 cm^{-1} Cr^{4+} local mode using time resolved resonance Raman measurements. The results prove that the 765 cm^{-1} local mode is involved in the energy transfer from the electronic system into the vibrational system. This is the first report on the dynamics of a laser ion's local modes during the nonradiative relaxation in an impurity-doped laser crystal; and
- (6) Characterization of the dynamics of the nonradiative decay and determination of characteristic parameters for the inter-electronic crossing, mother local mode lifetime and daughter phonon mode lifetime.

1.3 Thesis outline

Chapter 1 presents a general introduction to the relevance of the topic of the thesis, the thesis statement and its outline.

Chapter 2 gives a complete description of the experimental setup and conditions used for the steady state and time resolved resonance Raman experiments whose results are presented in Chapters 5 - 7. It starts with a detailed

presentation of the components and characteristics of the laser system which contains a mode locked Nd:YAG laser, a pulse compressor (for time resolved measurements) and a Rh-6G dye laser. Different scattering geometries are introduced, with their particularities, advantages and disadvantages, and specific notations (Porto's notation) used for Raman measurements. The acquisition system consisting of a triple spectrometer (whose spectral characteristics are discussed in detail) and the photoncounter (PIAS) together with the specially designed software package for data transfer and analysis are introduced. Finally the particularities of steady state and time resolved Raman setups are discussed.

Chapter 3 is entirely devoted to the Cr:Mg₂SiO₄ sample. The first part discusses the derivation of the phonon spectrum of the Mg₂SiO₄ host, the correlation between different types of symmetries (molecular, site, space group) using correlation tables and their connection to actual scattering geometries used in Raman experiments. The second part of this chapter focuses on the Cr⁴⁺ ion, starting with the multi-electronic structure of the free ion, followed by the changes introduced by a crystalline field of a given symmetry (Tanabe-Sugano diagrams). The crystal field parameters are calculated for Cr⁴⁺:Mg₂SiO₄ from site selective excitation spectra as : $B = 855 \text{ cm}^{-1}$, $C = 4190 \text{ cm}^{-1}$ and $Dq = 1000 \text{ cm}^{-1}$.

Chapter 4 presents the theoretical background for Raman and resonance Raman scattering, starting with a short history of the Raman effect followed by a qualitative description of Stokes and anti-Stokes processes in terms of creation and annihilation operators and Feynman diagrams. The quantum mechanical derivation of the Kramers-Heisenberg-Dirac dispersion relation is sketched, followed by the Placzek theory of electronic polarizability which gives the expression of the off-resonance Raman tensor, its symmetry and the applicable selection rules. The resonance Raman effect is discussed in terms of Albrecht's A and B terms whose implications are then discussed for the particular case of

$\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$. The chapter ends with a discussion of the relevance of electron-phonon coupling for impurity-doped systems.

Chapter 5 presents the identification and characterization of Cr^{4+} local modes from room temperature polarized resonance Raman spectra performed under 575 nm excitation corresponding to the ${}^3\text{A}_2 \rightarrow {}^3\text{B}_2({}^3\text{T}_1)$ dipole allowed Cr^{4+} transition. Seven (out of the expected nine) Cr^{4+} local modes were identified having the following energy and symmetry (the symmetry for each mode is given in both the site C_s and the undistorted T_d (in parenthesis) symmetries) : 765 cm^{-1} - $\text{A}'(\text{A}_1)$, 740 cm^{-1} - $\text{A}''(\text{T}_2)$, 690 cm^{-1} - $\text{A}'(\text{T}_2)$, 498 cm^{-1} - $\text{A}'(\text{E})$, 480 cm^{-1} - $\text{A}''(\text{E})$, 290 cm^{-1} - $\text{A}'(\text{T}_2)$, 253 cm^{-1} - $\text{A}'(\text{T}_2)$. Based on the values of the above measured local modes, the Cr-O and intra-tetrahedral O-O force constants are calculated for a $(\text{CrO}_4)^{-4}$ molecule and compared to the similar values for a $(\text{SiO}_4)^{-4}$ molecule. Force constant calculations show a decrease of 13 - 19% in the intra-tetrahedral force constants for a $(\text{CrO}_4)^{-4}$ molecule suggesting that such a complex is looser bound than the $(\text{SiO}_4)^{-4}$ host molecule.

Chapter 6 presents the low temperature (77 K) results of polarized resonance Raman spectra obtained for the ${}^3\text{A}_2 \rightarrow {}^3\text{B}_2({}^3\text{T}_1)$ Cr^{4+} transition. Due to improved resonance conditions and a lower background, weaker resonance enhanced modes are observed and reported in these spectra. A total number of 15 Cr^{4+} first order local modes, instead of maximum 9, were identified from fundamental and combinations and overtones of up to fourth order spectra. Following several proposed explanations it is concluded that they are due to second neighbor interactions. This is the first report of second neighbor interactions observed using resonance Raman scattering. Model calculations performed for the two breathing modes for the CrO_4Mg_4 molecule show that local modes have different degrees of localization, i.e. potential different involvement in nonradiative processes. The 15 local modes represent an anomalous high number of decay channels and partially explain the strength of nonradiative processes in

this material. Anharmonic constants have been calculated for different Cr^{4+} local modes from the higher order overtones measured resonance Raman spectra. The small values of the anharmonic constants ($X_{765} = -0.02 \text{ cm}^{-1}$ and $X_{742} = 0.08 \text{ cm}^{-1}$) lead to the conclusion that the sole responsible for the long observed overtone progression is the relative high value of the electron-phonon interaction.

Chapter 7 focuses on the dynamics of Cr^{4+} local modes during nonradiative relaxation obtained using time resolved resonance Raman scattering. This chapter starts with a presentation of proposed models for describing nonradiative processes followed by a review of different time resolved techniques. Section 7.5 presents the measured dynamics of the highest scattering cross section Cr^{4+} local mode at 765 cm^{-1} , during nonradiative relaxation following the ${}^3\text{B}_2({}^3\text{T}_1) - {}^1\text{E}$ bottleneck crossing. These experimental results were obtained using time resolved resonance Raman measurements performed with 500 fs pulses. The role and dynamics of local modes which act as decay channels during the nonradiative relaxation were experimentally demonstrated and measured for the first time. It was shown that following photoexcitation the ions relax nonradiatively by crossing between two electronic states. The transition towards the lower lying electronic state leads to an increase in the local mode (mothers) occupation number. The energy from the local modes is transferred to select phonon modes (daughters) which display a time-shifted nonequilibrium population. (It was shown that for the investigated system the intra-molecular decay pathway is forbidden). The daughter phonons decay due to anharmonic interactions with the phonon bath and the system returns to thermal equilibrium. The following parameters characterizing the nonradiative decay were estimated from time-resolved spectra : bottleneck transition time ~ 2.8 ps, local mode lifetime ~ 5.1 ps, phonon mode lifetime ~ 5 ps.

Finally, chapter 8 summarizes the conclusions of this research and discusses future experiments for verifying the proposed criteria for developing more efficient impurity-doped laser materials.

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Chapter 2

Experimental methods

2.1 Introduction

This chapter describes the experimental methods used to obtain the steady state and time resolved Raman results which will be presented in Chapters 5 - 7. The presentation of the experimental setup starts with a description of the laser system consisting of a mode locked Nd:YAG which synchronously pumps a dye laser. A subsection presents the pulse compressor used for measurements with temporal resolution. Section 2.3 considers different scattering geometries used for obtaining Raman spectra and discusses their advantages and limitations. The two main subsystems of the acquisition module of the experimental setup, the triple spectrometer and the Photoncounting Image Acquisition System (PIAS) are presented in Section 2.4. Section 2.5 describes the method used for data transfer and analysis. The last two sections present the actual setups used for obtaining steady state (Chapters 5 and 6) and time resolved (Chapter 7) Raman spectra.

2.2 Laser system

The laser system used for exciting the analyzed crystal samples consists of a mode locked Nd:YAG laser and a synchronously pumped dye laser. In the case of time resolved measurements, a pulse compressor is inserted between the two lasers, as will be shortly described. Each of the three above mentioned components are presented as follows.

2.2.1 Mode locked Nd:YAG laser

The mode locked Nd:YAG laser consists of a flash-lamp pumped Nd:YAG laser rod, two high reflectance end mirrors, two apertures (positioned between each mirror and the laser rod), a polarizer and an opto-acoustic crystal. A schematic picture of the mode locked Nd:YAG laser is presented in Fig. 2.1.

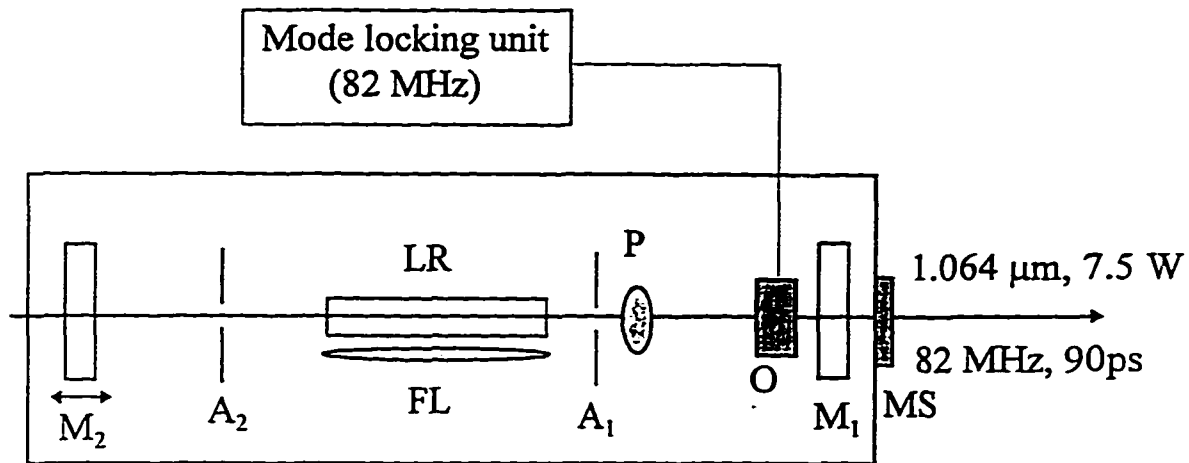


Figure 2.1 Schematic representation of the Nd:YAG mode locked laser.

The following notations have been used in Fig. 2.1 : M_1 , M_2 - output mirrors, A_1 , A_2 - apertures, P - polarizer, LR - laser rod, FL - flash lamp, OA - opto-acoustic crystal, MS - mechanical shutter. The mirror M_2 is mounted on a translation stage which allows its horizontal displacement, and the adjustment of the cavity length. All other components (except the laser rod, the flash lamp and the mechanical shutter, which are fixed) have two adjustments which allow translations (for A_1 , A_2 , OA) or rotations (for M_1 , M_2 and P) around two axes.

The mode locking unit drives the opto-acoustic crystal at 82 MHz and matches the round trip time for the laser pulses in the cavity. The mode locked Nd:YAG laser operates at a repetition rate of 82 MHz and emits at $1.064 \mu\text{m}$, with an output power of $\sim 7.5 \text{ W}$. The mechanical shutter MS is used for blocking the

infrared (IR) laser beam. The time duration of the output pulses is ~ 90 ps. The two main components which affect the duration of the $1.064\text{ }\mu\text{m}$ pulses are the laser's cavity length and the position of the opto-acoustic crystal. The duration of the pulses is critical in obtaining efficient second harmonic generation, and is more important than a high average output power. The pulse duration can be monitored with a sampling oscilloscope and a fast photodiode. In general, a good ($> 7\text{ W}$) IR power which does not provide at least $1.1 - 1.2\text{ W}$ of 532 nm excitation is an indication of poor mode locking (unless the KTP frequency doubling crystal is damaged) or of too long IR pulses. The remedy for this situation is to slightly change the position of the opto-acoustic crystal by translating it vertically. One also has to make sure that the crystal is "horizontal", i.e. positioned along the optical axis of the system. The optimal power for the second harmonic pulses is $\sim 1.3 - 1.4\text{ W}$ with excitation pulses of $\sim 7.5\text{ W}$.

Special care has to be taken to avoid Q-switching for the IR pulses, as this can damage (burn) the pulse compressor and the KTP crystal (see Sections 2.2.2, 2.2.3). The $1.064\text{ }\mu\text{m}$ pulse trains are constantly monitored by deflecting a small part of the output IR signal, using a beam splitter, into a photodiode connected to an oscilloscope. As soon as Q-switching is observed (as "spikes" on top of the flat trace of the laser pulses on the oscilloscope), the "fine frequency adjustment" knob on the mode locker unit has to be turned until the signal becomes "flat" (no Q-switching). If the Q-switching does not disappear when the fine adjustment knob is turned full range, the frequency of the mode locking unit has to be changed. If the gradual change in frequency by at most 40 Hz on each side of the preset operation frequency does not improve the Q-switching, the cavity length of the laser has to be slightly adjusted by horizontally translating with great care the output mirror M_2 in Fig. 2.1. It should be stressed that this is a critical operation and should be avoided if possible. Probably the most delicate and troublesome procedure is matching the driving frequency of the mode locking unit with the

laser's cavity length. For this reason it is advisable to very finely modify the laser's cavity length only if absolutely necessary.

In order to keep the laser operating under optimal conditions a few regular maintenance tasks have to be accomplished weekly. It is probably worth noting that these operations performed with regularity, as well as avoiding large changes in the laser's alignment will prevent the troublesome and time consuming situation when the system has to be realigned from "scratch". The mode locking unit has to be turned on in the beginning of every week, and turned off when the laser system is not used for more than one day. As the laser's output power gradually decreases in time due to dirty optics it is advisable that the polarizer P in Fig. 2.1 be cleaned in the beginning of each week. Before cleaning it, the power is measured in order to have a reference point. A wooden block is then placed between P and OA such that the laser beam is interrupted. The polarizer is released from its holder and taken out from its cylindrical container. The polarizer plate has to be taken out with great care, without touching it anywhere on its surface, as the hand grease destroys its coating. The plate is cleaned on both faces by gently sliding a sheet of lens paper impregnated with a droplet of methanol along the surface. The polarizer is then placed back into its holder and is loosely fixed in a "vertical position", i.e. with the top screw which changes the polarizer's angle, pointing upward. The wooden block is taken out allowing the laser beam to pass through the cavity. Typically the power will be low (~ 5 W) at this point. The polarizer is rotated in the vertical plane until maximum power is achieved (~ 6.4 W), and is fixed in this optimal position by tightening the two screws on the top of the holder. The following sequence of adjustments has to be repeated until the maximum power is obtained (~ 7.5 W or at least 0.3 W higher than the power measured before cleaning the polarizer) : (1) the polarizer's top screw is fine adjusted changing the angle of the polarizer till the maximum indication for the power is obtained; (2) the aperture A_1 is displaced in both vertical and horizontal planes to

obtain an improved reading for the power; (3) the output mirror M_1 is adjusted in the vertical plane (by its two adjustment screws) till the power is maximum. Steps (1), (2) and (3) are continuously repeated until the power is maximized.

The end mirror M_1 needs to be cleaned about every other month. This is done by turning its holder counter-clockwise and sliding it out, and by using, as in the case of the polarizer, a lens paper imbibed with a droplet of methanol. It should be noted that if the position of any of the output mirrors M_1 or M_2 is changed, the sequence of steps (1) - (3) has to be repeated in order to maximize the power. None of the above described procedures (not even a slight change in the position of an output mirror) can be performed while actual spectra are being measured, as they all lead to minute but detectable changes in alignment.

The filter for the cooling water of the laser's power supply has to be verified in the beginning of every week and should be changed as soon as it gets dirty. A dirty filter decrease the water flow such that the cooling is not effective any more and causes the laser to shut itself down.

The flash-lamp FL needs no maintenance but has to be changes after ~ 300 hours of use. An extensive list of eventual problems which may arise during the operation of the Nd:YAG laser and their trouble shooting is presented in the laser's technical manual [1].

2.2.2 Pulse compressor

In the case of time resolved measurements the $1.064 \mu\text{m}$, 90 ps output pulses of the Nd:YAG laser are further compressed by a fiber optic pulse compressor, down to ~ 6 ps. A schematic picture of the pulse compressor is shown in Fig. 2.2 where the following notations have been used : $\lambda/2$, $\lambda/4$ - half wave plate and quarter wave plates, respectively, MO - microscope objective, OF - optical fiber, PR_1 , PR_2 - prisms, G - grating, M_1 , M_2 - mirrors, KTP - second

harmonic generation crystal. The $1.064\ \mu\text{m}$, $7.5\ \text{W}$, $90\ \text{ps}$ mode locked IR pulses are focused into the optical fiber by the microscope objective. The quality of the mode locking and apparition of Q-switching (which has to be immediately rectified as it leads to burning of the optical fiber) are permanently monitored by an oscilloscope.

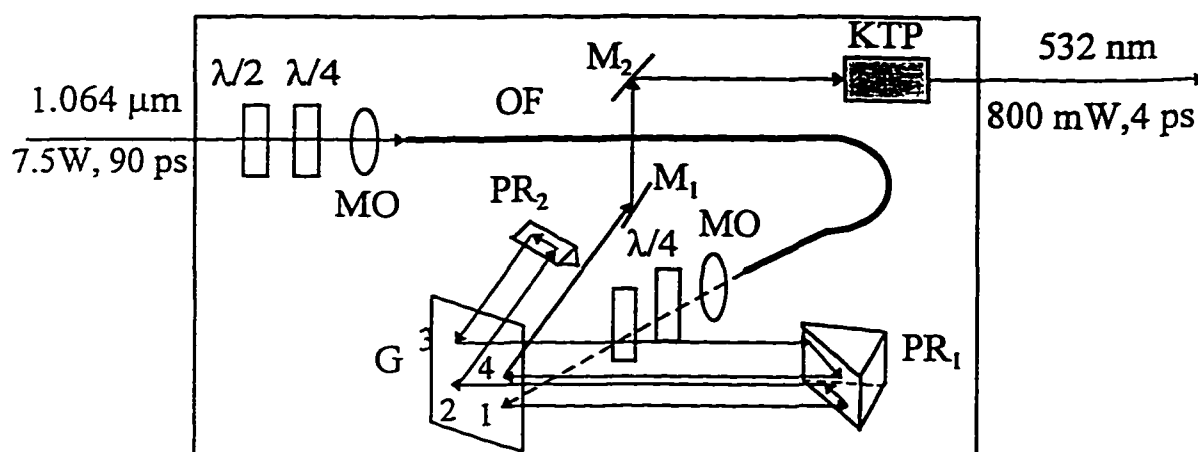


Figure 2.2 Schematic representation of the pulse compressor.

The $\lambda/2$ plate allows a continuous increase of the input power, such that gradual alignments are performed, for different power levels, preventing the optical fiber from being burned. The power measured after the optical fiber has to be at least $4.1\ \text{W}$ for maximum incident power ($7.5\ \text{W}$). Power values less than $4.1\ \text{W}$ may indicate that the fiber is burned and that it has to be cleaved using a single blade cleaver. The quality of the cut is extremely important as it insures the coupling of the fiber with the other optical components in the pulse compressor. A “jagged” cut will give rise to a lot of scattered light (which can be observed with an IR viewer) and to a low ($< 3.8\ \text{W}$) output power.

The optical fiber chirps the IR pulses which are then compressed by the multiple (four) pass through the diffraction grating (see Fig. 2.2) down to $\sim 6\ \text{ps}$. The average power of the compressed IR pulses is $\sim 4\ \text{W}$. These pulses are then

frequency doubled by a second harmonic generation KTP crystal such that 532 nm, 750 mW, 4 ps pulses are obtained at the output of the KTP crystal. The 532 nm pulses are used to synchronously pump the dye laser in order to achieve ultrashort 500 fs pulses used in time resolved measurements.

The pulse compressor needs to be aligned every time the alignment of the Nd:YAG laser changes, as, for example, is the case in the beginning of each week when the polarizer is cleaned. Although quite time consuming, the proper alignment of the pulse compressor is of paramount importance in obtaining good quality short pulses. If the pulse compressor is slightly misaligned, a minor change in the direction of the laser beam can cause the optical fiber to burn.

2.2.3 Dye laser

A synchronously pumped Rh-6G (Rhodamine - 6G) dye laser was used for most of the experiments presented in this thesis (Chapters 5 - 7). As Rh-6G which emits between 570 - 630 nm has the maximum of absorption at ~ 530 nm, the second harmonic of the Nd:YAG obtained from a KTP crystal is used to pump the dye laser. For steady state Raman measurements (Chapters 5, 6) where spectrally narrow pulses are desirable, the KTP crystal was attached directly at the output of the Nd:YAG laser. Otherwise, for time resolved measurements (Chapter 7) where short (500 fs) pulses are used, the 1.064 μm IR pulses are first compressed in a pulse compressor, and then frequency doubled (Section 2.2.2).

If the KTP crystal is attached directly to the output of the Nd:YAG laser, the average power of the 532 nm frequency doubled pulses is $\sim 1.3 - 1.4$ W. Under 1.4 W, 532 nm excitation, the output power of the dye laser varies between 100 - 500 mW, peaking around 585 - 600 nm. If the pulse compressor is used, i.e. if the dye laser is pumped with 750 mW, 532 nm pulses, the output power of the dye laser varies between 50 - 275 mW. Thus, the advantage of steady state

measurements is the availability of spectrally narrow pulses (under 3 cm^{-1}) and high power. On the other hand, the “price” for obtaining short (fs) pulses is a decrease in the average power of the dye laser.

While for several laser sources such as Argon, He-Ne, etc. the spectral width of the output laser line is fixed, one of the advantages of a mode locked synchronously pumped system is that it allows the modification of the spectral width of the output pulses by fine adjusting the cavity length of the sync pumped dye laser. The cavity length of the dye laser is matched to the cavity length of the Nd:YAG laser (in fact, the round trip times of the pulses in the two lasers are matched) by horizontally displacing the output mirror of the dye laser (which changes the cavity length). The fine adjustment of this mirror, in the vertical plane also affects the width of the output pulses.

The spectral width of the output pulses from the dye laser was monitored using a diffraction grating (which is removed during the actual measurements) and by observing on a remote (~ 12 feet) screen (wall) a high order (5 - 6) maximum of diffraction. A higher order of diffraction is chosen due to the proportionality between the linear dispersion D_l of the grating and the observed order k [2], as shown by Eq. (2.1) :

$$D_l = \frac{dx}{d\lambda} = \frac{lkn}{\cos i'} \quad (2.1)$$

where dx is the spatial distance between two spectral lines situated $d\lambda$ wavelength units apart in the spectrum, l is the distance to the wall, n - the number of grooves/mm of the grating and i' the diffraction angle. The linear dispersion D_l is usually given in units of mm/nm and is a main characteristic of a spectral device (spectrometer) giving the distance in the focal plane at which one can see two spectral lines situated 1nm apart. For example $D_l = 0.8 \text{ mm/nm}$ shows that two spectral lines which are 1 nm apart will be seen 0.8 mm apart in the focal plane. A large linear dispersion (given by a high k , for a given grating) is desirable as it

leads to a large spatial distance Δx ($\sim$ mm) between two different wavelengths. Thus, an excitation which contains several different wavelengths (spectrally broad) will appear as an elongated ellipse on the wall (large Δx). On the other hand a spectrally narrow “monochromatic” excitation, (as is desirable in steady state Raman measurements) will appear as a bright, narrow dot (small Δx). Different spectral widths, depending on the type of experiment to be performed, can be obtained for the same (central) wavelength pulse by adjusting the cavity length of the dye laser and observing the shape of the pulse on a screen using a diffraction grating.

The dye laser requires minimal maintenance. In order to provide optimal output power, the dye has to be changed every 6 - 8 months. The procedure for changing the Rh-6G dye is described as follows. Protective gloves have to be used throughout the dye changing procedure.

- (1) 1.44 g Rh-6G powder are mixed with 30 ml of methanol, for $\sim$ 1h using a magnetic stirrer.
- (2) The dye solution is then mixed with 1.47 l ethylene glycol in a plastic bottle which was previously rinsed with methanol.
- (3) The pump of the dye laser is turned off. The area under the pump must be covered with absorbing paper as spills are almost unavoidable. The lid of the container with used dye is unscrewed and the pipes are taken out. The container is emptied in a special waste bottle. ATTENTION : The dye solution is toxic and must be disposed of in an appropriate manner. Under no circumstances can the dye be thrown in the sink.
- (4) The filter under the metal bell-shaped housing is replaced with a new one every time the dye is changed by unscrewing the screw underneath. A collecting tray has to be placed under the housing as the filter is soaked in dye. After replacing the filter the screw below the housing is

tightened. A loose or inadequate position of the filter will cause spills during the operation of the pump.

- (5) The plastic pipes are introduced into the pump's container (see (3)) which is filled with new dye. The pump is turned on for a short while such that the dye is absorbed into the system.
- (6) Repeat the above operation till all the newly prepared dye was used.
- (7) Tighten cap and let the pump run. Check for eventual spills, especially at the filter housing.
- (8) If spills occur the whole system has to be emptied and the dye changing procedure has to be repeated starting with (1).
- (9) Everything has to be cleaned and rinsed with methanol. ATTENTION : All the papers, napkins, gloves, etc. which have been stained by dye have to be put in a special bag and disposed of in the appropriate manner. They can not be mixed with "ordinary" garbage because of the toxicity of the dye.

The dye laser's output mirrors need to be cleaned not more than once every three month. A lens paper soaked in methanol is used and the mirrors' surface is cleaned with radial outward movements.

2.3 Excitation configurations for Raman spectra for crystal samples

In order to obtain a Raman spectrum the excitation pulses from the laser system are focused into the polished, oriented single-crystal sample to be analyzed. Depending on the type of experiment (steady state or time resolved Raman) and on specific experimental requirements different converging focusing lenses and different scattering geometries need to be used. The advantages and disadvantages of various scattering configurations and their range of applicability are described in this section.

As opposed to the idealized picture given by geometrical optics where a parallel beam of light can be focused down to a dimensionless point, in reality a converging lens focuses the beam to a parabolic shape defined by a length L and diameter d , as shown in Fig. 2.3. After passing through the focusing lens, the beam is “squeezed” down to a minimal diameter d (“waist” or “focusing diameter”) which is preserved over a length L called length of focusing. Once the beam exits the focusing region, it diverges. From the practical point of view, the measurable, nonzero dimension of the focusing region implies that light collected from anywhere within the focusing cylinder of diameter d and length L can be focused into the spectral device used for measuring the Raman signal (e.g. spectrometer) and analyzed. If f is the focal length of the converging focusing lens ($f \sim \text{cm}$), a parallel laser beam of wavelength λ and diameter D (given for example by an aperture) is gradually focused down to a beam of waist d , and length of focusing L , given by [3] :

$$d = \frac{2.44\lambda f}{D} \quad (2.2)$$

$$L = \frac{2.44\lambda f^2}{D^2} \quad (2.3)$$

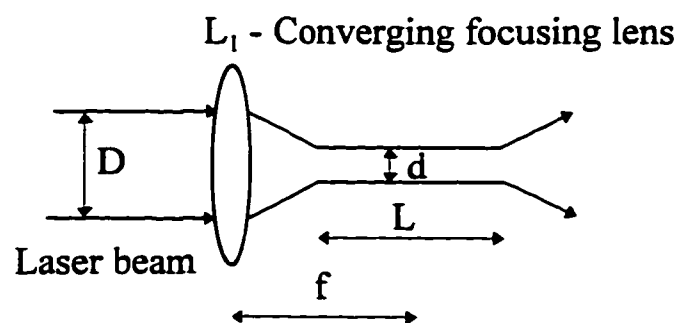


Figure 2.3 Schematic representation of the focusing diameter d and length of focusing L of a parallel beam focused by a converging lens.

Eqs. (2.2), (2.3) show that a short focal length lens ($f \sim 2 - 3$ cm) leads to “tight” focusing, i.e. to small focusing diameters d . At the same time, the length of focusing L for such a lens is short. On the other hand longer focal length lenses ($f \sim 20 - 30$ cm) lead to lower excitation densities due to larger values of d , but to a longer length of focusing L which allows the collection of light from the whole length of the focusing region. As will be further discussed, the latter situation is desirable when one wants to take advantage of a long spectrometer slit and illuminate it lengthwise. For example, using eqs. (2.2), (2.3) it can be shown that if a short converging focal length lens, $f = 2$ cm is used for focusing a 575 nm parallel laser beam of diameter $D = 4$ mm, the waist of the focused beam is $d \approx 7$ μm and length of focusing is $L \approx 35$ μm (see Fig. 2.4). On the other hand if the same beam is focused by a $f = 12$ cm converging lens, the focusing region has a waist of $d \approx 40$ μm and length of focusing $L \approx 1.5$ mm (see Fig. 2.5). As will be show in Chapters 7 and 5 the above mentioned typical beam diameter and focusing lens dimensions were used for obtaining time resolved and steady state resonance Raman spectra, respectively.

Short focal length lenses ($f \sim 1 - 2$ cm), such as microscope objectives, lead to high excitation densities due to small values of d , and are mainly used in backscattering configurations (180° scattering), as shown in Fig. 2.4. In a backscattering configuration the direction of the incident light $\vec{k}_i$ is opposite (180°) to the direction of the scattered light $\vec{k}_s$.

In a backscattering configuration the incident light is focused tight into the sample by a short focal length lens ($f \sim 1 - 2$ cm). The focusing region is usually chosen close to the surface of the sample (i.e. the lens is at its focal length away from the sample). The incident light quickly diverges as it passes through the sample. The collected signal (transformed into parallel light by the lens) comes

from the narrow focusing region of length L only. The scattered light from this region is collected backward (at 180°) by the same focusing lens and is transformed into parallel light which is further collimated into the spectrometer. Fig. 2.4 shows that a parallel 575 nm laser beam of diameter $D = 4$ mm is focused by a $f = 2$ cm converging focusing lens (microscope objective) down to a beam of waist $d = 7$ μm and length of focusing $L = 40$ μm .

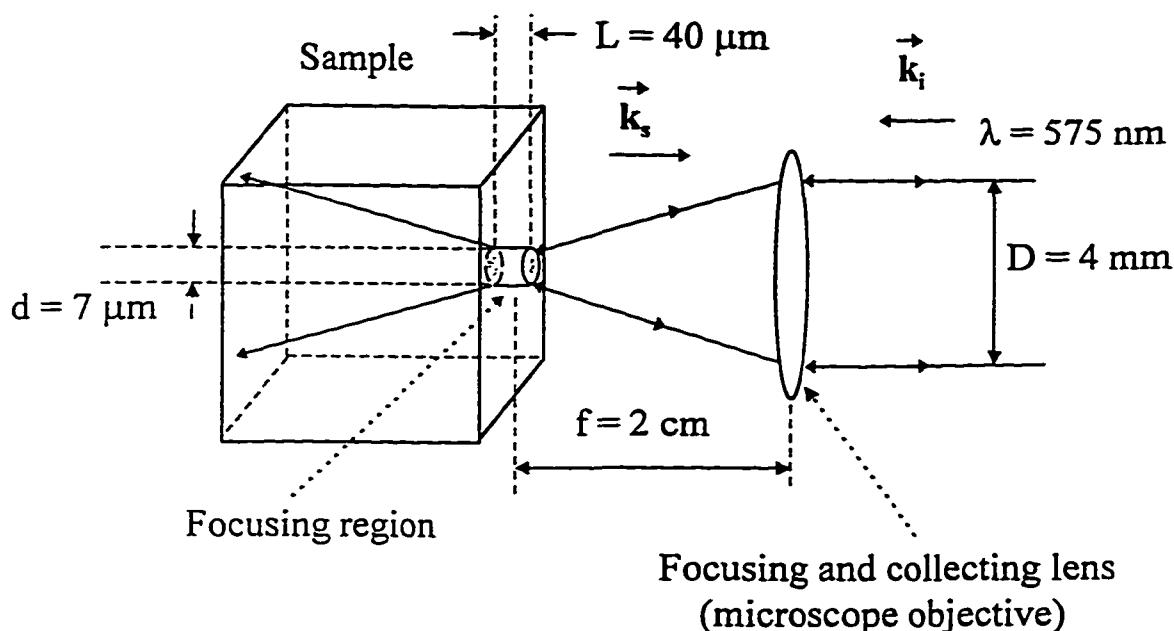


Figure 2.4 Backscattering configuration and typical system dimensions used for time resolved resonance Raman measurements.

A backscattering configuration, efficient due to the high excitation densities achieved in the focusing region, is desirable for highly absorbing samples where the incident light can not penetrate far into the sample. This arrangement is the only one which can be used for measurements with spectral resolution where the signal has to originate from a point-like region, such that no time delays are introduced between different points in the probed zone. For example, if a focusing lens produces an $L = 1$ mm length of focusing for a crystal sample with index of

refraction $n = 1.5$, the time delay between the signals originating at the end points of the focusing region is :

$$t = \frac{L}{v} = \frac{Ln}{c} = 2.2 \text{ ps} \quad (2.4)$$

where $c = 3 \times 10^8 \text{ m/s}$ is the speed of light in vacuum and $v = c/n$ is the speed of light in the crystal of index of refraction n . The 2.2 ps time delay value is totally unacceptable for experiments where the time scale of the observed phenomena is of the order of ps. If, on the other hand, a shorter focal length lens is used such that the length of focusing is only $L = 40 \text{ }\mu\text{m}$, a similar to the above calculation shows that the time delay introduced by the sample for the two endpoints in the region of focus is 20 fs, well under the temporal resolution of most ultrafast lasers. This calculation shows that very short focusing lenses ($f \sim 1 - 2 \text{ cm}$) have to be used for measurements with temporal resolution.

The disadvantage of the backscattering arrangement lies exactly in its strength : the narrowness of the probed region. Usually, spectrometer slits which determine the amount of light entering the detection system, are rectangular, with variable width ($\sim$ hundreds of μm) and height $\sim \text{cm}$. The most desirable situation which takes advantage of the height of the slit, is to have a long, parallel to the slit focusing region, such that signal is collected throughout the slit's length. As was previously shown this is not possible in a backscattering geometry where the object is point-like. On the other hand, a vertical, 90° scattering geometry uses a more significant length of the sample. In a 90° , vertical configuration the direction of the incident light $\vec{k}_i$ is perpendicular (at 90°) to the direction of the scattered light $\vec{k}_s$ (see Fig. 2.5). As previously calculated using eqs. (2.2), (2.3), Fig. 2.5 shows that a parallel 575 nm laser beam of diameter $D = 4 \text{ mm}$ is focused by a $f = 12 \text{ cm}$ converging focusing lens down to a beam of waist $d = 40 \text{ }\mu\text{m}$ and length of focusing $L = 1.5 \text{ mm}$.

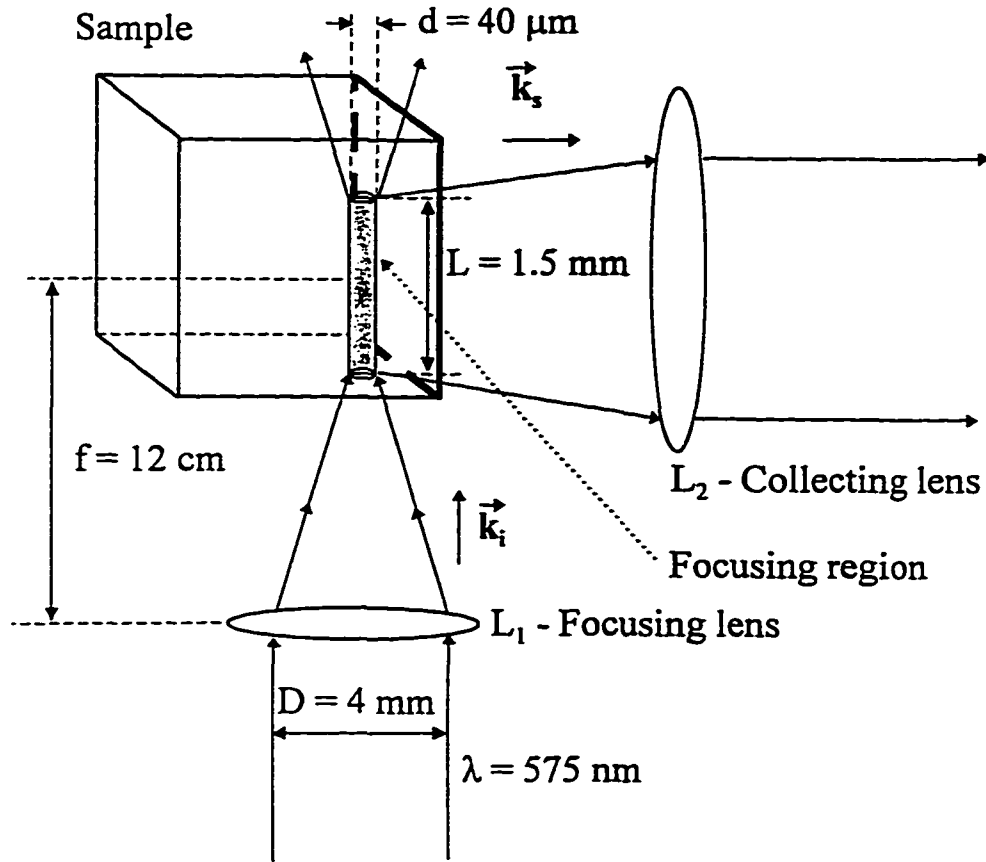


Figure 2.5 Vertical, 90° scattering geometry and typical system dimensions used for steady state resonance Raman measurements.

In Fig. 2.5 L_1 is the converging focusing lens ($f = 12$ cm) and L_2 the collecting lens which further collimates the scattered signal (together with a second collecting lens or by itself) into the entrance slit of the spectrometer. As shown by Fig. 2.5 in the vertical illumination it is desirable to focus along a longer focusing region ($\sim$ mm) where the signal is collected from. Using Eqs. (2.2), (2.3) it can be observed that a longer length of focusing L is obtained using long focal length lenses, f . Thus, a vertical scattering arrangement is more efficient from the point of view of the collected signal but can not be used for measurements with temporal resolution.

The major drawback of the 90° scattering arrangement for absorbing samples is the fact that if the incident laser beam enters the sample far from the face of the crystal sample through which the scattered signal is collected (i.e. facing the entrance slit of the spectrometer), outlined in Fig. 2.5, the Raman signal will be absorbed between the entrance point of the excitation beam and the collecting face of the sample. Thus, the sample has to be illuminated as close to the plane facing the detector as possible. As will be shown in Sections 2.7, 2.8, steady state Raman experiments presented in this thesis used vertical illumination provided by a 12 cm focal lens, while time resolved measurements used a 2 cm, 10x microscope objective.

The scattered signal is collected by one or two collecting lenses which focus it on the entrance slit S_1 of the spectrometer (see Section 2.4.1). The two lens system (different for steady state and time resolved experiments) was chosen due to a higher collection efficiency and a higher magnification. The last factor is important for measurements using vertical illumination where the size of the image of the length of focusing was ~ 1.5 mm.

2.4 Acquisition system

The acquisition system contains two main hardware components : a SPEX triple-spectrometer and a Hamamatsu Photoncounting Image Acquisition System (PIAS). Each of these two subsystems is discussed in detail as follows.

2.4.1 Triple spectrometer

The SPEX triple spectrometer has three compartments, delimited by three different slits S_1 , S_2 and S_3 (see Fig. 2.6). Each compartment contains a dispersive element (grating). While the first two stages (commonly denoted as

“filter stage”) supply undispersed light, only the combination of chosen grating and slit S_3 in the last stage (“spectrometer stage”) determines the resolution of the measurements.

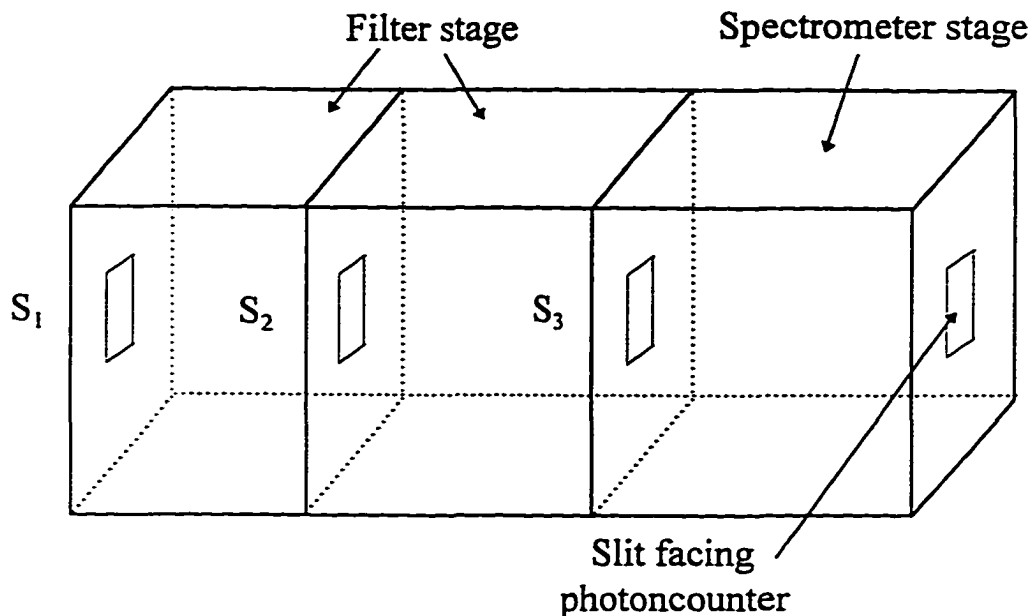


Figure 2.6 Schematic representation of the triple spectrometer.

The spectrometer offers a choice of three different gratings in the spectrometer stage, denoted as : grating #3 with 600 grooves/mm, grating #4 with 1200 grooves/mm and grating #5 with 1800 grooves/mm. The next question to be addressed is the effect of the three slits S_1 , S_2 and S_3 and of the chosen grating in the spectrometer stage, on the measured spectrum.

The resolution of the measurements is exclusively determined by the grating in the spectrometer stage and by the size of the slit S_3 in the spectrometer stage. In general, spectral lines are broadened by the spectrometer, such that the minimum measurable width of a spectral line is given by the band pass (BP), in mm, defined as :

$$BP = \frac{1}{D_1} \cdot SW \quad (2.5)$$

where D_1 is the linear dispersion (Eq. 2.1) and SW is the slit width (usually given in μm) of slit S_3 . D_1 is a constant for a given spectrometer (grating dependent) and its value is given in the technical manual. For example, in our case, for grating #4 [4], the inverse linear dispersion is :

$$\frac{1}{D_1} = \frac{\Delta\lambda}{\Delta x} = 1.4 \text{ nm} / \text{mm} \quad (2.6)$$

Using Eq. (2.5) and a slit opened at $300 \mu\text{m}$ ($SW = 300 \mu\text{m}$), the band pass is $BP = 0.4 \text{ nm}$. This calculation shows that : (a) spectral lines with a full width at half maximum (FWHM) smaller than 0.4 nm will be broadened by the spectrometer to 0.4 nm , and (b) two spectral lines closer than 0.4 nm can not be separated by the spectrometer. The band pass also determines the accuracy of the measured width of a spectral band. A practical rule-of-thumb is that bands with FWHM larger than $10BP$ can be accurately measured. For example, in the case presented above, only the profile of bands wider than 4 nm can be measured with accuracy.

In practice it is customary to give the band pass in units of energy (cm^{-1}) rather than in units of length (nm). The conversion between the two systems is given using the energy (E) - wavelength (λ) relationship :

$$E(\text{cm}^{-1}) = \frac{10^7}{\lambda(\text{nm})} \quad (2.7)$$

which leads to :

$$|\Delta E|(\text{cm}^{-1}) = \frac{10^7 \cdot \Delta\lambda(\text{nm})}{\lambda^2(\text{nm}^2)}, \text{ or } BP(\text{cm}^{-1}) = \frac{10^7 \cdot BP(\text{nm})}{\lambda^2(\text{nm}^2)} \quad (2.8)$$

Eq. (2.8) shows that the band pass expressed in cm^{-1} depends on the wavelength λ where the measurement is performed (not to be confused with the excitation wavelength - see next example). Using Eq. (2.8) it can be shown that a

Raman spectrum obtained under 550 nm excitation, measured with grating #4 and a slit width $SW=300\text{ }\mu\text{m}$ (i.e. with band pass $BP=0.4\text{ nm}$), is characterized by a band pass of $\sim 11\text{ cm}^{-1}$ for phonons measured at $\lambda \sim 580\text{nm}$, and a band pass of $\sim 10\text{ cm}^{-1}$ for phonons measured at $\lambda \sim 600\text{nm}$. Spectrometers which automatically scan a the spectral range also adjust the slit such that the band pass is kept fairly constant.

In the case of a spectrometer which can be adapted with a variety of gratings, the band pass is different for the same SW, for different gratings. The conversion between different gratings is done using the proportionality between the linear dispersion and the number of grooves per mm (Eq. (2.1)), which leads to

$$\frac{D_{l_1}}{D_{l_2}} = \frac{n_1}{n_2} \quad (2.9)$$

where D_{l_1} and D_{l_2} are the linear dispersions for the two gratings with n_1 and n_2 , respectively, grooves/mm. Using Eq. (2.9) and $1/D_{l_4} = 1.4\text{ nm/mm}$ for grating #4, it can be shown that the inverse linear dispersion for gratings #3 and #5, respectively, are $1/D_{l_3} = 2.8\text{ nm/mm}$ and $1/D_{l_5} = 0.9\text{ nm/mm}$.

Tab. 2.1 summarizes the results presented above regarding the computation of the band pass (in nm and cm^{-1}) for different slit widths (SW), for the three different gratings used by the spectrometer. Using Tab. 2.1 it can be shown that for a measurement at $\lambda = 600\text{ nm}$, using S_3 with $SW = 200\text{ }\mu\text{m}$, the corresponding band passes for the three gratings are : $BP_{\#3} = 16\text{ cm}^{-1}$, $BP_{\#4} = 8\text{ cm}^{-1}$, $BP_{\#5} = 5\text{ cm}^{-1}$.

Grating	n (grooves/mm)	$\frac{1}{D_1}(\frac{\text{nm}}{\text{mm}})$	BP (nm)	BP (cm ⁻¹)
#3	600	2.8	$2.8 \cdot \text{SW}(\mu\text{m})/1000$	$\frac{10^7 \cdot \text{BP}(\text{nm})}{\lambda^2(\text{nm}^2)}$
#4	1200	1.4	$1.4 \cdot \text{SW}(\mu\text{m})/1000$	
#5	1800	0.9	$0.9 \cdot \text{SW}(\mu\text{m})/1000$	

Table 2.1 Band pass (BP in nm and cm⁻¹) for different gratings, slit widths (SW) and wavelengths (λ).

Grating #5 was used for all the presented measurements. A larger slit opening provides a more intense signal, but as shown by Eqs. (2.5) and (2.8) also decreases the resolution of the measurement. A typical value of $\text{SW} = 200 \mu\text{m}$ was used for S_3 for all resonance Raman measurements, leading to a spectral resolution of $\sim 5 \text{ cm}^{-1}$.

The slit in the filter stage of the spectrometer, which supplies undispersed light, S_2 , determines the spectral coverage of the chosen grating and was opened to maximum (5 cm). As will be shown in Section 2.4.2 the collected signal is displayed by a 512 x 512 pixel screen. In order to correlate each of the 512 horizontal pixels with the corresponding wavelength for a given spectrum, the spectral coverage (range) was measured for each grating using a calibration Ne-lamp while keeping S_2 opened to maximum. It should be mentioned that the spectrometer displays only the grating number and the central wavelength (in nm) of a measured spectrum. A linear correlation was done between the change in the position (channel number) for each reference Ne line on the screen, when varying the central wavelength of the spectrometer by a given amount (1 nm). For example, as all spectra are displayed on 512 channels (pixels on the monitor), if

when varying the central wavelength on the spectrometer by 1nm the spectrum shifts by 33 channels, the spectral coverage (spectral domain corresponding to the 512 channels) for that particular grating is ~ 15.5 nm ($= 512/33$ nm). Similar measurements were performed for all three gratings, in the 500-670 nm spectral range. A mean-least-square program was used to determine the mean spectral coverage $\Delta\lambda$ for each grating. The same set of measurements also provided the difference between the actual reading on the spectrometer and the real wavelength (obtained from the calibration spectrum of the Ne-lamp), i.e. the correction $\delta\lambda$. The mean values and corresponding standard deviations (σ) for the spectral coverage and correction, for each of the three gratings are given in Tab. 2.2.

Grating	Spectral coverage (nm) $\Delta\lambda \pm \sigma_{\Delta\lambda}$	Correction (nm) $\delta\lambda \pm \sigma_{\delta\lambda}$
#3	51.1 ± 0.5	-3.7 ± 0.3
#4	25.5 ± 0.5	-1.8 ± 0.5
#5	15.5 ± 0.5	-0.9 ± 0.3

Table 2.2 Mean spectral coverages and corrections for the three gratings in the spectrometer stage.

For example, Tab.2.2 shows that the maximum spectral coverage ($S_2 = 5$ mm) for grating #4 is 25.5 nm, i.e. 12.8 nm on each side of the central wavelength displayed by the spectrometer. If grating #5 is used and the displayed central wavelength is 620.3 nm, then the actual central wavelength is $620.3 - 0.9$ nm = 619.4 nm and the observed spectral region extends from $619.4 - 12.8$ nm = 606.6 nm to $619.4 + 12.8$ nm = 632.2 nm.

It is important to stress that Tab.2.2 gives the mean corrections, which are important for preliminary measurements. But for an actual, good quality measurement where a difference of 0.3 nm can be translated in a shift as large as 10 cm^{-1} , each Raman spectrum has to be accompanied by a calibration spectrum taken with the Ne-lamp, which provides the exact correction for that particular spectral range. A software package was specially designed for accumulating, correcting and analyzing data (see Appendix A.1, A.2), with a choice of “average” and “local” corrections. Its structure will be described in Section 2.5.

Finally, the entrance slit S_1 determines the total amount of signal (and noise) which enter the spectrometer. Typically S_1 was opened to a slit width $SW = 200\text{ }\mu\text{m} - 300\text{ }\mu\text{m}$ providing good level signals.

2.4.2 Hamamatsu Photoncounting Image Acquisition System (PIAS)

A Hamamatsu Photoncounting Image Acquisition System (PIAS) photoncounter is attached at the output of the triple spectrometer and transforms the scattered signal into an image which can be displayed, stored and analyzed. It is mostly due to the impeccable performance of the detection system that high quality spectra were obtained. The two-dimensional PIAS model C1815 is an extremely sensitive image acquisition system capable of detecting signals as low as $10\text{ counts/sec/cm}^2$. It consists of a photocathode which converts the photons into photoelectrons. The electrons are amplified 10^9 times and hit a position sensitive detector connected to a position analyzer. The signal is digitized and displayed on a 512×512 pixel screen, where the x-coordinate represents the wavelength as determined by the spectrometer. “Bright” (white) regions represent high density photon zones in the spectral domain and give rise to spectral “lines”. Depending on the used scattering configuration the image of the scattered signal appears as a succession of vertical lines for the vertical illumination where a

significant length of the entrance slit S_1 is illuminated, while for a backscattering geometry the image appears as a succession of “spots” aligned along the horizontal (wavelength) axis. . The photoncounter operates between 280 - 820 nm [5], with maximum quantum efficiency between 300 - 700 nm and has low residual noise level (~ 8 counts/sec). The input signal has to be kept under 5000 counts/sec. Typical Raman spectra have between 80 - 3000 counts/sec. The photodetector automatically shuts down for signals higher than 10000 counts/sec. If the intensity of the signal is too strong neutral density (ND) filters should be used, and/or slits S_1 and/or S_3 can be gradually closed.

2.5 Data transfer and analysis. Software package

After a good quality spectrum is collected (with well defined regions of higher intensity, i.e. spectral lines) the image can be stored on 8.5” disks and/or it can be transferred to a faster PC. A special software package was especially designed for the data transfer and analysis. The programs are presented as follows.

The photoncounter’s computer software offers several options for saving and displaying the measured spectrum [5]. The downsize of these capabilities is the reduced processing speed and the limited graphic capabilities. Accordingly, it is desirable to transfer the image to a second, faster PC by first selecting a narrow display window (~ 40 channels high and 512 channels wide) containing the signal, from the initial 512 x 512 channel image. The measured image can always be positioned in the center of the screen by adjusting the collecting lenses. The program “DANA2” run on the photoncounter’s computer (see Appendix A.1) allows the user to choose the desired window height “h” such that the image is displayed by a 512 x h channel matrix. The program then integrates (adds) the data in each column (channel) and transforms it into a 512-long array, corresponding to the 512 collection channels in the spectral coverage range. The

program also requires the input of the grating number (3, 4 or 5), the central wavelength (nm) displayed by the spectrometer and the laser wavelength (nm), such that a 515-long array is transmitted to a faster PC (PC₂). The program “DANA8” (see Appendix A.2) has to be running on PC₂ in order to transfer, display, modify and store the data files. All created files have the default extension “.dat”.

Each good quality spectrum has to be accompanied by a calibration spectrum taken with the Ne-lamp as follows : (1) S₃ is closed to $\sim 10\ \mu\text{m}$ (or $\sim$ two ND3 filters are placed in front of the slit S₁); (2) the Ne-lamp is placed in front of the entrance slit S₁; (3) the laser beam is covered, such that only signal coming from the lamp enters the spectrometer; (4) a spectrum is acquired for ~ 10 sec. In the beginning and end of the set of measurements, an actual spectrum of the laser beam accompanied by a Ne-calibration spectrum has to be taken in order to accurately measure the excitation wavelength. ATTENTION : Extreme care has to be taken when the laser spectrum is taken, not to damage the sensitive detector. The slit S₃ is closed to $10\ \mu\text{m}$, and at least 1 ND3 filter is placed in the laser beam path. The slit S₁ is opened gradually. If the signal appears to be too high, S₁ is closed and more ND filters are used. All calibration spectra are transferred to PC₂. When plotted, using the same window for each measured spectrum and corresponding calibration spectrum, the correct, local correction is obtained instead of the mean one shown in Tab.2.2. The procedure for using the calibration data for correcting a measured spectrum is described as follows.

The code for the package of programs “DANA8” is given in Appendix A.2. When the program “DANA8” is run on PC₂ in order to transfer, display and analyze the collected spectra, the following options are available to the user :

1. **Transfer data file from Hamamatsu.**

This option enables the receiving of the 515 long data array sent by the photoncounter's computer. The data is stored in a file named by the user (the program prompts for inputting the file name), in a random-access-file which saves memory space. The size of the random access file is 1kB, while the size of the same file saved in ASCII format is 5kB.

2. **Type data file.**

This option enables the manual data input (used only for preliminary test).

3. **View/Modify data file.**

The 515 data contained in the file(s) named by the user at Option 1 can be viewed and modified, after inputting the name of the file to be viewed/modified. Sometimes, the user may input by mistake a wrong grating number, or laser wavelength, or central wavelength, when transferring data from PC₁. This option allows the correction of such mistakes. The new data will be automatically saved (overwritten) in the opened file.

4. **Plot.**

This option allows the user to plot data contained in the file of interest, whose name is required by the program. (This is the name under which the data-file was saved at Option 1). After choosing the file to be plotted, the following options are available : 1. **Preliminary plot** (Option 4.1), 2. **Final plot** (Option 4.2), and 3. **Exit** (Option 4.3).

Option 4.1 allows the user to display the data and gradually smooth it on 3, 5, 7, etc. adjacent channels. The smoothing is done by computing the mean value for N channels (N odd) and placing that value at the position

corresponding to channel $(N+1)/2$. The user can preview the spectrum under different degrees of smoothing and decide on the appropriate smoothing channels to be used for the final plot. Option 4.2 requires the input of the number of channels the final spectrum should be smoothed on, N odd. Often un-smoothed “raw” data is used ($N = 1$) for the final plot. The smoothing (and other types of processing) are done after saving the file in ASCII format (Option 4.2) with different types of software (Origin, Kaleidagraph, etc.). The full option capabilities of the program (reading any data, integrating, renormalization, etc.) as well as the function of different keys are explained on screen as the program is running.

Both Options 4.1 and 4.2 give two choices regarding the calibration of the spectrum : (1) **Use calibration values**, i.e. use a specific calibration - see Options 5 and 6, and (2) **Use program values**, i.e. use the mean corrections given in Tab. 2.2. If Option 1 is chosen, the calibration data file is requested. All calibration files are stored by default in the random access file “CALIB”. The way a calibration file is obtained and used is discussed at Option 5.

The program then offers a choice of displaying the measured spectrum in three different scales : (1) **Linear in Energy (meV)**, (2) **Linear in Wavelength (nm)**, (3) **Raman (1/cm)**. The user can then choose a screen window for plotting the spectrum (the default values use the whole screen and are ; $X0_{\text{left}} = 45$, $X0_{\text{right}} = 20$, $Y0_{\text{down}} = 48$, $Y0_{\text{up}} = 25$), add a title to the plot, display other information. The plot is then displayed. The user can rescale it by changing the minimum and/or maximum display values on the ordinate (y-axis). This is a useful option when the spectrum contains very “strong” (high intensity) and very “weak” (low intensity) peaks which may be suppressed by the limited screen resolution. By decreasing the maximum ordinate value (y_{max}) peaks above that value are cut by a horizontal line but the finer, weaker structure is resolvable. The plot can be printed at any

moment to a printer by pressing the “Print screen” key (or “Print Screen” + “Shift” keys) on the keyboard.

If the user is in the 4.1 Option, by pressing the key “y” (yes) the number of channels the program smoothes on is increased by 2 (from 1 to 3, to 5, etc.) and displayed. When a satisfactory spectrum was obtained the smoothing cycle is interrupted by pressing the key “n” (no).

If the user is in the 4.2 Option, a red arrow appears in the lower left hand side of the screen. In the upper right hand side of the screen the following information is displayed for the current position of the arrow: 1) X-axis value in different units (depending on the chosen scale : energy (meV), wavelength (nm), or Raman shift (1/cm)), 2) Y-axis value (intensity), 3) corresponding channel number, 4) integral value (the user can integrate the area under the spectrum between any two chosen points by pressing the “i” key; a green dot will appear once a point was chosen; after the second point (end of integration) was chosen by moving the arrow and pressing the “i” key again, a second green dot appears, as well as a green line connecting the beginning and end of the integrating interval). The arrow can be moved left by pressing the “4” (“←”) key and right by pressing the “6” (“→”) key, while it traces the shape of the displayed plot. The measured values at each point are displayed in the upper right hand corner. They allow the exact determination of the peak position, peak width, etc. In order to exit the plot screen, the user has to press the “n” (no) key. The program displays the integral ranges and values (if any) and offers the option of storing the file in ASCII format under a name chosen by the user. ASCII files can then be displayed and processed with any graphics software (Origin, Kaleida graph, etc.).

Option 4.3 (Exit) returns the user to the main menu.

5. Add data calibration.

It is recommendable to take a calibration spectrum with the Ne-lamp after each Raman measurement, or in any other situation when high accuracy is required. As previously mentioned, the calibration spectrum is taken by closing S_3 to $\sim 10\mu\text{m}$, blocking the laser beam, and placing the Ne-lamp in front of the slit S_1 . The calibration spectrum is taken for ~ 10 -20 seconds. The calibration spectrum will have the same grating number, central wavelength and laser wavelength as the Raman spectrum and has to be displayed using exactly the same window h (in program DANA2 running on PC₁) as was used for the Raman (or actual measured) pair spectrum. The calibration spectrum is transferred to PC₂ (Option 1), and plotted as final plot (Option 4.2) in wavelength (nm) units using the same number of smoothing channels as for the actual measurement (recommended $N = 1$, i.e. unsmoothed). The Option (2) **Use program values** has to be chosen for plotting. Once displayed, the red arrow indicates the corrected wavelength computed using the mean corrections given in Tab. 2.2. These values are compared with the actual, real values taken from the calibration table of the Ne-lamp. Generally, differences under ± 0.3 nm are expected between the mean corrected and actual values. The “local” correction is computed using the mean corrected and actual values. For example, if the Ne-line at 614.3 nm (table value) is measured by the arrow at 614.1 nm, a +0.2 nm correction is needed. As the only relevant wavelength for a calibration is the central wavelength, i.e. the wavelength (nm) corresponding to the central channel, 256 ($= 512/2$), readings (and corrections) are determined for two Ne-lines on both sides of the 256th channel. If the corrections are not identical (the program rounds all data to the first decimal point, i.e. 2.56 is displayed as 2.6 while 2.53 is displayed as 2.5), the mean value of the two corrections is taken. The arrow is placed on channel 256 and a reading is made (displayed in upper right hand side corner of the screen). Let us assume that

the displayed wavelength corresponding to channel 256 is 617.9 nm. Then the determined correction is made. For example, using the previous case where the correction was +0.2 nm, the actual (real) value for the central wavelength is $617.9 + 0.2 \text{ nm} = 618.1 \text{ nm}$. This value is marked (noted down) and will be used in the calibration file to be created.

The same procedure is repeated for determining the real laser wavelength, with the difference that we are interested in corrections on both side of the position of the laser line, which may not be on the central channel. For example, let us assume that a spectrum of the laser line was taken, it was plotted (Option 4.2) using option **(2) Linear in Wavelength (nm)**, Option **(2) Use program values** for calibration, and the peak of the laser line is situated on channel 210. The corresponding displayed value is 583.2 nm. When plotting the pair Ne-lamp calibration spectrum, in the same conditions, the closest Ne-lines on both sides of channel 210 are : on channel 156, 581.2 nm - displayed value and 581 nm real value, and on channel 319, 587.5 nm - displayed value and 587.3 nm real value. Both measurements show that a correction of -0.2 nm is required, i.e the real laser wavelength is $583.2 - 0.2 \text{ nm} = 583 \text{ nm}$. This value is also marked (noted down) and will be used in the calibration file to be created.

Only when the real central wavelength and laser wavelength are determined, as previously described, can Option 5 be used. When Option 5 is started, the program requires a name for the calibration file. ATTENTION, this is the name which will be used in Option 4 - **Plot (4.1 or 4.2)** when choosing **(1) Use calibration values**. It is recommendable to name this file with the same name as the spectrum it is associated with, chosen at Option 1. This calibration file is an entry in the file called "CALIB" and does not overwrite the file containing the 515 measured data. The calibration file is represented by three fields, all required by the program : calibration file name,

central wavelength (the corrected one, obtained using the Ne-calibration spectrum, i.e. 618.1 nm, in the example above), and laser wavelength (the corrected one, obtained using the Ne-calibration spectrum, i.e. 583 nm, in the previous example).

The file CALIB is a random access file containing three fields (previously mentioned). It was designed to hold at most 999 calibration files (triplets). The second field in the last entry contains the total number of data contained in the file. Each time a new set is added, this number is increased by one.

6. View/Modify data calibration.

This menu allows the modification of the central and/or laser wavelength used in a calibration spectrum created with Option 5, in case an error was made in the input values. The program requires the name of the calibration file (used for creating the file at Option 5) and displays, with an option to modify, the central wavelength and the laser wavelength. The (eventual) new values are automatically overwritten before exiting this option.

7. End.

Ends the program.

2.6 Porto's notation for Raman scattering configurations

The most commonly used notation for describing in a precise, compact manner the scattering geometry used for a Raman spectrum is given by Porto's notation. In Porto's notation the scattering geometry is given in terms of the crystal's axes by a sequence of four letters (axes) as : $x(yz)t$, where x is the direction of propagation (given by the k -vector) of the incident light, y is the

direction of polarization (given by the electric field) of the incident light, z is the direction of polarization of the scattered light (given by the position of the analyzer used for obtaining the Raman spectrum) and t is the direction of propagation of the scattered light. It is important to note that the symmetry of the phonons measured in a Raman spectrum is given, as shown in Chapters 3 and 4, by the polarization of the incident and scattered light, i.e. by the two directions inside the parenthesis in Porto's notation.

For example, an $a(ba)c$ configuration represents a 90° scattering geometry where the incident excitation enters the sample along the a -axis ($\vec{k}_i \parallel a$) while the scattered signal propagates along the perpendicular c -direction ($\vec{k}_s \parallel c$). The polarization of the incident excitation is along the b -axis ($\vec{E}_i \parallel b$), and the scattered signal is polarized along the a -axis ($\vec{E}_s \parallel a$). Using the table of the D_{2h} group (see Appendix A.3) it can be shown that for a crystal with D_{2h} space group symmetry, as is the case of the investigated $\text{Cr:Mg}_2\text{SiO}_4$ sample, using $a = x$, $b = y$, $c = z$, the $a(ba)c$ arrangement measures B_{1g} phonons, i.e. the representation having as basis the combination of incident and scattered polarizations ($ba = yx = xy$). On the other hand, a $c(bb)\bar{c}$ configuration represents a back-scattering geometry ($\bar{c}$ is used to denote a backward (180°) direction, as opposed to c which denotes a forward (0°) scattering), and measures A_g phonons having as basis $bb = b^2 = y^2$, for a crystal with D_{2h} space group symmetry.

2.7 Steady state resonance Raman setup

The actual experimental conditions used for obtaining the steady state Raman spectra presented in Chap. 5, 6 are presented as follows and shown in Fig. 2.7. The 7.5 W output power of the mode locked Nd:YAG laser was frequency doubled using a KTP crystal directly attached to the output holder of the

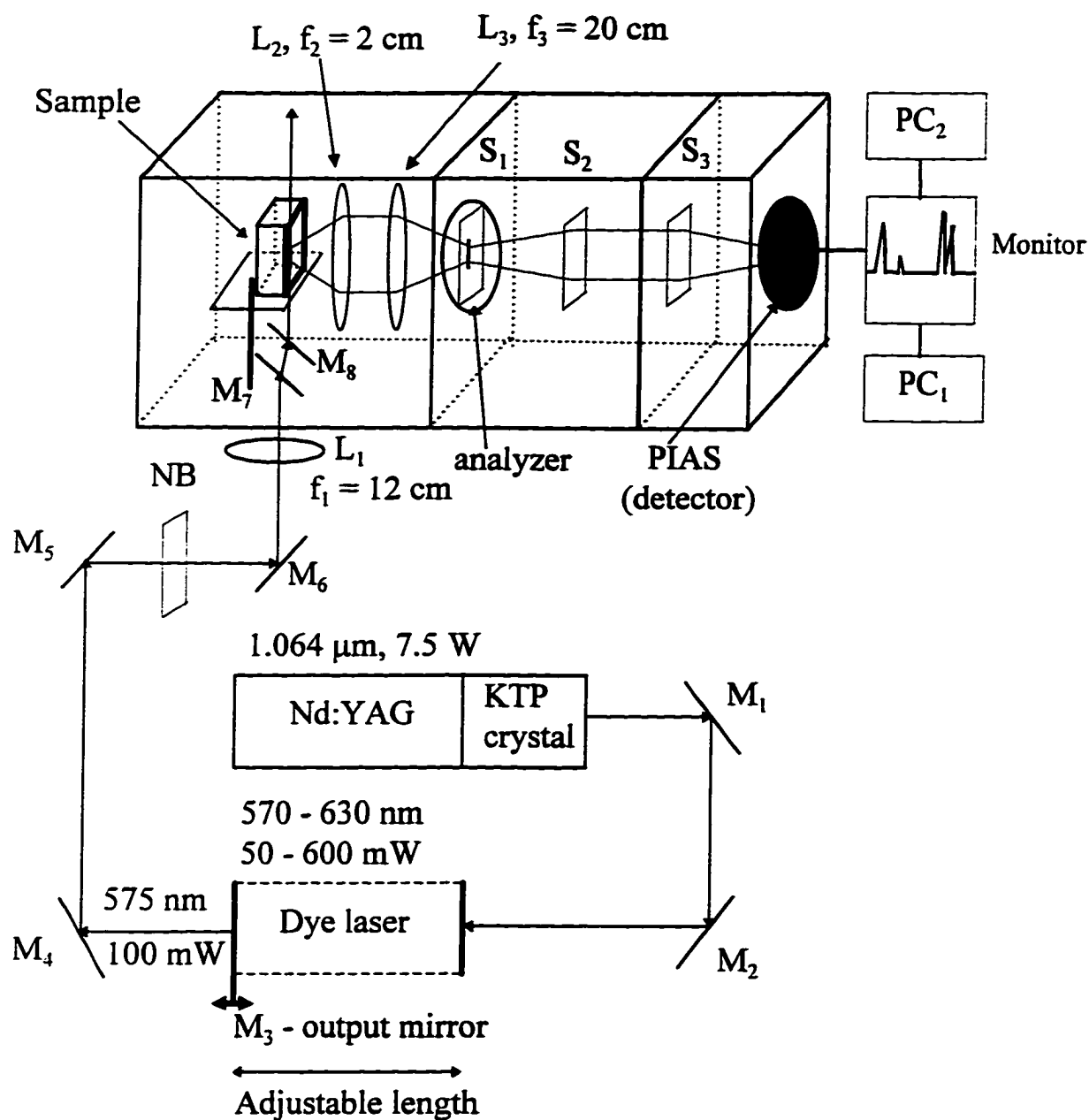


Figure 2.7 Experimental setup used for room temperature resonance Raman measurements.

laser. The average power of the 82 MHz, 532 nm pulses obtained from the KTP crystal was $\sim 1.3 \text{ W}$. The 532 nm pulses were used to pump a Rh-6G dye laser tunable between 570 - 630 nm. Room temperature resonance Raman experiments

used 575 nm linearly polarized excitation beams corresponding to the maximum of absorption (i.e. resonance enhancement) of the $\text{Cr}^{4+} \text{ } ^3\text{B}_2(^3\text{T}_1)$ band [6] (see Fig. 3.11 and Section 5.3), of average power ~ 100 mW.

The following notations were used in Fig. 2.7 : M_1 - M_8 - mirrors, NB - narrow band filter, L_1 - 12 cm converging focusing lens, L_2 - 2 cm focal length, 85 mm aperture (0.23 f-number) Canon collecting camera lens, L_3 - 20 cm focal length collecting lens, S_1 - S_3 - spectrometer's slits, PC_1 - photoncounter's computer, PC_2 - fast PC.

The cavity length of the dye laser was adjusted by translating M_3 in Fig. 2.7 for obtaining the spectrally "narrowest" pulses, monitored using a diffraction grating placed after the output mirror of the dye laser (see Section 2.2.3). As the width of the Raman lines is limited by the width of the laser line, in order to be able to detect modes of vibration which are spectrally close one has to use as narrow excitation line as possible. Wider laser pulses lead to an overlap of neighboring phonon modes and a reduced spectral resolution. The dye laser's cavity length was adjusted till a narrow, stable, "dot" (laser line) was obtained. It should be mentioned that it is often difficult to select one single mode (wavelength) of the dye laser, and instead the laser "jumps" between two neighboring modes. This appears as two maxima whose intensity fluctuates in time, in the image of the diffraction pattern projected on the wall. In order to avoid this problem one has to fine adjust either the direction of the 532 nm beam into the dye laser by changing the direction of the mirrors M_1 and M_2 (Fig. 2.7), or by changing the position of the dye laser's output mirror M_3 around the vertical and horizontal directions (without changing the dye laser's cavity length). Problems regarding the stability of the dye laser are especially acute for the "tails" of the emission spectrum, i.e. for $\lambda < 580$ nm and $\lambda > 620$ nm. Any instability in the excitation wavelength is reflected in the Raman spectrum which appears

doubled. The lines in each doublet may have very different intensities depending on the ratio of the intensities of the two competing modes.

By detuning the dye laser's cavity length to obtain spectrally narrow pulses, the power typically decreases to $\sim 1/2$. For example, if the maximum output power for the 575 nm excitation is 100 mW, the average power of the spectrally narrow pulses is ~ 50 mW. A narrow-band filter further ensures the monochromaticity of the excitation wavelength, but also further reduces the excitation power by $1/2$. The measured full width at half maximum (FWHM) of the laser pulses was $\sim 5 \text{ cm}^{-1}$, i.e. within the spectral resolution of the spectrometer.

The excitation pulses are focused into the sample using a 12 cm focus lens L_1 placed at its focal distance away from the sample. The sample is vertically illuminated (Fig. 2.7), i.e. with the direction of the incident beam parallel to the entrance slit S_1 of the spectrometer. For room temperature resonance Raman measurements the sample was placed on a specially designed holder which had a small hole ($\sim 2\text{mm}$ diameter) allowing the excitation beam to enter the sample. The 12 cm focusing lens was the optimum choice among a variety of other lenses and it lead to an estimated focusing diameter $d \approx 40 \text{ }\mu\text{m}$ and a length of focusing $L \approx 1.5 \text{ mm}$, calculated using eqs. (2.2) - (2.3) with $D = 4 \text{ mm}$. The length of focusing was further magnified by the collecting lenses L_2, L_3 such that its image on the entrance slit S_1 was $\sim 1.5 \text{ mm}$. In order to minimize the losses in the scattered signal due to absorption, the sample was illuminated close to the face directed towards S_1 (this face appears outlined in Fig. 2.7).

The scattered signal was collected in a 90° geometry using an 85 mm Canon camera lens L_2 with focal distance $f_2 = 2 \text{ cm}$ and a second collecting lens L_3 with focal distance $f_3 = 20 \text{ cm}$ which focuses the collected scattered signal on the entrance slit S_1 of the triple spectrometer. The camera lens L_2 was chosen for its high quality, versatility and large aperture (85 mm), efficient for signal

collection, and was placed at its focal distance away from the sample such that it transforms the collected signal into parallel light. The parallel light is collected by the second lens, L_3 which focuses it on the entrance slit of the spectrometer, i.e. the distance between L_3 and S_1 is f_3 . Fig. 2.7 suggests that the distance between L_2 and L_3 is not important and does not affect the image. This, however, is true only for light parallel to the optical axis of the system (horizontal). If the emergent parallel light from L_2 is not horizontal, but is tilted at angle α , it may easily “miss” L_3 if the latter is far from L_2 . Thus, from a practical point of view L_3 has to be as close to L_2 as possible and have a large aperture ($\sim 5 - 8$ cm). The long focal distance of L_3 ($f_3 = 20$ cm) allowed its placement close to L_2 and efficient collection of the scattered signal.

For resonance Raman measurements special care has to be given to the polarization of the incident light with respect to the crystal axes. As the absorption of the doped sample is polarization dependent, and the 575 nm wavelength corresponds to the maximum of absorption of the $\text{Cr}^{4+} {}^3\text{A}_2 \rightarrow {}^3\text{B}_2({}^3\text{T}_1)$ band for $E_{\parallel}||c$ (i.e. the incident excitation is polarized parallel to the c -crystallographic axis of the sample, see Fig. 3.11), in order to obtain a resonance Raman spectrum for the above mentioned band the incident light has to be polarized parallel the c -crystal axis. The polarization of the incident excitation can be easily checked with a polarizer.

Both the sample holder and the collecting lens L_3 are placed on 3-directional translation stages. A good focus is obtained when the image of the vertical excitation beam passing through the crystal is clearly observed as a thin luminous line on the entrance slit S_1 . This is achieved by moving both the sample holder and L_3 along the optical axis of the system (horizontally).

The polarized signal is measured using a polarizer (analyzer) placed in front of S_1 . The analyzer can be rotated in the vertical plane. The complete scattering

arrangement is described using Porto's notation (Section 2.6) where all directions are given in terms of crystal axes in standard *Pnma* notation (see Chapter 3).

Special care has to be given to the position of the crystal and the "degree of polarization" of the incident laser light. If the crystal is slightly rotated around a vertical axis, $\vec{E}_i$ can be decomposed along two crystal axes such that Raman modes of different symmetry will "leak" into the spectrum. This may be very annoying especially when one measures weak nontotally symmetric modes where, often, strong totally symmetric modes appear as parasites. In order to determine the optimum position of the crystal such that depolarization does not appear (or is minimal), preliminary measurements have to be done for the highest scattering cross section phonons in the system (in our case, for the high frequency A_g modes - see Fig. 3.5), most likely to "leak". If a nontotally symmetric spectrum (ex. $b(cb)a$, for B_{3g} modes) also contains A_g (cc) modes, the crystal and/or the analyzer in front of the slit S_1 have to be slightly rotated in order to minimize the parasite modes. An additional polarizer for the excitation beam may have to be used in order to eliminate any parasite depolarization introduced by reflections on the mirrors.

All polarized room temperature Stokes Raman spectra were obtained under 575 nm excitation, by monitoring the signal corresponding to phonon energies above 150 cm^{-1} . This limit of the spectral region was imposed by the closeness to the laser line which gives rise to higher background values and covers the Raman signal. The upper limit for the investigated Raman spectrum was $\sim 1000\text{ cm}^{-1}$ for room temperature measurements [7] (Chapter 5) and up to 3200 cm^{-1} for low temperature measurements [8] (Chapter 6). The upper limit was imposed by the increased emission from the Cr^{3+} fluorescence R_1 line at 692 nm [6]. The following formula was used for computing the wavelength λ (nm) where a phonon

of energy ΔE (cm^{-1}) is observed, under excitation wavelength λ_0 (nm), in a Stokes spectrum :

$$\lambda(\text{nm}) = \frac{10^7}{\frac{10^7}{\lambda_0(\text{nm})} - \Delta E(\text{cm}^{-1})} \quad (2.10)$$

A similar formula is used for an anti-Stokes spectrum ($\lambda < \lambda_0$), where the “-” sign in Eq. (2.10) is changed into “+”.

The slit widths used for collecting Raman signals were : $S_1 = 200 \mu\text{m}$, $S_2 = 5 \text{ cm}$, $S_3 = 200 \mu\text{m}$. The polarized scattered Stokes Raman signal was collected by a Photoncounting Image Acquisition System (PIAS Hamamatsu model C1815), for exposure times varying between 5 min - 35 min, depending on the signal level (lower for geometries corresponding to nontotally symmetric modes). All spectra were displayed on the monitor and stored as images, on PC₁ (Fig. 2.7). Data was also transferred to a second PC (PC₂), used for analyzing data and storing it in ASCII format using the software package described in Section 2.5.

The experimental setup and experimental conditions used for obtaining low temperature resonance Raman measurements [8] (Chapter 6) were identical to those previously described in this section and shown in Fig. 2.7, except for the following modifications :

- a) resonance Raman spectra were obtained under 572 nm excitation corresponding to maximum resonance enhancement of the local modes. 532 nm excitation was used for obtaining third and fourth order resonance Raman spectra due to its blue shift which allowed the investigation of higher order spectra, without being hindered by the high energy emission tail of the Cr^{3+} R_1 line. Reference off-resonance Raman spectra used for identifying Cr^{4+} local modes were obtained from the $\text{Cr:Mg}_2\text{SiO}_4$ crystal using off-resonance 582 nm excitation

(see Chapter 6). Appropriate NB filters were used for each of the previously mentioned excitation wavelengths.

- (b) As measurements were performed at low temperatures (4K using liquid He and 77K using liquid N₂) the sample was placed into a Dewar attached to a suspended platform which could be displaced in the horizontal plane by two fine adjustment screws (see Fig. 2.8).

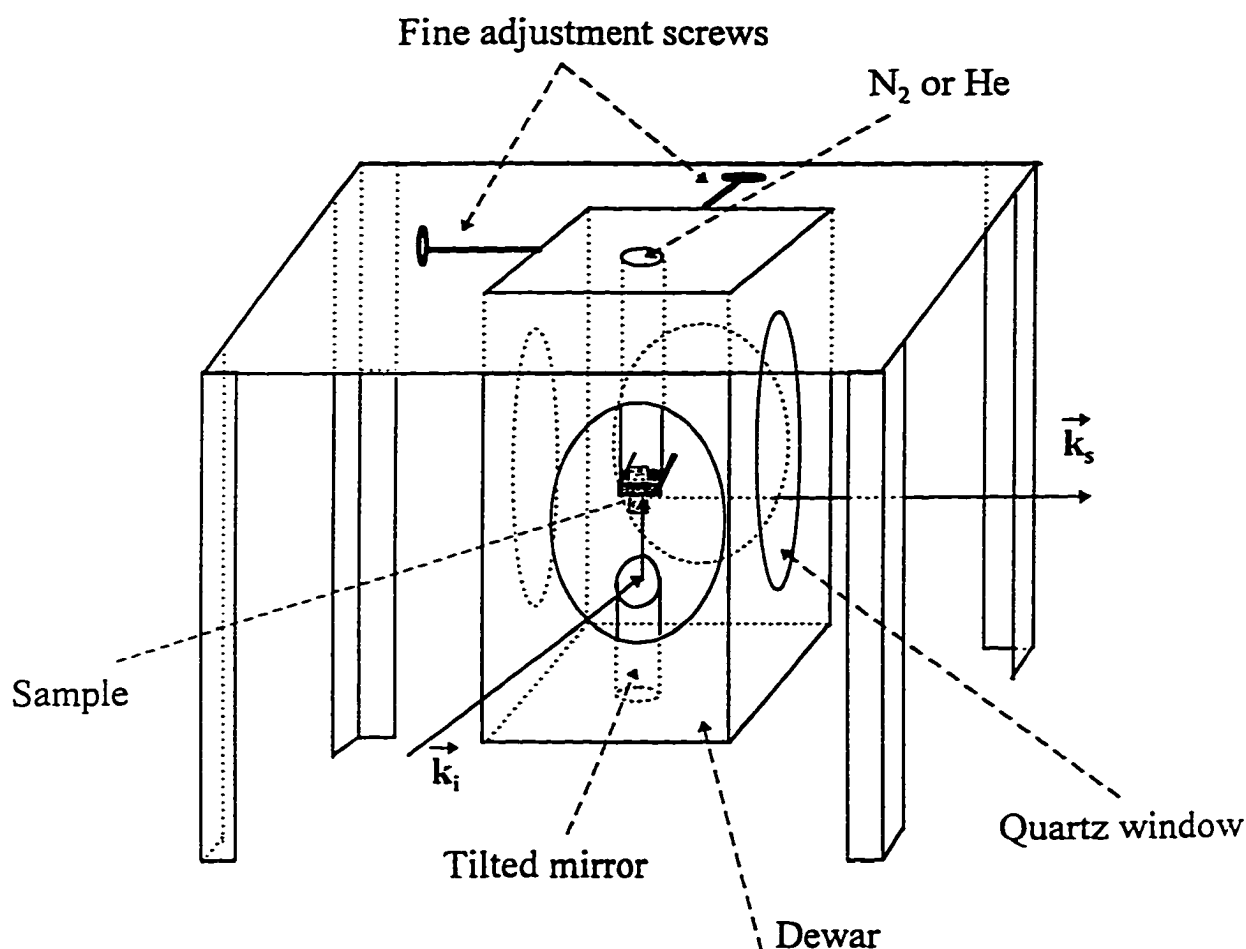


Figure 2.8 Schematic representation of sample positioning for low temperature measurements.

The Dewar has quartz windows on each of the four vertical walls which allow the sample to be irradiated. In order to use the vertical, more efficient

illumination described in Section 2.3, a mirror tilted at 45° was introduced inside the Dewar such that the excitation beam was directed along the vertical axis inside the sample (Fig. 2.8) and, at the same time, parallel to the entrance slit of the spectrometer. The temperature inside the Dewar was monitored throughout the experiments with a temperature controller. It should be mentioned that it was necessary to first pump the air out of the Dewar containing the sample, using a vacuum pump, and only then was the coolant pumped into the system. If the quality of the vacuum is poor, or if air leaks in, the quartz windows freeze and make the measurement impossible.

2.8 Time resolved resonance Raman setup

The experimental conditions used for obtaining the time resolved resonance Raman spectra presented in Chapter 7 are presented as follows and shown in Fig. 2.9. The following notations were used in Fig. 2.9 : $M_1 - M_5$ - mirrors, $BS_1 - BS_3$ - beamsplitters, TD - time delay unit, NB - narrow band filter, MO - $f = 2$ cm, 10 $\times$ focusing and collecting microscope objective, L - $f = 30$ cm collecting lens, A - analyzer (polarizer), PC₁ - PIAS computer, PC₂ - faster PC.

The 7.5 W, 90 ps, 1.064 μm output pulses of the mode locked Nd:YAG laser enter the optical fiber pulse compressor, where they are compressed and frequency doubled by a KTP crystal. The 750 mW, 6 ps, 532 nm output pulses of the pulse compressor synchronously pump the Rh-6G dye laser whose output pulses can be further compressed down to 500 fs by translating the output mirror M_3 (Fig. 2.7). The temporal length of the pulses is first assessed using a diffraction grating as described in Section 2.7. The main difference is that for time resolved measurements the desirable spectral beam profile is broad (elongated ellipse projected on a remote wall), corresponding to short temporal pulses, instead

of the “narrow dot” used in steady state measurements. The width of the diffracted beam (ellipse) can be maximized by adjusting both the cavity length of the dye laser and the position of the output mirror relative to the vertical plane. It should be noted that the actual duration of the laser pulses is determined with the autocorrelator.

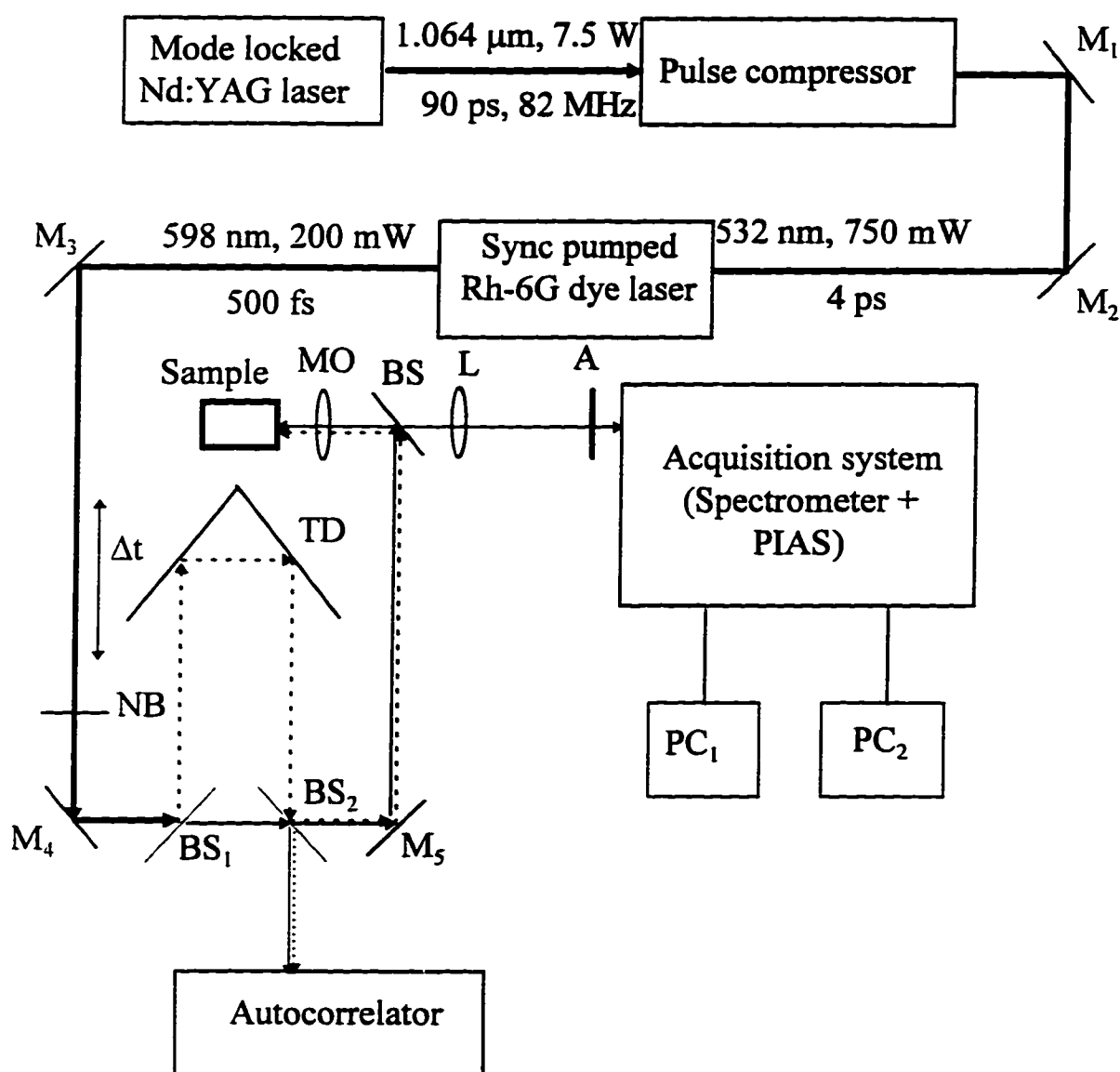


Figure 2.9 Experimental setup used for room time resolved resonance Raman measurements.

Time resolved resonance Raman measurements used linearly polarized along the *c*-crystallographic axis, in *Pnma* notation (see Chapter 3), 598 nm excitation pulses [9], corresponding to the maximum enhancement for the anti-Stokes 765 cm^{-1} Cr^{4+} tetrahedral breathing mode (Chapter 5). A $600 \pm 5\text{ nm}$ narrow band filter (slightly rotated such that the incident beam is not normal to it, which allowed the transmission maximum to be shifted towards lower wavelengths) was used to minimize any residual background due to the laser excitation. The 50 mW excitation beam was divided by a beamsplitter (BS_1 in Fig. 2.9) into a pump and a probe pulse with intensity ratios 2/1, respectively. The weaker probe entered an adjustable time delay unit and was retarded with respect to the pump by a determined time Δt . The pump and probe are then recombined by BS_2 and focused into the sample by a $f=2\text{ cm}$, 10x microscope objective, in a backscattering geometry (as discussed in Section 2.3). The microscope objective acts both as focusing lens and as collection lens. Using Eqs. (2.2), (2.3), the focal length of the microscope objective $f = 2\text{ cm}$, $\lambda = 598\text{ nm}$ and $D = 4\text{ mm}$, the diameter of the focusing region is $d = 7\text{ }\mu\text{m}$ and the length of focusing is $L = 36\text{ }\mu\text{m}$ (40 times shorter than for steady state measurements). This value of the length of focusing leads to a maximum time delay between signals originating in different parts of $L \sim 18\text{ fs}$, well under the widths of the used pulses. This calculation shows that no measurable time delay is introduced by the sample itself under the given experimental conditions.

The signal is scattered backwards and collected by the microscope objective and a 30 cm lens which focuses it into the entrance slit of the spectrometer. Due to the backscattering type of illumination the signal displayed by the photoncounter's computer is made of bright "dots", not lines as was the case for vertical illumination (Section 2.7). As will be shown in Chapter 7, time resolved Raman measurements investigate the anti-Stokes spectrum, i.e. the central wavelength on

the spectrometer is lower (at higher energy) than the excitation wavelength. The slits were opened at $S_1 = 300 \text{ } \mu\text{m}$, $S_2 = 5 \text{ cm}$, $S_3 = 400 \text{ } \mu\text{m}$. All spectra used grating #5 (finest with 1800 grooves/mm). Using Tab. 2.1 and the above setting for the spectrometer it can be shown that the spectral resolution was 10 cm^{-1} . This does not affect the quality of the measurements as the width of the laser pulses was 35 cm^{-1} . The level of the signal was $\sim 120 \text{ counts/sec}$ and each spectrum was taken for $\sim 30 \text{ min}$.

One of the main difficulties in a time resolved experiment is to determine the zero-time delay (reference) between pump and probe. The first step is to get good quality, narrow (500 fs) pulses. The time duration of the pulses is changed as previously described, and monitored by covering any of the two pump or probe beams (in order to avoid interferences) and observing on the oscilloscope the signal from the autocorrelator. If pulses are “squeezed” too hard they tend to become unstable. After obtaining short, stable pulses, the second step is to get signals from the autocorrelator for both pump and probe, one at a time (by alternately blocking the other beam). The traces of the two beams on the oscilloscope should have comparable intensities. If one trace is too weak, it will be completely covered by the trace of the second pulse, such that the determination of zero-time delay is impossible. It is very important to remember that in order to determine the correct zero-time delay, the pump and probe signal to be monitored (sent into the autocorrelator) has to be taken after BS₂ (after the two beams have been recombined). A mirror placed after BS₂ (which will be removed during the actual measurements) directs the pump and probe pulses into the autocorrelator. When the two pulses are within ps of each other, their trace on the oscilloscope has three peaks, due to the shaking mirror of the autocorrelator [10]. When the TD unit is moved by the automated Unidex translation stage by a determined amount (which is linearly transformed into a time delay as : 150 units = 1 ps) the two exterior peaks in the trace start “moving” towards or away from the central peak.

Due to the finite width of the peaks, which makes it difficult to determine when the two exterior pulses coincide exactly with the central pulse (zero time delay), the reference of the measurements is chosen as half the distance between the positions when the two pulses “interchange” symmetrically. For example, let us assume that for a given position of the translation stage x_1 -units, the two peaks are 2 divisions on both sides of the central peak on the oscilloscope. Once the translation stage is moved, the two peaks seem to “converge” toward the central line, “melt” into it, interchange and start moving away from it. The translation stage is moved till the two peaks are again 2 divisions on both sides of the central peak on the oscilloscope. If this new position corresponds to x_2 units on the translation stage, then the zero-time delay is at position $(x_2 + x_1)/2$. The translation stage is fixed at this position and reset (0 units). The operation is repeated several times in order to check the accuracy of the determined zero. Once the zero-time delay is determined the mirror after BS₂ is removed and different time delays Δt are introduced between pump and probe. It should be noted that strong interference occur between the pump and probe at zero-time delay, such that measurements for this point should be avoided.

During the actual measurements the trace on the autocorrelator monitors the quality of the pulses. Any change of any kind in the system, which needs to be corrected will imply a change in the path of the excitation beams and the loss of zero. Measurements taken under different conditions can not be compared. Many times, especially during the day, the laser is unstable and several fine adjustments have to be done, which lead to the loss of all previous measurements.

2.9 References

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Chapter 3

Vibrational and electronic state characterization of chromium-doped forsterite

3.1 Background

The material under investigation is chromium-doped forsterite ($\text{Cr:Mg}_2\text{SiO}_4$), the first Cr^{4+} -based tunable solid state laser material emitting in the near-infrared spectral region, between 1000 - 1500 nm [1, 2]. Before the development of $\text{Cr:Mg}_2\text{SiO}_4$, all Cr-doped laser active materials ($\text{Cr:Al}_2\text{O}_3$ - ruby, $\text{Cr:BeAl}_2\text{O}_4$ - alexandrite, $\text{Cr:Be}_3\text{Al}_2(\text{SiO}_3)_6$ - emerald, etc.) had Cr^{3+} as lasing center. The major deficiency of Cr^{3+} is that it usually occupies an octahedrally coordinated position which, due to the inversion center, makes the dipole ($\hat{P}$) transition forbidden for d-electrons described by the even wavefunction $|\Psi_d\rangle$ (i.e. $\langle \Psi_d | \hat{P} | \Psi_d \rangle = 0$). This means that pure d-electrons can not be excited by one-photon absorption. The absorption spectra of Cr^{3+} is due to Russell-Saunders coupling (discussed in Section 3.3.1) which describes Cr^{3+} ions in terms of multielectronic wavefunctions instead of pure, even, d-wavefunctions. On the other hand, Cr^{4+} occupies (as will be shown) a tetrahedrally coordinated position which allows dipole transitions due to the lack of inversion center. The higher excitation efficiency makes Cr^{4+} ions highly desirable as laser active centers. $\text{Cr:Mg}_2\text{SiO}_4$ was the first major step on the path of developing tetrahedrally coordinated Cr^{4+} laser materials.

This chapter presents the spectroscopic properties of $\text{Cr:Mg}_2\text{SiO}_4$ by first analyzing the structure of Mg_2SiO_4 host and correlating it to the phonon spectrum in section 3.2. The characterization of the free Cr^{4+} ion (laser center) and the

optical properties of Cr^{4+} doped into the Mg_2SiO_4 host are presented and discussed in section 3.3. The B, C and Dq field parameters are determined for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ from the polarized absorption spectra in section 3.4.

3.2 Normal modes of vibration of forsterite

Forsterite belongs to the olivine family and is a naturally occurring gem. The arrangement of the constituent ions inside a forsterite unit cell can be derived from the symmetry and number of Raman and infrared modes of vibration (phonons), while the energy of these phonons gives information on the interaction strength between different ions. Olivines have chrysoberyl (Al_2BeO_4) arrangement with 4 formula units per unit cell [3]. As for a material with N atoms per unit cell a total of 3N normal modes of vibration are expected (3 low frequency acoustic and $3N - 3$ optic (Raman, infrared active and inactive) modes), Mg_2SiO_4 has a total of $3 \times 4 \times (2 + 1 + 4) = 84$ phonons. The symmetry of phonon modes determines the selection rules and the particular geometry in which different modes are excited in IR and Raman spectra. Using group theory the symmetry of the 84 phonon modes of forsterite and the type of vibration they describe i.e. translations, rotations or molecular internal vibrations, will be determined and analyzed in Section 3.2.2.

3.2.1 Molecular, site - and space group symmetry. Correlation tables

In order to accurately describe a crystal structure, three different types of symmetry are considered : (i) molecular symmetry, (ii) site symmetry and (iii) space group symmetry.

(i) If the unit cell contains structures (molecules) which can not be treated as point-like entities (as is the case of SiO_4 in Mg_2SiO_4), the symmetry of the

unperturbed molecule i.e. molecular symmetry (G_M) has to be considered and the rotations and internal modes of vibration have to be derived. In general, G_M is described by a group with high symmetry such as T_d or O_h , and the normal modes of vibration are degenerate.

(ii) Each ion or molecule is placed inside the unit cell in a position with a specific symmetry determined by the lattice. The symmetry of the location of an ion (atom, molecule) inside the unit cell is called site (or point) symmetry (G_S). The site symmetry is the symmetry the lattice imposes in a particular point inside the unit cell. A molecule having its own symmetry G_M is distorted when placed into the crystal such that it ends up being described not by G_M but by the symmetry of the site where it was inserted, G_S . It should be noted that in general the site symmetry is lower than G_M and the degeneracy of the unperturbed molecule is partially lifted when inserted into the lattice.

(iii) The symmetry of the unit cell as a whole is called space group (or crystal) symmetry (G). All spectroscopic properties of a material are described in terms of the space group. As a consequence, all other types of symmetry (G_M , G_S) have to be expressed in terms of G . It should be noted that as each particular location of an atom or molecule inside the crystal is part of the unit cell, the group describing the site symmetry has to be a subgroup of the space group ($G_S \subset G$). The symmetry of the crystal is completely described by correlating G , G_S and G_M , using correlation tables [4]. This procedure will be illustrated for the 84 normal modes of vibration of Mg_2SiO_4 in the next section.

3.2.2 Determination of symmetry and selection rules for the normal modes of vibration of Mg_2SiO_4

Mg_2SiO_4 belongs to the D_{2h}^{16} space group [3]. It is important to note that D_{2h} contains only one-dimensional representations which means that the degeneracy of all wavefunctions describing the crystal (or any ion doped into it) is completely lifted. In $Pnma$ notation (standard) [5] indicating a rectangular ($\alpha = \beta = \gamma = \pi/2$) primitive cell with unequal lattice constants ($a \neq b \neq c$), the unit cell has the following dimensions : $a = 10.22 \text{ \AA}$, $b = 5.99 \text{ \AA}$ and $c = 4.73 \text{ \AA}$ [3]. The $Pnma$ notation will be used throughout this thesis. The transition from $Pnma$ to other crystal notations ($Pbnm$, $Pnmb$, etc.) is obtained by the permutation of the crystal's axes (Ref. 5, pag. 37) and is given in Tab. 3.1.

Lattice constants ($\text{\AA}$)	$Pnma$	$Pbnm$	$Pmnb$
10.22	a	b	b
5.99	b	c	a
4.76	c	a	c

Table 3.1 Correlation between $Pnma$, $Pbnm$ and $Pmnb$ crystal notations and the crystal lattice constants.

The lattice constants a , b and c are identified as the x , y , z axes, respectively and used as such from now on. The unit cell of Mg_2SiO_4 contains 4 formula units, thus giving rise to a total of 84 normal modes of vibration, all of them nondegenerate. A forsterite unit cell is depicted in Fig. 3.1.

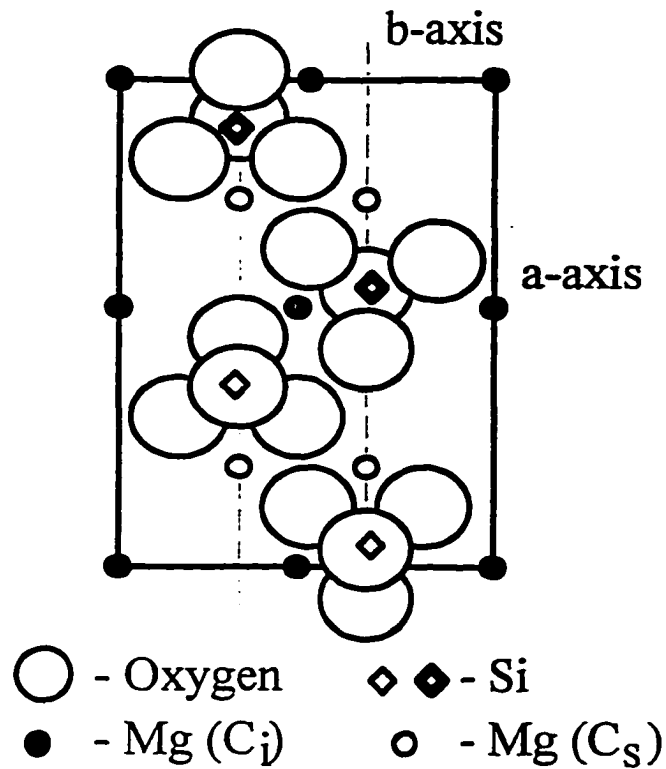


Figure 3.1 Unit cell of forsterite.

The normal mode analysis is done by first considering point-like structures, described by three translations each, inside the unit cell. The next step involves the characterization of those structures which can not be described as point-like, and the derivation of the modes of vibration due to rotations and internal vibrations of such molecules. As will be shown, due to the strongly bound SiO_4 molecules, the analysis of Mg_2SiO_4 normal modes of vibration first considers two point-like types of constituents : Mg^{2+} and $(\text{SiO}_4)^{4-}$ ions. As shown in Ref. 3 for the isostructural to Mg_2SiO_4 , Al_2BeO_4 , 4 Mg ions are in (a) positions, 4 Mg ions are in (c) positions and the 4 Si ions are in (c) positions. Ref. 5 gives the point symmetry group of these sites as : C_i for (a) and C_s for (c). The two non-equivalent sets of Mg ions are denoted as : Mg(I) - in C_i site and Mg(II) - in C_s site [6]. Each of the above mentioned types of ions is described by 3 phonon

modes due to the 3 translational degrees of freedom. The next step will be to consider the internal structure of SiO_4 and add the rotations and internal vibrations of this molecule to the phonon spectrum. The four relevant point groups describing Mg_2SiO_4 are : C_i , C_s , D_{2h} and T_d . The character tables for these groups are given in Appendix A.3.

3.2.2.1 Translations of Mg in C_i Site (Mg(I))

The 4 Mg ions in C_i site will contribute with 3×4 modes of translation to the 84 normal modes of vibration of Mg_2SiO_4 . As Mg is considered point-like, the only correlation is $G_S \rightarrow G$. The $C_i \rightarrow D_{2h}$ correlation table is presented in Tab.3.2. The table is filled from left to right as indicated by the arrow.



$n = 4$	f	t	Basis	C_i	D_{2h}	c_ξ	a_ξ
	12	3	x, y, z	A_u	A_u B_{1u} B_{2u} B_{3u}	1 1 1 1	3 3 3 3

Table 3.2 $C_i \rightarrow D_{2h}$ correlation table for Mg(I) in Mg_2SiO_4 .

The leftmost column contains the number of equivalent ions ($n = 4$). The next column (f) contains the total dimension of the considered object, as given by all contributing ions (in our case $12 = 4$ Mg ions $\times$ 3 translations (third column), each). The fourth column (Basis) contains the actual basis for the operation of interest (x, y, z for translations). The fifth column has as heading the name of the site group (C_i) and contains the representation(s) having as basis the operation of

interest. As shown by the character table for C_i (Appendix A.3) all three translations x , y and z are basis for the A_u representation. The next three columns establish the symmetry of the 12 translations expressed in terms of the crystal's space group D_{2h} . The sixth column has as heading the space group of the unit cell (D_{2h}) and contains all the representations which, upon lowering the symmetry from G to G_S (D_{2h} to C_i), contain A_u (the representation in column 5). The $G \rightarrow G_S$ correlations are found in Ref. 4, pag. 203. There are 4 representations in D_{2h} which are reduced to A_u in C_i : A_u , B_{1u} , B_{2u} and B_{3u} . The seventh column (c_ξ) contains the dimension of each of these representations. Finally, the last column (a_ξ) contains the contribution of each representation (coefficients) to the total (12) number of vibrations : $a_\xi = f / \sum c_\xi$ ($a_\xi = 12 / 4 = 3$). In the end we obtain that the 12 translations due to Mg(I) have the following symmetry in D_{2h} :

$$\Gamma_{Mg(I),C_i}^{tr} = 3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u} \quad (3.1)$$

As all representations are odd (u) they are only infrared active, or , in the case of A_u , inactive (see character table for D_{2h} in Appendix A.3).

3.2.2.2 Translations for Mg in C_s Site (Mg(II))

The $C_s \rightarrow D_{2h}$ correlation table for Mg(II) is given by Tab. 3.3 which shows that the space group symmetry of the 12 translations due to Mg(II) in C_s is :

$$\Gamma_{Mg(II),C_s}^{tr} = 2A_g + B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + B_{2u} + 2B_{3u} \quad (3.2)$$

Some observations should be made regarding Tab. 3.3. As opposed to the case of C_i , both representations of C_s (A' and A'') have as basis translation vectors : A' - x and y , and A'' - z . When looking at the $D_{2h} \rightarrow C_s$ correlation (Ref. 4, pag. 203), three choices are possible depending on the direction of lowering the symmetry (obviously, only one is correct). The proper correlation to be chosen is given in Ref. 4, pag. 46, where the space group and site ((c) for Mg(II), as

previously shown) are correlated by a particular direction (element of symmetry) which enables the lowering of symmetry. For D_{2h}^{16} , for a (c) site (as is the case for C_s), the correlating plane is $\sigma(zx)$ [4].

$\sigma(zx)$							
$n = 4$	f	t	Basis	C_s	D_{2h}	c_ξ	a_ξ
	8	2	x, y	A'	$\rightarrow A_g$ $\rightarrow B_{2g}$ $\rightarrow B_{1u}$ $\rightarrow B_{3u}$	1 1 1 1	2 2 2 2
	4	1	z	A''	$\rightarrow B_{1g}$ $\rightarrow B_{3g}$ $\rightarrow A_u$ $\rightarrow B_{2u}$	1 1 1 1	1 1 1 1

Table 3.3 $C_s \rightarrow D_{2h}$ correlation table for Mg(II) in Mg_2SiO_4 .

3.2.2.3 Translations for (SiO_4) in C_s site

The 12 translations for any 4 point-like equivalent objects on C_s site are given by Eq. (3.2). Therefore, the space group symmetry of the (SiO_4) translational modes is :

$$\Gamma_{SiO_4, C_s}^{tr} = 2A_g + B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + B_{2u} + 2B_{3u} \quad (3.3)$$

Eqs. (3.1) - (3.3) give the symmetry of all 36 translations in Mg_2SiO_4 . It should be noted that 3 of them are acoustic vibrations (those having basis x, y and z in D_{2h} , i.e. B_{1u} , B_{2u} and B_{3u} , respectively), while the other 33 translations are

optical phonons. We now proceed to considering the rotations and internal vibrations of the SiO_4 molecules.

3.2.2.4 Rotations for (SiO_4) in C_s site

Each of the 4 SiO_4 molecules in the unit cell of forsterite contribute with 3 rotations (R_x , R_y , R_z) to the phonon spectrum. The correlation table for the 12 rotations is constructed in the same manner as for the translations, the only difference being that now the basis of interest in column 4 are the 3 rotations. Tab. 3.4 details the $C_s \rightarrow D_{2h}$ correlation for the 12 modes of rotation :

n = 4	f	t	Basis	$\xrightarrow{\sigma(zx)}$		c_ξ	a_ξ
				C_s	D_{2h}		
	4	1	R_z	A'	$\rightarrow A_g$ $\rightarrow B_{2g}$ $\rightarrow B_{1u}$ $\rightarrow B_{3u}$	1 1 1 1	1 1 1 1
	8	2	R_x, R_y	A''	$\rightarrow B_{1g}$ $\rightarrow B_{3g}$ $\rightarrow A_u$ $\rightarrow B_{2u}$	1 1 1 1	2 2 2 2

Table 3.4 $C_s \rightarrow D_{2h}$ correlation table for the 12 (SiO_4) rotations.

Table 3.4 gives the space group symmetry of the 12 rotations due to (SiO_4) in C_s site as :

$$\Gamma_{\text{SiO}_4, C_s}^{\text{rot}} = A_g + 2B_{1g} + B_{2g} + 2B_{3g} + 2A_u + B_{1u} + 2B_{2u} + B_{3u} \quad (3.4)$$

3.2.2.5 Internal vibrations for SiO_4

Up to this point there was no need to consider the structure of a molecule in determining the symmetry of translations and rotations, but internal vibrations are closely connected to the particular arrangement of ions inside a molecule. In this case the molecular symmetry G_M is lowered to G_S which is then correlated to G . A new block containing the molecular symmetry and its correlation to G_S has to be added to the leftmost part of the correlation table. The rest of the table connecting G_S to G is similar to the cases already illustrated by Tabs. 3.2 and 3.3.

We will start by looking at the number and symmetry of the internal vibrations of a free $(\text{SiO})_4$ molecule. A molecular complex with N atoms has $3N - 5$ internal vibrations if the molecule is linear, and $3N - 6$ internal vibrations if the molecule is nonlinear. For the tetrahedral SiO_4 molecule ($N = 5$), $3 \times 5 - 6 = 9$ internal vibrations are expected (the 6 modes which were “discarded” are 3 translations and 3 rotations; these modes were already accounted for in Eqs. (3.3) and (3.4)). In order to determine the symmetry of the $3N-6$ internal vibrations, one has to first consider the symmetry of the total number of modes Γ_{tot} ($3N$) and determine the characters of the $3N \times 3N$ matrices of transformation of the molecule under all operations of the molecular group G_M . A table containing two lines is constructed (Tab. 3.5) such that the first line contains all the operations of symmetry of the group describing the free molecule and the second line contains the characters (traces) of the $3N \times 3N$ matrices of transformation for each particular operation of the group G_M . The derivation of the characters in Tab. 3.5 is discussed as follows

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\Sigma_d$
Γ_{tot}	15	0	-1	-1	3

Table 3.5 Characters describing the 15 modes of vibration of the tetrahedral SiO_4 molecule.

As a molecule can be seen as a separate collection of N atoms, each with 3 degrees of freedom (translations), the identity operator E is given by a $3N \times 3N$ diagonal matrix ($E_{ij} = \delta_{ij}$) whose trace is :

$$\chi(E) = \sum_{i=1}^{3N} \delta_{ii} = 3N \quad (3.5)$$

For SiO_4 , $N = 5$, which gives (second column in Tab. 3.5) :

$$\chi(E) = 3 \times 5 = 15 \quad (3.6)$$

The character χ_φ of a matrix describing a rotation of angle φ is given by :

$$\chi(\varphi) = (1 + 2\cos\varphi) \times p \quad (3.7)$$

where p is the number of atoms which do not change position under the rotations (the atoms on the axis of rotation). The character for C_3 (rotation of angle $2\pi/3$) is (third column in Tab. 3.5) :

$$\chi(C_3) = (1 + 2\cos(\frac{2\pi}{3})) \times p = (1 - 1) \times p = 0 \quad (3.8)$$

The character for C_2 (rotation of angle π) is :

$$\chi(C_2) = (1 + 2\cos(\pi)) \times p = (1 - 2) \times p = -p \quad (3.9)$$

Fig. 3.2 depicts a rotation of angle π and indicates that only one atom (atom #5) does not change its position under the rotation (while atom #1 permutes with atom #2, and atom #3 permutes with atom #4), i.e. in Eq. (3.8), $p = 1$ which gives (fourth column in Tab. 3.5) :

$$\chi(C_2) = -1 \quad (3.10)$$

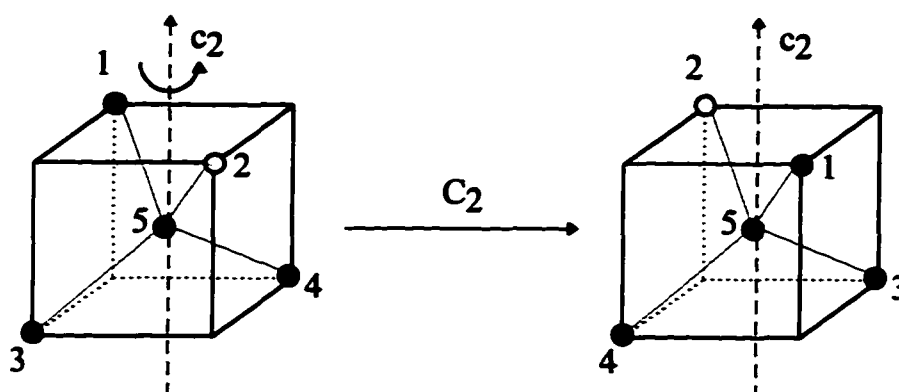


Figure 3.2 Rearrangement of atoms in a tetrahedral molecule ($N = 5$) after rotation of angle π .

The character $\chi(S_\varphi)$ of a matrix describing an improper rotation of angle φ is :

$$\chi(S_\varphi) = (-1 + 2 \cos \varphi) \times p \quad (3.11)$$

For an improper rotation of order 4, Eq. (3.11) leads to :

$$\chi(S_4) = (-1 + 2 \cos(\frac{2\pi}{4})) \times p = -p \quad (3.12)$$

Fig. 3.3 depicts an improper rotation S_4 (rotation of angle $2\pi/4$ followed by a reflection in the plane perpendicular to the axis of rotation) and shows that only atom #5 does not change its position under the improper rotation, while atoms 1 ÷ 4 permute as $P = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 3 & 4 & 2 & 1 \end{pmatrix}$. This leads to $p = 1$, i.e. (fifth column in

Tab. 3.5) :

$$\chi(S_4) = -1 \quad (3.13)$$

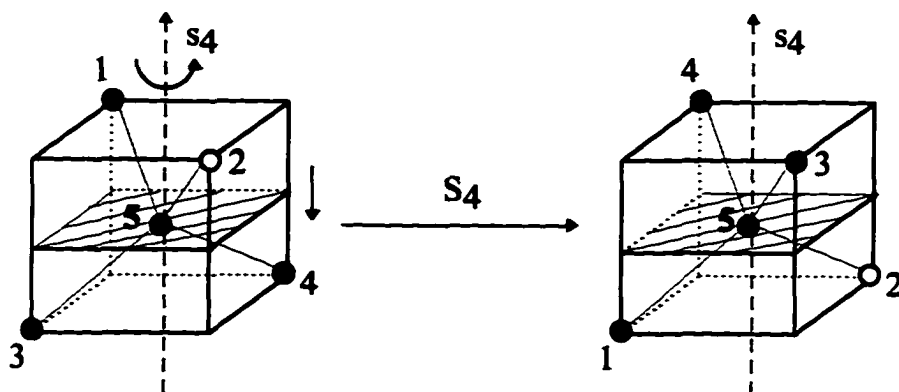


Figure 3.3 Rearrangement of atoms in a tetrahedral molecule ($N = 5$) after an improper rotation of angle $2\pi/4$ (S_4).

The character $\chi(\Sigma)$ under a reflection is :

$$\chi(\Sigma) = 1 \times p \quad (3.14)$$

Fig. 3.4 shows that for the chosen diagonal plane (σ_d) for SiO_4 , $p = 3$ (atoms #3, #4 and #5 do not change their position under the reflection), which gives the character in column 6, Tab. 3.5, using Eq. (3.14) as :

$$\chi(\Sigma_d) = 1 \times 3 = 3 \quad (3.15)$$

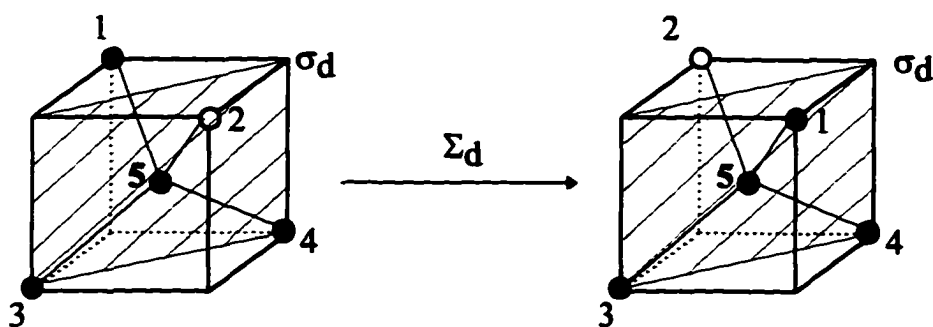


Figure 3.4 Rearrangement of atoms in a tetrahedral molecule ($N = 5$) after a reflection in a diagonal plane.

After all characters presented in Tab. 3.5 have been obtained, Γ_{tot} is decomposed in the irreducible representations of T_d by the standard method described in any group theory book (e.g. [7]) as :

$$\Gamma_{\text{tot}} = \sum_j a_j \Gamma_j \quad (3.16)$$

with

$$a_j = \frac{1}{\mathcal{N}} \chi_i(\Gamma_{\text{tot}}) \cdot \chi(\Gamma_{O_i}) \cdot m(O_i) \quad (3.17)$$

where Γ_{tot} is the structure to be decomposed, Γ_j are the irreducible representations (basis) of the molecular group, a_j are the integer coefficients of Γ_j (to be determined), $\mathcal{N}$ is the order of the group (total number of elements in the group), $\chi_i(\Gamma_{\text{tot}})$ is the character of Γ_{tot} under the operation O_i , $\chi(\Gamma_{O_i})$ is the character of representation Γ_j under the operation O_i , and $m(O_i)$ is the multiplicity of operation O_i . Applying Eqs. (3.16) - (3.17) to the particular case of a 5 atom tetrahedral molecule (as is the case of SiO_4) and using Tab. 3.5 (for $\chi_i(\Gamma_{\text{tot}})$) and the character table for the T_d group (for $\chi(\Gamma_{O_i})$ and $m(O_i)$), one obtains :

$$\Gamma_{\text{tot}} = a_1 A_1 + a_2 A_2 + a_3 E + a_4 T_1 + a_5 T_2 \quad (3.18)$$

where

$$a_1 = \frac{1}{24} (15 \cdot 1 \cdot 1 + 0 \cdot 1 \cdot 8 + (-1) \cdot 1 \cdot 3 + (-1) \cdot 1 \cdot 6 + 3 \cdot 1 \cdot 6) = 1 \quad (3.19)$$

$$a_2 = \frac{1}{24} (15 \cdot 1 \cdot 1 + 0 \cdot 1 \cdot 8 + (-1) \cdot 1 \cdot 3 + (-1) \cdot (-1) \cdot 6 + 3 \cdot (-1) \cdot 6) = 0 \quad (3.20)$$

$$a_3 = \frac{1}{24} (15 \cdot 2 \cdot 1 + 0 \cdot (-1) \cdot 8 + (-1) \cdot 2 \cdot 3 + (-1) \cdot 0 \cdot 6 + 3 \cdot 0 \cdot 6) = 1 \quad (3.21)$$

$$a_4 = \frac{1}{24} (15 \cdot 3 \cdot 1 + 0 \cdot 0 \cdot 8 + (-1) \cdot (-1) \cdot 3 + (-1) \cdot 1 \cdot 6 + 3 \cdot (-1) \cdot 6) = 1 \quad (3.22)$$

$$a_5 = \frac{1}{24}(15 \cdot 3 \cdot 1 + 0 \cdot 0 \cdot 8 + (-1) \cdot (-1) \cdot 3 + (-1) \cdot (-1) \cdot 6 + 3 \cdot 1 \cdot 6) = 3 \quad (3.23)$$

Eqs. (3.19) - (3.23) lead to :

$$\Gamma_{\text{tot}} = A_1 + E + T_1 + 3T_2 \quad (3.24)$$

After eliminating the 3 rotations (T_1) and 3 translations (T_2), we are left with the modes of internal vibration of a 5-atom tetrahedral molecule given by :

$$\Gamma_{\text{int}} = A_1 + E + 2T_2 \quad (3.25)$$

The 4 modes given by Eq. (3.25) are usually denoted as follows : the non-degenerate A_1 mode as ν_1 (totally symmetric tetrahedral stretching (breathing) mode); the double degenerate E mode as ν_2 (symmetric tetrahedral bending mode), the triple degenerate T_2 mode as ν_3 (anti-symmetric tetrahedral stretching mode) and the second the triple degenerate T_2 mode as ν_4 (anti-symmetric tetrahedral bending mode). The direction of oscillation of every atom in each of the four modes $\nu_1 \div \nu_4$ is depicted in [8]. Each of these 4 modes will be discussed in greater detail in Chapter 5. It should be noted that, as expected, the total dimensionality of the internal modes is $1 + 2 + 3 + 3 = 9$ ($= 3 \times 5 - 6$). The 4 modes of internal vibration given by Eq. (3.25) will appear in the leftmost part of the correlation table, and will be connected to the site symmetry G_S . The construction of the correlation table (Tab. 3.6) proceeds from now on in the typical manner previously described.

Tab. 3.6 shows that the symmetry of the 9×4 internal modes of vibration for the 4 SiO_4 molecules inside a forsterite unit cell is :

$$\Gamma_{\text{SiO}_4, C_s}^{\text{int}} = 6A_g + 3B_{1g} + 6B_{2g} + 3B_{3g} + 3A_u + 6B_{1u} + 3B_{2u} + 6B_{3u} \quad (3.26)$$

The symmetry of the 84 modes of vibration given by a unit cell of forsterite is obtained by adding Eqs. (3.1) $\div$ (3.4), (3.26) :

$$\Gamma_{\text{Mg}_2\text{SiO}_4}^{\text{tot}} = 11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g} + 10A_u + 14B_{1u} + 10B_{2u} + 14B_{3u} \quad (3.27)$$

n=4	f	t	T_d	$\rightarrow$		$\xrightarrow{\sigma(zx)}$		D_{2h}	$c_2(C_s)$	$c_2(C_s)$
				C_s	$c_2(C_s)$	$a_2(C_s)$	$a_2(C_s)$			
	4	1	A_1	A'	1	4		A_g B_{2g} B_{1u} B_{3u}	1 1 1 1	1 1 1 1
	8	2	E	A'	1	4		A_g B_{2g} B_{1u} B_{3u}	1 1 1 1	1 1 1 1
				A''	1	4		B_{1g} B_{3g} A_u B_{2u}	1 1 1 1	1 1 1 1
				A'	1	4		A_g B_{2g} B_{1u} B_{3u}	1 1 1 1	1 1 1 1
				A''	1	4		A_g B_{2g} B_{1u} B_{3u}	1 1 1 1	1 1 1 1
	12	3	T_2	A'	1	4		A_g B_{2g} B_{1u} B_{3u}	1 1 1 1	1 1 1 1
				A'	1	4		A_g B_{2g} B_{1u} B_{3u}	1 1 1 1	1 1 1 1
				A''	1	4		B_{1g} B_{3g} A_u B_{2u}	1 1 1 1	1 1 1 1
				A''	1	4		B_{1g} B_{3g} A_u B_{2u}	1 1 1 1	1 1 1 1
	12	3	T_2	A'	1	4		A_g B_{2g} B_{1u} B_{3u}	1 1 1 1	1 1 1 1
				A'	1	4		A_g B_{2g} B_{1u} B_{3u}	1 1 1 1	1 1 1 1
				A''	1	4		B_{1g} B_{3g} A_u B_{2u}	1 1 1 1	1 1 1 1
				A''	1	4		B_{1g} B_{3g} A_u B_{2u}	1 1 1 1	1 1 1 1

Table 3.6 $T_d \rightarrow C_s \rightarrow D_{2h}$ correlation table for the 4 x 9 (SiO_4) internal vibrations

Tab. 3.7 summarizes the types (translations, rotations, internal vibrations) of the 84 modes of vibration given by a unit cell of forsterite, as they appear in each representation in D_{2h} :

D_{2h} representations	Total	Translations	Acoustic	Rotations	Internal vibrations
A_g	11	4		1	6
B_{1g}	7	2		2	3
B_{2g}	11	4		1	6
B_{3g}	7	2		2	3
A_u	10	5		2	3
B_{1u}	14	6	1	1	6
B_{2u}	10	4	1	2	3
B_{3u}	14	6	1	1	6

Table 3.7 Types of the 84 modes of vibration of a unit cell of forsterite, grouped according to the representations in D_{2h} .

The symmetry of the 81 optical phonon modes characterizing a unit cell of forsterite is given by Eq. (3.28) which is obtained by subtracting the three acoustic modes (the modes having as basis the 3 translations x , y and z , i.e. B_{3u} , B_{2u} and B_{1u} , respectively) from Eq. (3.27) :

$$\Gamma_{\text{Mg}_2\text{SiO}_4}^{\text{opt. phonon}} = 11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g} + 10A_u + 13B_{1u} + 9B_{2u} + 13B_{3u} \quad (3.28)$$

It should be stressed that all of the above was derived in $Pnma$ notation. The correlation between $Pnma$ and other crystal notations is obtained by the appropriate permutation of axes and shown in Tab. 3.1. As an example, the complete correlation between $Pnma$ ($a = x = 10.22 \text{ \AA}$, $b = y = 5.99 \text{ \AA}$ and $c = z =$

4.73 Å) and $Pbnm$ ($a = x = 4.73$ Å, $b = y = 10.22$ Å and $c = z = 5.99$ Å), another widely used crystal notation [9] is given in Tab. 3.8 :

Represent- tation in $Pnma$ (D_{2h})	Basis in $Pnma$	Crystal axes in $Pnma$	Crystal axes in $Pbnm$	Basis in $Pbnm$	Represent-tation in $Pbnm$ (D_{2h})
	x y z	a b c	b c a	y z x	
A_g	x^2, y^2, z^2	a^2, b^2, c^2	a^2, b^2, c^2	x^2, y^2, z^2	A_g
B_{1g}	xy	ab	bc	yz	B_{3g}
B_{2g}	xz	ac	ba	xy	B_{1g}
B_{3g}	yz	bc	ca	xz	B_{2g}
A_u	-	-	-	-	A_u
B_{1u}	z	c	a	x	B_{3u}
B_{2u}	y	b	c	z	B_{1u}
B_{3u}	x	a	b	y	B_{2u}

Table 3.8 Correlation between $Pnma$ and $Pbnm$ crystal notations.

3.2.2.6 Selection rules

Knowledge of the symmetry of the energy levels of a system allows one to determine the selection rules, i.e. the conditions under which a transition between two given states is permitted. The basic relation which determines if a specific transition is possible is :

$$\langle \Psi_i | \hat{\mathbf{O}} | \Psi_f \rangle = \sum_j a_j \Gamma_j \supset \Gamma_1 \quad (3.29)$$

where $|\Psi_i\rangle$ and $|\Psi_f\rangle$ are the initial and final, respectively, wavefunctions describing the system which undergoes the transition, and $\hat{\mathbf{O}}$ is the operator inducing the transition $i \rightarrow f$. The symmetry of different operators responsible for various types of transitions is given in Appendix A.4. The left-hand side integral is in fact the product of the three representations having as basis $|\Psi_i\rangle$, $|\Psi_f\rangle$ and $\hat{\mathbf{O}}$, in the group describing the system. The product can be decomposed in the representations of the group $\sum_j a_j \Gamma_j$ (see Eqs. (3.16), (3.17)). The transition $i \rightarrow f$ is allowed only if the system remains invariant under all operations of the group, i.e. if and only if $\sum_j a_j \Gamma_j$ contains the totally symmetric representation Γ_1 ($\sum_j a_j \Gamma_j \supset \Gamma_1$).

In the case of normal vibrations (phonons), assuming that the system is initially in the ground state (ex. Stokes process), thus that $|\Psi_i\rangle$ is totally symmetric, the left-hand side of Eq. (3.29) is reduced to the product $\langle \hat{\mathbf{O}} | \Psi_f \rangle$. Using the orthogonality of a group's representations ($\Gamma_i \Gamma_j = \delta_{ij}$) it can be shown that the transition to the one-phonon mode $|\Psi_f\rangle$ is allowed only if the operator producing the transition and $|\Psi_f\rangle$ have the same symmetry, i.e. belong to the same representation. For example, as shown in Appendix A.4, IR active phonons belong to representations which have as basis x , y or z (cartesian coordinates), while Raman active phonons belong to representations which have as basis x^2 , xy , yz ,... (squares of coordinates). The basis of a given representation X also gives the geometry in which a phonon of the same symmetry X is obtained. For example, in

a D_{2h} group, a B_{1g} Raman active mode can be excited only in a B_{1g} configuration (i.e. using xy or yx linearly polarized incident and scattered light, respectively), while a B_{3u} IR active mode is excited in a B_{3u} configuration (i.e. using x-polarized light). The table of characters for D_{2h} shows that all “g” (even) modes are Raman active, A_u is inactive, and all the other “u” (odd) modes are IR active.

3.2.3 Experimental results and force constant calculations for the Mg_2SiO_4 phonon spectrum

Eq. (3.28) together with Tab. 3.8 predict the appropriate experimental configurations required for obtaining the 36 Raman active Mg_2SiO_4 modes. The complete room temperature Raman spectrum [9] is shown in Fig. 3.5, in $Pnma$ crystal notation. The scattering configuration used for obtaining each set of phonon modes is given in Porto’s notation $x(yz)t$ (see Section 2.6) where (yz) gives the symmetry of the component of the Raman tensor responsible for the excitation of the observed phonon mode and, at the same time, the symmetry of the excited phonon mode for a one phonon process (see Section 3.2.2.6). The energies and symmetries of the Raman active phonon modes for Mg_2SiO_4 are summarized in Tab 3.9 [9], in $Pnma$ notation. Additional information on the energy and symmetry of the 35 IR active phonons is given in Ref. 9, in $Pbnm$ notation. Tab. 3.8 can be used to express the symmetry of all measured phonon modes in $Pnma$ notation.

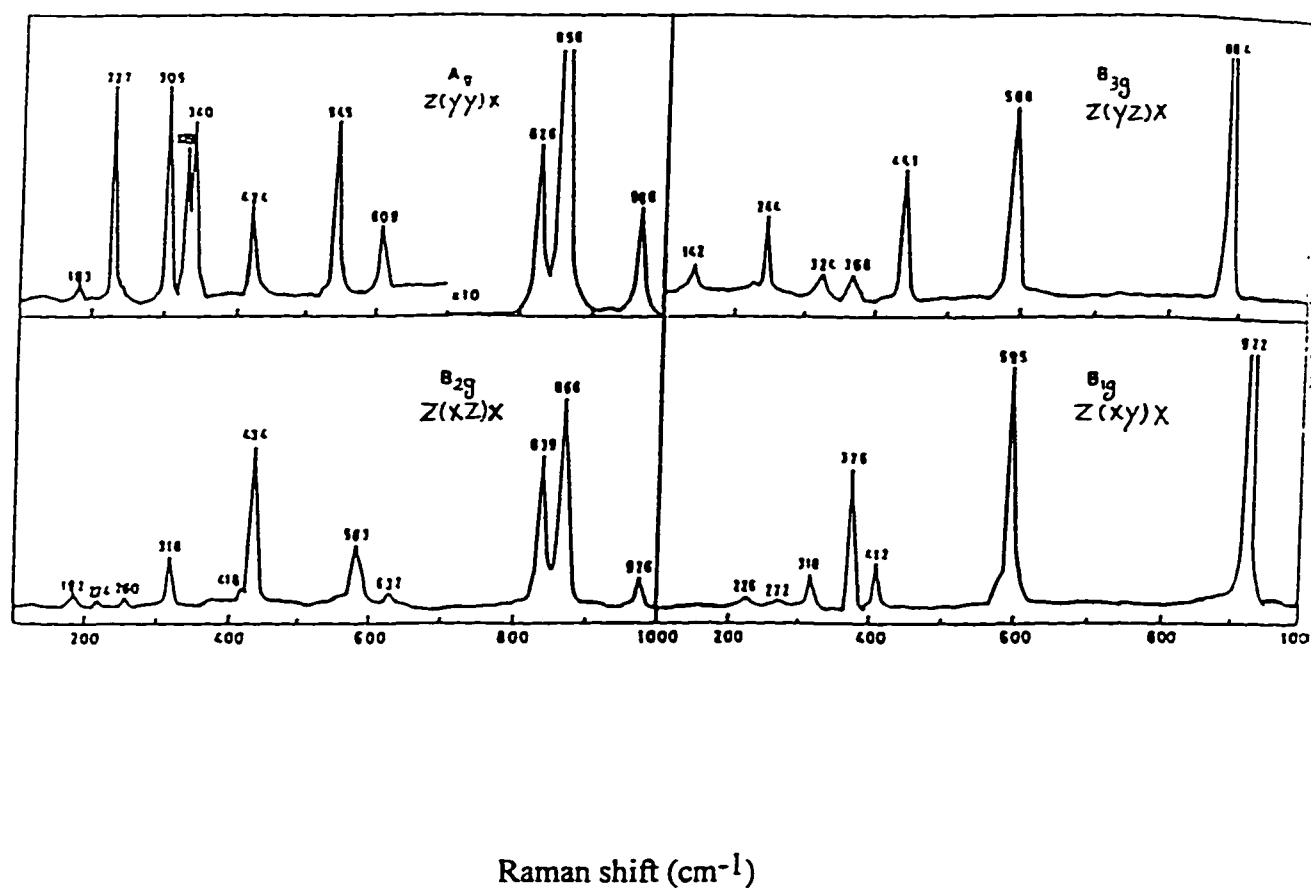


Figure 3.5 Polarized Raman spectra of forsterite. The scattering configurations and representations of D_{2h} are given in $Pnma$ notation.

Mode Symmetry	Experimental (cm ⁻¹)	Calculated (RI) (cm ⁻¹)	Assignment	Mode Symmetry	Experimental (cm ⁻¹)	Calculated (RI) (cm ⁻¹)	Assignment
A _g	966	958	v ₃	B _{2g}	976	961	v ₃
	856	888	v ₃		866	891	v ₃
	826	837	v ₁		839	846	v ₁
	609	606	v ₄		632	629	v ₄
	546	535	v ₄		583	583	v ₄
	424	414	v ₂		434	412	v ₂
	340	358	R(SiO ₄ :z)		418	396	R(SiO ₄ :z)
	329	287	T(MgII:y)		318	316	T(MgII:y)
	305	269	T(MgII, SiO ₄ :x)		260	276	T(MgII, SiO ₄ :x)
	227	228	T(MgII, SiO ₄ :y)		224	230	T(MgII, SiO ₄ :x)
183	157	T(MgII, SiO ₄ :x)	192	180	T(MgII, SiO ₄ :y)		
B _{1g}	922	894	v ₃	B _{3g}	884	891	v ₃
	595	580	v ₄		588	591	v ₄
	412	411	v ₂		441	451	v ₂
	376	367	R(SiO ₄ :z)		368	362	R(SiO ₄ :y)
	318	304	R(SiO ₄ :y)		324	306	R(SiO ₄ :x)
	272	277	T(MgII:z)		244	267	T(SiO ₄ :z)
	226	234	T(SiO ₄ :z)		142	166	T(MgII:z)
R : rotational lattice modes, T : translational lattice modes.							

Table 3.9 Experimental and theoretical phonon frequencies of the Raman spectrum in forsterite (from Ref. 9), in *Pnma* notation.

It is interesting to note from Tab. 3.9 that there are three groups of phonons arranged according to the type of motion they describe as follows : the highest frequency phonons ($\sim 400 \div 960 \text{ cm}^{-1}$) are due to internal vibrations of the SiO_4 tetrahedron; the second group situated at intermediate frequencies ($\sim 350 \div 400 \text{ cm}^{-1}$) represent rotations of the SiO_4 tetrahedron as a whole; and, finally, the lowest frequency group ($\sim 150 \div 350 \text{ cm}^{-1}$) describes translational modes of Mg ions and of SiO_4 tetrahedra.

Based on the energies of the experimentally measured Mg_2SiO_4 phonon spectrum, force constant calculations were made in different models [9]. In the rigid-ion (RI) model the calculated intra-tetrahedral force constants are :

$$k_1(\text{Si-O}) = 3.75 \text{ mdyn/\AA}, \quad k_2(\text{O-O}) = 0.716 \text{ mdyn/\AA} \quad (3.30)$$

where k_1 is the Si-O force constant and k_2 is the mean O-O force constant. These values will be compared with those obtained for a $(\text{CrO}_4)^{-4}$ tetrahedron (Section 5.6) in order to estimate the local changes induced by the $\text{Cr}^{4+} \rightarrow \text{Si}^{4+}$ substitution.

3.3 The Cr^{4+} ion. Electronic structure and symmetry

Chromium is a transition metal situated in the 4B group, IVth period of the periodic table, with $Z = 24$ and atomic weight $A = 52.01 \text{ m.u.}$ Its natural isotopes and their relative abundance are (Ref. 10, pag. B236) : Cr_{24}^{50} - 4.35%, Cr_{24}^{52} - 83.79%, Cr_{24}^{53} - 9.5% and Cr_{24}^{54} - 2.36%. The ground state electronic configuration for Cr is (Ref. 10, pag. B236):

$$\text{Cr} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5 \quad (3.31)$$

Chromium has one s and five d valence electrons and may have the following oxidation numbers : Cr^{2+} , Cr^{3+} , Cr^{4+} , Cr^{6+} . As our studies focus on the $\text{Cr}^{4+} \rightarrow \text{Si}^{4+}$ substitution in a $(\text{SiO}_4)^{-4}$ tetrahedron, we will first analyze what are the

conditions under which Cr^{4+} can display tetrahedral coordination. First, the symmetry of the molecular orbitals which support a tetrahedral coordination is derived.

In a tetrahedral coordination (of type XY_4) the central ion X forms bonds along the diagonals of the tetrahedron, i.e. X has to have four orbitals r_i , $i = 1 \div 4$ directed towards the four ligands Y as shown in Fig. 3.6.

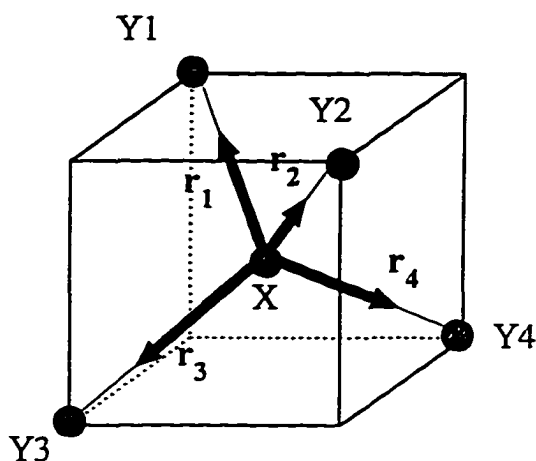


Figure 3.6 Tetrahedrally coordinated X ion. r_i , $i = 1 \div 4$ are the molecular orbitals which belong to X, and tetrahedrally coordinate the ligands Y.

In order to determine what types of the 4 orbitals ensure tetrahedral coordination, one has to investigate how does the set $\{r_i\}$ change under the operations of T_d .

Let Γ_4 be the representation which describes the 4 orbitals r_i in T_d . The characters for Γ_4 are given in Tab. 3.10 and were obtained as follows :

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_4	4	1	0	0	2

Table 3.10 Characters describing the four σ orbitals of the central ion, for tetrahedral coordination.

The transformation of the system of four orbitals r_i , under the identity operator E is described by a diagonal unitary 4×4 matrix, with trace 4 (i.e. $\chi(E) = 4$). $\chi(C_3)$ is obtained as shown by Eq. (3.8), leading to $\chi(C_3) = 0$. $\chi(C_2) = 0$ and $\chi(S_4) = 0$ are given by Eq. (3.9) and Eq. (3.12), respectively, with $p = 0$, as all four orbitals permute under c_2 and s_4 . Finally, $\chi(\Sigma_d) = 2$, as shown by Eq. (3.14), where $p = 2$ is the number of orbitals contained in the diagonal plane σ_d . Γ_4 is decomposed in the irreducible representations of T_d as shown by Eq. (3.18) leading to :

$$\Gamma_4 = A_1 + T_2 \quad (3.32)$$

The table of characters for T_d (Appendix A.3) gives as basis for A_1 $x^2 + y^2 + z^2 \equiv r^2$, i.e. an s orbital, and for T_2 (x, y, z) , i.e. three p orbitals or (xy, xz, yz) , i.e. three d orbitals. Thus, in order to achieve tetrahedral coordination, the central ion X has to have on the last electronic shell at least one s and three p electrons (sp^3 hybridization) or one s and three d electrons (sd^3 hybridization).

The six Cr electrons on the last shell $n = 4$, given by Eq. (3.31), will participate to the tetrahedral bond as follows : one s and three d electrons will be used to construct the σ bonds r_i as shown in Fig. 3.9. Although the four electrons are shared with the O^{2-} ligand, the bond can be considered as having strong ionic character, case in which Cr is “stripped” of the 4 electrons becoming Cr^{4+} . The remaining two d valence electrons will be responsible for the optical properties of Cr^{4+} ions and give a d^2 configuration to the Cr^{4+} ion.

3.3.1 Two d electronic structure of Cr^{4+} . Free ion case

In order to explain the optical properties of a d^N (N d electrons) system, one has to start by constructing the energy diagram of the multi-electronic free ion. The electronic Hamiltonian for a free ion can be written as :

$$H = \sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right) + \frac{1}{2} \sum_{i,j} \frac{e^2}{r_{ij}} + \sum_i \xi_{n_i, l_i} \vec{l}_i \vec{s}_i + \sum_{i,j} J_{ij} \vec{s}_i \vec{s}_j \quad (3.33)$$

where the first term represents the energy of the i^{th} electron in the field of a nucleus of charge Ze (a screening factor due to the filled electronic shells can be taken into account), m is the mass of the electron and r_i is the electron-nucleus distance; the second term represents the electron-electron repulsion, where

$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the i^{th} and j^{th} electrons; the third term represents the spin-orbit interaction and the last term represents the spin-spin interaction.

The total angular momentum $\vec{J}$ for an N -multielectronic system, can be calculated in two distinct ways, depending on the relative magnitude of the electron-electron and spin-interaction terms in Eq. (3.33). If the electron-electron repulsion is stronger than the spin-orbit and spin-spin interactions, as is the case for light, transition metal atoms, the $\vec{L} - \vec{S}$ (Russel-Saunders) coupling is applied (Ref. 11, pag. 421). In the Russel-Saunders coupling $\vec{J} = \vec{L} + \vec{S}$ where $\vec{L} = \sum_{i=1}^n \vec{l}_i$,

total orbital angular momentum, and $\vec{S} = \sum_{i=1}^n \vec{s}_i$, total spin. $\vec{l}_i$ and $\vec{s}_i$ are the orbital angular momentum and the spin for the i^{th} electron, respectively. If, on the other hand, the spin-orbit and/or spin-spin interactions are stronger than the electron-electron repulsion, as is the case for heavy, rare-earth atoms, the $\vec{J} - \vec{J}$ coupling is applied (Ref. 11, pag. 430). In the $\vec{J} - \vec{J}$ coupling $\vec{J} = \sum_{i=1}^n \vec{j}_i$ where $\vec{j}_i = \vec{l}_i + \vec{s}_i$ is the total angular momentum for the i^{th} electron.

Cr^{4+} is a transition metal ion described by the Russel-Saunders coupling. As was shown in Section 3.3 Cr^{4+} is a d^2 system. For a d^2 system we have two d valence electrons $N = 2$, $l_{1\text{max}} = l_{2\text{max}} = 2$ (d electrons, i.e. $l = 2$) and $s_{1\text{max}} =$

$s_{2\max} = 1/2$ (electronic spin). This leads to the following values for the total orbital angular momentum L : $|L_{\max}| = l_{1\max} + l_{2\max} = 2 + 2 = 4$ and $|L_{\min}| = l_{1\max} - l_{2\max} = 2 - 2 = 0$, i.e. $|L| = 4, 3, 2, 1, 0$, which shows that the multi-electronic structure for a free d^2 ion contains : S ($L=0$), P ($L=1$), D ($L=2$), F ($L=3$) and G ($L=4$) states. Capital letters are used for a multi-electronic structures, as opposed to lower-case letters used for one-electron configurations. Each of the above mentioned L -states are M_L degenerate due to the orbital angular momentum, with $M_L = 2L+1$ (ex. a P-state is triple degenerate, an F-state is 7-times degenerate, etc. - see Tab. 3.11). The total spin is computed in a similar manner, leading to $|S_{\max}| = s_{1\max} + s_{2\max} = 1/2 + 1/2 = 1$ and $|S_{\min}| = s_{1\max} - s_{2\max} = 1/2 - 1/2 = 0$, i.e. $|S| = 1, 0$. The degeneracy due to the total spin is $M_S = 2S+1$. For example, an $S = 0$ state is nondegenerate, $M_S=1$, while an $S=1$ state is triple degenerate, $M_S = 2 \times 1 + 1 = 3$. Using the Russel-Saunders spectroscopic notation for an electronic state : $^{M_S} X_L$, where X is the state with orbital angular momentum L (see Tab. 3.11) one can conclude that a d^2 system contains only $M_S=2 \times 1 + 1 = 3$ (triplet states) and $M_S=2 \times 0 + 1 = 1$ (singlet states) with total angular momentum $X = S, P, D, F$ and G . At this point, the spin multiplicity for each of the above mentioned states is unknown.

L	0	1	2	3	4
Name (X)	S	P	D	F	G
Degeneracy M_L	1	3	5	7	9

Table 3.11 Notations and degeneracy for different orbital angular momentum states.

Using Pauli's exclusion principle, a simple diagram can be constructed for determining the spin multiplicity for the above multielectronic d^2 states. The two d electrons have to be in (l, s) states which differ either in terms of orbital angular momentum, l or in terms of spin, s . As each electron can have spin $+1/2$ (+ spin-state) or $-1/2$ (- spin-state) any combination of the two d electrons can be represented as the pair (l_1, l_2) called a "microstate", where each l_i can have superscript "+" or "-". The constructed diagram will contain all possible combinations of pairs of l_i 's for each given L , $|L|$ from 0 to 4. For example, if $L=4$, the only possible combination of electrons to give rise to such a state is 2^+2^- (as 2^+2^+ and 2^-2^- are not allowed by Pauli's exclusion principle). On the other hand, $L=2$ can be obtained from different combinations of $2^{\pm}0^{\pm}$ or $1^{\pm}1^{\pm}$. Tab. 3.12 calculates all $l_1^{\pm}l_2^{\pm}$ combinations for a d^2 multi-electronic configuration and gives the spin degeneracy for each state as follows: one S state (^1S), three P states (^3P), one D state (^1D), three F states (^3F) and one G state (^1G). The notations (name) for each state has been determined according to the degeneracy as shown in Tab. 3.11. Although the energies of these states which describe the free Cr^{4+} ion in the Russel-Saunders approximation are not known (nor is their order in energy scale), the ground state can be determined using Hund's rule which states that "The ground state is the state with maximum spin; if there are several states with maximum spin, the ground state is the state with maximum orbital angular momentum". According to Hund's rule the ground state for Cr^{4+} is ^3F .

In order to find the energy of the multi-electronic states, the last two terms containing spin interactions in Eq. (3.33) are neglected at this stage. The Hamiltonian of the unperturbed system (first term in Eq. (3.33)) is similar to that of a hydrogen-like atom. As a consequence, the basis one-electron wavefunctions can be written as the product of a radial function and a spherical harmonic :

$$\Psi_{nlm}(\vec{r}_i) = R_{nl}(r_i) \cdot Y_{lm}(\theta, \varphi) \quad (3.34)$$

L	Possible combinations for pairing 2 <i>d</i> electrons								
	S=1 ($l_1^+ l_2^+$)		S=0 ($l_1^+ l_2^-$)					S=-1 ($l_1^- l_2^-$)	
4			$2^+ 1^-$						
3	$2^+ 1^+$		$2^+ 0^-$	$2^+ 1^+$				$2^+ 1^-$	
2	$2^+ 0^+$		$2^+ -1^-$	$2^+ 0^+$	$1^+ 1^-$			$2^+ 0^-$	
1	$2^+ -1^+$	$1^+ 0^+$	$2^+ -1^-$	$2^+ -1^+$	$1^+ 0^-$	$1^+ 0^+$		$2^+ -1^-$	$1^+ 0^-$
0	$2^+ -2^+$	$1^+ -1^+$	$2^+ -2^-$	$2^+ -2^+$	$1^+ -1^-$	$1^+ -1^+$	$0^+ 0^-$	$2^+ -2^-$	$1^+ -1^-$
-1	$-2^+ 1^+$	$-1^+ 0^+$	$-2^+ 1^-$	$-2^+ 1^+$	$-1^+ 1^-$	$-1^+ 0^+$		$-2^+ 1^-$	$-1^+ 0^-$
-2	$-2^+ 0^+$		$-2^+ 0^-$	$-2^+ 0^+$	$-1^+ 0^-$			$-2^+ 0^-$	
-3	$-2^+ -1^+$		$-2^+ -1^-$	$-2^+ -1^+$				$-2^+ -1^-$	
-4			$-2^+ -1^-$						
Degeneracy M_L (No. of states)	7	3	9	7	5	3	1	7	3
Name	F	P	G	F	D	P	S	F	P

Table 3.12 Types and multiplicity of the electronic states for a d^2 system.

It should be stressed that the radial function is not necessary that of an atomic orbital (hydrogen-like). For a two-electron system, the energy due to the electron-electron interaction is :

$$W^{(1)} = \langle \Psi_{nlm} \left| \frac{e^2}{r_{12}} \right| \Psi_{nlm} \rangle \quad (3.35)$$

where, Ψ_{nlm} is the total wavefunction given by Eq. (3.34) and r_{12} is the distance between the two valence d electrons. The reciprocal of r_{12} can be expanded in terms of spherical harmonics [12] as :

$$\frac{1}{r_{12}} = 4\pi \sum_k \frac{1}{2k+1} \cdot \frac{r_{<}^k}{r_{>}^{k+1}} \sum_{q=-k}^k (-1)^q Y_{k,q}(\theta_1, \varphi_1) Y_{k,-q}(\theta_2, \varphi_2) \quad (3.36)$$

where $r_{<}$ is the lesser and $r_{>}$ is the greater of r_1 and r_2 . The energies of the multielectronic states for a d^N system can be expressed in terms of three Slater integrals (Slater-Condon parameters) cf. Ref. 12, pag. 64 : F^0 , F^2 and F^4 , where F^k is defined as :

$$F^k(dd) = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_d^2(r_1) R_d^2(r_2) \frac{r_{<}^k}{r_{>}^{k+1}} \quad (3.37)$$

with $R_d(r)$ is the radial part of the wavefunction. The three Slater integrals used for d electrons are renormalized as :

$$F_0 = F^0, \quad F_2 = \frac{1}{49} F^2, \quad F_4 = \frac{1}{144} F^4 \quad (3.38)$$

In a completely equivalent form, the energies of the multielectronic d levels for a free ion can be expressed in terms of Racah A, B and C parameters defined as :

$$\begin{aligned} A &= F_0 - 49F_4 \\ B &= F_2 - 5F_4 \\ C &= 35F_4 \end{aligned} \quad (3.39)$$

The dependence of the energies of the multielectronic d states on the A, B and C Racah parameters are tabulated in Ref. 14, pag. 254. The energies of the multielectronic states of a free d^2 ion given by Tab. 3.12 are :

$$\begin{aligned}
{}^3F &= A - 8B \\
{}^3P &= A + 7B \\
{}^1G &= A + 4B + 2C \\
{}^1D &= A - 3B + 2C \\
{}^1S &= A + 14B + 7C
\end{aligned} \tag{3.40}$$

As we are interested in the optical transitions, i.e. in the energy difference between each state and the ground ${}^3F$ state, the values of the energy for the multielectronic levels given by Eq. (3.40) are renormalized by subtracting from each the value of the ${}^3F$ level :

$$\begin{aligned}
{}^3F &= 0 \\
{}^3P &= 15B \\
{}^1G &= 12B + 2C \\
{}^1D &= 5B + 2C \\
{}^1S &= 22B + 7C
\end{aligned} \tag{3.41}$$

By dividing Eqs. (3.41) by B, the Energy-to-B ratio can be expressed in terms of the C/B variable as :

$$\begin{aligned}
(E / B)_{3F} &= 0 \\
(E / B)_{3P} &= 15 \\
(E / B)_{1G} &= 12 + 2 \cdot (C / B) \\
(E / B)_{1D} &= 5 + 2 \cdot (C / B) \\
(E / B)_{1S} &= 22 + 7 \cdot (C / B)
\end{aligned} \tag{3.42}$$

The dependence of the energies on the C/B ratio given by Eqs. (3.42) is graphically depicted in Fig. 3.7.

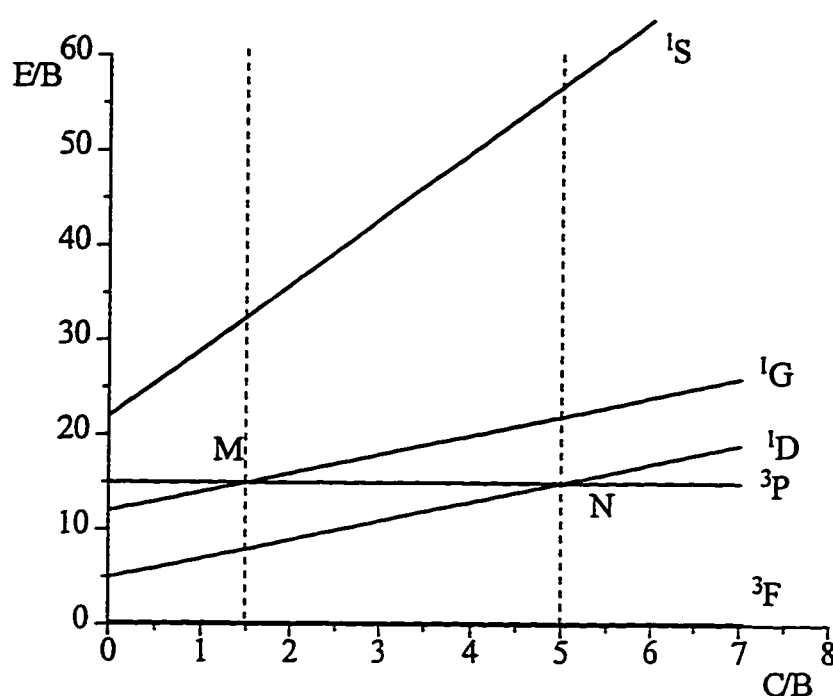


Figure 3.7 Dependence of the energy to B ratio on C/B for the multielectronic states of a d^2 system.

Fig. 3.7 shows the following : the ^3P state does not depend on C/B; the intersections between different states occur at $C/B = 1.5$ (point M) and $C/B = 5$ (point N). The ascending order in energy scale of the multielectronic states is :

- a) if $0 < C/B < 1.5$, the order is ^3F , ^1D , ^1G , ^3P , ^1S .
- b) if $1.5 < C/B < 5$, the order is ^3F , ^1D , ^3P , ^1G , ^1S .
- c) if $C/B > 5$, the order is ^3F , ^3P , ^1D , ^1G , ^1S .

If $C/B = 1.5$, the ^3P and ^1G states coincide. If $C/B = 5$, the ^3P and ^1D states coincide. The B and C values for free ions can be found in different tables. It can be shown (Ref. 12, pag. 106) that for transition metal ions in the iron group ($3d$) C/B has almost constant value, $C/B \sim 4.2 \div 4.9$ such that case b) applies and the ascending order of the multielectronic states of a free d^2 ion is : ^3F , ^1D , ^3P ,

$^1G, ^1S$. The B and C values for free Cr^{4+} ions are (Ref. 13, pag. 164) : $B = 1039 \text{ cm}^{-1}$, $C = 4238 \text{ cm}^{-1}$.

3.3.2 Cr^{4+} ion in a crystal field. Tanabe-Sugano diagrams

When an ion is doped into a lattice, the effective crystal field created by the lattice acts as a perturbation and displaces or removes the degeneracy of the electronic states of the free ion. The crystal field appears as an additional term (H_C) in the electronic Hamiltonian given by Eq. (3.33). Two extreme cases can be considered :

1) **Weak field approximation.** This is the case when the crystal field is weaker than the electron-electron interaction, but stronger than the spin-orbit term. In such a situation one first constructs the **multielectronic** states for the free ion as shown in Section 3.3.1 and acts with the crystal field on these states. The multielectronic states split due to the crystal field.

2) **Strong field approximation.** This is the case when the crystal field is stronger than the electron-electron interaction. In such a situation one first acts with the crystal field on the **electronic** states of the free ion (d orbitals). The crystal field partially removes the degeneracy of the 5-time degenerate d orbitals. It will be shown that a cubic field splits a d state into a double degenerate e level and a triple degenerate t_2 level (lower case is used to denote one-electron configurations). The electron-electron repulsion then acts on the e and t_2 states.

As the above mentioned extreme cases describe the same system, it is only natural that they are correlated and that a continuous transition can be made from the weak to the strong field although the first derivative of the energy can be discontinuous [12]. The dependence of the position of electronic levels on the strength of the crystalline field Dq and on B and C Racah parameters are called

Tanabe-Sugano diagrams. Such diagrams were calculated for different d^N systems [12]. The d^2 Tanabe-Sugano diagram is discussed in more detail as follows.

1) Weak field approximation.

The preferential “surrounding” (crystal field) symmetry for transition metal ions is O_h or T_d cubic fields depicted in Fig. 3.8. As the character tables for T_d and O (group of rotations) are identical, and as O_h can be written as the direct product between O and the group inversion C_i as $O_h = O \times C_i$ (see Appendix A.3), in order to find out how do the multielectronic states given by Eq. (3.41) (weak field approximation) split under a cubic field it is enough to analyze how does the rotation group O act on these states.

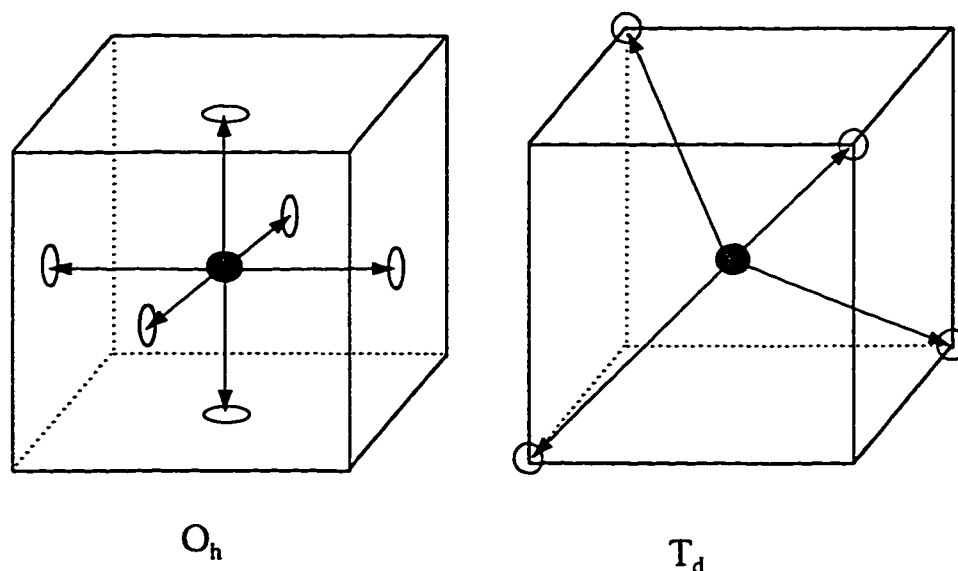


Figure 3.8 Octahedral (O_h) and tetrahedral (T_d) crystal field surroundings. The black dot represents the central ion and the white dots represent the ligands.

We further analyze what is the effect of a T_d or O_h set of ligands as the ones shown in Fig. 3.8 on the multi-electronic levels of a d^2 ion, by computing the

splitting of these states under the operations of the O group. Since all operations of O are rotations C_α of different azimuthal angles $2\pi/\alpha$, and since the angular dependence of the wavefunctions of the central ion is given by spherical harmonics

$$Y_{lm}(\theta, \varphi) \sim P_l^m(\cos\theta)e^{im\varphi} \quad (3.43)$$

where $P_l^m(\cos\theta)$ are associated Legendre polynomials, independent of the azimuthal angle φ , C_α rotations will act only on the $e^{im\varphi}$ term. For a given orbital angular momentum L, the magnetic quantum number M takes all integer values from -L to L, i.e. the azimuthal part of the wavefunction for an state with given L can be written as the $2L+1$ dimensional vector :

$$\Phi_i(\varphi) = \begin{pmatrix} e^{iL\varphi} \\ e^{i(L-1)\varphi} \\ e^{i(L-2)\varphi} \\ \dots \\ e^{-iL\varphi} \end{pmatrix} \quad (3.44)$$

A counter clockwise rotation C_α changes the angle φ into $\varphi+\alpha$, such that the final state achieved after the rotation can be written as the $2L+1$ dimensional vector :

$$\Phi_f(\varphi) = \begin{pmatrix} e^{iL(\varphi+\alpha)} \\ e^{i(L-1)(\varphi+\alpha)} \\ e^{i(L-2)(\varphi+\alpha)} \\ \dots \\ e^{-iL(\varphi+\alpha)} \end{pmatrix} \quad (3.45)$$

The $(2L+1) \times (2L+1)$ diagonal matrix describing the rotation C_α connecting the initial and final states given by Eqs. (3.44) - (3.45) is :

$$M_{\alpha} = \begin{pmatrix} e^{iL\alpha} & 0 & \dots & 0 \\ 0 & e^{i(L-1)\alpha} & \dots & 0 \\ \dots & \dots & \dots & 0 \\ 0 & 0 & 0 & e^{-iL\alpha} \end{pmatrix} \quad (3.46)$$

The trace of the matrix of transformation given by Eq. (3.46) is :

$$\Gamma(\alpha) = \sum_{M=-L}^L e^{iM\alpha} = \begin{cases} \frac{\sin((L+1/2)\alpha)}{\sin(\alpha/2)} & \alpha \neq 0 \\ 2L+1 & \alpha = 0 \end{cases} \quad (3.47)$$

In order to determine the effect of the group of rotations on a given state L , one has to construct a table similar to Tab. 3.5, with the first line containing the operations of the group O , and the second line contains the trace of the matrix of transformation M_{α} for the L -state under each operation of O , as given by Eq. (3.47).

The multielectronic states of a d^2 system split in a cubic field as follows :

a) ^1S state ($L = 0, M = 0$).

O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$
Γ_S	1	$\frac{\sin((1/2) \times 2\pi/3)}{\sin(1/2 \times 2\pi/3)}$ = 1	$\frac{\sin((1/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ = 1	$\frac{\sin((1/2) \times 2\pi/4)}{\sin(1/2 \times 2\pi/4)}$ = 1	$\frac{\sin((1/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ = 1

Table 3.13 Characters of transformation of an S state under the operations of O .

Tab. 3.13 shows that all characters are 1, i.e. $\Gamma_S = A_1$ in O or T_d . As the representations preserve the parity of the original states, ("g", for d states), $\Gamma_S = A_{1g}$ in O_h . In conclusion, an S state becomes A_1 or A_{1g} in a cubic field.

b) ^3P state ($L = 1, M = -1, 0, 1$).

O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$
Γ_P	$2 \times 1 + 1$ $= 3$	$\frac{\sin((3/2) \times 2\pi/3)}{\sin(1/2 \times 2\pi/3)}$ $= 0$	$\frac{\sin((3/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ $= -1$	$\frac{\sin((3/2) \times 2\pi/4)}{\sin(1/2 \times 2\pi/4)}$ $= 1$	$\frac{\sin((3/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ $= -1$

Table 3.14 Characters of transformation of a P state under the operations of O.

Tab. 3.14 shows that. $\Gamma_P = T_1$ in O or T_d (see Appendix A.3) and $\Gamma_P = T_{1g}$ in O_h , indicating that a P state becomes T_1 or T_{1g} in a cubic field.

c) ^1D state ($L = 2, M = -2, -1, 0, 1, 2$).

O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$
Γ_D	$2 \times 2 + 1$ $= 5$	$\frac{\sin((5/2) \times 2\pi/3)}{\sin(1/2 \times 2\pi/3)}$ $= -1$	$\frac{\sin((5/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ $= 1$	$\frac{\sin((5/2) \times 2\pi/4)}{\sin(1/2 \times 2\pi/4)}$ $= -1$	$\frac{\sin((5/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ $= 1$

Table 3.15 Characters of transformation of a D state under the operations of O.

The representation Γ_D can be decomposed as shown by Eqs. (3.16) - (3.18) yielding : $\Gamma_D = E + T_2$ in O or T_d and $\Gamma_D = E_g + T_{2g}$ in O_h , showing that a D state splits in a cubic field in an E and a T_2 state.

d) ^3F state ($L = 3, M = -3, -2, -1, 0, 1, 2, 3$).

O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$
Γ_F	$2 \times 3 + 1$ $= 7$	$\frac{\sin((7/2) \times 2\pi/3)}{\sin(1/2 \times 2\pi/3)}$ $= 1$	$\frac{\sin((7/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ $= -1$	$\frac{\sin((7/2) \times 2\pi/4)}{\sin(1/2 \times 2\pi/4)}$ $= -1$	$\frac{\sin((7/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ $= -1$

Table 3.16 Characters of transformation of an F state under the operations of O.

The representation Γ_F can be decomposed using Eqs. (3.16) - (3.18). One obtains $\Gamma_F = A_2 + T_1 + T_2$ in O or T_d and $\Gamma_F = A_{2g} + T_{1g} + T_{2g}$ in O_h , showing that an F state splits in a cubic field in a A_2 , T_1 and a T_2 state.

e) ^1G state ($L = 4, M = -4, -3, -2, -1, 0, 1, 2, 3, 4$).

O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$
Γ_G	$2 \times 4 + 1$ $= 9$	$\frac{\sin((9/2) \times 2\pi/3)}{\sin(1/2 \times 2\pi/3)}$ $= 0$	$\frac{\sin((9/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ $= 1$	$\frac{\sin((9/2) \times 2\pi/4)}{\sin(1/2 \times 2\pi/4)}$ $= 1$	$\frac{\sin((9/2) \times 2\pi/2)}{\sin(1/2 \times 2\pi/2)}$ $= 1$

Table 3.17 Characters of transformation of a G state under the operations of O.

The representation Γ_G can be decomposed using Eqs. (3.16) - (3.18) leading to : $\Gamma_G = A_1 + E + T_1 + T_2$ in O or T_d and $\Gamma_G = A_{1g} + E_g + T_{1g} + T_{2g}$ in O_h , showing that a G state splits in a cubic field in an A_1 , E, T_1 and a T_2 state.

The splitting of multielectronic states for a d^2 system due to the presence of a cubic field can be summarized as follows :

$$\begin{aligned}
 \Gamma_{1S} &= {}^1A_1 \\
 \Gamma_{3P} &= {}^3T_1 \\
 \Gamma_{1D} &= {}^1E + {}^1T_2 \\
 \Gamma_{3F} &= {}^3A_2 + {}^3T_1 + {}^3T_2 \\
 \Gamma_{1G} &= {}^1A_1 + {}^1E + {}^1T_1 + {}^1T_2
 \end{aligned} \tag{3.48}$$

The states on the left-hand side of Eq. (3.48) are obtained for a free d^2 ion and appear on the left-hand side of a Tanabe-Sugano diagram (no crystal field) in the order discussed in section 3.3.1, i.e. ${}^3F$, ${}^1D$, ${}^3P$, ${}^1G$, ${}^1S$. The states on the right-hand side of Eq. (3.48) are obtained by acting with the cubic field of the surrounding lattice on the multielectronic states of the impurity ion and appear on the right-hand side (non-zero crystal field) in a d^2 Tanabe-Sugano diagram (Ref. 12, pag. 108). The crystal field splits the free ion's states as shown by Eq. (3.48). For example a d^2 Tanabe-Sugano diagram shows that an F state splits due to the cubic crystal field in an A_2 , a T_1 and a T_2 states. Eq. (3.48) shows that the multiplicity of each state is preserved : for example a G state (9 - time degenerate, see Tab. 3.11) splits into a one (non-) degenerate A_1 state, a double degenerate E state and two triple degenerate T states (T_1 and T_2), such that the relationship between the initial and final degeneracy is : $9 = 1 + 2 + 3 + 3$. It should be mentioned that the above results apply regardless of the spin multiplicity of the initial state, i.e. both a ${}^1D$ and a ${}^2D$ state will split into an E and a T_2 state. The states obtained due to the presence of the cubic field preserve the spin multiplicity of the original multielectronic state such that ${}^1D \rightarrow {}^1E + {}^1T_2$, while ${}^2D \rightarrow {}^2E + {}^2T_2$.

The energy distance between the multielectronic states in a cubic field depends on the strength of the crystal field Dq . The Dq parameter is determined from experimental data (absorption, emission spectra), and is defined as :

$$Dq = \frac{e^2 Z_l \overline{r^4}}{6a^5} \quad (3.49)$$

where Z_l is the charge of the ligand, e is the charge of the d -electron, a is the ion-ligand distance and $\overline{r^4}$ is the mean fourth power of the radius of the orbit of d electrons. Eq. (3.49) shows that if $N > 5$, a d^N system of electrons ($e < 0$) can be treated as a d^{10-N} system of holes ($e > 0$), which implies that the sign of Dq changes from a d^N system to a d^{10-N} system. Eq. (3.49) also shows that the strength of the crystal field Dq decreases as the size of the central ion or ligands increase, i.e. as the ion-ligand distance “ a ” increases. Tanabe-Sugano diagrams calculate the dependence of the energies of the multielectronic states E/B given by Eq. (3.48) as a function of the intensity of the crystal field Dq/B , for a given value of C/B (see for example Ref. 12, pag. 108).

2) Strong field approximation.

In the strong field approximation the electron-electron repulsion which gives rise to the multielectronic states described by Eq. (3.42) is weaker than the intensity of the crystal field, such that the crystal field acts on the one-electron d states which are then mixed by the electron-electron repulsion. It was previously shown in this section that a d state splits in a cubic field in an e and a t_2 state. The distance in energy scale between the e_g and t_{2g} levels due to an orthorhombic crystal field O_h of intensity Dq can be calculated by expanding the crystal field in spherical harmonics (Ref. 13, pag. 73). It can be shown that the t_{2g} levels are

stabilized by the amount $-4 Dq$ and the e_g levels are destabilized by the amount $6 Dq$, as shown in Fig. 3.9.

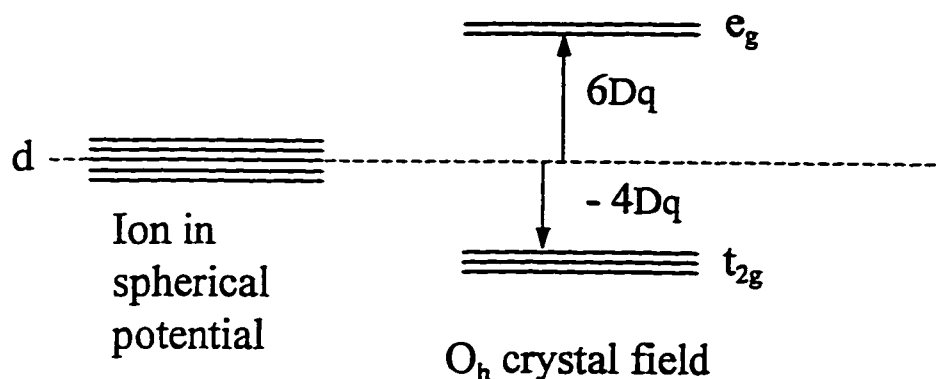


Figure 3.9 Splitting of a d level due to an orthorhombic crystal field Dq .

The important information contained in Fig. 3.9 is that the energy required to promote an electron from a t_{2g} state to an e_g state is $10Dq$. The diagram depicted in Fig. 3.9 can be interpreted as follows, using the fact that the splitting between an e and a t_2 state is $10 Dq$ [13] : a d state can accommodate 10 electrons (2 electrons of opposite spin on each of the five levels). Taking the energy E of the d states as reference and considering that the t_{2g} levels which can accommodate 6 electrons (2×3) are stabilized by the amount “ x ”, while the e_g levels which can accommodate 4 electrons (2×2) are destabilized by the amount “ y ”, one can write

$$10E = 6(E - x) + 4(E + y) \quad (3.50)$$

On the other hand the distance between the t_{2g} and e_g levels is $10 Dq$:

$$x + y = 10Dq \quad (3.51)$$

Solving Eqs. (3.50) - (3.51) one obtains $x = 4Dq$ and $y = 6Dq$ which shows that t_{2g} levels are stabilized by $4Dq$ while e_g levels are destabilized by $6Dq$ by an orthorhombic crystal field. The order of the e_g and t_{2g} states can be understood by considering the basis for these two representations in an O_h group (see Appendix

A.3). e_g has as basis $(x^2+y^2-2z^2, x^2-y^2)$, functions which are directed along the x, y and z axes (see for example Ref. 14, pag. 53), while t_{2g} has as basis (xy, yz, zx) directed at 45° between the axes. On the other hand the 6 ligands responsible for the orthorhombic field are directed along the x, y and z axes. Thus, one expects that the electron-electron repulsion between the electrons of the central ion and those of the ligand is strong for the e_g orbitals leading to their destabilization. The same type of argument applied to a tetrahedral field where the bases for e and t_2 are the same as above but the 4 ligands are situated along the main diagonals of the cube, as shown in Fig. 3.8, indicates that a T_d field destabilizes the t_2 states by $6Dq$ and stabilizes the e states by $4Dq$. The change in the order of the t_2 and e states in O_h and T_d crystal fields is obtained simply by formally considering $Dq < 0$ for a T_d field. It should be noted that the intensities of a T_d and O_h crystal field are not equal for ligands which can be inscribed in the same cube (as the ones shown in Fig. 3.8), i.e.

$$10Dq(T_d) = -(4/9) \times 10Dq(O_h) \quad (3.52)$$

Taking into account that in the strong field approximation one has t_2 and e available states, the following combinations are possible for a d^2 system:

- a) both electrons in a t_2 state : t_2^2 , or in strong field notation, γ^2 .
- b) both electrons in an e state : e^2 , or in strong field notation, ϵ^2 .
- c) one electron is in a t_2 state and one in an e state : t_2e , or in strong field notation, $\gamma\epsilon$.

As was already shown, the ascending order of the states in an O_h field is t_{2g}^2 , $e_{2g}t_{2g}$, e_g^2 , with a spacing of $10Dq$ between each of them. In a T_d field the order of the states is reversed, i.e. e^2 , et_2 , t_2^2 .

The symmetry of the multielectronic states in the strong field approximation is obtained by decomposing the corresponding direct products in the irreducible

representations of the group describing the field (O_h or T_d). The following results are obtained for a d^2 system in T_d symmetry (the subscript “g” is added for O_h field) :

$$\text{a) two } t_2 \text{ electrons - } t_2^2 : t_2 \times t_2 = A_1 + E + T_1 + T_2 \quad (3.53)$$

$$\text{b) two } e \text{ electrons - } e^2 : e \times e = A_1 + A_2 + E \quad (3.54)$$

$$\text{c) one } e \text{ and one } t_2 \text{ electron - } et_2 : e \times t_2 = t_2 \times e = T_1 + T_2 \quad (3.55)$$

The spin multiplicity of the above states is not known, but the states derived in the strong field approximation have to be identical to those derived in the weak field approximation in Eq. (3.48). Noting that for the et_2 combination the two electrons may have parallel or anti-parallel spin, leading to both triplets and singlets ($^3T_1$, $^3T_2$, $^1T_1$, $^1T_2$), the number of states given by Eq. (3.48) and Eqs. (3.53) - (3.55) coincide, as expected. In order to determine the spin of the above states correlation diagrams are used (Ref. 13, pags. 93 - 98). The multielectronic states given by Eqs. (3.48), (3.53) - (3.55) sometimes have in parenthesis the state they originate from, in either weak or strong field notation. For example the only $^3A_2$ state can be denoted either as $^3A_2(^3F)$ indicating that it originates in the ^3F multielectronic state in weak field notation (Eq. (3.48)) or as $^3A_2(d\varepsilon^2)$ indicating that it originates in a state where both electrons are on an E state in strong field notation (Eq. (3.54)). t_2 states are denoted by γ and e states are denoted by ε in strong field approximation. The upper index denotes the number of electrons on that particular state, and the “d” in front of the state indicates the original d electrons.

Tanabe-Sugano diagrams calculate the position of electronic levels taking into account both electron-electron repulsion and crystal field effects. Ref. 12, pags. 294 - 301 tabulates the matrices used for computing the energies of the electronic terms for different d^N systems starting with the Coulomb interaction. The d^2 case will be considered in detail.

The eleven electronic states for a d^2 system are given by Eq. (3.48) which shows that there are seven distinct types of states : $^1A_1$ (two states), $^3A_2$ (one state), ^1E (two states), $^1T_1$ (one state), $^3T_1$ (two states), $^1T_2$ (two states) and $^3T_2$ (one state). As all the above states are linear independent, being irreducible representations (bases) of the cubic group describing the crystal field (T_d or O_h if subscripts "g" are added), only states of the same symmetry and spin will interact with each other., as shown in Tab. 3.18. The diagonal matrices describing the Coulomb interaction for a d^2 system, schematically depicted in Tab. 3.18, are given in Ref. 12, pag. 295.

	$^1A_1$	$^1A_1$	$^3A_2$	^1E	^1E	$^1T_1$	$^3T_1$	$^3T_1$	$^1T_2$	$^1T_2$	$^3T_2$
$^1A_1$	X	X									
$^1A_1$	X	X									
$^3A_2$			X								
^1E				X	X						
^1E				X	X						
$^1T_1$						X					
$^3T_1$							X	X			
$^3T_1$							X	X			
$^1T_2$									X	X	
$^1T_2$									X	X	
$^3T_2$											X

Table 3.18 Non-zero elements in the electron-electron interaction matrix for a d^2 system in a (weak) cubic field.

The contribution of the crystal field in the strong field approximation is considered by taking into account the fact that the energy required to promote one electron from a t_2 to an e state is $10Dq$. Thus, if one considers the energy of an et_2 state to be zero in a strong field, the energy of a t_2^2 state is $-10Dq$ and the energy of an e^2 state is $+10Dq$. It should be noted that the relative order of these states

depends on the sign of Dq ($Dq > 0$ for O_h and $Dq < 0$ for T_d). The matrixes of interaction M given in Ref. 12, pag. 295 contain both weak- and strong-field notations for each state. In order to find the energies of the electronic states of a d^2 system one has to find the eigenvalues W of each matrix of interaction, i.e. to solve for W the secular equation :

$$\det(M - WI) = 0 \quad (3.56)$$

where I is the identity operator. The energies of the electronic levels of a d^2 system are determined as follows.

i) $^1A_1$ (^1G , ^1S) states

As shown by Eq. (3.48) there are two $^1A_1$ states : one of them arises from the ^1G state and the other from the ^1S state. The symmetric matrix of Coulomb interaction is (Ref. 12, pag. 295) :

$$M = \begin{matrix} & \begin{matrix} t_2^2 & e^2 \end{matrix} \\ \begin{pmatrix} 10B + 5C & \sqrt{6}(2B + C) \\ \sqrt{6}(2B + C) & 8B + 4C \end{pmatrix} \end{matrix} \quad (3.57)$$

Taking into account the strong field correction, the secular equation to be solved is:

$$\begin{vmatrix} 10B + 5C - 10Dq - W & \sqrt{6}(2B + C) \\ \sqrt{6}(2B + C) & 8B + 4C + 10Dq - W \end{vmatrix} = 0 \quad (3.58)$$

Eq. (3.58) represents a quadratic equations which admits two solutions. The assignment of the two solutions to the multielectronic ^1G and ^1S states is made as follows. In the particular case $Dq = 0$, Fig. 3.7 shows that the higher energy state is ^1S . If one calculates the two solutions of Eq. (3.58) in the particular case $Dq = 0$, the higher energy solution originates in ^1S , while the lower energy solution originates in ^1G . By solving Eq. (3.58) the energies of the two $^1A_1$ states are obtained as :

$$W_{A_1(^1G)} = \frac{1}{2}(18B+9C - \sqrt{100B^2 + 25C^2 + 100BC + 400Dq^2 - 40CDq - 80BDq}) \quad (3.59)$$

$$W_{A_1(^1S)} = \frac{1}{2}(18B+9C + \sqrt{100B^2 + 25C^2 + 100BC + 400Dq^2 - 40CDq - 80BDq}) \quad (3.60)$$

ii) $^1E (^1D, ^1G)$ states

Eq. (3.48) shows that there are two ^1E states : one of them arises from ^1D and the other from ^1G . The symmetric matrix of Coulomb interaction is (Ref. 12, pag. 295) :

$$M = \begin{pmatrix} t_2^2 & e^2 \\ B+2C & -2\sqrt{3}B \\ -2\sqrt{3}B & 2C \end{pmatrix} \quad (3.61)$$

Taking into account the strong field correction, the secular equation to be solved is:

$$\begin{vmatrix} B+2C-10Dq-W & -2\sqrt{3}B \\ -2\sqrt{3}B & 2C+10Dq-W \end{vmatrix} = 0 \quad (3.62)$$

Using the values of the two solutions of Eq. (3.62) at $Dq = 0$, and Fig. 3.7 which shows that the ^1G state has higher energy than the ^1D state, the solutions of Eq. (3.62) are:

$$W_{^1E(^1D)} = \frac{1}{2}(4C+B - \sqrt{400Dq^2 + 49B^2 - 40BDq}) \quad (3.63)$$

$$W_{^1E(^1G)} = \frac{1}{2}(4C+B + \sqrt{400Dq^2 + 49B^2 - 40BDq}) \quad (3.64)$$

iii) $^1T_2 (^1D, ^1G)$ states

Eq. (3.48) shows that there are two $^1T_2$ states : one of them arises from ^1D and the other from ^1G . The symmetric matrix of Coulomb interaction is (Ref. 12, pag. 295) :

$$M = \begin{matrix} & \begin{matrix} t_2^2 & t_2e \end{matrix} \\ \begin{pmatrix} B+2C & 2\sqrt{3}B \\ 2\sqrt{3}B & 2C \end{pmatrix} \end{matrix} \quad (3.65)$$

Taking into account the strong field correction, the secular equation to be solved is:

$$\begin{vmatrix} B+2C-10Dq-W & 2\sqrt{3}B \\ 2\sqrt{3}B & 2C-W \end{vmatrix} = 0 \quad (3.66)$$

According to the discussion at ii), the higher energy state originates in ^1G and the lower energy state originates in ^1D . The solutions of Eq. (3.66) are :

$$W_{^1T_2(^1D)} = \frac{1}{2}(-10Dq + 4C + B - \sqrt{100Dq^2 + 49B^2 - 20BDq}) \quad (3.67)$$

$$W_{^1T_2(^1G)} = \frac{1}{2}(-10Dq + 4C + B + \sqrt{100Dq^2 + 49B^2 - 20BDq}) \quad (3.68)$$

iv) $^3T_1(^3F, ^3P)$ states

Eq. (3.48) shows that there are two $^3T_1$ states : one of them arises from ^3F and the other from ^3P . The symmetric matrix of Coulomb interaction is (Ref. 12, pag. 295) :

$$M = \begin{matrix} & \begin{matrix} t_2^2 & t_2e \end{matrix} \\ \begin{pmatrix} -5B & 6B \\ 6B & 4B \end{pmatrix} \end{matrix} \quad (3.69)$$

Taking into account the strong field correction, the secular equation to be solved is:

$$\begin{vmatrix} 5B - 10Dq - W & 6B \\ 6B & 4B - W \end{vmatrix} = 0 \quad (3.70)$$

As shown in Fig. 3.7, the higher energy state originates in ^3P and the lower energy state originates in ^3F . The solutions of Eq. (3.70) are :

$$W_{^3T_1(^3F)} = \frac{1}{2}(-10Dq - B - \sqrt{100Dq^2 + 225B^2 + 180BDq}) \quad (3.71)$$

$$W_{^3T_1(^3P)} = \frac{1}{2}(-10Dq - B + \sqrt{100Dq^2 + 225B^2 + 180BDq}) \quad (3.72)$$

v) $^1T_1(^1G)$ - t_2e -state

Eq. (3.48) shows that the only $^1T_1$ state originates from ^1G . The matrix of Coulomb interaction is (Ref. 12, pag. 295) :

$$M = 4B + 2C \quad (3.73)$$

Taking into account the strong field correction, the secular equation to be solved is:

$$4B + 2C - W = 0 \quad (3.74)$$

Eq. (3.74) has the solution :

$$W_{^1T_1(^1G)} = 4B + 2C \quad (3.75)$$

vi) $^3T_2(^3F)$ - t_2e state

Eq. (3.48) shows that the only $^3T_2$ state originates from ^3F . The matrix of Coulomb interaction is (Ref. 12, pag. 295) :

$$M = -8B \quad (3.76)$$

Taking into account the strong field correction, the secular equation to be solved is:

$$-8B - W = 0 \quad (3.77)$$

Eq. (3.77) has the solution :

$$W_{^3T_2(^3F)} = -8B \quad (3.78)$$

vii) $^3A_2(^3F)$ - e^2 state

Eq. (3.48) shows that the only $^3A_2$ state originates from ^3F . The matrix of Coulomb interaction is (Ref. 12, pag. 295) :

$$M = -8B \quad (3.79)$$

Taking into account the strong field correction, the secular equation to be solved is:

$$-8B + 10Dq - W = 0 \quad (3.80)$$

Eq. (3.80) has the solution :

$$W_{^3A_2(^3F)} = -8B + 10Dq \quad (3.81)$$

The B, C and Dq parameters are obtained by fitting the energies of the above calculated electronic states to experimentally determined values from absorption spectra. As the position of all peaks in the absorption spectra is given by the energy difference between a given electronic level and the ground state, the next question to be addressed is which of the above calculated levels is the ground state for a d^2 ion in T_d crystal field. It was shown that the ground state for a free d^2 ion is ^3F and that this state splits in a cubic field in three states : $^3T_1$, $^3T_2$ and $^3A_2$, (Eq. (3.48)) with energies given by Eqs. (3.71), (3.78) and (3.81), respectively. As a tetrahedral field is formally described by $Dq < 0$, the $^3A_2$ state has lower energy than the $^3T_2$ state (see Eqs. (3.78), (81)). Thus the possible candidates for the ground state are $^3A_2$ and $^3T_1$. Using Eqs. (3.71), (3.78) it is straightforward to show that $W_{^3A_2(^3F)} < W_{^3T_1(^3F)}$ for any values of Dq and B, i.e. in a T_d field, $^3A_2(^3F)$ is the ground state. It is interesting to note that in an O_h field $^3T_1(^3F)$ is the ground state.

The energies of the eleven multielectronic states W_i given by Eqs. (3.59), (3.60), (3.63), (3.64), (3.67), (3.68), (3.71), (3.72), (3.75), (3.78), (3.81) can be rescaled with respect to the ground state ${}^3A_2({}^3F)$, by subtracting the energy of the ground state from each electronic state :

$$\Delta W_i = W_i - W_{{}^3A_2({}^3F)} \quad (3.82)$$

The dependence of the ratio $\Delta W_i / B \equiv W / B$ on Dq/B , for a given C/B value represents a Tanabe-Sugano diagram. An example of such a diagram for a d^2 ion in a T_d field is plotted in Fig. 3.10 for $C/B = 4.9$.

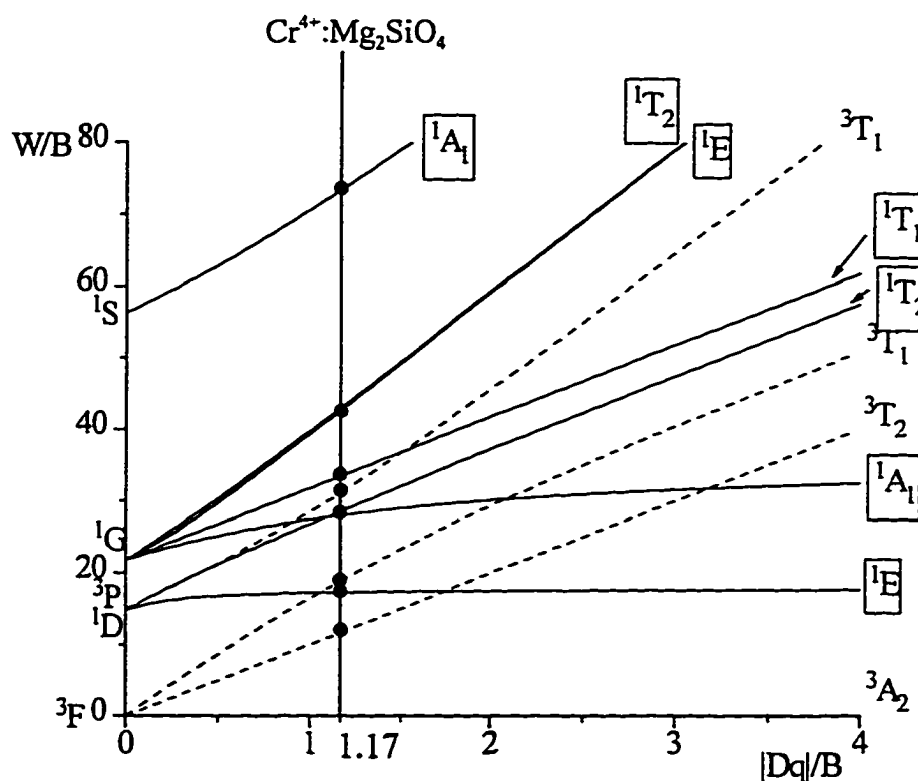


Figure 3.10 Tanabe-Sugano diagram for a d^2 ion in the T_d field, for $C/B = 4.9$. The dotted lines represent states which do not depend on the C/B ratio. The continuous lines, boxed names, represent states which depend on the C/B ratio. The vertical line gives the position of $Cr^{4+}:Mg_2SiO_4$ electronic levels in the energy diagram.

As will be shown in Section 3.4 $C/B = 4.9$ is the value for Cr^{4+} in Mg_2SiO_4 as determined from absorption spectra. The intersection between the vertical line at $|Dq|/B = 1.17$ and the d^2 electronic levels in Fig. 3.10 (marked with a dot •) gives the position of Cr^{4+} electronic states in Mg_2SiO_4 (see Section 3.4), in the tetrahedral approximation for the crystal field, i.e. when the effect of the C_s site symmetry is not taken into account.

Fig. 3.10 shows that for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ the ground state is $^3A_2$. The first excited state is $^3T_2$, followed by $^3T_1$ which is positioned very close to ^1E . The next two states $^1A_1$ and $^1T_2$ are also very close but are not expected to be observed in an absorption spectrum due to the spin forbidden character of the transition. Still higher in energy scale is another pair of levels $^1T_1$ and $^3T_1$, and finally, $^1T_2$ and ^1E having approximately the same energy, and $^1A_1$. The actual measured position of the lower lying electronic states and the calculation of crystal field parameters are given in the next section.

3.4 Determination of B, C and Dq parameters for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$

The average energy of Cr^{4+} electronic states in tetrahedral approximation, in forsterite has been reported [1, 2], [6] from absorption spectra as :

$$\begin{aligned}
 W_{^3A_2} &= 0 \\
 W_{^3T_2(^3F)} &= 10140 \text{ cm}^{-1} \\
 W_{^3T_1(^3F)} &= 15610 \text{ cm}^{-1} \\
 W_{^1E(^1D)} &= 15875 \text{ cm}^{-1} \\
 W_{^3T_1(^3P)} &= 26810 \text{ cm}^{-1} \\
 W_{^1T_1(^1G)} &= 28735 \text{ cm}^{-1}
 \end{aligned}
 \tag{3.83}$$

Eqs. (3.83) indicate that, as shown by Fig. 3.10, the $^3T_1$ and ^1E states are positioned close to each other, as are, relatively, the $^3T_1$ and $^1T_1$ states. The values of the crystal field parameters B, C and Dq are calculated using Eqs. (3.59) - (3.82) and the corresponding position of the electronic states as determined from the absorption or site selective excitation spectrum, and are presented as follows.

Using Eqs. (3.78) and (3.81), the rescaled energy of the $^3T_2(^3F)$ state (with respect to the ground state) is $10|Dq|$. It is interesting to note that this result shows that the value of the Dq parameter for a d^2 ion in a T_d field is given, at least in the first approximation, by the energy of the $^3T_2(^3F)$ level divided by 10. Using the measured energy of the $^3T_2(^3F)$ state given by Eqs. (3.83) one obtains :

$$|Dq| = 1014 \text{ cm}^{-1} \quad (3.84)$$

The value for Dq given by Eq. (3.84) and B and C for a free ion (see Section 3.3.1) are the starting values for fitting the experimentally determined positions of the energy levels given by Eqs. (3.83) with the theoretical values given by Eqs. (3.58) - (3.81).

A program entitled "Tanabe" which finds the optimal values for the B, C, and Dq parameters using Eqs. (3.58) - (3.82) and the experimentally measured energies of the $^3T_2(^3F)$, $^3T_1(^3F)$, $^1E(^1D)$, $^3T_1(^1P)$ and $^1T_1(^1G)$ (given in our case by Eq. (3.83)) electronic levels such that the sum of the differences squared between the measured and calculated values is minimized, was written. The code for this program is given in Appendix A.5. Each line in the program where the energy of a state is calculated has a reference to the corresponding equation which was used. The determined optimal values for B, C and Dq are :

$$B = 855 \text{ cm}^{-1}, C = 4190 \text{ cm}^{-1} \text{ and } Dq = 1000 \text{ cm}^{-1} \quad (3.85)$$

As mentioned before, the input values for the crystal field parameters were the values for the free ion for B and C (i.e. $B = 1039 \text{ cm}^{-1}$ and $C = 4238 \text{ cm}^{-1}$ - see Section 3.3.1) and $Dq = 1014 \text{ cm}^{-1}$ given by eq. (3.84). Using the values given by

Eq. (3.85) one obtains : $C/B = 4.9$ and $Dq/B = 1.17$. Tab. 3.19 gives the comparison between the average values of the electronic levels of a Cr^{4+} ion in forsterite and the computed values in the tetrahedral field approximation with the parameters given in Eq. (3.85).

State	Measured energy (cm^{-1})	Calculated energy (cm^{-1})
${}^3\text{A}_2({}^3\text{F})$	0	0
${}^3\text{T}_2({}^3\text{F})$	10140	10100
${}^1\text{E}({}^1\text{D})$	15875	14900
${}^3\text{T}_1({}^3\text{F})$	15610	16300
${}^1\text{A}_1({}^1\text{G})$	-	24150
${}^1\text{T}_2({}^1\text{D})$	-	24660
${}^3\text{T}_1({}^3\text{P})$	26810	26890
${}^1\text{T}_1({}^1\text{G})$	28735	28860
${}^1\text{T}_2({}^1\text{G})$	-	37140
${}^1\text{E}({}^1\text{G})$	-	36790
${}^1\text{A}_1({}^1\text{S})$	-	63270

Table 3.19 Comparison between measured and calculated energies of the electronic levels of a Cr^{4+} ion in forsterite, in the tetrahedral field approximation.

In fact the B, C and Dq parameters do not describe the ion correctly, since the real symmetry of the Cr^{4+} ion is lowered by the surrounding lattice from T_d to C_s (site symmetry) such that all energy levels are nondegenerate representations of C_s , and not degenerate representations of T_d . The measured energies of the

electronic levels reported in Tab. 3.19 are calculated as the mean energies of the C_s states. For example, the ${}^3T_1({}^3F)$ state splits in three components under the C_s field, measured at 13850, 15300 and 17670 cm^{-1} . This approximation for the position of the T_d levels is a major source of error. Thus, one expects the crystal fields and the Racah parameters to be only an indicator of the behavior of the ion in the surrounding ligand field, without being able to predict exact values for the energy levels. It should be noted that the orthorhombic distortion C_s is sometimes approximated by C_{2v} [6]. The correlation between the T_d , C_s and C_{2v} groups is given in Tab. 3.20 [4]:

T_d	C_s	C_{2v}	C_s
A_1	A'	A_1	A'
A_2	A''	A_2	A''
E	$A'+A''$	B_1	A'
T_1	$A'+2A''$	B_2	A''
T_2	$2A'+A''$		

Table 3.20 Correlation between the representations of T_d , C_s and C_{2v} groups.

Tab. 3.20 shows that a T_1 T_d state splits due to the orthorhombic C_s distortion in an A' and two A'' states. Indeed, the site selective excitation spectrum [1, 2], [6] of $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ shows that the ${}^3T_1$ state with the reported mean energy of 15610 cm^{-1} consists of three distinct bands, obtained under different polarizations of the incident light which were measured at 13850, 15300 and 17670 cm^{-1} . The main problem in determining the symmetry of the three bands from the polarized absorption spectrum is to correlate the directions of the polarized light given with respect to the crystal axes, to the symmetry of the dipole moment expressed in terms of the site symmetry. In other words, the selection

rules are computed in C_s (or C_{2v}) but they are determined from the polarization of the incident light given in D_{2h} , i.e. with respect to the crystal axes. The symmetry of the above mentioned bands is obtained as follows from the polarized absorption or site selective excitation spectra.

i) The absorption band at 13850 cm^{-1} is obtained under incident light parallel to the b axis in the $Pbnm$ notation used by Refs. [1, 2], [6], i.e. under incident light parallel to the a axis in $Pnma$ notation (see Tab. 3.8). This means that the transition is induced by the x-component of the dipole moment, in standard $Pnma$ notation for D_{2h} . The representation which has as basis the x axis in D_{2h} is B_{3u} (see Tab. 3.8). Using the $C_s \rightarrow D_{2h}$ correlation table (see Tab. 3.4), the C_s representation correlated to B_{3u} is A' , i.e. the symmetry of the component of the dipole moment responsible for the transition is $\hat{O} = A'$. The ground state has symmetry A_2 in T_d , i.e. A'' in C_s (see Tab. 3.20), i.e. $\Psi_i = A''$. The final state Ψ_f whose symmetry has to be determined, has to be such that the product $\Psi_i \cdot \hat{O} \cdot \Psi_f$ contains the totally symmetric representation A' (Eq. (3.29)). It can be shown that the only possible combination such that $A'' \cdot A' \cdot \Psi_f = A'$ is $\Psi_f = A''$. (The other possibility would be $\Psi_f = A'$ which leads to $A'' \cdot A' \cdot \Psi_f = A''$ - forbidden). Thus the polarized absorption indicates that the symmetry of the band at 13850 cm^{-1} is ${}^3A''$ in C_s .

ii) The absorption band at 17670 cm^{-1} is obtained under incident light parallel to the a axis in the $Pbnm$ notation, i.e. under incident light parallel to the c axis in $Pnma$ notation (see Tab. 3.1). This means that the transition is induced by the z-component of the dipole moment, in standard $Pnma$ notation for D_{2h} . The representation which has as basis the z axis in D_{2h} is B_{1u} (see Tab. 3.8). Using the $C_s \rightarrow D_{2h}$ correlation table (see Tab. 3.4), the C_s representation correlated to B_{1u} is A' , i.e. the symmetry of the component of the dipole moment responsible

for the transition is $\hat{O} = A'$. Following the previous argument it follows that the symmetry of the band at 17670 cm⁻¹ is ${}^3A''$ in C_s .

Rigorous correlation tables (such as Tab. 3.4) can not be used for determining the symmetry of the band in C_{2v} , but using Tab. 3.20 it can be concluded that the symmetry of the A'' states is A_2 and B_2 in C_{2v} . Considering the actual arrangement of the ions inside a distorted tetrahedron, given by [8], it can be shown that the c -crystallographic axis (in $Pnma$ notation) can be approximated by the z - C_{2v} axis (z -direction of the crystal field). The state with higher energy of A_2 and B_2 , i.e. the one which is destabilized by the crystal field, is the state which contains a z -orbital and is repelled due to Coulomb interaction by the electrons of the ligand (as in the case of the splitting of d levels into t_2 and e discussed previously). As B_2 has as basis yz , it is destabilized by the ligand field. Thus in C_{2v} approximation the symmetry of the energy level at 17670 cm⁻¹ is ${}^3B_2$ and the symmetry of the energy level at 13850 cm⁻¹ is ${}^3A_2$

iii) The absorption band at 15300 cm⁻¹ is obtained under incident light parallel to the c axis in the $Pbnm$ notation, i.e. under incident light parallel to the b axis in $Pnma$ notation (see Tab. 3.1). This means that the transition is induced by the y -component of the dipole moment, in standard $Pnma$ notation for D_{2h} . The representation which has as basis the y axis in D_{2h} is B_{2u} (see Tab. 3.8). Using the $C_s \rightarrow D_{2h}$ correlation table (see Tab. 3.4), the C_s representation correlated to B_{2u} is A'' , i.e. the symmetry of the component of the dipole moment responsible for the transition is $\hat{O} = A''$. Using the fact that the ground state has symmetry A'' in C_s , the final state Ψ_f whose symmetry has to be determined, has to be such that $A'' \cdot A'' \cdot \Psi_f = A'$, leading to $\Psi_f = A'$. Thus, the polarized absorption indicates that the symmetry of the band at 15300 cm⁻¹ is ${}^3A'$ in C_s . Using Tab. 3.20 and the $T_d - C_{2v}$ correlation, it can be inferred that the symmetry of this state is ${}^3B_1$ in C_{2v} .

The polarized site-selective excitation spectra depicting the three ${}^3T_1({}^3F)$ states and their symmetries as derived from the measured spectra are shown in Fig. 3.11 [6].

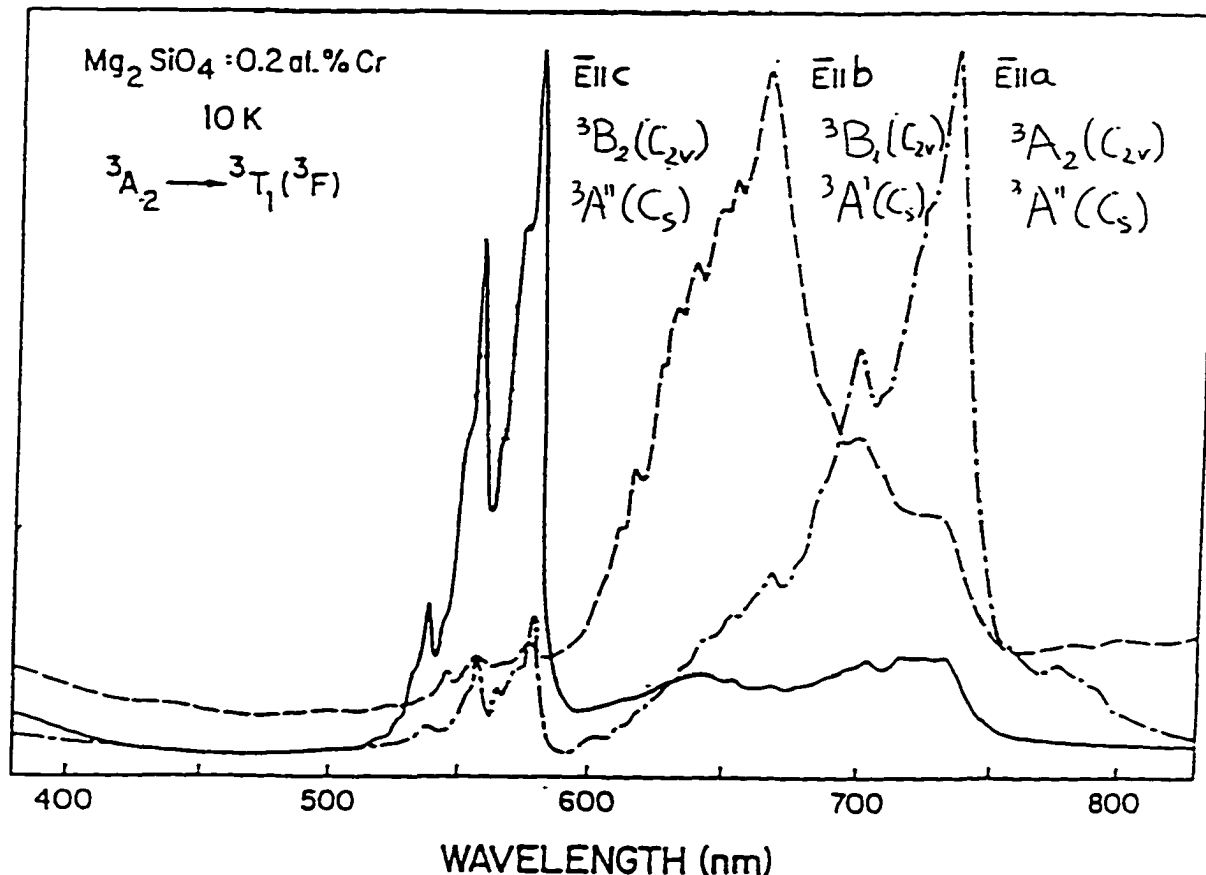


Figure 3.11 Polarized site-selective excitation spectrum of the $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ ${}^3T_1({}^3F)$ states and their symmetry (in C_{2v} and C_s) as derived in Section 3.5, in $Pnma$ notation.

Using a similar type of argument, it can be shown the polarized absorption spectrum establishes the symmetry of the ${}^3T_2$ energy levels as follows [6] (the representation in parenthesis gives the symmetry of the state in C_{2v} notation) : ${}^3A'$ (${}^3A_1$) at 9150 cm^{-1} (the metastable level), ${}^3A'$ (${}^3B_1$) at 9820 cm^{-1} and ${}^3A''$ (${}^3B_2$) at 11470 cm^{-1} . No orthorhombic splitting was reported for the ${}^1E$ level.

Low temperature measurements[6] reveal an even finer structure in the absorption spectrum due to spin-orbit coupling which splits all triplet states into

three distinct components. In addition to all these features, the ${}^3B_2({}^3T_1)$ band at 17670 cm^{-1} displays two additional higher energy replicas due to the coupling of the electronic state with a high frequency ($\sim 750\text{ cm}^{-1}$) Cr^{4+} local mode. Using symmetry arguments it can be shown that this has to be a strong totally symmetric A' mode which can be identified as the 765 cm^{-1} tetrahedral stretching mode (see Chapter 6).

3.5 Presence of Cr^{3+} in $\text{Cr:Mg}_2\text{SiO}_4$

It should be mentioned that a $\text{Cr:Mg}_2\text{SiO}_4$ sample contains both Cr^{4+} and Cr^{3+} ions. Using Eq. (3.31) it can be shown that Cr^{3+} has a d^3 structure. While Cr^{4+} ions substitute for Si^{4+} , Cr^{3+} substitutes for Mg^{2+} in both C_i and C_s positions, as $\text{Cr}^{3+}(\text{I})$ and $\text{Cr}^{3+}(\text{II})$, respectively. Doping of the host in a different atmosphere favors one particular type of ions : Cr^{3+} is favored by a reducing growing atmosphere while Cr^{4+} is favored by an oxidized atmosphere.

Although an absorption spectrum contains contributions from all types of ions, site selective excitation spectra are able to differentiate the contribution of individual types of ions. In a site selective excitation spectrum one monitors the change in the intensity of the maximum of emission corresponding to each type of impurity, as a function of excitation wavelength. The contributions of Cr^{3+} and Cr^{4+} ions are separated by monitoring the maximum of emission at 14437 cm^{-1} (692.7 nm) for $\text{Cr}^{3+}(\text{I})$, 11600 cm^{-1} (862.1 nm) for $\text{Cr}^{3+}(\text{II})$ and 9137 cm^{-1} (1094.5 nm) for Cr^{4+} [6]. Site selective excitation spectra obtained for $\text{Cr:Mg}_2\text{SiO}_4$ demonstrate that the structure at $530 - 600\text{ nm}$ is due exclusively to the ${}^3A''({}^3T_1)\text{Cr}^{4+}$ electronic level.

3.6 References

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Chapter 4

Raman and resonance Raman scattering

4.1. Light scattering

Light scattering is divided into: a) elastic scattering (Rayleigh process), and b) inelastic scattering (Raman and Brillouin processes). In general, most of the incident photons do not interact with the molecules of the considered medium (gas, liquid or solid), and only one in every $\sim 10^6$ photons is scattered off the sample. Out of the total number of scattered phonons, most of them interact elastic with the molecules of the investigated material, such that their frequency ν_S is equal to the frequency of the incident photons ν_0 , but their direction of propagation is eventually changed. An elastic scattering process where, $\nu_S = \nu_0$ is called Rayleigh scattering.

Only about one in every 10^3 scattered photons, i.e. only one in every 10^9 incident photons undergoes an inelastic scattering (Raman process) such that $\nu_S \neq \nu_0$. As most of the medium's molecules are in the ground state, part of the energy of the incident photon is transferred to the molecule and one (or several) molecular modes of vibration are excited. The scattered photon leaves the medium with a changed frequency $\nu_S = \nu_0 - \nu_V$ where ν_V is the frequency of the molecular vibration (see Fig. 4.1). A Raman process where $\nu_S < \nu_0$ is called a Stokes process. A very restricted number of molecules, given by the Boltzman factor (see Section 4.2.2) are initially in the excited vibrational state ν_V . In this case, the scattered photon leaves the system with enhanced energy $\nu_S = \nu_0 + \nu_V$. A Raman process where $\nu_S > \nu_0$ is called an anti-Stokes process. A schematic picture of a Stokes, Rayleigh and anti-Stokes processes, respectively is given in Fig.4.1.

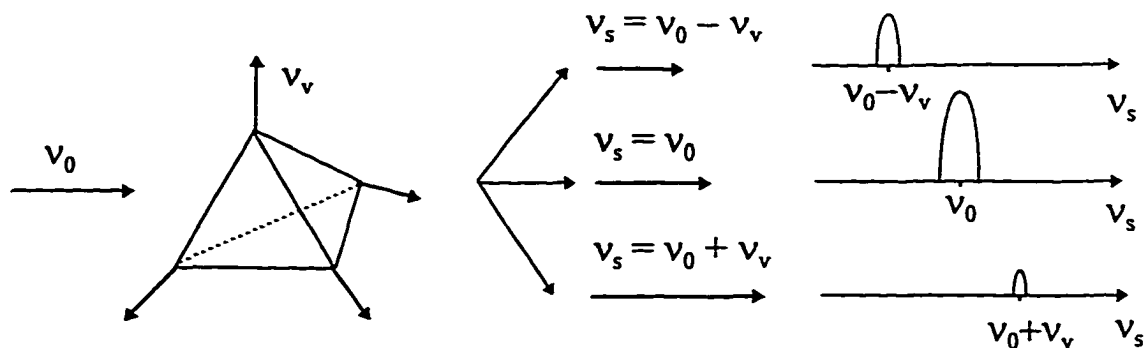


Figure 4.1 Schematic picture of a Stokes, Rayleigh and anti-Stokes processes.

As will be shown in Section 4.2 a Raman spectrum consists of lines whose energy measured from the excitation wavelength provides the energy of the phonon modes ν_v which characterize the molecular motion. The energy shift (energy of phonon modes) is usually measured in cm^{-1} (wavenumbers) and is calculated as :

$$E = \left| \frac{1}{\lambda_0} - \frac{1}{\lambda_s} \right| \quad (4.1)$$

where the wavelength of the incident and of the scattered radiation λ_0 and λ_s , respectively, are expressed in cm.

The scattered photons provide important information regarding fundamental characteristics of the investigated material such as : inter-atomic distances, inter-nuclear force constants, phonon spectrum (energy, symmetry, density of states), molecular moments of inertia, anharmonic constants, etc.

4.2 Raman scattering

Although light scattering was investigated early this century by several scientists such as Rayleigh, Born, Smekal, Kramers and Heisenberg, it was only in

1928 that Raman realized the full significance of inelastic light scattering, based on experiments performed in different types of media. Raman first used as excitation source natural sun light which was passed through several narrow band filters, and later a mercury vapor lamp which emitted almost monochromatic light. By analyzing the spectrum of the scattered light with a spectrometer, Raman made the startling observation that the spectrum contained a number of sharp lines or bands which were not present in the emission spectrum of the excitation source. The presence of these lines was initially verified in more than 80 liquids and amorphous substances. Each material displayed a specific pattern of such energy shifted lines. Raman observed that the frequency shifts of these new lines are independent of the incident radiation but are characteristic for each given material. In 1928 Raman published his results on inelastic light scattering [1] which would later come to be known as the Raman effect, while the series of energy shifted lines would be called a Raman spectrum. It is interesting to mention that similar results on light scattering in crystals were independently published a few weeks later by Landsberg and Mandelstam in Russia.

4.2.1 Stokes and anti-Stokes processes

A first order scattering Raman process involves an incoming photon of energy $\hbar\omega_i$, an outgoing scattered photon of energy $\hbar\omega_s$ and the creation or annihilation of a phonon (vibration) of energy $\hbar\omega_v$. The process where a phonon is created (Stokes process) is depicted in Fig. 4.2 (a). The energy and momentum conservation for a Stokes process are given by Eqs. (4.2) and (4.3), respectively as

$$\hbar\omega_i = \hbar\omega_s + \hbar\omega_v \quad (4.2)$$

$$\vec{k}_i = \vec{k}_s + \vec{k}_v \quad (4.3)$$

where $\vec{k}_i$, $\vec{k}_s$ and $\vec{k}_v$ are the momenta of the incident and scattered photons and of the created phonon, respectively.

The process where a phonon is annihilated (anti-Stokes process) is depicted in Fig. 4.2 (b). The energy and momentum conservation for an anti-Stokes process are given by Eqs. (4.4) and (4.5), respectively as :

$$\hbar\omega_i = \hbar\omega_s - \hbar\omega_v \quad (4.4)$$

$$\vec{k}_i = \vec{k}_s - \vec{k}_v \quad (4.5)$$

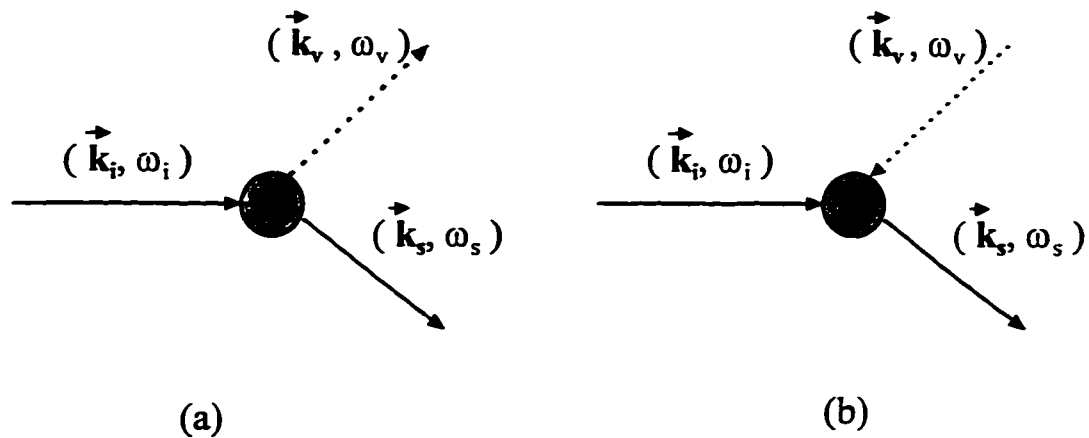


Figure 4.2 Schematic representation of a first order (a) Stokes and (b) anti-Stokes scattering Raman processes.

The filled circle in Fig. 4.2 represents the interaction region between the electromagnetic radiation and matter (the material under investigation).

A more explicit representation of the interaction region is given by Feynman diagrams which show that Raman Stokes and anti-Stokes processes involve the creation of an electron-hole pair, as depicted in Figs. 4.3 (a), (b), respectively. The diagrams in Figs. 4.3 suggest that : (i) a first order Raman process has to be treated as a second order process in the radiation-matter interaction (due to the two vertices at points M and N), (ii) each vertex involves

one single photon, i.e. the perturbation Hamiltonian is linear in the vector potential A describing the radiation field, and (iii) the depicted scattering events are first order process in the phonon field (i.e. only the linear term in the vibrational coordinate is retained in the perturbation Hamiltonian, as a single phonon is created or annihilated at point P). Moreover, Figs. 4.3 show that a Raman process is induced by the interaction between the electromagnetic field (photon) with the electronic system only (points M and N), and that there is no direct photon-phonon coupling. The phonon at point P (representing the ionic system) is created (or annihilated) due to interactions with the electronic system only. Figs. 4.3 also show the absence of two photon processes, which would be given by A^2 terms. The above mentioned aspects are discussed in more detail from the theoretical point of view in Section 4.2.5.

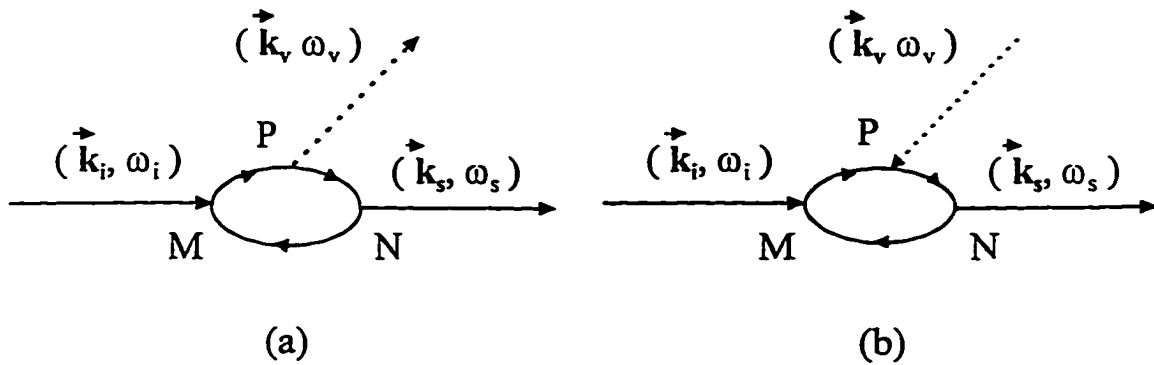


Figure 4.3 Feynman diagrams for first order (a) Stokes and (b) anti-Stokes Raman processes.

According to Figs. 4.3 a Raman process can be described as follows : an incoming photon interacts with the electrons in the system, slightly changing their state. The perturbed electrons interact with the ions which “adjust” their motion to “match” the new electronic configuration by creating or destroying a phonon. The photon leaves the system with different energy and momentum due to the created

(or annihilated) phonon. It is worth noting that the electron-hole pair created in a Raman process is, with the exception of the resonance case (Section 4.3), virtual, i.e. Raman scattering does not involve a transition to a real electronic state, as is shown in Figs. 4.4. One of the most attractive characteristics of Raman scattering is based on this particular feature and is the fact that a Raman process takes place under any excitation wavelength $\lambda_i = 2\pi c/\omega_i$. Nevertheless, it should be noted that a particular case of Raman scattering, resonance Raman processes which are discussed in Section 4.3, are wavelength dependent and occur only when the excitation wavelength is in resonance with an electronic state of the system (like in the case of absorption which occurs only for particular wavelengths).

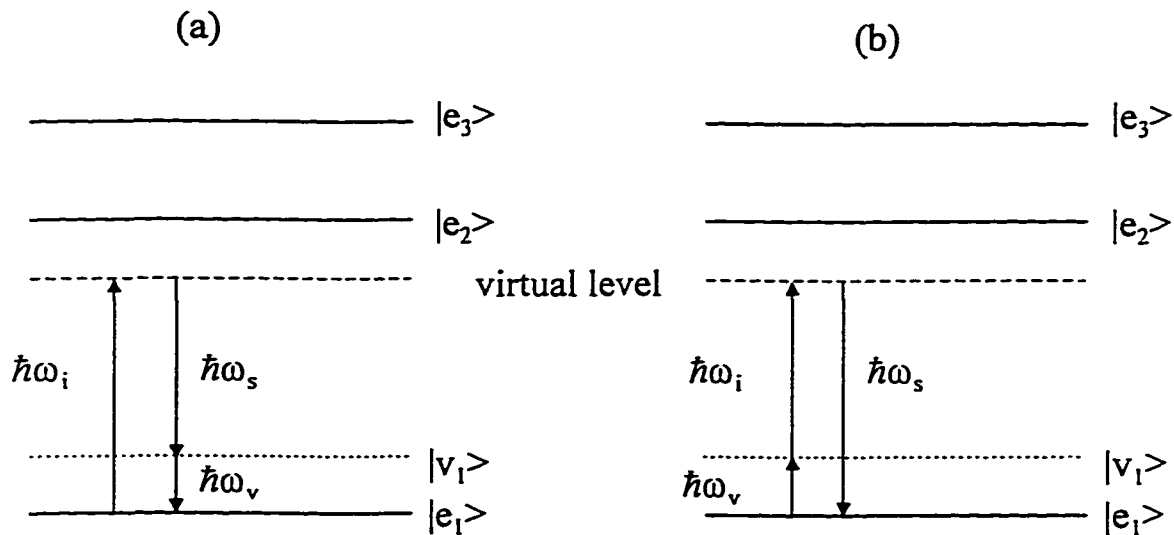


Figure 4.4 Schematic representation in energy space of first order (a) Stokes and (b) anti-Stokes scattering Raman processes.

In Figs. 4.4 $|e_i\rangle$, $i = 1, 2, \dots$ are electronic levels of the system under investigation and $|v_1\rangle$ a vibrational level. The above figure shows that in a Stokes process a vibration of energy $\hbar\omega_v$ is created (Fig. 4.4 (a)) and in an anti-Stokes process a vibrational quanta is destroyed (Fig. 4.4 (b)). In both cases (a) and (b) the system makes a transition to a virtual level, which, as will be shown in Section 4.2.5, is

given by the virtual off-resonance transitions to all electronic and vibrational states of the system.

Another feature of Raman scattering is given by Eqs. (4.3), (4.5) which show which types of phonons can be probed using Raman scattering. The module of the phonon's momentum involved in a Raman process is :

$$|\vec{k}_v| = \sqrt{k_i^2 + k_s^2 - 2|\vec{k}_i||\vec{k}_s| \cos \alpha} \quad (4.6)$$

where α is the angle between the wavevectors of the incident and scattered photons, ultimately given by the scattering geometry (e.g. $\alpha = 90^\circ$ for 90° scattering, $\alpha = 180^\circ$ for backscattering, etc.). Eq. (4.6) shows that phonons with momenta whose maximum value is $k_v = k_i + k_s \approx 2k_i$ can be probed by Raman scattering.

As a photon's wavevector is inversely proportional to its wavelength, the maximum value of a phonon's momentum probed with visible radiation $\lambda_i = 400$ nm is $k_v \approx 2 \times \frac{2\pi}{400} \text{ nm}^{-1} = 2\pi \times \frac{1}{200} \text{ nm}^{-1}$. By comparing this value with the maximum value of the phonon's momentum at the edge of the Brillouin zone $k_{\text{max}} = 2\pi/a$, where a is the linear size of the crystal's unit cell (typically $a \sim 1$ nm), it follows that $k_v \approx 0.5\% \times k_{\text{max}}$, i.e. only zone-center phonons ($k_v \sim 0$) can be investigated by Raman scattering. Although a solid state system is generally described by two types of phonons (optical and acoustic), Raman scattering refers only to processes involving optical zone-center phonons. Scattering processes occurring on acoustic phonons are termed as Brillouin scattering.

4.2.2 Creation and annihilation operators

As Stokes and anti-Stokes processes involve the creation or annihilation of a vibrational quanta, respectively, they can be described in terms of creation (a^+) and annihilation (a) operators defined as :

$$a^+|n\rangle = \sqrt{n+1}|n+1\rangle \quad (4.7)$$

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad (4.8)$$

A Stokes process takes the system from a state with n vibrations to a state with $n+1$ vibrations, i.e. the intensity of a Stokes line is given by the square of the amplitude of a $n \rightarrow n+1$ transition :

$$I_{\text{Stokes}} \sim |\langle n+1|a^+|n\rangle|^2 = (n+1)|\langle n+1|n+1\rangle|^2 = n+1 \quad (4.9)$$

where, for a system in thermal equilibrium at a temperature T , n is the Bose-Einstein factor for the considered mode of vibration ω_v , given by

$$n = \frac{1}{e^{\frac{\hbar\omega_v}{kT}} - 1} \quad (4.10)$$

On the other hand, an anti-Stokes process takes the system from a state with n vibrations to a state with $n-1$ vibrations, i.e. the intensity of an anti-Stokes line is given by the square of the amplitude of a $n \rightarrow n-1$ transition :

$$I_{\text{anti-Stokes}} \sim |\langle n-1|a|n\rangle|^2 = n|\langle n-1|n-1\rangle|^2 = n \quad (4.11)$$

The ratio between the anti-Stokes to Stokes lines for a mode of vibration of frequency ω_v is given by the Boltzman factor and is obtained by taking the ratio of Eqs. (4.11) and (4.9), which leads to :

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} \approx e^{-\frac{\hbar\omega_v}{kT}} \quad (4.12)$$

Eq. (4.12) does not include the $(\omega_i - \omega_v)^4 / (\omega_i + \omega_v)^4$ correction for the intensity of the scattered light. Using the above equation it can be shown that for a system at room temperature ($T = 300\text{K}$) the intensity of the anti-Stokes line for an 800 cm^{-1} phonon mode is only 2% of the intensity of the Stokes line for the same mode. The difference in intensities for the Stokes and anti-Stokes spectra indicates that whenever possible, one prefers to analyze a Stokes spectrum for identifying the Raman lines of a system in thermal equilibrium. It should be pointed out that Eq. (4.12) holds only for the case of “regular” (non-resonant) Raman scattering. For the resonance case, the ratio of the intensities of the anti-Stokes and Stokes lines is also dependent on the incident wavelength (on the resonance condition) and in some cases the anti-Stokes line has higher intensity under a particular excitation wavelength, than the Stokes line.

4.2.3 Number of phonon modes

It is important to note that only the number of modes of vibration is conserved in a system, while the total number of phonons is generally not conserved. Some modes of vibration appear as Raman lines in a scattering spectrum. As discussed in Chapter 3, the number of modes of vibration given by a unit cell with N atoms is equal to $3N$ (three modes of translation for each atom). For a lattice where translational invariance is obeyed, the $3N$ phonon modes can be categorized as : 1 longitudinal acoustic (LA), 2 transverse acoustic (TA), $(N - 1)$ longitudinal optic (LO) and $2(N - 1)$ transverse optical modes (TO). The acoustic modes are investigated by Brillouin scattering while the optical modes are investigated by Raman (and/or infrared) scattering. The $3N - 3$ optical modes of vibration will give rise to at most $3N - 3$ Raman modes. The number of Raman modes can be smaller due to degeneracy and to selection rules which may make

some modes Raman-inactive (see Chapter 3). The Raman lines are visible in a spectrum as bands (they have a finite width) due to the contributions of all unit cells in the crystal. Thus, in a more rigorous way, for a crystal with S unit cells there are $S \cdot (3N - 3)$ optical modes of vibration.

The modes of vibration can also be categorized according to the type of motion they describe into translations, rotations and internal vibrations. A molecule with N atoms gives rise to $3N - 6$ internal vibrations for nonlinear molecules and to $3N - 5$ internal vibrations for linear molecules. Out of the 6 (5) remaining modes, 3 describe molecular translations and the rest, rotations.

The Raman (and infra-red) lines in a scattering spectrum are usually referred to as “phonons”, although rigorously speaking they represent modes of vibration, while the total number of such lines is usually referred to as “the total number of phonons”. As previously discussed this term is not exactly appropriate as the total number of phonons is temperature dependent and is not conserved, while the total number of modes of vibration (i.e. lines in a scattering spectrum) is conserved. It is important to stress that in fact a mode of vibration consists of several phonons of similar energies. Nevertheless we will refer from now on to the modes of vibration in a lattice, as phonons.

4.2.4 Classical approach to the Raman effect

The change in frequency for the light scattered by a given medium can be obtained from classical considerations [2]. The electric dipole moment $\vec{p}$ induced in a medium by an electric field $\vec{E}$ is given by :

$$\vec{p} = \alpha \vec{E} \quad (4.13)$$

where α is the polarizability of the medium. Eq. (4.13) shows that $\vec{p}$ is the linear response of the medium to the applied electric field. Let $\vec{E}$ be an oscillating field, of frequency ω_i , and amplitude E_0 given by :

$$E = E(t) = E_0 \cos \omega_i t \quad (4.14)$$

Let us assume that the molecules of the medium vibrate with a frequency ω_v , such that the distance r between two neighboring molecules changes in time as :

$$r(t) = r_0 + A \cos(\omega_v t + \phi_v) \quad (4.15)$$

where r_0 is the equilibrium value of the intermolecular distance, and A and ϕ_v are the amplitude and phase of the molecular oscillation, respectively. The polarizability α has to reflect the particularities of the considered medium, i.e. it is reasonable to assume that α depends and changes with the intermolecular coordinate. By expanding α in a Taylor series and keeping the linear term in the molecular displacement one obtains :

$$\alpha = \alpha(r) = \alpha(r_0) + \left(\frac{\partial \alpha}{\partial r}\right)_{r_0} (r(t) - r_0) + \dots \quad (4.16)$$

Substituting Eq. (4.15) into Eq. (4.16) the expression for the polarizability becomes :

$$\alpha = \alpha(r_0) + \left(\frac{\partial \alpha}{\partial r}\right)_{r_0} \cdot A \cos(\omega_v t + \phi_v) \quad (4.17)$$

Using Eq. (4.17) the expression for the dipole moment given by Eq. (4.13) becomes :

$$p = \alpha(r_0) E_0 \cos \omega_i t + \left(\frac{\partial \alpha}{\partial r}\right)_{r_0} A E_0 \cos(\omega_v t + \phi_v) \cdot \cos \omega_i t = \quad (4.18)$$

$$p = \alpha(r_0) E_0 \cos \omega_i t + \left(\frac{\partial \alpha}{\partial r}\right)_{r_0} A E_0 \cos(\omega_v t + \phi_v) \cdot \cos \omega_i t = \quad p_v]$$

$= \alpha_0 E_0 \cos \omega_i t + \left(\frac{\partial \alpha}{\partial r}\right)_{r_0} \frac{A E_0}{2} \cos[(\omega_i - \omega_v)t - \phi_v] + \left(\frac{\partial \alpha}{\partial r}\right)_{r_0} \frac{A E_0}{2} \cos[(\omega_i + \omega_v)t + \phi_v]$ where the frequency of the scattered light is the same as that of the incident light. The second term describes a scattering process where the frequency of the scattered

light is $\omega_i - \omega_v$ (Stokes process) and the last term in Eq. (4.18) describes a process where the frequency of the scattered light is $\omega_i + \omega_v$ (anti-Stokes process).

The classical approach to Raman scattering suggests that the molecular vibration “modulates” the incident electromagnetic field such that the outgoing radiation can have different frequency if compared to the incident field, given by the sum and difference between the frequency of the incident field and the molecular frequency of vibration. It also shows that the operator responsible for Raman scattering is the polarizability α , i.e. it is the polarizability which gives the selection rules for the Raman effect. Although it provides the above mentioned results, the classical approach to Raman scattering is incomplete as, for example, it can neither explain the different intensities of the Stokes and anti-Stokes spectra, nor the selection rules for Raman scattering. In order to understand the real nature of inelastic light scattering, quantum mechanical methods have to be used.

4.2.5 Quantum mechanical theory

The quantum mechanical theory of Raman scattering was developed by Kramers, Heisenberg [4] and Dirac [5] who derived the expression for the Raman tensor, which is referred to as the KHD (Kramers - Heisenberg - Dirac) dispersion formula (Eq. (4.20)). Placzek [6] extended the theory of electronic polarizability (the Placzek polarizability theory) and showed that if : (i) the ground electronic state is nondegenerate and (ii) the excitation wavelength is off resonant, then the vibrational Raman intensities are approximately given by the vibrational matrix elements of the electronic polarizability and the KHD dispersion formula can be expressed in terms of the electronic polarizability tensor.

The differential cross section for the Raman scattering σ_R , is defined for given polarizations of the incident and scattered photons as the ratio between the number of scattered photons per unit solid angle around the direction of

observation, to the number of incident photons. The differential cross section σ_R is proportional to the sum squared over σ and ρ :

$$\sigma_R \sim \left| \sum_{\rho, \sigma} (\bar{\rho} \bar{l}_s)(\bar{\sigma} \bar{l}_i) a_{\rho\sigma} \right|^2 \quad (4.19)$$

where $\rho, \sigma = x, y, z$, $\bar{l}_i$ and $\bar{l}_s$ are the unit vectors for the direction of polarization for the incident and scattered photon, respectively, and $a_{\rho\sigma}$ is the Raman tensor, derived using second order perturbation theory, given by [4]:

$$a_{\rho\sigma}(f \leftarrow i) = \sum_e \left\{ \frac{\langle i | \mu_\sigma | e \rangle \langle e | \mu_\rho | f \rangle}{h(\nu_e - \nu_i - \nu_0) - i\Gamma_e} + \frac{\langle i | \mu_\rho | e \rangle \langle e | \mu_\sigma | f \rangle}{h(\nu_e - \nu_f + \nu_0) - i\Gamma_e} \right\} \quad (4.20)$$

$|i\rangle$, $|e\rangle$ and $|f\rangle$ are the initial, intermediate and final states, respectively, $h\nu_j$, ($j = i, e, f$) is the energy of state j , $h\nu_0$ is the energy of the exciting radiation, $i\Gamma_e$ the damping term for state $|e\rangle$ (given by its half-bandwidth and related to its lifetime) and μ_ρ the ρ component of the dipole moment. The notation Σ' indicates that $|i\rangle$ and $|f\rangle$ are excluded from the summation. Eq. (4.20) is the KHD dispersion relation.

A complete derivation of Eq. (4.20) is given by Birman [7] and will be briefly outlined as follows. The Hamiltonian of an interacting system of ions and electrons is given by :

$$H_0 = \sum_i \frac{1}{2m} \mathbf{p}_i^2 + \sum_\alpha \frac{1}{2M} \mathbf{P}_\alpha^2 + \sum_i \frac{e^2}{|\mathbf{x}_i - \mathbf{x}_i'|} + \sum_\alpha \frac{ZZ'e^2}{|\mathbf{X}_\alpha - \mathbf{X}_\alpha'|} - \sum_{i,\alpha} \frac{Ze^2}{|\mathbf{X}_\alpha - \mathbf{x}_i|} \quad (4.21)$$

where the latin indexes and lower case letters denote electronic operators, while greek indexes and upper case letters denote ionic operators. Eq. (4.21) contains the following terms : the first term represents the kinetic energy of the electronic system (m and $\mathbf{p}_i$ are the mass and momentum of an electron, respectively), the second term is the kinetic energy of the ionic system (M and $\mathbf{P}_\alpha$ are the mass and momentum of an ion, respectively), the third term is the electron-electron

interaction (x_i is the electronic coordinate), the fourth term is the ion-ion interaction (X_α is the ionic coordinate), and the last term is the electron-ion Coulomb interaction. As mentioned in Section 4.2.1 the Raman tensor contains the product of two terms describing the matter-radiation interaction (vertices M and N in Fig. 4.3).

The interaction of the system of electrons and ions with an incident electromagnetic field is introduced by the vector potential A . The Hamiltonian of the system given by Eq. (4.21) is changed by the presence of the field, which acts as a perturbation, by making the following substitutions :

$$\bar{p} \rightarrow (\bar{p} - \frac{e\bar{A}}{c}) \quad (4.22)$$

$$\bar{P} \rightarrow (\bar{P} + \frac{Ze\bar{A}}{c}) \quad (4.23)$$

Substituting Eqs. (4.22), (4.23) into Eq. (4.21) and making the expansion, the Hamiltonian of a system of electrons and ions interacting with an electromagnetic field is obtained as :

$$H = H_0 + \sum_i \frac{e}{mc} \bar{A} \bar{p}_i + \sum_\alpha \frac{Ze}{Mc} \bar{A} \bar{P}_\alpha + \sum_i \frac{1}{2m} (\frac{e}{c})^2 \bar{A}^2 + \sum_\alpha \frac{1}{2M} (\frac{Ze}{c})^2 \bar{A}^2 \quad (4.24)$$

The perturbation Hamiltonian H' used for computing the transition amplitudes usually contains only the linear terms in the vector potential from Eq. (4.24), i.e. :

$$H' = \sum_i \frac{e}{mc} \bar{A} \bar{p}_i + \sum_\alpha \frac{Ze}{Mc} \bar{A} \bar{P}_\alpha \quad (4.25)$$

The first term in Eq. (4.25) represents the electron-photon coupling while the second term represents a direct phonon-photon coupling. In order to assess the relative magnitude of these two terms a smallness parameter is introduced as [7] :

$$\frac{m}{M} = \kappa^4 \quad (4.26)$$

It can be shown that the phonon-photon coupling term is of the order of $Z\kappa^3$. For example, for Cr_{24}^{52} , the direct photon-phonon coupling is $\sim 4 \times 10^{-5}$ times the magnitude of the electron-photon coupling. This is the reason why many textbooks neglect this second term altogether stating that there is no direct photon-phonon interaction. Rigorously speaking, this term can not be discarded and will be incorporated, as shown next, in the dipole moment of the electron-ion pair.

As shown by Eq. (4.25) the usual approximation for deriving the Raman tensor is to neglect the A^2 terms which represent two-photon processes in Eq. (4.24). This approximation is valid in general for insulators but is no longer appropriate for the case of metals where a high density of free carriers is present [7]. It can be shown that in certain cases the A^2 terms are exactly zero (for example in the case of a transition between two states in different bands, or for vibrational transitions in the same electronic manifold), but attention has to be paid to whether the particularities of the system under investigation allow one to neglect the A^2 terms. This terms can be neglected for Raman scattering in insulators, which is the case of the material under investigation ($\text{Cr:Mg}_2\text{SiO}_4$).

By making the assumption that the electrons are localized at the ion or cell sites [8], the electronic index in Eq. (4.25) can be replaced with the ionic index, such that a general term in the perturbation Hamiltonian can be written as :

$$H'_\alpha = \left(\frac{e}{m} \bar{\mathbf{p}}_\alpha - \frac{Ze}{M} \bar{\mathbf{P}}_\alpha \right) \bar{\mathbf{A}} \quad (4.27)$$

Using the definition for the momentum operators :

$$\mathbf{p}_\alpha = m \frac{d\mathbf{r}_\alpha}{dt} \quad (4.28)$$

$$\mathbf{P}_\alpha = M \frac{d\mathbf{R}_\alpha}{dt} \quad (4.29)$$

where $\mathbf{r}_\alpha$ and $\mathbf{R}_\alpha$ are electronic and ionic displacements from some unperturbed position, the electron-ion term in Eq. (4.27) can be written as :

$$\frac{e}{m} \mathbf{p}_\alpha - \frac{Ze}{M} \mathbf{P}_\alpha = \frac{d}{dt}(\mathbf{e}\mathbf{r}_\alpha - Ze\mathbf{R}_\alpha) = \frac{d\boldsymbol{\mu}_\alpha}{dt} \quad (4.30)$$

where

$$\boldsymbol{\mu}_\alpha = \mathbf{e}\mathbf{r}_\alpha - Ze\mathbf{R}_\alpha \quad (4.31)$$

is the dipole operator of the electron-ion pair in cell α . The matrix element of the $d\boldsymbol{\mu}_\alpha/dt$ operator can be computed using Heisenberg's equation of motion :

$$\frac{d\boldsymbol{\mu}_\alpha}{dt} = \frac{i}{\hbar} [\mathbf{H}, \boldsymbol{\mu}_\alpha] \quad (4.32)$$

where $\mathbf{H}$ is the total Hamiltonian of the system. Using Eqs. (4.28) - (4.32), the perturbation given by Eq. (4.27) can be written as :

$$\mathbf{H}'_\alpha = \frac{i}{\hbar} [\mathbf{H}, \boldsymbol{\mu}_\alpha] \bar{\mathbf{A}} \quad (4.33)$$

The transition amplitude from an initial state $|i\rangle$ to a final state $|f\rangle$ due to a perturbation $\mathbf{H}'$ is given by :

$$A_{i \rightarrow f} \sim \sum_e \frac{\langle f | \mathbf{H}' | e \rangle \langle e | \mathbf{H}' | i \rangle}{E_e - E_i - \hbar\nu_0} \quad (4.34)$$

where $|e\rangle$ is an intermediate state of the system. After quantizing the radiation field, substituting Eq. (4.33) into Eq. (4.34), and acting with the Hamiltonian on its eigenfunctions in Eq. (4.34), one obtains an expression for the transition amplitude:

$$A_{i \rightarrow f} \sim \sum_e \frac{\langle f | \boldsymbol{\mu}_\alpha | e \rangle \langle e | \boldsymbol{\mu}_\alpha | i \rangle}{E_e - E_i - \hbar\nu_0} \quad (4.35)$$

formally similar to Eq. (4.20).

The KHD dispersion can be put in a more useful form using the adiabatic approximation [9] where the electronic $|m\rangle$ and vibrational $|n\rangle$ parts of the wavefunctions are separated :

$$|i\rangle = |g\rangle |i\rangle \quad (4.36)$$

$$|f\rangle = |g\rangle|j\rangle \quad (4.37)$$

$$|e\rangle = |e\rangle|v\rangle \quad (4.38)$$

As we are interested in a vibrational Raman transition, i.e. having the same initial and final electronic state, Eqs. (4.36), (4.37) were written for a system starting and ending in the ground electronic state $|g\rangle$, but suffering a change in the vibrational occupation number (from $|i\rangle$ to $|j\rangle$). The intermediate state $|e\rangle$ was also separated in its electronic $|e\rangle$ and vibrational $|v\rangle$ parts. Using the adiabatic approximation, Eq. (4.20) becomes :

$$a_{\rho\sigma}(j \leftarrow i) = \sum_{e \neq g} \sum_v \left\{ \frac{(i|[g|\mu_\sigma|e]|v)(v|[e|\mu_\rho|g]|j)}{h(\nu_{ev,gi} - \nu_0) - i\Gamma_{ev}} + \frac{(i|[g|\mu_\rho|e]|v)(v|[e|\mu_\sigma|g]|j)}{h(\nu_{ev,gj} + \nu_0) - i\Gamma_{ev}} \right\} \quad (4.39)$$

where $\nu_{ev,gi}$ and $\nu_{ev,gj}$ are the transition energies for the processes $|g\rangle|i\rangle \rightarrow |e\rangle|v\rangle$ and $|g\rangle|j\rangle \rightarrow |e\rangle|v\rangle$, respectively.

We are now using Placzek's second condition which states that the excitation energy $h\nu_0$ is far from the resonance energy $h\nu_{ev,gi}$. Using the fact that the electronic energies are much larger than the vibrational energies (as is the case for our system, see Chapter 3), the denominators in Eq. (4.39) can be approximated as :

$$h(\nu_{ev,gi} - \nu_0) - i\Gamma_{ev} \sim h(\nu_{e0,g0} - \nu_0) \quad (4.40)$$

$$h(\nu_{ev,gj} + \nu_0) - i\Gamma_{ev} \sim h(\nu_{e0,g0} + \nu_0) \quad (4.41)$$

In Eqs. (4.40), (4.41) both the vibrational energies and the damping constant which is comparable to the vibrational energies were neglected when compared to the electronic energies. Substituting Eqs. (4.40), (4.41) into Eq. (4.39), the only terms involved in the summation over the vibrational states are :

$$\sum_v |v\rangle\langle v| = 1 \quad (4.42)$$

The above equation expresses the closure relation for the vibrational wavefunctions. The Raman tensor given by Eq. (4.39) becomes :

$$a_{\rho\sigma}(j \leftarrow i) = (i | \sum_{e \neq g} \left\{ \frac{[g | \mu_\sigma | e][e | \mu_\rho | g]}{h(\nu_{e0,g0} - \nu_0)} + \frac{[g | \mu_\rho | e][e | \mu_\sigma | g]}{h(\nu_{e0,g0} + \nu_0)} \right\} | j) = (i | \alpha_{\rho\sigma} | j) \quad (4.43)$$

where $\alpha_{\rho\sigma}$ is the $\rho\sigma$ component of the electronic polarizability tensor. Eq. (4.43) shows that a Raman process is represented as the virtual (off-resonance) transitions to all electronic states in the system and that in the Placzek polarizability theory the Raman tensor is given by the polarizability tensor. Eq. (4.43) gives the selection rules for Raman processes and shows that the Raman tensor is real and symmetric due to the symmetry of the polarizability tensor, i.e. for off-resonance processes :

$$a_{\rho\sigma} = a_{\sigma\rho} \quad (4.44)$$

However, it should be stressed that the Raman tensor for a resonance process is not necessary symmetric any longer.

4.2.6 Symmetry of the Raman tensor. Selection rules for Raman processes

In this section it will be shown that the polarizability α changes like the squares of coordinates x^2 , xy , zy , etc., such that it is the squares of coordinates who give the selection rules for Raman processes. An example illustrating the selection rules and the connection between the symmetry of a Raman mode and the scattering geometry is given at the end of this section.

In all the following equations the double index summation convention is applied, i.e. summation is made whenever an index is double :

$$a_{ij}a_{jk} \equiv \sum_{j=1}^3 a_{ij}a_{jk} = a_{i1}a_{1k} + a_{i2}a_{2k} + a_{i3}a_{3k} \quad (4.45)$$

The polarizability tensor $\hat{\alpha}$ is given by Eq. (4.13). If a unitary, orthogonal transformation R :

$$R \cdot R^{-1} = 1, \text{ i.e. } (R^{-1})_{ij} = R_{ji} \quad (4.46)$$

is applied to both $\bar{p}$ and $\bar{E}$ in Eq. (4.13), after the transformation they become $\bar{p}'$ and $\bar{E}'$, given by :

$$\bar{p}' = R\bar{p} \quad (4.47)$$

$$\bar{E}' = R\bar{E} \quad (4.48)$$

We are looking for the transformation for the polarizability $\hat{\alpha}'$ written in the new basis :

$$\bar{p}' = \hat{\alpha}' \bar{E}' \quad (4.49)$$

Equating Eqs. (4.47) and (4.49), and writing $\bar{E}'$ as given by Eq. (4.48), one obtains

$$R\bar{p} = \hat{\alpha}' R\bar{E} \quad (4.50)$$

The left-hand multiplication of Eq. (4.50) by R^{-1} gives :

$$\bar{p} = R^{-1} \hat{\alpha}' R\bar{E} \quad (4.51)$$

The comparison between Eq. (4.51) and Eq. (4.13) yields :

$$\hat{\alpha} = R^{-1} \hat{\alpha}' R \quad (4.52)$$

which can be inverted, leading to :

$$\hat{\alpha}' = R\hat{\alpha}R^{-1} \quad (4.53)$$

The ij^{th} component of the above equation can be written, using Eq. (4.46) as :

$$\alpha'_{ij} = R_{ik} \alpha_{kl} R_{lj}^{-1} = R_{ik} R_{jl} \alpha_{kl} \quad (4.54)$$

Eq. (4.54) gives the transformation of the polarizability tensor.

On the other hand, the coordinate vectors change under the unitary transformation as :

$$\bar{X}' = R\bar{X} \quad (4.55)$$

The i^{th} component of Eq. (4.55) can be written as :

$$X'_i = R_{ik} X_k \quad (4.56)$$

It follows that the squares of coordinates change as :

$$X'_i X'_j = R_{ik} X_k R_{jl} X_l = R_{ik} R_{jl} (X_k X_l) \quad (4.57)$$

Eq. (4.57) is formally identical to Eq. (4.54) showing that the polarizability tensor changes in the same way as the squares of coordinates. As shown in Section 3.2.2.6 the amplitude of transition for a one phonon process is given by the product between the representation corresponding to the operator inducing the transition (which is the polarizability for a Raman process, as shown above) and the representation corresponding to the wavefunction of the created (or annihilated phonon). It was also shown that due to the orthogonality of the representations of a group, the operator and the phonon wavefunction have to belong to the same representation, or, using Eqs. (3.54) and (3.57), for a first order Raman process a phonon wavefunction has to change as the polarizability, i.e. as the squares of coordinates. The formal identity between Eqs. (3.54) and (3.57) gives the selection rules for first order Raman processes as follows : a phonon mode is Raman active if it belongs to a representation having as basis the square of coordinates.

The above rule will be illustrated with an example as follows. In Section 4.2.5 it was shown that the operator inducing Raman scattering is the polarizability which changes like the squares of coordinates (see also Appendix A.4). Let us consider a crystal with D_{2h} space group symmetry, where a Stokes process is observed. In a Stokes process the system is initially in the vibrational ground state which is totally symmetric, i.e. $\Psi_i = A_{1g}$, where Ψ_i is the wavefunction of the initial (vibrational) state, and A_{1g} is the totally symmetric representation in a D_{2h} group (see Appendix A.3). Let us assume that the experiment is performed in a $a(ca)b$ scattering geometry given in Porto's notation (see Section 2.6), i.e a 90° arrangement with the incident light parallel to the c -crystal axis and the analyzer (giving the polarization of the scattered light) along the a axis. This means that we are observing a process due to the ca -component of the polarizability (α_{ca}), or

using Cartesian notations, due to the zx -component of the polarizability. Using again the table for D_{2h} in Appendix A.3 we find that the representation which has as basis zx ($= xz$ as the Raman tensor is symmetric) is B_{2g} . We know at this point the symmetry of the initial state - A_{1g} and the symmetry of the operator inducing the transition (Raman process) - B_{2g} . In order for the transition to be allowed the symmetry of the final vibrational state Ψ_f , i.e. the symmetry of the created phonon (as in a Stokes process the initial and final vibrational states differ only by one phonon which was created during the process) has to be such that $\Psi_i \cdot \alpha_{xz} \cdot \Psi_f = A_{1g}$, as shown by Eq. (3.29). Using the fact that the totally symmetric representation is the neutral element of the group, Ψ_f has to be determined such that $\alpha_{xz} \cdot \Psi_f = B_{2g} \cdot \Psi_f = A_{1g}$. Applying the orthonormality of a group's representations it follows that $\Psi_f = B_{2g}$ i.e. the phonons observed using an $a(ca)b$ scattering geometry in a D_{2h} crystal, are of B_{2g} symmetry.

The above result is in fact a very general one which can be extended to anti-Stokes processes too, where the vibrational wavefunction of the final state is totally symmetric. Based on the orthogonality of a group's representations the general result is that for one-phonon processes, the symmetry of the observed phonons is the same as the symmetry of the component of the polarizability producing the scattering. For example, using the group tables given in Appendix A.3 and the above selection rule it follows that for a T_d group where only the A_1 , E and T_2 representations have as basis squares of coordinates, the only phonons which are Raman active are those of symmetry A_1 , E or T_2 . Moreover, using the fact that T_2 has as basis (xy, xz, yz) , it follows that T_2 phonons can be observed only in scattering configurations where that polarizer and analyzer are perpendicular to each other (i.e. in Porto's notation (xy) or (xz) or (yz)). The same T_2 phonons can not be observed if the polarizations of the incident and scattered beams are parallel to each other.

4.3 Resonance Raman scattering

The theory of resonance enhancement was pioneered by Albrecht [10] and Shorygin [11] and later developed by Tonks [12], Nafie [13] and Hassing [14]. The basic ideas of resonance Raman enhancement can be found in different textbooks (see e.g. [9]) and are underlined in this section.

If the incident wavelength $h\nu_0$ is in resonance with an intermediate state $|e\rangle|v\rangle$, the second Placzek condition is not valid any more and the approximation given by Eqs. (4.40), (4.41) can not be used. We start again with Eq. (4.39) where an analytical form of the intermediate resonant state $|e\rangle$ is obtained using first order time independent theory. It should be reminded that the first order correction $|\Psi^{(1)}\rangle$ to the wavefunction of the unperturbed system $|u_n\rangle$ due to a perturbation H' is :

$$|\Psi^{(1)}\rangle = \sum_{n \neq m} \frac{H'_{nm}}{E_n - E_m} |u_n\rangle \quad (4.58)$$

The Hamiltonian of the system is expanded into a Taylor series in the normal vibrational coordinates Q_a of the ground state, retaining only the linear term :

$$H = H_{el} + H_{vib} + \sum_a \left(\frac{\partial H_{ev}}{\partial Q_a} \right)_{|0} Q_a \quad (4.59)$$

where H_{el} is the electronic Hamiltonian at the equilibrium position of the nuclei, in the ground state, H_{vib} is the vibrational Hamiltonian. The last term which represents the perturbation, can be rewritten as :

$$H' = \sum_a \left(\frac{\partial H_{ev}}{\partial Q_a} \right)_{|0} Q_a = \sum_a h_a Q_a \quad (4.60)$$

where h_a is the electron-phonon coupling operator defined as the derivative of the electron-vibrational coupling operator H_{ev} with respect to the normal coordinates, calculated at the position of equilibrium. It should be noted that h_a is an operator which depends on electronic coordinates. Applying first order perturbation theory

to the intermediate electronic state $|e\rangle$, using Eq. (4.58) and the perturbation Hamiltonian in Eq. (4.60), the first order correction to the electronic wavefunction due to electron-phonon coupling is :

$$|e^{(1)}\rangle = \sum_{s \neq e} \sum_a \frac{(h_a Q_a)_{se}}{h(\nu_{s0} - \nu_{e0})} |s_0\rangle = \sum_{s \neq e} \sum_a \frac{[e_0 | h_a | s_0]}{h(\nu_{s0} - \nu_{e0})} Q_a |s_0\rangle \quad (4.61)$$

where $|e_0\rangle, |s_0\rangle$ are unperturbed electronic functions such that :

$$H_{el} |e_0\rangle = \nu_{e0} |e_0\rangle \quad (4.62)$$

$$H_{el} |s_0\rangle = \nu_{s0} |s_0\rangle \quad (4.63)$$

The corrected electronic wavefunction can be written from Eq. (4.61) as :

$$|e\rangle = |e_0\rangle + \sum_a \sum_{s \neq e} \frac{[e_0 | h_a | s_0]}{h(\nu_{s0} - \nu_{e0})} Q_a |s_0\rangle \equiv |e_0\rangle + |e^{(1)}\rangle \quad (4.64)$$

When Eq. (4.64) is substituted into Eq. (4.39) the Raman tensor becomes :

$$a_{\rho\sigma} = \sum_{c \neq g} \sum_v \frac{(i)[g|\mu_\sigma|(|e_0\rangle + |e^{(1)}\rangle)](v)(v)[(|e_0\rangle + |e^{(1)}\rangle)|\mu_\rho|g]|j)}{h(\nu_{cv} - \nu_{gi} - \nu_0) - i\Gamma_{cv}} + \text{a similar term} \quad (4.65)$$

The second term in Eq. (4.65) is formally identical to the first term, the difference being that μ_ρ and μ_σ permute, and the denominator of the second term is $h(\nu_{cv} - \nu_{gi} + \nu_0) - i\Gamma_{cv}$. The numerator will give four terms of the form :

$$a_{\rho\sigma} \sim |e_0\rangle [e_0 + |e^{(1)}\rangle] [e^{(1)} + |e^{(1)}\rangle] [e_0 + |e^{(1)}\rangle] [e^{(1)}] \quad (4.66)$$

As in the case of the Hamiltonian, only linear terms in Q_a ($|e^{(1)}\rangle$) are kept, i.e. the last term which represents a two phonon process is neglected. The first term in Eq. (4.66) gives the so called A-Albrecht term to the Raman tensor given by Eq. (4.65) as :

$$A = \sum_{c \neq g} \sum_v \frac{[g_0|\mu_\sigma|e_0][e_0|\mu_\rho|g_0](i|v)(v|j)}{h(\nu_{cv} - \nu_{gi} - \nu_0) - i\Gamma_{cv}} \quad (4.67)$$

It should be noted that the second term in Eq. (4.39) gives rise to a similar to the above term where μ_ρ and μ_σ permute and the denominator is $\hbar(\nu_{ev} - \nu_{gi} + \nu_0) - i\Gamma_{ev}$.

Several observations can be made regarding the A term :

- (i) The A-term is non-zero if the transition from the electronic ground state $|g_0\rangle$ to the resonance state $|e_0\rangle$ is dipole allowed, i.e. $[g_0|\mu_{\sigma,\rho}|e_0] \neq 0$.
- (ii) As the vibrational wavefunctions are representations of the group describing the molecule of interest, using the orthogonality of representations it follows that the A term is non-zero only if the initial, final and intermediate one phonon vibrational wavefunctions $|i\rangle$, $|j\rangle$ and $|v\rangle$, respectively, have the same symmetry. As in general the initial (for a Stokes process) or the final (for an anti-Stokes process) vibrational wavefunctions describe the system in the ground state, i.e. are totally symmetric, it follows that only totally symmetric modes give rise to the A-Albrecht term.
- (iii) The A term is zero for a zero Stokes shift (i.e. if the overlap integrals also called Franck-Condon integrals $\langle i|v\rangle$ or $\langle v|j\rangle$ are zero). As a significant Stokes shift is associated with a strong electron-phonon interaction (see Section 4.5), it follows that only totally symmetric modes for which the electron-phonon coupling is sizable are resonance enhanced due to the A-term.

The second and third term (linear in the first order correction to the electronic wavefunction) in Eq. (4.66) give rise to the B-Albrecht term. By substituting these terms given by Eq. (4.55) into Eq. (4.39) one obtains, taking into account that Q_a acts only on the vibrational part of the wavefunction :

$$B = \sum_{e \neq g} \sum_a \sum_{v \neq e} \frac{[g_0|\mu_\rho|e_0][e_0|h_a|s_0][s_0|\mu_\sigma|g_0](i|Q_a|v)(v|j)}{\hbar(\nu_{e0} - \nu_{s0})[\hbar(\nu_{ev} - \nu_{gi} - \nu_0) - i\Gamma_{ev}]} +$$

$$+ \frac{[g_0|\mu_\sigma|e_0][e_0|h_a|s_0][s_0|\mu_\rho|g_0](i|v)(v|Q_a|j)}{h(\nu_{e0} - \nu_{s0})[h(\nu_{ev} - \nu_{gi} - \nu_0) - i\Gamma_{ev}]} \quad (4.68)$$

As for the A-term, two more similar terms are obtained from the second term in Eq. (4.39) with the only difference that μ_ρ and μ_σ permute and that the denominator is $h(\nu_{e0} - \nu_{s0})[h(\nu_{ev} - \nu_{gi} + \nu_0) - i\Gamma_{ev}]$. The following remarks can be made regarding the existence of the B-term :

- (i) The B-term requires the existence of a second excited electronic state $|s_0\rangle$ which is vibronically coupled with the resonance state $|e_0\rangle$, such that $[s_0|h_a|e_0]/h(\nu_{e0} - \nu_{s0}) \neq 0$. The closer the two electronic states are (i.e. the smaller the denominator) the larger the B term.
- (ii) The B-term is nonzero if the transition from the ground state to two excited electronic states $|e_0\rangle$ and $|s_0\rangle$, which are coupled by the electron-phonon operator h_a , is dipole allowed, i.e. $[g_0|\mu_\rho|e_0] \neq 0$ and $[s_0|\mu_\sigma|g_0] \neq 0$
- (iii) The symmetry of the two excited electronic states has to be such that $[e_0|h_a|s_0] \neq 0$, where the symmetry of h_a is the same as that of the phonon mode Q_a enabling the transition (see Section 4.4).
- (iv) As the B-term involves a change by one in the occupation number of the mode Q_a , the initial and final vibrational states don't have to have the same symmetry any longer, i.e. B-terms account for the resonance enhancement of nontotally symmetric modes.

The Raman tensor for a resonance process can be written using the A and B terms given by Eqs. (4.67) and (4.68) as :

$$a_{\rho\sigma}(j \leftarrow i) = A + B \quad (4.69)$$

Eqs. (4.67), (4.68) show that some modes of vibration of a system (phonons or local modes) can be enhanced due to resonance effects obtained by any of the A

or B mechanisms, if the incident excitation ν_0 is in resonance with an excited electronic state $|e\rangle$, i.e. is in an absorption band of the material under investigation, such that :

$$\nu_0 \approx \nu_{ev} - \nu_{gi} \quad (4.70)$$

Eq. (4.70) leads to a significant increase in the magnitude of the A and B terms due to the smallness of the denominator. It should be noted that the absorption band $|e\rangle$ where the incident laser wavelength is tuned in order to obtain resonance Raman scattering can be the conduction band of the crystal for the case of resonance enhancement of phonon modes, or an electronic state of the impurity ion, usually situated in the band gap of the crystal host, for the case of resonance enhancement of local modes.

4.4 Particularities of resonance Raman scattering for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$

As throughout this thesis the focus is on resonance enhanced local modes of Cr^{4+} , Eqs. (4.67) and (4.68) will be considered for the particular case of this ion. In Chapter 3 it was shown that Cr^{4+} substitutes for Si^{4+} in Mg_2SiO_4 in a position with C_s site symmetry. Thus, the group which has to be considered for determining the selection rules for Cr^{4+} local modes is C_s . The table of characters of the group C_s is given in Appendix A.3 and shows that this group contains only two (orthogonal) representations : a totally symmetric representation A' and a totally anti-symmetric representation A'' . The following multiplication laws can be written for C_s :

$$A' \times A' = A'' \times A'' = A' \quad (4.71)$$

$$A' \times A'' = A'' \times A' = A'' \quad (4.72)$$

It should be reminded (see Eq. (3.29)) that a transition is allowed only if the product of representations of the wavefunctions for the initial and final states and

of the operator inducing the transition contains the totally symmetric representation (A' in our case).

All resonance experiments presented in Chapters 5 - 7 excite Cr^{4+} ions from the ${}^3A_2$ ground state (expressed in the approximate to C_s , C_{2v} symmetry) to the excited ${}^3B_2$ electronic state at ~ 575 nm. As showed in Section 3.4 it is more appropriate to write all Cr^{4+} states in terms of the real C_s symmetry. The symmetry of the Cr^{4+} electronic states is, expressed in C_s (see Section 3.4) : ground state $|g_0\rangle - {}^3A''$, excited state $|e_0\rangle$ at 575 nm - ${}^3A''$, neighboring states $|s_0\rangle$ which can be vibronically coupled with $|e_0\rangle$, at 15300 cm^{-1} - ${}^3A'$ and at 15875 cm^{-1} ${}^1E$ (in C_{2v}) which becomes ${}^1A' + {}^1A''$ in C_s . The upper left-hand side index of the electronic states gives the spin multiplicity. According to observation (i) for the B-term (see Section 4.3), the largest resonance enhancement of the B-type modes of vibration is given by the closest to $|e_0\rangle$ neighboring electronic state $|s_0\rangle$, i.e. the B-type local modes obtained under 575 nm excitation are expected to be due to the coupling between the state at 13850 cm^{-1} with any of the states at 15300 and at 15875 cm^{-1} .

The $|g_0\rangle \leftrightarrow |e_0\rangle$ transition is dipole allowed if the dipole moment belongs to A' , as only in this case the transition amplitude of symmetry $A'' \times A' \times A'' = A'$ is nonzero. According to the expression of the A-term in Eq. (4.67) it follows that totally symmetric A' Cr^{4+} local modes are absent from the resonance Raman spectrum only if they do not induce a Stokes shift, i.e. if the electron-phonon coupling is weak for them. It can also be noted that the A-term is in general nonzero if $|j\rangle = A'$. But for multiphonon processes (like the observation of combinations or mode overtones - see Chapter 6) this implies, from Eqs. (4.71), (4.72) that $|j\rangle$ has to contain an even number of A'' phonons, as $(A'')^{2k} = A'$ with k an integer. Thus, in principle, the A-term also accounts for overtones and combinations of A' modes and/or an even number of A'' vibrations. The A term can not account for the creation or annihilation of one A'' vibration.

We will now look under what conditions can A'' (B-type) local modes be observed in the resonance Raman spectrum of Cr^{4+} . Such a type of Stokes process requires $|j\rangle = A''$ (creation of an A'' vibration) in Eq. (4.68), and $|i\rangle = A'$ (symmetric ground state). A similar argument can be made for an anti-Stokes process where $|i\rangle = A''$ and $|j\rangle = A'$ (the system ends up in the ground state). In order for the first term in Eq. (4.68) to be nonzero :

$$(v|j) = A' \quad (4.73)$$

and

$$(i|Q_a|v) = A' \quad (4.74)$$

Using Eq. (4.72), Eq. (4.73) gives $|v\rangle = A''$. In order for Eq. (4.74) to hold (with $|i\rangle = A'$), $Q_a = A''$. This means that a nontotally symmetric mode Q_a was created. On the other hand this mode has to couple the two excited electronic states $|e_0\rangle$ and $|s_0\rangle$. As the Hamiltonian of interaction given by Eq. (4.60) is a scalar (i.e. totally symmetric) it follows that due to the orthogonality of the representations in a group, h_a and Q_a have to have the same symmetry. Returning to the case of Cr^{4+} , this means that if $Q_a = A''$ then $h_a = A''$. Using $|e_0\rangle = A''$ (the state at 575 nm), in order to have nonzero vibronic coupling, $|s_0\rangle = A'$. But this condition is satisfied for both neighboring to $|e_0\rangle$ states at 15300 and 15875 cm^{-1} .

Summarizing, it was shown that the B term only is responsible for one-phonon A'' processes which occur only if the A'' vibration couples two neighboring excited electronic states of different symmetries (A' and A''). The absence of an A'' local mode from the resonance Raman spectrum signals the fact that this particular mode does not effectively couple the $|e_0\rangle$ and $|s_0\rangle$ excited states.

4.5 Electron-phonon coupling

In this section we will consider the effect of electron-phonon coupling on the energetic configuration of an impurity ion embedded into a lattice and the correlation between the Stokes shift and the electron-phonon coupling.

Let us start by considering an impurity ion which can be described as a perfect harmonic oscillator vibrating with frequency ω along the coordinate Q_a . In the case of a one-dimensional chain, Q_a is the deviation from the equilibrium position of the inter-nuclear distance. For a three-dimensional lattice, Q_a is the generalized coordinates. It is worth noting that for a molecule with N ions there are $3N$ modes of vibration, each of them having associated a generalized coordinate Q_a , $a = 1 \div 3N$. In the approximation of a harmonic system each mode of vibration is independent, such that the molecule is described in a $3N$ -dimensional energy space by a system of $3N$ independent harmonic oscillators. For simplicity, but without affecting the generality of the problem, only one of the $3N$ harmonic oscillators will be considered.

In the case when the electronic and the vibrational parts of the system are independent (uncoupled), i.e. when the motion of the electrons and of the ions can be separated, the energy of an excited state is given by the sum of the electronic energy (E_{el}) and the vibrational energy (E_{vib}). If the energy of the ion is calculated as a function of the coordinate Q_a in the harmonic approximation, only the energy of vibration depends on Q_a while the electronic energy is a constant (does not depend on the coordinate Q_a as the electronic and vibrational motions are independent). The energy for an ion where there is no electron-vibrational (electron-phonon) coupling can be written as :

$$E = E_{el} + E_{vib} = C + \frac{1}{2} \omega^2 Q_a^2 \quad (4.75)$$

Eq. (4.75) shows that the “pure” electronic energy does not depend on Q_a and was denoted as a constant C , while the vibrational energy (second term) is given by the classical formula for a harmonic oscillator where the mass of the oscillator was absorbed in the generalized coordinate. Eq. (4.75) gives the energy for a system with no electron-phonon coupling and was written taking as reference the ground state. If the energy given by Eq. (4.75) is plotted as a function of Q_a it is immediately obtained that the excited electronic state is a parabola having its minimum given by :

$$\frac{\partial E}{\partial Q_a} = 0 = \omega^2 Q_a \Rightarrow Q_a = 0 \quad (4.76)$$

Thus, the excited state is “vertically shifted” with respect to the ground state, having its minimum in the vibrational position of equilibrium ($Q_a = 0$). Eq. (4.75) also shows that the excited state has its minimum situated at :

$$E_{\min} = E(Q_a = 0) = C \quad (4.77)$$

The energy diagram for a system with no electron-phonon coupling is shown in Fig. 4.5 (a). A very interesting observation is that for Fig. 4.5 (a) an electronic transition (marked by the thick vertical arrows) produces only zero-phonon transitions ($|0\rangle \rightarrow |0\rangle$, $|1\rangle \rightarrow |1\rangle$, etc.), i.e. transitions where the vibrational occupation number does not change. The electronic transitions are “vertical” as they are fast compared to the period of oscillations of the ions, so that the ionic coordinate Q_a does not have time to change during the electronic transition. For a system with no electron-phonon interactions the absorption and emission bands coincide (are not shifted) and the Stokes shift (which is measured as the “horizontal” shift of the excited state along the generalized coordinate) is zero. The overlap integrals given by Eq. (4.67) are zero (due to the zero Stokes shift) as a change by one in the phonon occupation number is not possible. Thus, a system with no electron-phonon interaction is characterized by a zero Stokes shift

and zero Franck-Condon integrals (implying, for example, that it can not give rise to A - Albrecht terms in a resonance Raman spectrum - see Eq. (4.67)).

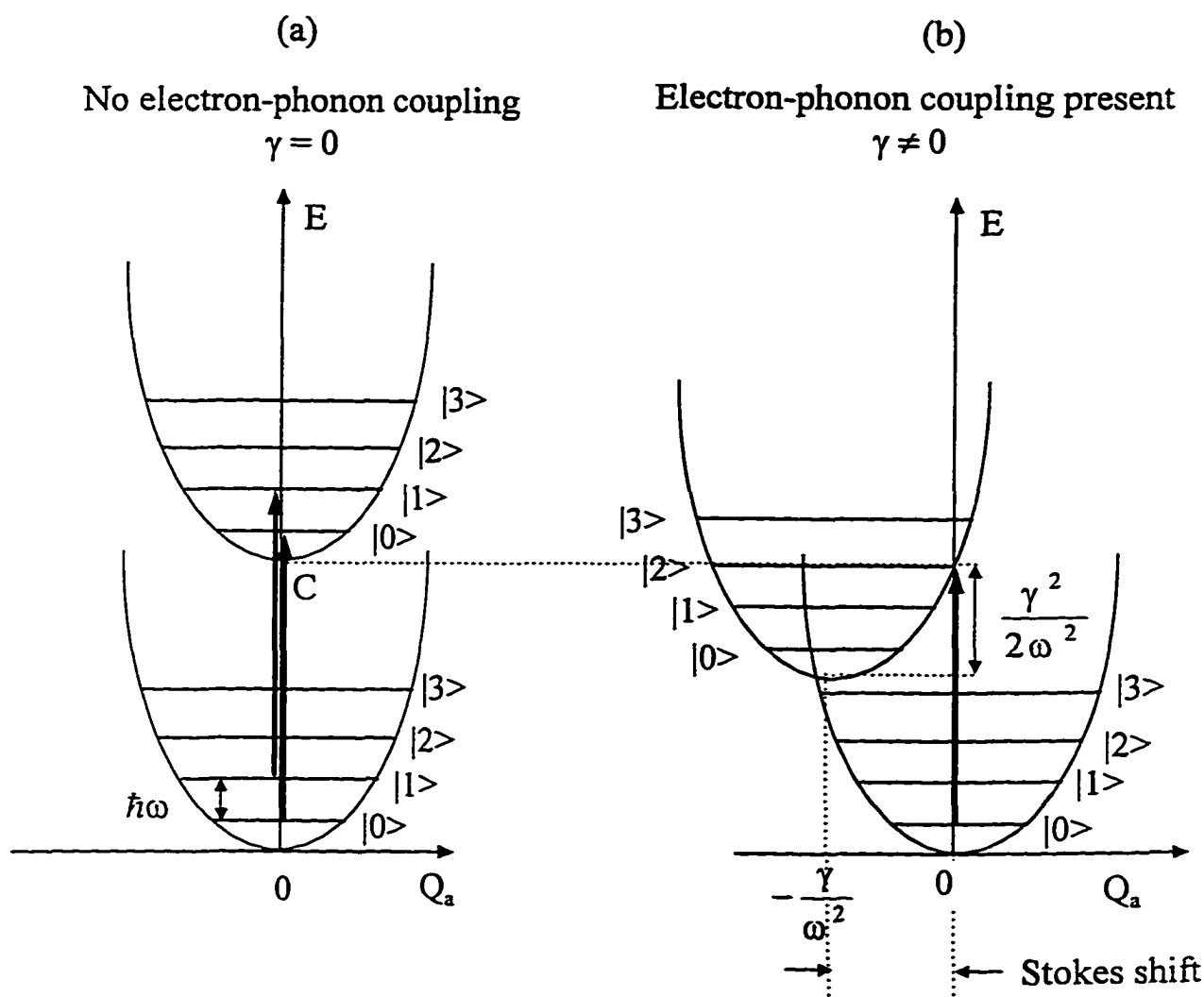


Figure 4.5 Schematic diagram of electron-phonon interaction effects.

If we now consider a system where electron-phonon coupling is present, the energy of the system given by Eq. (4.75) has to contain an additional "cross-term" mixing the electronic and the vibrational motions. As shown by Eqs. (4.59), (4.60) the cross-term is obtained by expanding the Hamiltonian of interaction in powers of Q_a and keeping only the linear term. Considering Eq. (4.60) for the case of a

single harmonic oscillator, the electron-phonon interaction energy can be written as :

$$E_{\text{el-ph}} = h_a Q_a \stackrel{\text{not}}{=} \gamma Q_a \quad (4.78)$$

h_a in the above equation is the electron-phonon coupling operator and depends on the electronic coordinates. Q_a , on the other hand depends on the nuclear coordinates, such that the term given by Eq. (4.78) is indeed a cross term of the electronic and nuclear motion. As we are considering one harmonic oscillator, Q_a is one-dimensional (scalar). Taking into account the fact that the energy is also a scalar, it follows that in the case of one harmonic oscillator h_a is a scalar which was denoted in Eq. (4.78) as γ .

The energy of a system where electron-phonon interaction is present ($\gamma \neq 0$) is given by summing Eqs. (4.75), (4.78) as :

$$E = E_{\text{el}} + E_{\text{vib}} + E_{\text{el-ph}} = C + \frac{1}{2} \omega^2 Q_a^2 + \gamma Q_a \quad (4.79)$$

It can be noted that Eq. (4.75) describing a system with no electron-phonon interactions can be obtained from Eq. (4.79) for $\gamma = 0$. As before, if the energy of the excited state given by Eq. (4.79) is plotted as a function of the normal coordinate, its minimum is given by :

$$\frac{\partial E}{\partial Q_a} = 0 = \omega^2 Q_a + \gamma \quad \Rightarrow \quad Q_a = -\frac{\gamma}{\omega^2} \quad (4.80)$$

The above equation shows that the minima of the ground and excited states for a system where electron-phonon interaction is present do not coincide in coordinate space any longer, and that they are “horizontally” shifted by the amount γ / ω^2 (see Fig. 4.5 (b)). Thus, the first consequence of the presence of electron-phonon interaction is the apparition of a Stokes shift ($Q_a \neq 0$) which is proportional to the electron-phonon interaction operator.

The minimum value of the energy in the presence of electron-phonon coupling is obtained from Eqs. (4.79), (4.80) at :

$$E_{\min} = E(Q_a = -\frac{\gamma}{\omega^2}) = C + \frac{\omega^2}{2}(-\frac{\gamma}{\omega^2})^2 + \gamma(-\frac{\gamma}{\omega^2}) = C - \frac{\gamma^2}{2\omega^2} \quad (4.81)$$

The above equation shows that the second effect of electron-phonon coupling is that the excited state is “pulled” toward the ground state by the amount $\gamma^2/2\omega^2$. Eq. (4.81) shows that the stronger the electron-phonon coupling, the closer the two states get. The effects of electron-phonon interaction on the energy levels of an impurity ion are schematically depicted in Fig. 4.5 (b)

The most important effect of electron-phonon interactions is the presence of a Stokes shift which depends on the electron-phonon coupling and allows transitions where the vibrational quantum number is changed (see Fig. 4.5 (b)). Fig. 4.5 (b) suggests that the stronger the electron-phonon coupling, the larger the Stokes-shift and the larger the change in the vibrational occupation number. It is interesting to stress the fact that following this argument, a long progression of overtones (ω , 2ω , 3ω , ...) for a mode of vibration ω indicates relative strong electron-phonon coupling for this particular mode [15].

As mentioned in Section 4.3 it is only modes with Stokes shifts (i.e. which experience electron-phonon interactions) which give rise to A-type resonance enhanced modes. As a consequence, the absence of an A-type term from the resonance Raman spectrum can be connected to the weakness of electron-phonon interactions for this mode. It is also interesting to note that as shown by Eq. (4.60) each mode of vibration Q_a is characterized by a different electron-phonon operator h_a , i.e. for impurity-doped systems electron-phonon interactions are not a “global” characteristic, but rather a local, mode-dependent one.

A second consequence of the Stokes shift is the fact that the maxima of absorption and emission do not coincide any more (the emission is usually red-shifted with respect to the absorption). Thus, the most straightforward proof of the

presence of a Stokes shift (and of electron-phonon interactions) is to measure the shift between the absorption and emission peaks for a given electronic state. Unfortunately there are cases (e.g. the ${}^3B_2({}^3T_1)$ Cr^{4+} state in $Cr:Mg_2SiO_4$) when the radiative emission is absent, and the ion relaxes nonradiatively by tunneling to a lower lying electronic state and sliding down the electronic parabola (see Chapter 7). The second disadvantage of assessing electron-phonon interactions from comparing the absorption and emission peaks is the fact that both absorption and emission are global processes which include the contribution of all modes of vibration. Thus, the “global” Stokes shift given by absorption and emission spectra can be interpreted as the convolution of all Stokes shifts given by all the modes of vibration in the system. On the other hand, resonance Raman spectra resolves the strength of the individual electron-phonon coupling for each mode of vibration. For example, if the resonance Raman spectrum given by the transition to an electronic state is measured, different intensities for different resonance enhanced modes are ultimately given by different overlap integrals in Eq. (4.67). But, as discussed above, the overlap integrals depend on the Stokes shifts for individual resonance enhanced modes, given by electron phonon coupling for each mode (see Eq. 4.80). Thus, the resonance Raman spectrum gives an “individual” picture of the electron-phonon coupling for each resonance enhanced mode.

4.6 References

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Chapter 5

Characterization of Cr^{4+} local modes in $\text{Cr:Mg}_2\text{SiO}_4$ using room temperature resonance Raman measurements

5.1 Background. Phonon and local modes

The normal modes of vibration of a crystal (see section 3.2.2) are measured using infrared (IR) and Raman scattering. It can be shown using group theory considerations and the fact that only representations which have as basis squares of coordinates are Raman active (see Section 4.2.6 and Appendix A.3), that if a system has center of inversion (c_i) its vibrations are either IR-active (the odd vibrations, i.e. “u”), or Raman active (the even vibrations, i.e. “g”). This is, for example, the case of a system with D_{2h} symmetry, like Mg_2SiO_4 (see Appendix A.3) where the A_g , B_{1g} , B_{2g} and B_{3g} representations are Raman active, i.e. have as basis the square of coordinates, while the B_{1u} , B_{2u} and B_{3u} representations are IR active, i.e. have as basis the Cartesian coordinates. On the other hand, a system without center of inversion can have modes of vibration which are both IR and Raman active. This is the case of the T_2 representation belonging to the T_d group and the case of both A' and A'' representations belonging to the C_s group (see Appendix A.3).

A “perfect” crystal, without impurities, inclusions or other defects is invariant under translations, i.e. can be completely reconstructed by translating the unit cell along the three crystal axes. The solution of the Schrodinger equation describing the ionic oscillations of a crystal lattice is periodic both in $\vec{r}$ (coordinate) and $\vec{k}$ (reciprocal momentum) space and is called a phonon [1, 2]. It should be reminded that the total number of phonons (in fact phonon bands) and their symmetry is given by the space, site and molecular symmetry, as well as by

the number of ions in the unit cell (see Section 3.2). Polarized Raman and/or IR measurements of a crystal will determine the energy of the phonon modes at $\bar{\mathbf{k}} \cong 0$, i.e. at the center of the Brillouin zone [2].

Once impurity ions are randomly introduced into the lattice host, the translational invariance is broken as the unit cells are not equivalent any more; some of them now contain the randomly distributed impurity ions. The vibrational spectrum for such a system can not be rigorously described by phonons any longer. The vibrational spectrum now contains features from both host and the impurity ion. When the doping level is low ($< 0.1 - 0.2$ at %) the following approximation can be made : the vibrational spectrum of the impurity-doped crystal consists of the unperturbed phonon spectrum of the host plus the modes (bands) of vibration of the impurity ion (local modes). It should be noted that the above approximation no longer holds at high doping levels when the system behaves like an alloy, and the energy (frequency) of phonon modes is a function of the doping level.

As previously shown in Section 3.2 there are three types of modes of vibration : translations, rotations and internal vibrations. Due to the low doping level only one in every $10^4 - 10^5$ molecules which contribute to the collective modes of translation and rotation is “different” due to the presence of the impurity. Accordingly, the frequency shift it produces for a given translation/rotation mode is practically zero if compared to the similar spectrum of the undoped host. On the other hand, each molecule has its independent modes of internal vibration. The molecules containing impurity ions, i.e. the impurity ion surrounded by the first neighboring lattice ions, are expected to vibrate at different frequencies than the analog host molecules. This Raman signal describing a different frequency of vibration of the impurity molecule if compared to a similar lattice host molecule, although weak, is detectable unless it overlaps with a strong phonon mode. One expects the vibrational spectrum of a low-doping-level impurity-doped crystal to

be identical to the phonon spectrum of the host and to contain additional weak features due to internal vibrations of the impurity molecule.

The technique used to compensate for the reduced number of impurity ions leading to a weak Raman signal arising from the local modes, is resonance Raman scattering (see Section 4.3). When the excitation wavelength ν_0 is tuned inside an absorption band of the impurity ions under investigation (see Eqs. (4.67) - (4.70)), the mode of vibration of the impurity only are selectively enhanced up to 3 - 4 orders of magnitude [3] such that they have intensities comparable to the phonon modes of the host and appear in addition to the phonon spectrum. If the excitation wavelength is tuned outside the absorption band, sometimes by as little as 5-10 nm (see Section 6.3), the impurity's local modes "disappear" while the phonon modes of the host remain invariant.

For the general case of transition-metal-ion doped olivine hosts, the visible excitation wavelength corresponding to an absorption band of the impurity ion under investigation plays two roles : (a) it produces a Raman spectrum for the host, and (b) it produces a resonance Raman spectrum for the impurity ion. The crystal host has a wide band gap and is transparent for visible light. The host gives rise to the phonon spectrum by regular Raman scattering. On the other hand, the impurity ions (Cr^{4+}) have several absorption bands in the visible region, such that the doped crystal appears colored. As the absorption is polarization dependent (see Fig. 3.11) the doped crystal has different colors if viewed along different crystal directions, using a polarizer. If the excitation wavelength is tuned to one of the Cr^{4+} absorption bands, and the appropriate polarization which gives rise to the absorption band is used, the resonance Raman spectrum of the impurity is observed in addition to the phonon spectrum of the host.

Thus, the identification of the local mode spectrum of an impurity requires the following steps :

- (1) The absorption spectrum of the impurity doped crystal is measured.
- (2) The polarized Stokes-Raman spectrum of the undoped host is measured, providing the phonon reference spectrum. Preferably, the measurement is taken using the excitation wavelength corresponding to the maximum of absorption of the impurity band under investigation determined at (1), the same which will be used for obtaining the resonance Raman spectrum, λ_0 . Although the Raman spectrum is independent of the excitation wavelength (except for the fourth power of the frequency), λ_0 is chosen for measuring the phonon spectrum in order to maintain identical experimental conditions for Raman measurements of the undoped and doped host.
- (3) The polarized Stokes Raman spectrum of the doped crystal is measured under identical conditions as those used at (2). Special care has to be taken if the absorption of the sample is polarization dependent, to use the appropriate polarization for λ_0 . In a resonance Raman spectrum the order of the incident-scattered polarization, in Porto's notation (Section 2.6) is crucial, as opposed to a Raman spectrum where it does not matter. In order to observe Cr^{4+} local modes for the ${}^3\text{A}_2 \rightarrow {}^3\text{B}_2({}^3\text{T}_1)$ electronic absorption, the 575 nm incident excitation wavelength has to be polarized along the c -crystallographic axis (Fig. 3.11), i.e. only the following resonance spectra can be obtained, using Porto's notation (see Section 2.6) : $s(ca)t$, $s(cb)t$, $s(cc)t$, where s and t are any of the three crystallographic axes a , b , c .

For example, Appendix A.3 shows that for a D_{2h} crystal, the B_{2g} representation has as basis xz , i.e. in order to obtain a B_{2g} Raman spectrum the polarizer has to be oriented along the $x = a$ crystal axis and the analyzer has to be oriented along the $z = c$ crystal axis, or the other way around. (In Porto's notation a B_{2g} phonon spectrum can be

obtained in any configuration of the type $s(ca)t$ or $s(ac)t$ where, as above, s and t are any of the a , b or c crystal axes). This “interchangeability” of the analyzer and polarizer is valid for a Raman spectrum only (i.e. only for phonon modes) and is due to the symmetry of the Raman tensor (see Section 4.2.6). If, on the other hand, one wants to observe a B_{2g} resonance Raman spectrum, under 575 nm excitation, the polarizer has to be oriented along the c -crystal axis in order to have dipole allowed absorption, which leaves the only choice for the analyzer as parallel to the a -crystal axis, i.e. a B_{2g} resonance Raman spectrum under 575 nm excitation can be observed only in a $s(ca)t$ configuration

It is interesting to note that for crystals with a relative large number of atoms per unit cell (28 for Mg_2SiO_4) and different types of bonds (ionic, covalent, etc.) the large number of phonon modes and relatively complicate manner of deriving their symmetry (see Section 3.2.2) is compensated by the fact that the direction of the incident and scattered light ($\vec{k}_i$ and $\vec{k}_s$) is of no significance to the symmetry of the measured Raman spectrum. For example, the same B_{2g} Raman spectrum is obtained in a $b(ca)b$ backscattering configuration, in a $b(ca)c$ 90° configuration, or in a $b(ca)b$ forward scattering geometry. This “irrelevance of the wavevector” is due to the fact that the symmetry of the unit cell is given by certain ionic sites and does not depend on the direction the cell is probed on (i.e. the cell has the same symmetry viewed along any axis or combination of axes). This, however is not the case for highly symmetric crystals with low numbers of ions per unit cell, such as diamond, Si, Ge, semiconductors and XY materials in general (two atoms per unit cell), like NaCl, KF, etc. In such cases different directions inside the unit cell have different symmetry in k -

space, i.e. for such materials the Raman spectrum and the selection rules are different, for example, along the (1, 0, 0) and the (1, 1, 1) directions. Thus, for such materials apart from the polarizations of the incident and scattered light, one also has to consider the directions of propagation (k-vectors) for the incident and scattered radiation which give the momentum of the created or annihilated phonon as shown by Eqs. (4.3), (4.5), respectively. A complete derivation of selection rules for such materials is given by Ref. [4].

- (4) A comparison between similar spectra for the undoped and doped samples will identify modes which appear in addition to the phonon modes and are present in the doped material only. These are the local modes.
- (5) The correct identification of the local modes can be “double checked” by taking two polarized Stokes-Raman spectra for the doped sample under identical scattering geometry, but using different excitation wavelengths, one of them in the maximum of absorption of the studied impurity (λ_0), and one outside the absorption band (off-resonance). The off-resonance spectrum contains only phonon modes, while the resonance spectrum contains local modes which appear as additional to phonon peaks. Considering the previous example of the ${}^3A_2 \rightarrow {}^3B_2({}^3T_1)$ $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ absorption band, using Fig. 3.11, it can be concluded that all Cr^{4+} local modes should “disappear” or dramatically reduce their intensity under excitation with $\lambda_0 > 585$ nm. On the other hand, the phonon intensity will be insensitive to the change in excitation wavelength from 575 to 585 nm.

The local modes are those modes of vibration which appear in a Raman spectrum under resonance conditions only, (i.e. when the excitation wavelength is tuned inside an absorption band of the impurity under investigation), in addition to

phonon modes (or, seldom, overlapping with them but displaying enhanced intensity), and “disappear” or drastically reduce their intensity once the excitation wavelength is tuned outside the absorption band. It should be noted that this behavior is valid for Stokes -Raman local mode spectra. Different behavior in the local mode intensity-dependence on the excitation wavelength (excitation profiles) appear in an anti-Stokes Raman spectrum.

5.2 Experimental setup and experimental method

In order to identify the local mode spectrum of Cr^{4+} in the Mg_2SiO_4 host, polarized resonance Raman measurements were performed on a 10x8x6 mm oriented single crystal of $\text{Cr:Mg}_2\text{SiO}_4$ with low doping level, $\sim 3 \times 10^{18}$ ions/cm³ (0.02 at%) [5]. An undoped 15x12x5 mm oriented single crystal of Mg_2SiO_4 was used as reference, for identifying the phonon spectrum. Under resonance conditions, i.e. under 575 nm, linearly polarized along the *c*-crystallographic axis excitation, corresponding to the maximum of absorption of the ${}^3\text{B}_2({}^3\text{T}_1)$ Cr^{4+} electronic state [6] (see Fig. 3.11), the Stokes Raman spectrum of the doped sample is expected to contain additional to phonon modes, which will be identified as Cr^{4+} local modes. The reference phonon spectrum is provided by the undoped sample. Different local modes are expected to appear in different incident-scattered polarization arrangements. The number and symmetry of Cr^{4+} local modes and their correlation to different polarization arrangements will be discussed in Sections 5.3 and 5.5. Additional information which can be extracted from the local mode spectrum, such as local force constant changes at the impurity site, is discussed in Section 5.6. Both crystal samples were free of visible inhomogeneities such as inclusions, cracks or bubbles. Details on the experimental method and results are given as follows.

The experimental setup used for identifying the Cr^{4+} local mode spectrum is presented in detail in Section 2.7, Fig. 2.7, and is briefly described as follows. The mode-locked Nd:YAG laser ($\sim 7\text{W}$ output power at $1.064\ \mu\text{m}$) with a repetition rate of 82 MHz, has attached at its output a KTP crystal which doubles the frequency providing 532 nm pulses with $\sim 1.3\ \text{W}$ average power. The frequency doubled Nd:YAG laser synchronously pumped the Rh-6G dye laser which is tunable between 572 - 630 nm. The dye laser was tuned to 575 nm, corresponding to the maximum of absorption of the $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$, for incident excitation polarized along the *c*-crystallographic axis in *Pnma* notation, as shown in Figs. 3.11 and 5.1. The average output power of the dye laser at 575 nm was $\sim 50\text{mW}$. Reflections on mirrors and a 575 narrow band filter further reduced the power, such that the sample was effectively irradiated with a 15 mW beam, focused down to a diameter of $\sim 40\ \mu\text{m}$ along a lens of focusing $L \sim 1.5\ \text{mm}$, using a 12 cm focus lens (see Section 2.6). All Raman spectra were recorded at room temperature in a 90° scattering geometry, such that the excitation beam was parallel to the entrance slit of the spectrometer, as shown in Fig. 2.7.

The scattered signal was collected by a system of two lenses : an 85-mm Canon camera lens placed 2 cm (at its focal distance) away from the sample, and a 20 cm focal lens, placed at its focal distance away from the spectrometer's entrance slit (and close to the camera lens in order to minimize losses). The signal was collected by a SPEX triple spectrometer, using grating #5 with 1800 grooves/mm. The following combination of slits was used : $S_1 = 200\ \mu\text{m}$, $S_2 = 5\ \text{cm}$ and $S_3 = 200\ \mu\text{m}$, leading to a spectral resolution of $\sim 5\ \text{cm}^{-1}$ [7]. The Raman images were detected by a PIAS Hamamatsu photoncounter, and further processed, analyzed and saved (as images, and in ASCII format) using two PCs, together with the specifically designed software (see Section 2.5).

The scattering geometry is given for all spectra in Porto's notation (see Section 2.6). As previously discussed, in order to obtain resonance Raman spectra

under 575 nm excitation the incident light has to be polarized along the *c*-crystal axis. Thus, in order to obtain a B_{3g} spectrum for a crystal with space group symmetry D_{2h} , as is the case of Mg_2SiO_4 , using the fact that the basis for the B_{3g} representation is $yz = zy = cb$ (see Appendix A.3) the incident excitation has to be polarized along the *c*-crystal axis and the scattered signal is collected polarized along the *b*-crystal axis, or in Porto's notation a $a(cb)c$ 90° arrangement can be used. On the other hand, the only possible 90° scattering configurations used for obtaining an A_g resonance Raman spectrum (where A_g has as basis $x^2 = aa$, $y^2 = bb$ and $z^2 = cc$ coordinates - see Appendix A.3) are $b(cc)a$ or $a(cc)b$. Although, as previously mentioned, the order of the analyzer and polarizer can be interchanges in a Raman spectrum (for the undoped host) identical scattering configurations were used for the doped and undoped samples, for consistency.

Raman (for the undoped sample) and resonance Raman (for the doped sample) spectra obtained in the above described experimental conditions are presented and analyzed in Section 5.4.

5.3 Vibrational analysis. Expected number and symmetry of Cr^{4+} local modes

Cr^{4+} local modes originate in the tetrahedrally distorted CrO_4 molecule, where Cr^{4+} substitutes for Si^{4+} , in a position with C_s site symmetry. As discussed in Section 4.1, the most likely to be observed are the $3N-6$ internal vibration of such an N-atomic molecule, i.e. 9 internal vibration are expected (Section 3.2.2.5). It should be noted that, in general, while an eventual lower number of observed local modes can be attributed to low scattering cross sections, and the absence of specific enhancement conditions, such as Stokes shifts for totally symmetric modes [8], an eventual higher number of observed local modes requires a closer and more careful analysis (see Chapter 6).

The symmetry of the internal vibrations for a XY_4 molecule has been discussed in Section 3.2.2.5, and it was shown that it gives rise to one nondegenerate (A_1), one double degenerate (E) and two triple degenerate (T_2) modes of vibration (Eq. 3.25). The degeneracy is completely lifted by the C_s site symmetry which describes the real symmetry of the molecule such that out of the 9 internal modes of vibration, 6 are totally symmetric (A') and 3 are nontotally symmetric (A''):

$$\Gamma_{C_s} = 6A' + 3A'' \quad (5.1)$$

Tab. 3.6 gives the complete $T_d \rightarrow C_s \rightarrow D_{2h}$ correlation for the unit cell. Tab. 5.1 summarizes the molecular, site and space group correlations from Tab. 3.6 for the 9 $(CrO_4)^{4-}$ internal local modes of vibration and indicates the exact scattering geometries, in Porto's notation (see Section 2.6), under which different local modes are observed. As before, s and t are any of the a , b or c crystal axes and for reasons previously discussed in Section 5.2 they are irrelevant for the symmetry of the local and phonon modes, and describe only the geometrical arrangement under which a certain Raman spectrum was obtained (90° , 180° , etc.).

The first column in Tab. 5.1 gives the four internal modes of vibration for an XY_4 tetrahedral molecule (Eq. 3.25) and shows how they split due to the C_s site symmetry (second column). For example, Tab. 5.1 shows that a triple degenerate T_2 tetrahedral mode splits under C_s symmetry in $2A' + 1A''$ modes. As shown in Tab. 3.6, A' modes can be observed in a Raman spectrum in configurations corresponding to A_g or B_{2g} space group (D_{2h}) representations, while A'' modes can be observed in configurations corresponding to B_{1g} or B_{3g} representations.

As discussed in Section 5.2, for a resonance Raman spectrum obtained under 575 nm excitation the incident light has to be polarized along the c -crystallographic axis. It was also shown that the symmetry of the observed

spectrum is given by the combination of incident and scattered light polarizations which match the basis for the considered representation.

T_d	C_s	D_{2h}	Number of totally symmetric modes	Number of nontotally symmetric modes	Scattering geometry to be used
A_1	A'	A_g or B_{2g}	1	0	$s(cc)t$ $s(ca)t$
E	A'	A_g or B_{2g}	1	0	$s(cc)t$ $s(ca)t$
	A''	B_{1g} or B_{3g}	0	1	- $s(cb)t$
T_2	A'	A_g or B_{2g}	1	0	$s(cc)t$ $s(ca)t$
	A'	A_g or B_{2g}	1	0	$s(cc)t$ $s(ca)t$
	A''	B_{1g} or B_{3g}	0	1	- $s(cb)t$
T_2	A'	A_g or B_{2g}	1	0	$s(cc)t$ $s(ca)t$
	A'	A_g or B_{2g}	1	0	$s(cc)t$ $s(ca)t$
	A''	B_{1g} or B_{3g}	0	1	- $s(cb)t$
			6	3	

Table 5.1 Number, symmetry and corresponding scattering geometry for obtaining Cr^{4+} local modes under resonance excitation in the ${}^3B_2({}^3T_1)$ electronic level.

For example, an A_g D_{2h} representation has as basis $z^2 = cc$ (in terms of crystal axes) - see Appendix A.3. In order to obtain a resonance A_g Raman spectrum a $s(cc)t$ scattering configuration has to be used, with s and t any of the a , b or c crystal axes (Tab. 5.1). As already discussed, the choice of s and t gives the scattering geometry only and is irrelevant for symmetry considerations. Thus an

A_g resonance Raman spectrum can be obtained in any of the following scattering arrangements, given in Porto's notation (section 2.6) : $a(cc)b$ or $b(cc)a$ (90^0) and $b(cc)\bar{b}$ (180^0).

A B_{1g} D_{2h} representation has as basis $xy = ab$ (in terms of crystal axes). As both axes are different from c it follows that a B_{1g} resonance Raman spectrum can not be obtained under excitation corresponding to the ${}^3A_2 \rightarrow {}^3B_2({}^3T_1)$ level at 575 nm. (B_{1g} spectra are obtained only under (ab) or (ba) polarizer-analyzer configurations).

A B_{2g} D_{2h} representation has as basis $xz = zx = ca$ (in terms of crystal axes). In order to obtain a resonance B_{2g} Raman spectrum a $s(ca)t$ scattering configuration has to be used, with s and t any of the a , b or c crystal axes (Tab. 5.1). Thus a B_{2g} resonance Raman spectrum can be obtained in any of the following scattering arrangements : $a(ca)b$ or $b(ca)c$ (90^0) or $b(ca)\bar{b}$ (180^0).

Finally a B_{3g} D_{2h} representation has as basis $yz = zy = cb$ (in terms of crystal axes). In order to obtain a resonance B_{3g} Raman spectrum a $s(cb)t$ scattering configuration has to be used, with s and t any of the a , b or c crystal axes (Tab. 5.1). Thus a B_{3g} resonance Raman spectrum can be obtained in any of the following scattering arrangements : $a(cb)c$ or $b(cb)a$ (90^0) or $a(cb)\bar{a}$ (180^0).

The table of the D_{2h} group (Appendix A.3) shows that only the "g" (gerade) representations are Raman active. All the possible scattering geometries for obtaining resonance Raman spectra corresponding to the ${}^3A_2 \rightarrow {}^3B_2({}^3T_1)$ level under c -polarized 575 nm incident excitation have been discussed above and are summarized in the last column of Tab. 5.1. The table also correlates different scattering geometries with the symmetry of the local modes given in the C_s group, in the second column. Tab. 5.1 shows that, for example, A' C_s local modes can be obtained in $s(cc)t$ or $s(ca)t$ configurations while A'' C_s modes can be obtained only in $s(cb)t$ configurations, where s and t are any of the a , b or c crystal axes.

5.4 Experimental results

All polarized Stokes Raman spectra measured at room temperature for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ and undoped Mg_2SiO_4 were obtained under linearly polarized along the c -crystallographic axis 575 nm excitation, corresponding to the maximum of absorption of the ${}^3\text{B}_2({}^3\text{T}_1)$ Cr^{4+} electronic state. The absorption spectrum for this electronic band is shown in Fig. 5.1.

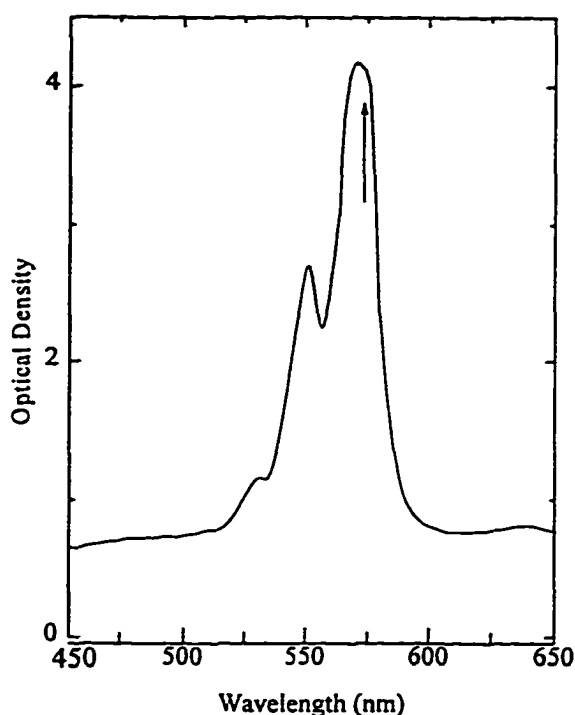


Figure 5.1 Room temperature absorption spectrum for $\text{Cr}:\text{Mg}_2\text{SiO}_4$, obtained under incident excitation polarized along the c -crystallographic axis. The arrow position indicates the excitation wavelength ($\lambda_0 = 575$ nm) used for obtaining the resonance Raman spectra shown in Figs. 5.2 - 5.4.

The maximum of absorption, which corresponds to the maximum resonance enhancement for the local modes, at 575 nm, is marked by an arrow. The two other local maxima at ~ 550 nm and ~ 530 nm are phonon replicas of the first

maximum of absorption (zero phonon line at 575 nm). Using the spacing between the maxima and selection rules it can be shown that these two higher order maxima are due to the electron-phonon (in fact local mode) coupling between the ${}^3B_2({}^3T_1)$ band and the Cr^{4+} local mode at 764 cm^{-1} which is (as will be shown), the tetrahedral breathing mode A_1 .

The polarized Stokes Raman spectra at room temperature for $Cr^{4+}:Mg_2SiO_4$ (continuous line) and undoped Mg_2SiO_4 (dotted line) obtained under 575 nm linearly polarized excitation are shown in Figs. 5.2 (a)-(c), 5.3 (a)-(b) and 5.4. In each figure, the lower spectrum, corresponding to the undoped host contains only the phonon (reference) modes, while the upper spectrum corresponding to the Cr^{4+} -doped host also contains local modes which appear in addition to the phonon modes. All local modes are boxed. Each figure gives the phonon mode symmetry and the corresponding scattering geometry in Porto's notation (see Tab. 5.1).

Figs. 5.2 (a) - (c) present the 5 totally symmetric A' local modes obtained in $b(cc)a$ scattering configuration corresponding to A_g space group symmetry (see Tab. 5.1), for different spectral ranges. The measured energy of the 5 A' local modes is : 253, 290, 498, 690 and 764 cm^{-1} .

Figs. 5.3 (a), (b) present the 2 nontotally symmetric A'' local modes obtained in $a(cb)c$ scattering configuration corresponding to B_{3g} space group symmetry (see Tab. 5.1), for different spectral ranges. The energy of the 2 A'' local modes is : 480 and 740 cm^{-1} .

Fig. 5.4 presents the only A' local mode obtained in $b(ca)c$ scattering configuration corresponding to B_{2g} space group symmetry, measured at 690 cm^{-1} . No other resonance modes were detected outside the spectral ranges shown in Figs. 5.2 - 5.4. Tab. 5.2 summarizes the energy and symmetry of the measured Cr^{4+} local modes shown in Figs. 5.2 - 5.4. The estimated accuracy of the measured

frequency of the Raman spectra was $\sim \pm 3 \text{ cm}^{-1}$ and the spectral resolution was $\sim 5 \text{ cm}^{-1}$.

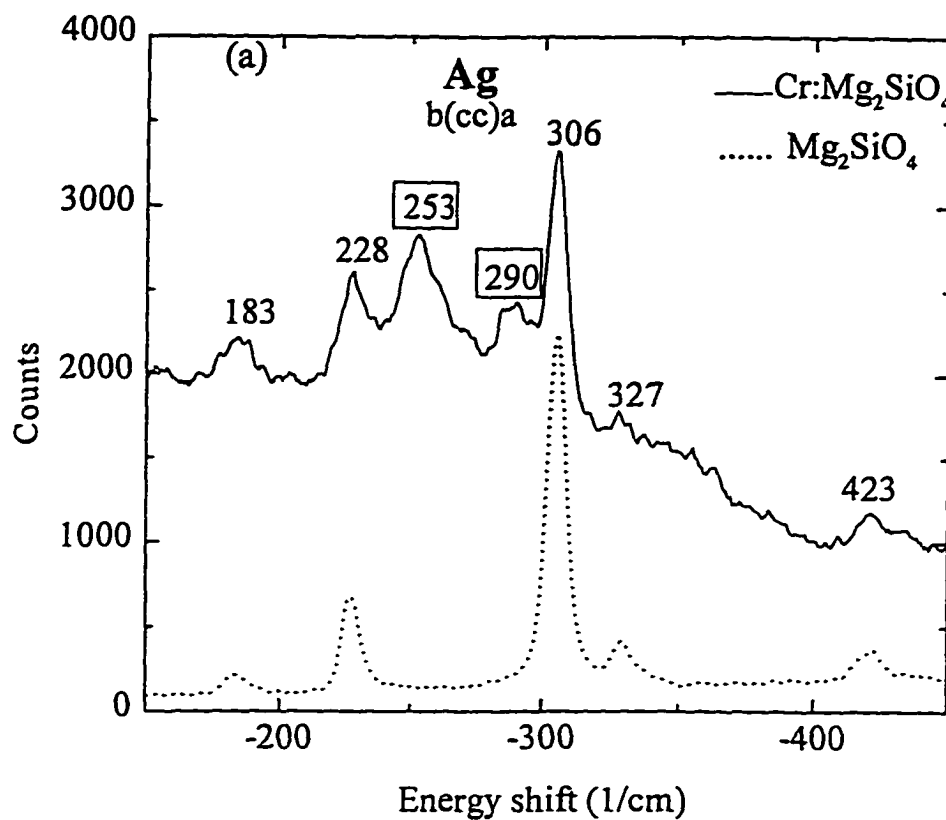
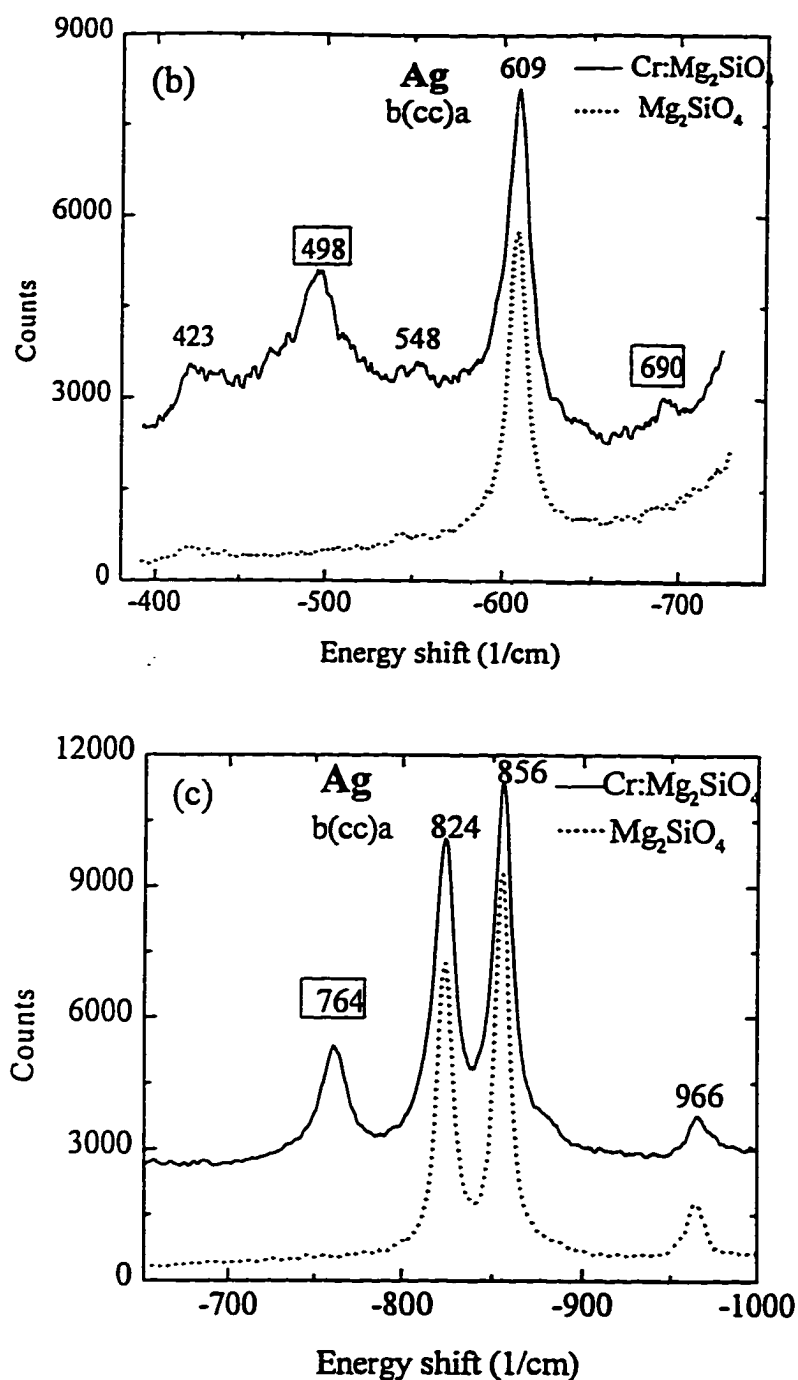
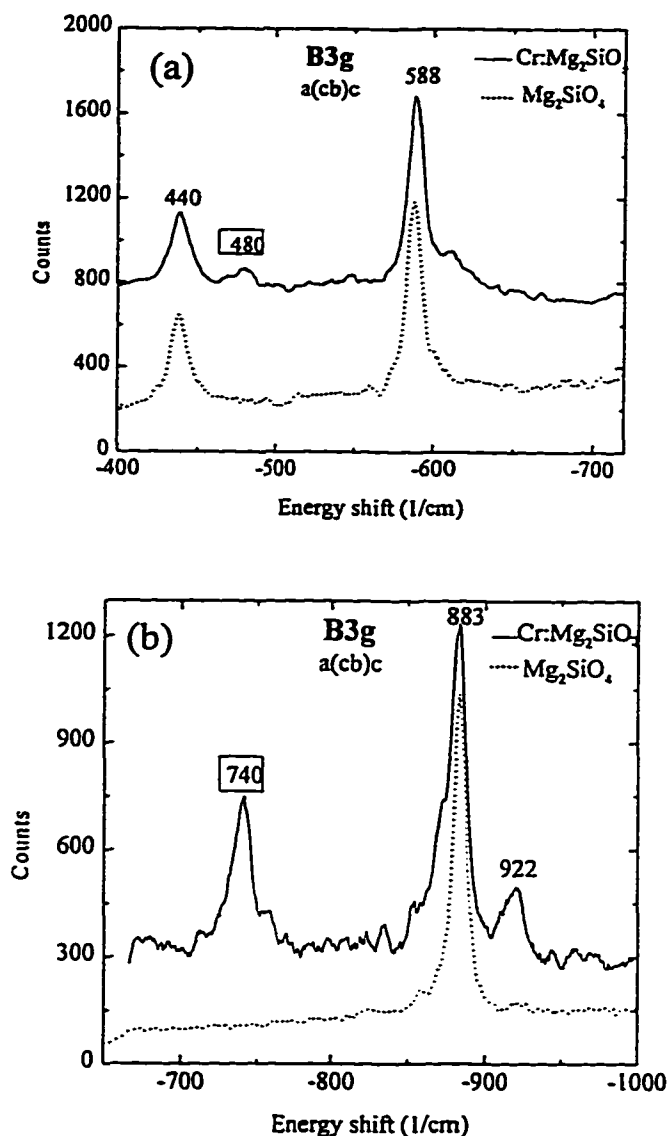


Figure 5.2 (a) Polarized Raman for Mg_2SiO_4 (....) and resonance Raman (—) for $\text{Cr:Mg}_2\text{SiO}_4$ spectra at room temperature, in $b(cc)a$ configuration for A_g modes, in the $150 - 450 \text{ cm}^{-1}$ spectral region. The intensity of the modes is given in arbitrary units.



Figures 5.2 (b), (c) Polarized Raman for Mg_2SiO_4 (...) and resonance Raman (—) for $\text{Cr:Mg}_2\text{SiO}_4$ spectra at room temperature, in $b(cc)a$ configuration for Ag modes, in the 380 - 720 cm^{-1} and 650 - 1000 cm^{-1} spectral regions, respectively. The intensity of the modes is given in arbitrary units.



Figures 5.3 (a), (b) Polarized Raman for Mg_2SiO_4 (...) and resonance Raman (—) for $\text{Cr:Mg}_2\text{SiO}_4$ spectra at room temperature, in $a(cb)c$ configuration for B_{3g} modes, in the 400 - 720 cm^{-1} and 650 - 1000 cm^{-1} spectral regions, respectively. The intensity of the modes is given in arbitrary units.

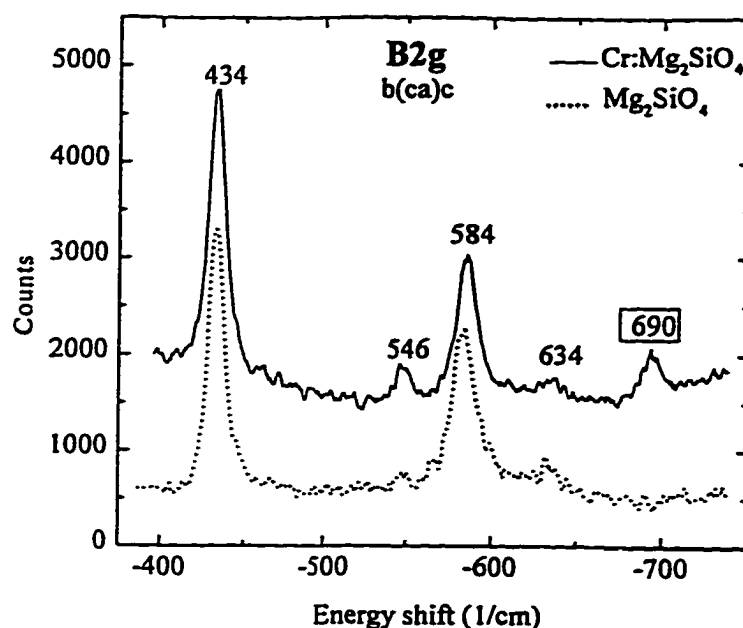


Figure 5.4 Polarized Raman for Mg_2SiO_4 (....) and resonance Raman (—) for $\text{Cr:Mg}_2\text{SiO}_4$ spectra at room temperature, in $b(ca)c$ configuration for B_{2g} modes, in the $375 - 720 \text{ cm}^{-1}$ spectral region. The intensity of the modes is given in arbitrary units.

$A_g (A')$	$B_{2g} (A')$	$B_{3g} (A'')$
765 cm^{-1}	690 cm^{-1}	740 cm^{-1}
690 cm^{-1}		
498 cm^{-1}		
290 cm^{-1}		480 cm^{-1}
253 cm^{-1}		

Table 5.2 Energies (cm^{-1}) and symmetry assignment in D_{2h} (C_s) symmetry of the measured resonance enhanced Cr^{4+} local modes in $\text{Cr:Mg}_2\text{SiO}_4$.

5.5 Determination of Cr^{4+} local mode symmetry. Missing modes

Instead of the expected 6 resonance enhanced totally symmetric modes and the 3 non-totally symmetric modes only 5 and 2 were observed, respectively. As discussed in Section 4.3 the total intensity of the resonance Raman spectrum is proportional to the sum of the A and B Albrecht terms [9]. According to Albrecht's theory the resonance enhanced totally symmetric modes correspond to configurations with large Franck-Condon overlap integrals and are given by the A term [8] (Eq. 4.67). Thus for a particular local mode, the A term will be non-zero for a non-zero Franck-Condon overlap which requires the presence of a Stokes shift due to electron-phonon interactions (see Section 4.5). Therefore, a possible explanation for the absence of one totally symmetric mode would be that the Stokes shift is small for this particular mode (i.e. electron-phonon interactions are weak for this mode - see Sections 4.3 - 4.5).

The mechanism for obtaining non-totally symmetric resonance enhanced modes is different, and is connected to the B term [8], Eq. (4.68). The existence of a non-totally symmetric mode requires the presence of a second excited state $|s_0\rangle$ coupled with the excited state (${}^3\text{B}_2({}^3\text{T}_1)$ in our case). The absence of one of the three expected non-totally symmetric modes would occur if the coupling term is weak or zero, or if the scattering cross section for the third nontotally symmetric local mode A'' is small.

Next, the symmetry of the 7 measured local modes will be determined in terms of the original (undistorted) tetrahedral symmetry. In the undoped crystal the frequencies of the four types of T_d modes of vibration given by Eq. (3.25), denoted as $\nu_1(\text{A}_1)$, $\nu_2(\text{E})$, $\nu_3(\text{T}_2)$ and $\nu_4(\text{T}_2)$, having Si as central ion are in the following ranges (see [10], and Tab. 3.9) : $\nu_3 \in (850 - 980) \text{ cm}^{-1}$, $\nu_1 \in (830 - 840) \text{ cm}^{-1}$, $\nu_4 \in (500 - 600) \text{ cm}^{-1}$ and $\nu_2 \in (420 - 480) \text{ cm}^{-1}$. Taking this positioning in energy scale into account, and the results presented in Table 5.2, the following conclusions can be drawn:

- (1) The 764 cm^{-1} mode is the tetrahedral breathing mode $\nu_1(A_1)$. The arguments which support this assignment are :
- (a) the most enhanced modes in resonance Raman experiments are the totally symmetric ones. The 764 cm^{-1} is about 10 times more intense than any of the other resonance enhanced modes.
 - (b) although it is not the only totally symmetric mode (taking into account the C_s site symmetry there should be six), it is the only one which originates in a totally symmetric representation in $T_d - A_1$. The other 5 totally symmetric modes originate in E and T_2 (non-totally symmetric) representations.
- (2) The 740 cm^{-1} , 690 cm^{-1} group belongs to $\nu_3(T_2)$. Due to the complete removal of degeneracy caused by the C_s site symmetry, 3 distinct modes are expected : 2 totally symmetric and 1 non-totally symmetric (Tab. 5.1). Instead, one totally symmetric (690 cm^{-1}) and one non-totally symmetric (740 cm^{-1}) were observed. One totally symmetric mode is missing. Possible explanations have been previously mentioned. It is interesting to remark that the 690 cm^{-1} mode is the only one present in both A_g and B_{2g} representations. This fact supports two possible explanations. The first one is that the 690 cm^{-1} vibration is the same mode in both representations and it merely reflects a high degree of depolarization which is in perfect accordance with its originating in a non-totally symmetric T_d mode as A_g and B_{2g} correspond to the $I(\perp)$ and $I(\parallel)$ scattering configurations, respectively. A second explanation is that the 690 cm^{-1} A_g mode is different from the 690 cm^{-1} B_{2g} mode. This could be explained if it is assumed that more than one Cr^{4+} ion is present in each unit cell (which can accommodate up to four Cr ions). Such a situation is not probable if we take into account the low, uniform doping concentration of the

sample ($N \approx 3 \times 10^{18}$ ions/cm³). At the same time, the different positioning inside the unit cell should be reflected by other modes, but is not. All of these arguments suggest that the first explanation is the valid one and we have one totally and one non-totally symmetric mode for ν_3 (T_2).

- (3) If the 498 cm⁻¹ and 480 cm⁻¹ local modes are assigned to ν_4 (T_2) then the two A' local modes at 290 cm⁻¹ and 253 cm⁻¹ belong to ν_2 (E). But ν_2 should split into one totally symmetric mode and one non-totally symmetric (Tab. 5.1). Thus the only possible assignment remains : 498 cm⁻¹ and 480 cm⁻¹ belong to ν_2 (E) while 290 cm⁻¹ and 253 cm⁻¹ belong to ν_4 (T_2).

The local mode assignment discussed above is summarized in Tab. 5.3.

T_d mode symmetry	$(SiO_4)^{4-}$ in Mg_2SiO_4 (cm ⁻¹)	$(CrO_4)^{4-}$ in Mg_2SiO_4 (cm ⁻¹)
$\nu_1(A_1)$	830 ÷ 840	764
$\nu_2(E)$	420 ÷ 480	498 480
$\nu_3(T_2)$	850 ÷ 980	740 690 ?
$\nu_4(T_2)$	500 ÷ 600	290 253 ?

Table 5.3 Local mode assignment in terms of tetrahedral symmetry.

5.6 Local effects at the Cr^{4+} site. General results for a tetrahedral XY_4 molecule. Calculation of force constants for the $(\text{CrO}_4)^{4-}$ molecule in T_d approximation

Using the tetrahedral approximation for a XY_4 -type molecule, as is the case of the undistorted $(\text{CrO}_4)^{4-}$, the frequencies of all four T_d internal modes of vibration given by Eq. (3.25) can be expressed in terms of four parameters : (1) mass of central ion X (i.e. Cr^{4+}) - M ; (2) mass of one of the four equivalent Y ions (i.e. O^{2-}) - m ; (3) X-Y (i.e. Cr-O) force constant - k_1 ; and (4) intra-tetrahedral Y-Y (i.e. O-O) force constant - k_2 . For a given molecule, the masses of the two types of ions are known, such that only the two force constants remain to be determined using two of the four equations for the internal modes of vibration. The remaining two equations can be used to calculate the expected energy of the modes, and can be compared with the actual measured value, as will be shown in this section. This also constitutes a test for the correctness of the mode assignment and calculation of the frequency of vibration. It should be mentioned that these calculations assume a tetrahedral, isolated molecule, where the distortions introduced by the site symmetry are neglected and the central ion's interactions are restricted to the first neighbors' sphere.

The Lagrangeian of the XY_4 tetrahedral molecule will be written for each mode of internal vibration. The equations of motion are then obtained and solved for each corresponding frequency of vibration. The actual mean measured values for the local modes will be used to determine the force constants for a tetrahedron containing a Cr^{4+} ion instead of a Si^{4+} ion. The comparison between the force constants in a $(\text{SiO}_4)^{4-}$ and a $(\text{CrO}_4)^{4-}$ tetrahedron will give the local effects introduced by the $\text{Cr}^{4+} \rightarrow \text{Si}^{4+}$ substitution.

In order to write the Lagrangeian of the system, one has to know the kinetic and potential energy of the ions which are treated as harmonic oscillators, i.e. the eigenvectors describing the motion of the 5 ions for each type of vibration have to

be known. The eigenvectors describing the motion of the four equivalent Y (O) ions, for each of the four tetrahedral internal modes of vibration are given by Ref. 11, as “S-vectors” (internal symmetry coordinates), which represent the linear combination of the four eigenvectors. The complete motion of the ions in each of the four internal modes of vibration, including the central X (Cr^{4+}) ion, are schematically depicted in [12]. The 5-dimensional vector having as components the ionic eigenvectors is derived such that it transforms under the operations of T_d like the mode of vibration it describes. It is important to remember that the motion of the five constituent ions of the tetrahedral molecule has to be such that the center of mass of the molecule is at rest (does not move) :

$$m \sum_{i=1,4} \vec{r}_i + M\vec{R} = 0 \quad (5.2)$$

where $\vec{r}_i$ is the displacement for the i^{th} Y ion and $\vec{R}$ is the displacement of the central ion.

The equations of motion for the tetrahedral modes of vibration of an XY_4 molecule, given by Eq. (3.25) are derived as follows.

1) Symmetric stretching (breathing) mode $\nu_1(A_1)$.

The S-vector for the A_1 mode is [11] :

$$S = \frac{1}{\sqrt{4}}(\vec{r}_1 + \vec{r}_2 + \vec{r}_3 + \vec{r}_4) \quad (5.3)$$

The expression of the S-vector shows that in the breathing mode the four equivalent ions Y oscillate along the diagonals of the tetrahedron. As the $\vec{r}_i$, $i = 1 \div 4$ vectors are of equal magnitude (unitary), in order to preserve the center of mass the central ion X has to be at rest at all times, or in other words, as :

$$\sum_{i=1}^4 \vec{r}_i = 0 \quad (5.4)$$

from Eq. (5.2) one gets :

$$\bar{\mathbf{R}} = 0 \quad (5.5)$$

Eq. (5.5) shows that the central ion is not displaced in a breathing mode. The symmetric stretching mode A_1 is shown in Fig. 5.5 [12].

As the kinetic energy T of a classical particle of mass m , moving with speed $v = \dot{q}$, where q is the displacement of the particle, can always be written as

$$T = \frac{m\dot{q}^2}{2} \quad (5.6)$$

then the kinetic energy of the system of 4 identical ions is :

$$T = 4 \cdot \frac{m\dot{q}^2}{2} = 2m\dot{q}^2 \quad (5.7)$$

where

$$|\bar{\mathbf{r}}_1| = |\bar{\mathbf{r}}_2| = |\bar{\mathbf{r}}_3| = |\bar{\mathbf{r}}_4|^{not} = q \quad (5.8)$$

is the displacement of each of the four equivalent Y-ions.

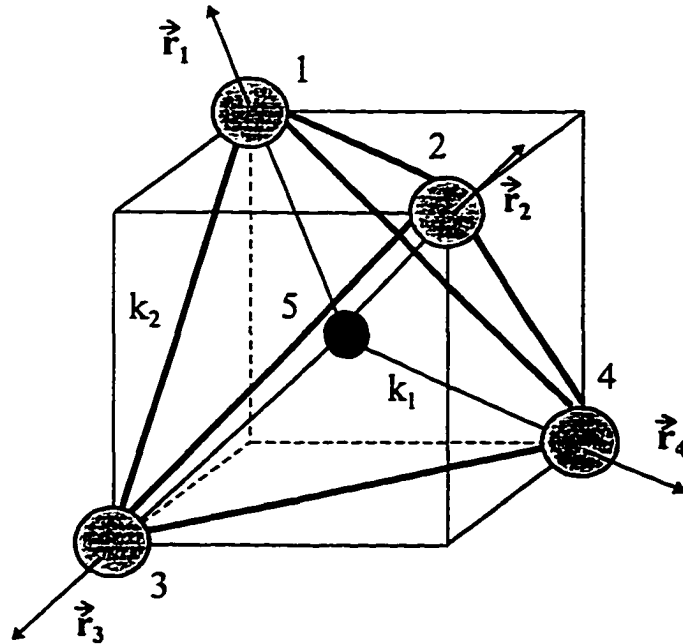


Figure 5.5 Ionic displacement $\bar{\mathbf{r}}_i$ in the $\nu_1(A_1)$ tetrahedral breathing mode. k_1 is the X-Y force constant and k_2 the Y-Y force constant.

The potential energy is due to stretching (or compressing) of the bonds and will be calculated in the harmonic approximation as :

$$V = \frac{ky^2}{2} \quad (5.9)$$

where k is the bond's force constant and y its deformation. As the molecule contains two types of bonds, each is treated separately.

The vectors $\vec{r}_i$ act along the four X-Y bonds and deform each of them by an amount “ q ” such that the potential energy for these bonds is :

$$V_1 = 4 \cdot \frac{k_1 q^2}{2} = 2k_1 q^2 \quad (5.10)$$

The vectors $\vec{r}_i$ also deform the Y-Y bonds, but only the projections of $\vec{r}_i$ along the bond stretch it. The component of a deformation vector perpendicular to the bond does not change its length ($q = 0$) and does not contribute to the harmonic potential energy term. Fig. 5.6 shows that the deformation of an Y-Y bond is $2q \cos \alpha$, where α is the angle between a tetrahedral diagonal of length $a\sqrt{3}$ and a face diagonal of length $a\sqrt{2}$ of the tetrahedron inscribed in the cube of side “ a ”.

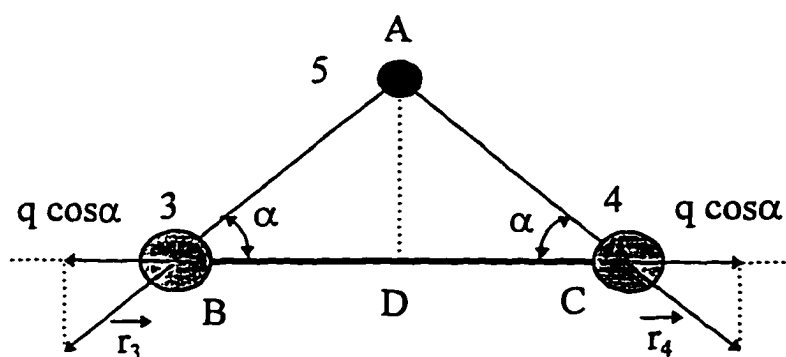


Figure 5.6 Deformation of an Y-Y (BD) bond under a symmetric stretch.

The angle α can be calculated from the above triangle as :

$$\cos \alpha = \frac{AD}{AB} = \frac{a\sqrt{2}/2}{a\sqrt{3}/2} = \sqrt{\frac{2}{3}}; \quad \sin \alpha = \frac{1}{\sqrt{3}} \quad (5.11)$$

As there are 6 Y-Y (O-O) bonds of k_2 force constant, and each is being deformed by an amount $2q \cos \alpha$, the potential energy for these bonds is :

$$V_2 = 6 \frac{k_2 (2q \cos \alpha)^2}{2} = 8k_2 q^2 \quad (5.12)$$

Using Eqs. (5.7), (5.10), (5.12) the Lagrangeian of the system can be written as :

$$\mathcal{L} = T - V_1 - V_2 = 2m\dot{q}^2 - 2k_1 q^2 - 8k_2 q^2 \quad (5.13)$$

The equation of motion is given by the Lagrange equation :

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{q}} \right) - \frac{\partial \mathcal{L}}{\partial q} = 0 \quad (5.14)$$

which, combined with Eq. (5.13) gives :

$$\ddot{q} + \frac{(k_1 + 4k_2)}{m} q = 0 \quad (5.15)$$

Eq. (5.15) is the equation for a harmonic oscillator with eigenfrequency :

$$\boxed{\omega^2 = \frac{k_1 + 4k_2}{m}} \quad (5.16)$$

Eq. (5.16) gives the (angular) frequency of oscillation of the tetrahedral breathing mode $\nu_1(A_1)$ as a function of the tetrahedral force constants k_1 and k_2 and the mass m of the Y (O) ions. As the central ion does not get displaced in the tetrahedral breathing mode, its mass does not affect the frequency of this mode. This means that if one would measure the tetrahedral breathing mode for two molecules each having as central ions an isotope of the same element such that only M , but not k_1 change, and the same surrounding ions (ex. : $(\text{Cr}^{52}\text{O}_4)^{4-}$ and $(\text{Cr}^{53}\text{O}_4)^{4-}$), one would expect to obtain the same energy for the breathing mode, for both molecules.

2) Symmetric bending mode $\nu_2(E)$.

As the symmetric bending mode E is double degenerate, there are two S-vectors which act as basis for this mode, S_{2a} and S_{2b} , such that both have the same eigenfrequency ω . Thus, no matter which of the two vectors is used for calculating the frequency of vibration, the result should be the same. In fact the second S-vector can, and will be used for checking the result of the first computation. A bending mode vector α_{12} , for example is represented by the shearing-type motion of the pair of ions #1 and #2, and determines their motion perpendicular to the X-Y bond, as shown in Fig. 5.7. The expressions for the two S-vectors for the symmetric bending mode E is [11] :

$$S_{2a} = \frac{1}{\sqrt{12}}(2\alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{24} + 2\alpha_{34}) \quad (5.17)$$

$$S_{2b} = \frac{1}{\sqrt{4}}(\alpha_{13} - \alpha_{14} - \alpha_{23} + \alpha_{34}) \quad (5.18)$$

where α_{ij} are unitary bending mode vectors. We will start by looking at the effect of one bending mode vector α_{12} on the tetrahedral bonds X-Y and Y-Y. α_{12} is represented by a pair of equal-length vectors q_1 and q_2 , of length q , perpendicular on the tetrahedral diagonals 1-5 and 2-5, respectively, as shown in Fig. 5.7.

As the vectors q_1 and q_2 are perpendicular to the bonds 1-5 and 2-5, they will not change their length, i.e. these bonds will not enter the harmonic potential energy term. On the other hand, all Y-Y bonds will be affected by the α_{12} bending vector. The effect of the q_1 vector will be analyzed, as follows. The effect of the pairing q_2 vector is obtained by analogy. These general results will be used for any bending vector α_{ij} .

Vector q_1 acts on ion 1 which is connected with three other identical ions by the bonds 1-2, 1-3 and 1-4 (Y-Y bonds), thus vector q_1 acts on three bonds. q_1 will be decomposed, for each of the three bonds, in a perpendicular component, and a parallel component, along the bond. The perpendicular component will be

discarded as it does not produce any elongation of the bond, i.e. does not enter the potential energy term. The elongation produced by the perpendicular component will be calculated, and will lead to the contribution to the harmonic potential energy for that bond.

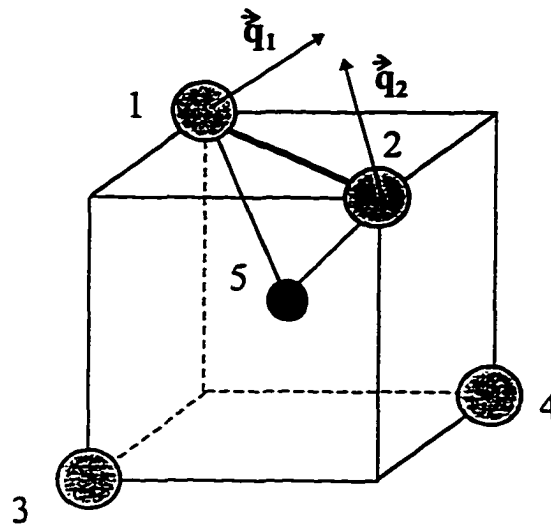


Figure 5.7 Bending mode α_{12} .

1) Bond 1-2.

Fig. 5.8 shows the components of q_1 on, and perpendicular to the bond 1-2. The same figure depicts the fact that q_1 compresses the bond 1-2 by the amount $q \cdot \sin \alpha$. The following convention will be adopted :

Convention : 1) If a bond is compressed, the deformation has a “-” (minus) sign.

2) If a bond is stretched, the deformation has a “+” (plus) sign.

Thus, using Fig. 5.8, and Eq. (5.11) the deformation of bond 1-2 produced by q_1 is

$$\Delta l_{1-2} = -\frac{q}{\sqrt{3}} \quad (5.19)$$

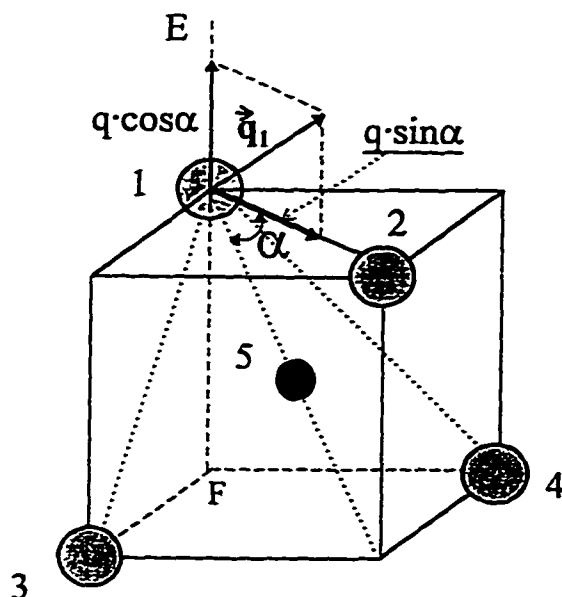


Figure 5.8. Perpendicular and parallel (underlined) to the 1-2 bond components of the q_1 deformation vector.

2) Bond 1-3.

Fig. 5.9 shows that both components of q_1 act on the 1-3 bond and stretch it as follows: a) The $q \cdot \cos \alpha$ component can be decomposed along and perpendicular to the 1-3 bond as shown in Fig. 5.9.

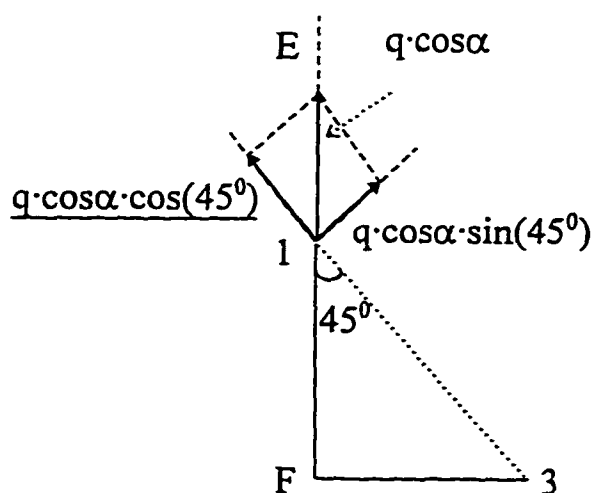


Figure 5.9 Perpendicular and parallel (underlined) to the 1-3 bond components of the $q \cdot \cos \alpha$ deformation vector.

Only the longitudinal component $q \cdot \cos \alpha \cdot \cos(45^\circ)$ stretches the bond 1-3. Fig. 5.9 and Eq. (5.11) show that the stretching of bond 1-3 produced by $q \cdot \cos \alpha$ is :

$$\Delta l_{1-3}^{(1)} = +q \cdot \sqrt{\frac{2}{3}} \cdot \frac{1}{\sqrt{2}} = +\frac{q}{\sqrt{3}} \quad (5.20)$$

b) The $q \cdot \sin \alpha$ component can be projected along the 1-3 bond in the equilateral 123 triangle of side $a\sqrt{2}$ as shown in Fig. 5.10.

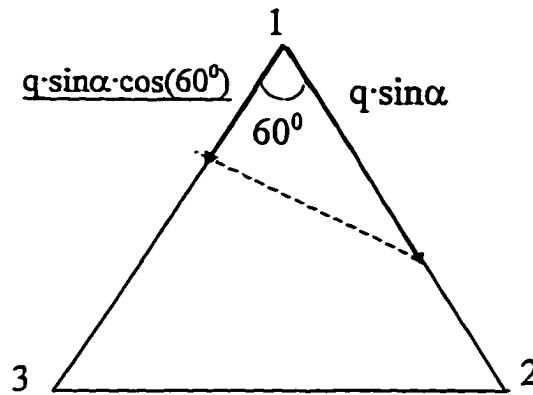


Figure 5.10 Projection along the 1-3 bond of the $q \cdot \sin \alpha$ deformation vector. The parallel to the 1-3 bond component of the deformation vector is underlined.

Fig. 5.10 shows that the $q \cdot \sin \alpha$ component shrinks the bond 1-3 and, together with Eq. (5.11) shows that the shrinkage of bond 1-3 produced by $q \cdot \sin \alpha$ is :

$$\Delta l_{1-3}^{(2)} = -q \cdot \sin \alpha \cdot \cos(60^\circ) = -q \cdot \frac{1}{\sqrt{3}} \cdot \frac{1}{2} = -\frac{q}{2\sqrt{3}} \quad (5.21)$$

Eqs. (5.20), (5.21) show that the total stretch of the 1-3 bond due to the q_1 vector is

$$\Delta l_{1-3} = \Delta l_{1-3}^{(1)} + \Delta l_{1-3}^{(2)} = \frac{q}{\sqrt{3}} - \frac{q}{2\sqrt{3}} = \frac{q}{2\sqrt{3}} \quad (5.22)$$

3) Bond 1-4.

Bond 1-4 is obtained by reflecting bond 1-3 in the plane 12F (Fig. 5.8), i.e. in the diagonal plane of the tetrahedron. Thus, the result obtained for this bond is identical to the one given by Eq. (5.22), as the vector producing the deformation lies in the reflection plane. Thus, the deformation of bond 1-4 produced by the vector $\mathbf{q}_1$ is :

$$\Delta l_{1-4} = \frac{q}{2\sqrt{3}} \quad (5.23)$$

Equations (5.19), (5.22) and (5.23) give the deformation of the three adjacent bonds under one of the bending mode pair vectors, acting in the point of intersection of the three bonds.

Eq. (5.17) describes the displacement of the four equivalent ions only. The displacement of the central ion $\bar{\mathbf{R}}$ has to be derived from Eq. (5.2). Figs. 5.7 - 5.8 show that the two $\mathbf{q}$ vectors describing a bending mode vector α_{ij} can be decomposed, each, in two components : one along the bond between the two vectors (bond 1-2 in Fig. 5.8), and one perpendicular to it, along vertical axes (FE in Fig. 5.8). The two components along the bond are equal and opposite, of magnitude $q \cdot \sin \alpha$, thus they cancel each other, in Eq. (5.2). The two vertical components $q \cdot \cos \alpha$ have the same upward direction, and have to be added giving a total contribution $2 \cdot q \cdot \cos \alpha$. This means that only the vertical components have to be calculated for each vector α_{ij} .

Under a closer look, it can be noted that the α_{34} vector has the same vertical component as α_{12} , but directed downwards ($-2 \cdot q \cdot \cos \alpha$), canceling out the α_{12} contribution. In a similar manner α_{13} cancels with α_{24} and α_{14} cancels with α_{23} (i.e. pairs of bending vectors involving opposite pairs of ions). This means that the sum of the displacements of the four ions is zero (Eq. (5.4)), thus the central ion has to be at rest at all times. Like in the tetrahedral breathing mode, the central ion does not move in the symmetric bending mode E.

We will now proceed to calculate the deformation of each of the six Y-Y bonds, determined by the six bending mode vectors given by Eq. (5.17). The effect of each bending mode α_{ij} is calculated by considering contributions from both $\mathbf{q}_i$, $\mathbf{q}_j$ vectors as given by Eqs. (5.19), (5.22), (5.23). The deformations produced by the bending mode vectors are given in Tab. 5.4. In Tab. 5.4 the contributions of the $\mathbf{q}_i$ vectors have been multiplied with the factor corresponding to the α_{ij} vector.

Bending mode	$\mathbf{q}_i$	Bond 1-2	Bond 1-3	Bond 1-4	Bond 2-3	Bond 2-4	Bond 3-4
$2\alpha_{12}$	$\mathbf{q}_1$	$-2q/\sqrt{3}$	$q/\sqrt{3}$	$q/\sqrt{3}$			
	$\mathbf{q}_2$	$-2q/\sqrt{3}$			$q/\sqrt{3}$	$q/\sqrt{3}$	
$-\alpha_{13}$	$\mathbf{q}_1$	$-q/2\sqrt{3}$	$q/\sqrt{3}$	$-q/2\sqrt{3}$			
	$\mathbf{q}_3$		$q/\sqrt{3}$		$-q/2\sqrt{3}$		$-q/2\sqrt{3}$
$-\alpha_{14}$	$\mathbf{q}_1$	$-q/2\sqrt{3}$	$-q/2\sqrt{3}$	$q/\sqrt{3}$			
	$\mathbf{q}_4$			$q/\sqrt{3}$		$-q/2\sqrt{3}$	$-q/2\sqrt{3}$
$-\alpha_{23}$	$\mathbf{q}_2$	$-q/2\sqrt{3}$			$q/\sqrt{3}$	$-q/2\sqrt{3}$	
	$\mathbf{q}_3$		$-q/2\sqrt{3}$		$q/\sqrt{3}$		$-q/2\sqrt{3}$
$-\alpha_{24}$	$\mathbf{q}_2$	$-q/2\sqrt{3}$			$-q/2\sqrt{3}$	$q/\sqrt{3}$	
	$\mathbf{q}_4$			$-q/2\sqrt{3}$		$q/\sqrt{3}$	$-q/2\sqrt{3}$
$2\alpha_{34}$	$\mathbf{q}_3$		$q/\sqrt{3}$		$q/\sqrt{3}$		$-2q/\sqrt{3}$
	$\mathbf{q}_4$			$q/\sqrt{3}$		$q/\sqrt{3}$	$-2q/\sqrt{3}$
Total longitudinal deformation		$-2q\sqrt{3}$	$q\sqrt{3}$	$q\sqrt{3}$	$q\sqrt{3}$	$q\sqrt{3}$	$-2q\sqrt{3}$

Table 5.4 Longitudinal deformations (along the bond) produce by the S_{2a} bending mode vectors given by Eq. (5.17).

For example, as Eq. (5.17) contains a term $2\alpha_{12}$, Eqs. (5.19), (5.22) and (5.23) have been multiplied by a factor of 2. This table also shows that for a given bending mode $+\alpha_{ij}$, the bond i-j is compressed by $-2q / \sqrt{3}$, i.e by $-q / \sqrt{3}$ due to each vector q_i and q_j , and that bonds containing either ion "i" or "j" are affected (stretched by $+q / 2\sqrt{3}$). Table 5.4 describes the motion of the ions in the $\nu_{2a}(E)$ symmetric bending mode. The actual ionic displacement for this mode is shown in Fig. 5.11 [12].

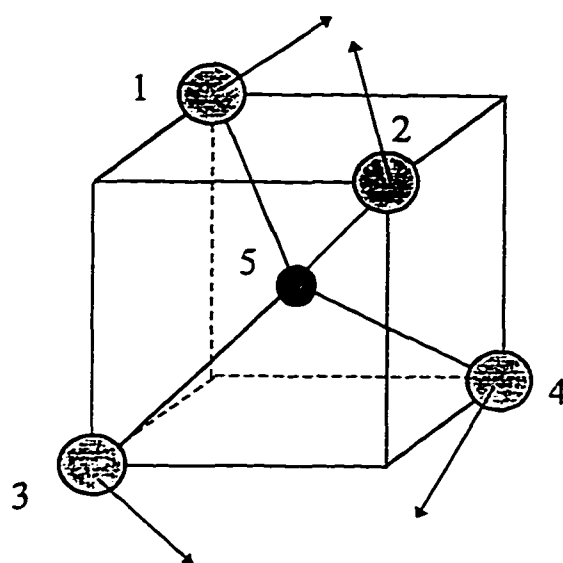


Figure 5.11 Ionic displacement in the $\nu_{2a}(E)$ symmetric bending mode.

The kinetic energy of the system is calculated as the sum of the kinetic energies of the four identical ions. The displacement of each ion will be written in a system of Cartesian coordinates (X' , Y' , Z') chosen as shown in Fig. 5.12, and will provide the Cartesian components of the instantaneous speed to be used in the kinetic energy term of the Lagrangeian.

1) Kinetic energy of ion 1.

Ion #1 is involved in the motion affecting three bonds : 1-2, 1-3 and 1-4. The magnitude of contraction ("-") or stretching ("+") of each bond is given in the last line of Tab. 5.4. Attention has to be paid to the fact that these values represent the total deformation as symmetrically produced by both ions at the end of the bond. Thus, each ion is displaced by half the value on the last line in Tab. 5.4. For example, for bond 1-2, ion #1 is displaced towards ion #2 by $q\sqrt{3}$, while for bond 1-3, the same ion is displaced away from ion #3 by $q\sqrt{3}/2$.

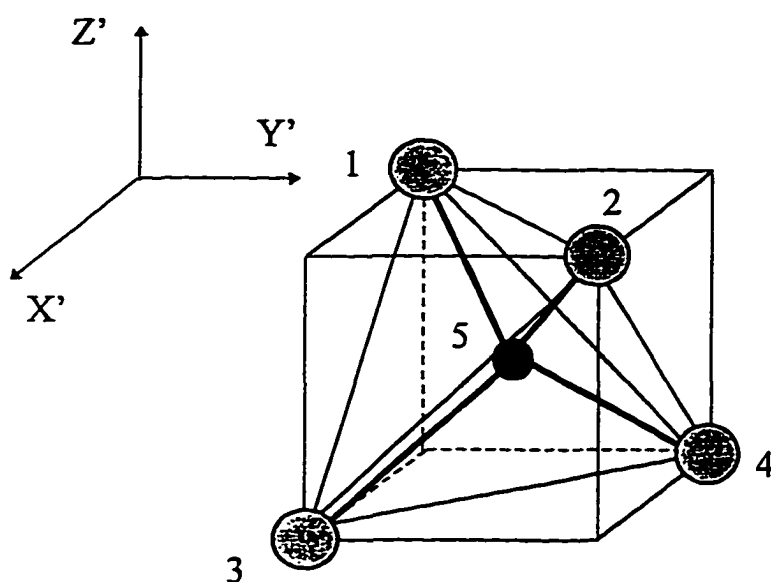


Figure 5.12 System of Cartesian coordinates associated to the ionic motion.

As bond 1-2 is in the plane $X'Y'$ (Fig. 5.12), and makes an angle of 45° with each axis, the Cartesian components of the displacement of ion #1 (see Tab. 5.4 and the above observation) produced by bond 1-2 is :

$$\Delta l_{1-2}^{(1)} = q \cdot \left(\sqrt{\frac{3}{2}}, \sqrt{\frac{3}{2}}, 0 \right) \quad (5.24)$$

Bonds 1-3 and 1-4 are in the $X'Z'$ and $Y'Z'$ planes, respectively, and make angles of 45° with the Z' axis. Ion #1 moves such as to stretch both bonds, i.e. its displacement has components along the $-X'$ and $-Z'$ axes, respectively. The displacement of ion #1 produced by bonds 1-3 and 1-4 are (see also Tab. 5.4):

$$\Delta l_{1-3}^{(1)} = q \cdot \left(-\frac{1}{2}\sqrt{\frac{3}{2}}, 0, \frac{1}{2}\sqrt{\frac{3}{2}}\right) \quad (5.25)$$

$$\Delta l_{1-4}^{(1)} = q \cdot \left(0, -\frac{1}{2}\sqrt{\frac{3}{2}}, \frac{1}{2}\sqrt{\frac{3}{2}}\right) \quad (5.26)$$

The Cartesian components of the total displacement for ion #1 are obtained by adding Eqs. (5.24) - (5.26) and gives :

$$\Delta l^{(1)} = q \cdot \left(\frac{1}{2}\sqrt{\frac{3}{2}}, \frac{1}{2}\sqrt{\frac{3}{2}}, \sqrt{\frac{3}{2}}\right) \quad (5.27)$$

The kinetic energy of ion #1 is obtained from Eq. (5.27) as :

$$T_1 = \frac{m(\Delta l^{(1)})^2}{2} = \frac{m}{2} \dot{q}^2 \left(\frac{1}{4} \cdot \frac{3}{2} + \frac{1}{4} \cdot \frac{3}{2} + \frac{3}{2}\right) = \frac{9}{8} m \dot{q}^2 \quad (5.28)$$

The displacement of ion #2 produced by bonds 2-1, 2-3 and 2-4, the total displacement and the kinetic energy of ion #2 can be computed in a similar fashion as described for ion #1, from Tab. 5.4. The above mentioned values are, respectively :

$$\Delta l_{2-1}^{(2)} = q \cdot \left(-\sqrt{\frac{3}{2}}, -\sqrt{\frac{3}{2}}, 0\right) \quad (5.29)$$

$$\Delta l_{2-3}^{(2)} = q \cdot \left(0, \frac{1}{2}\sqrt{\frac{3}{2}}, \frac{1}{2}\sqrt{\frac{3}{2}}\right) \quad (5.30)$$

$$\Delta l_{2-4}^{(2)} = q \cdot \left(\frac{1}{2}\sqrt{\frac{3}{2}}, 0, \frac{1}{2}\sqrt{\frac{3}{2}}\right) \quad (5.31)$$

$$\Delta l^{(2)} = q \cdot \left(-\frac{1}{2}\sqrt{\frac{3}{2}}, -\frac{1}{2}\sqrt{\frac{3}{2}}, \sqrt{\frac{3}{2}}\right) \quad (5.32)$$

$$T_2 = \frac{m}{2} \dot{q}^2 \left(\frac{3}{8} + \frac{3}{8} + \frac{3}{2} \right) = \frac{9}{8} m \dot{q}^2 \quad (5.33)$$

The displacement of ion #3 produced by bonds 3-1, 3-2 and 3-4, the total displacement and the kinetic energy of ion #3 are, respectively :

$$\Delta l_{3-1}^{(3)} = q \cdot \left(\frac{1}{2} \sqrt{\frac{3}{2}}, 0, -\frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.34)$$

$$\Delta l_{3-2}^{(3)} = q \cdot \left(0, -\frac{1}{2} \sqrt{\frac{3}{2}}, -\frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.35)$$

$$\Delta l_{3-4}^{(3)} = q \cdot \left(-\sqrt{\frac{3}{2}}, \sqrt{\frac{3}{2}}, 0 \right) \quad (5.36)$$

$$\Delta l^{(3)} = q \cdot \left(-\frac{1}{2} \sqrt{\frac{3}{2}}, -\frac{1}{2} \sqrt{\frac{3}{2}}, -\sqrt{\frac{3}{2}} \right) \quad (5.37)$$

$$T_3 = \frac{m}{2} \dot{q}^2 \left(\frac{3}{8} + \frac{3}{8} + \frac{3}{2} \right) = \frac{9}{8} m \dot{q}^2 \quad (5.38)$$

The displacement of ion #4 produced by bonds 4-1, 4-2 and 4-3, the total displacement and the kinetic energy of ion #4 are, respectively :

$$\Delta l_{4-1}^{(4)} = q \cdot \left(0, \frac{1}{2} \sqrt{\frac{3}{2}}, -\frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.39)$$

$$\Delta l_{4-2}^{(4)} = q \cdot \left(-\frac{1}{2} \sqrt{\frac{3}{2}}, 0, -\frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.40)$$

$$\Delta l_{4-3}^{(4)} = q \cdot \left(\sqrt{\frac{3}{2}}, -\sqrt{\frac{3}{2}}, 0 \right) \quad (5.41)$$

$$\Delta l^{(4)} = q \cdot \left(\frac{1}{2} \sqrt{\frac{3}{2}}, -\frac{1}{2} \sqrt{\frac{3}{2}}, -\sqrt{\frac{3}{2}} \right) \quad (5.42)$$

$$T_4 = \frac{m}{2} \dot{q}^2 \left(\frac{3}{8} + \frac{3}{8} + \frac{3}{2} \right) = \frac{9}{8} m \dot{q}^2 \quad (5.43)$$

The total kinetic energy for the XY_4 molecule is obtained by summing up the individual kinetic energy terms T_i , $i = 1 \div 4$, i.e. by adding Eqs. (5.28), (5.33), (5.38) and (5.43), which leads to :

$$T = \sum_{i=1}^4 T_i = 4 \cdot \frac{9}{8} m \dot{q}^2 = \frac{9}{2} m \dot{q}^2 \quad (5.44)$$

The harmonic potential energy is obtained as shown by Eq. (5.9) where y is the sum of the squares of the deformations of all Y-Y bonds, obtained from the last line in Tab. 5.4. The force constant of all Y-Y bonds is k_2 . The potential energy of the system for an $\nu_{2a}(E)$ mode can be written as :

$$V = \frac{k_2}{2} q^2 [(2\sqrt{3})^2 + (\sqrt{3})^2 + (\sqrt{3})^2 + (\sqrt{3})^2 + (\sqrt{3})^2 + (2\sqrt{3})^2] = 18k_2 q^2 \quad (5.45)$$

Using Eqs. (5.44), (5.45) the Lagrangeian of the system can be written as :

$$\mathcal{L} = T - V = \frac{9}{2} m \dot{q}^2 - 18k_2 q^2 \quad (5.46)$$

The equation of motion is given by the Lagrange equation (5.14) which, combined with Eq. (5.46) gives :

$$\ddot{q} + \frac{4k_2}{m} q = 0 \quad (5.47)$$

Eq. (5.47) is the equation for a harmonic oscillator with eigenfrequency :

$$\boxed{\omega^2 = \frac{4k_2}{m}} \quad (5.48)$$

Eq. (5.48) gives the (angular) frequency of the symmetric bending mode $\nu_{2a}(E)$ as a function of the Y-Y (O-O) force constant k_2 and the mass m of the Y ions. Eq. (5.48) shows that neither the mass nor the force constant of the bonds involving the central ion X affect the frequency of this mode.

The second S-vector (S_{2b}) given by Eq. (5.18) can be used in the same manner as S_{2a} for obtaining the (same) eigenfrequency for the symmetric bending mode ν_{2a} . Using a similar argument as that used for the S_{2a} vector, it can be

shown that the central ion has to remain stationary at all times in order to preserve the center of mass of the molecule. A table similar to Tab. 5.4, Tab. 5.5, gives the longitudinal deformations of the bonds as :

Bending mode	q_i	Bond 1-2	Bond 1-3	Bond 1-4	Bond 2-3	Bond 2-4	Bond 3-4
α_{13}	q_1	$q / 2\sqrt{3}$	$-q / \sqrt{3}$	$q / 2\sqrt{3}$			
	q_3		$-q / \sqrt{3}$		$q / 2\sqrt{3}$		$q / 2\sqrt{3}$
$-\alpha_{14}$	q_1	$-q / 2\sqrt{3}$	$-q / 2\sqrt{3}$	$q / \sqrt{3}$			
	q_4			$q / \sqrt{3}$		$-q / 2\sqrt{3}$	$-q / 2\sqrt{3}$
$-\alpha_{23}$	q_2	$-q / 2\sqrt{3}$			$q / \sqrt{3}$	$-q / 2\sqrt{3}$	
	q_3		$-q / 2\sqrt{3}$		$q / \sqrt{3}$		$-q / 2\sqrt{3}$
α_{24}	q_2	$q / 2\sqrt{3}$			$q / 2\sqrt{3}$	$-q / \sqrt{3}$	
	q_4			$q / 2\sqrt{3}$		$-q / \sqrt{3}$	$q / 2\sqrt{3}$
Total longitudinal deformation		0	$-q\sqrt{3}$	$q\sqrt{3}$	$q\sqrt{3}$	$-q\sqrt{3}$	0

Table 5.5 Longitudinal deformations (along the bond) produce by the S_{2b} bending mode vectors, given by Eq. (5.18).

The displacement of each of the four ions is calculated as previously shown from the last line in Tab. 5.5, by taking half the total displacement, for each ion participating in each bond. The individual displacements allow the calculation of the kinetic energy for each ion as follows. The notations have the same significance as those used for obtaining the kinetic energy for the S_{2a} vector.

1) Ion #1

$$\Delta l_{1-2}^{(1)} = q \cdot (0,0,0) \quad (5.49)$$

$$\Delta l_{1-3}^{(1)} = q \cdot \left(\frac{1}{2} \sqrt{\frac{3}{2}}, 0, -\frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.50)$$

$$\Delta l_{1-4}^{(1)} = q \cdot \left(0, -\frac{1}{2} \sqrt{\frac{3}{2}}, \frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.51)$$

$$\Delta l^{(1)} = q \cdot \left(\frac{1}{2} \sqrt{\frac{3}{2}}, -\frac{1}{2} \sqrt{\frac{3}{2}}, 0 \right) \quad (5.52)$$

$$T_1 = \frac{m}{2} \dot{q}^2 \left(\frac{3}{8} + \frac{3}{8} \right) = \frac{3}{8} m \dot{q}^2 \quad (5.53)$$

2) Ion #2

$$\Delta l_{2-1}^{(2)} = q \cdot (0, 0, 0) \quad (5.54)$$

$$\Delta l_{2-3}^{(2)} = q \cdot \left(0, \frac{1}{2} \sqrt{\frac{3}{2}}, \frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.55)$$

$$\Delta l_{2-4}^{(2)} = q \cdot \left(-\frac{1}{2} \sqrt{\frac{3}{2}}, 0, -\frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.56)$$

$$\Delta l^{(2)} = q \cdot \left(-\frac{1}{2} \sqrt{\frac{3}{2}}, \frac{1}{2} \sqrt{\frac{3}{2}}, 0 \right) \quad (5.57)$$

$$T_2 = \frac{m}{2} \dot{q}^2 \left(\frac{3}{8} + \frac{3}{8} \right) = \frac{3}{8} m \dot{q}^2 \quad (5.58)$$

3) Ion #3

$$\Delta l_{3-1}^{(3)} = q \cdot \left(-\frac{1}{2} \sqrt{\frac{3}{2}}, 0, \frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.59)$$

$$\Delta l_{3-2}^{(3)} = q \cdot \left(0, -\frac{1}{2} \sqrt{\frac{3}{2}}, -\frac{1}{2} \sqrt{\frac{3}{2}} \right) \quad (5.60)$$

$$\Delta l_{3-4}^{(3)} = q \cdot (0, 0, 0) \quad (5.61)$$

$$\Delta l^{(3)} = q \cdot \left(-\frac{1}{2}\sqrt{\frac{3}{2}}, -\frac{1}{2}\sqrt{\frac{3}{2}}, 0\right) \quad (5.62)$$

$$T_3 = \frac{m}{2} \dot{q}^2 \left(\frac{3}{8} + \frac{3}{8}\right) = \frac{3}{8} m \dot{q}^2 \quad (5.63)$$

4) Ion #4

$$\Delta l_{4-1}^{(4)} = q \cdot \left(0, \frac{1}{2}\sqrt{\frac{3}{2}}, -\frac{1}{2}\sqrt{\frac{3}{2}}\right) \quad (5.64)$$

$$\Delta l_{4-2}^{(4)} = q \cdot \left(\frac{1}{2}\sqrt{\frac{3}{2}}, 0, \frac{1}{2}\sqrt{\frac{3}{2}}\right) \quad (5.65)$$

$$\Delta l_{4-3}^{(4)} = q \cdot (0, 0, 0) \quad (5.66)$$

$$\Delta l^{(4)} = q \cdot \left(\frac{1}{2}\sqrt{\frac{3}{2}}, \frac{1}{2}\sqrt{\frac{3}{2}}, 0\right) \quad (5.67)$$

$$T_4 = \frac{m}{2} \dot{q}^2 \left(\frac{3}{8} + \frac{3}{8}\right) = \frac{3}{8} m \dot{q}^2 \quad (5.68)$$

The total kinetic energy for the XY_4 molecule is obtained by summing up the individual kinetic energy terms T_i , $i = 1 \div 4$, i.e. by adding Eqs. (5.53), (5.58), (5.63) and (5.68), which leads to :

$$T = 4 \cdot \frac{3}{8} m \dot{q}^2 = \frac{3}{2} m \dot{q}^2 \quad (5.69)$$

The potential energy is obtained as shown by Eq. (5.9) where y is the sum of the squares of the deformations of all Y-Y bonds, obtained from the last line in Tab. 5.5. The force constant of all Y-Y bonds is k_2 . The potential energy of the system can be written as :

$$V = \frac{k_2}{2} q^2 [0 + (\sqrt{3})^2 + (\sqrt{3})^2 + (\sqrt{3})^2 + (\sqrt{3})^2 + 0] = 6k_2 q^2 \quad (5.70)$$

Using Eqs. (5.69), (5.70) the Lagrangeian of the system can be written as :

$$\mathcal{L} = T - V = \frac{3}{2}m\dot{q}^2 - 6k_2q^2 \quad (5.71)$$

The equation of motion is given by the Lagrange equation (5.14) which, combined with Eq. (5.71) gives :

$$\ddot{q} + \frac{4k_2}{m}q = 0 \quad (5.72)$$

Eq. (5.71) is the equation for a harmonic oscillator with eigenfrequency :

$$\boxed{\omega^2 = \frac{4k_2}{m}} \quad (5.73)$$

Eq. (5.73) gives the (angular) frequency of the symmetric bending mode $\nu_2(E)$ as the eigen value of the S_{2b} vector and is identical, as expected, with the eigenvalue of the S_{2a} vector in Eq. (5.48). The above example shows that in the case of an n-degenerate mode of vibration, it is sufficient to consider any of the n S-vectors to obtain the frequency of vibration for the considered mode.

3) Anti-symmetric stretching mode $\nu_3(T_2)$.

The three S-vectors for the $\nu_3(T_2)$ mode are [11] :

$$S_{3a} = \frac{1}{\sqrt{4}}(\bar{r}_1 + \bar{r}_2 - \bar{r}_3 - \bar{r}_4) \quad (5.74)$$

$$S_{3b} = \frac{1}{\sqrt{4}}(\bar{r}_1 - \bar{r}_2 - \bar{r}_3 + \bar{r}_4) \quad (5.75)$$

$$S_{3c} = \frac{1}{\sqrt{4}}(\bar{r}_1 - \bar{r}_2 + \bar{r}_3 - \bar{r}_4) \quad (5.76)$$

The S_{3a} vector which indicates that ions #1 and #2 stretch the X-Y bonds, while ions #3 and #4 compress them, as shown in Fig. 5.13 [12], will be used for computing the frequency of oscillation for the T_2 mode. As in the previous cases the displacement $\bar{R}$ of the central ion has to be determined from Eq. (5.2). Fig.

5.8 shows that a stretching vector can be decomposed in a component along the bond $q \cdot \cos \alpha$, and a vertical component $q \cdot \sin \alpha$. The longitudinal components cancel each other (for $\vec{r}_1$ and $\vec{r}_2$, and for $-\vec{r}_3$ and $-\vec{r}_4$), but the vertical components add up giving a total contribution of $4q \cdot \sin \alpha$. Eq. (5.2) becomes, as projected on the vertical axis Z' (Fig. 5.13) :

$$4qm \sin \alpha + MR = 0 \quad (5.77)$$

with $\sin \alpha$ given by Eq. (5.11). Eq. (5.77) shows that in order to maintain the center of mass at rest, the central ion is displaced downwards, along Z' by :

$$R = -\frac{4qm}{M\sqrt{3}} \quad (5.78)$$

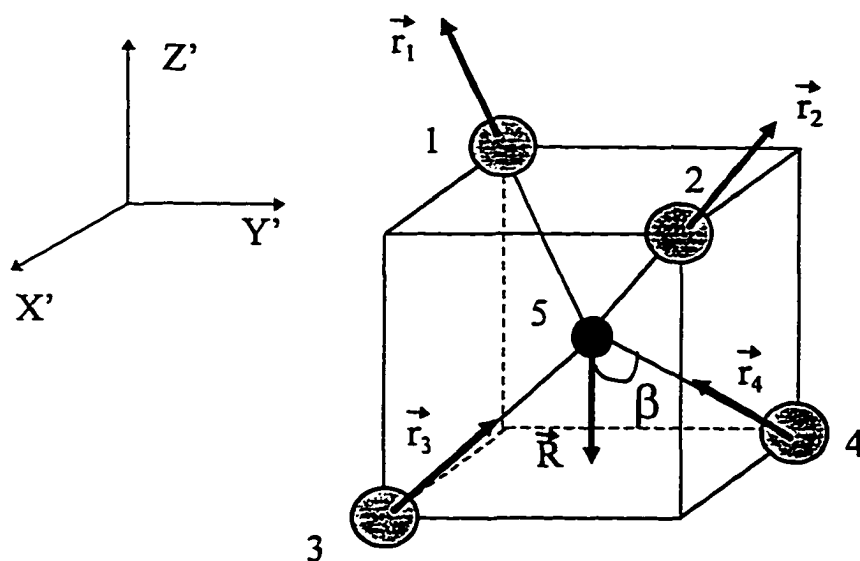


Figure 5.13 Ionic displacement in the $v_3(T_2)$ anti-symmetric stretching mode described by S_{3a} .

Using the fact that the displacements of the four equivalent ions are $+q$ (for ions #1 and #2) and $-q$ (for ions #3 and #4), and Eq. (5.78) which gives the displacement of the central ion, the kinetic energy of the molecule is :

$$T = 4 \cdot \frac{m\dot{q}^2}{2} + \frac{M\dot{R}^2}{2} = 2m\dot{q}^2 + \frac{M}{2} \cdot \frac{16m^2\dot{q}^2}{3M^2} = 2m(1 + \frac{4m}{3M})\dot{q}^2 \quad (5.79)$$

Fig. 5.13 shows that the angle between the displacement of the central ion and the X-Y bonds is β , where β is the complementary of α ($\alpha + \beta = \pi/2$), thus using Eq. (5.11) :

$$\cos\beta = \frac{\sqrt{3}}{3}, \quad \sin\beta = \sqrt{\frac{2}{3}} \quad (5.80)$$

The projection of the displacement of the central ion on each of the four X-Y bonds is then $R \cdot \cos\beta$. Using Eqs. (5.78), (5.80) and Fig. 5.13 it can be shown that each of the four X-Y bonds are stretched (bonds 1-5 and 2-5), or compressed (bonds 3-5 and 4-5) (see Fig. 5.13) by the amount :

$$\Delta l = q + |R| \cos\beta = q(1 + \frac{4m}{3M}) \quad (5.81)$$

Using the above equation, the harmonic potential energy of the four X-Y bonds can be written as :

$$V_1 = \frac{k_1}{2} \cdot 4 \cdot q^2 (1 + \frac{4m}{3M})^2 = 2k_1 (1 + \frac{4m}{3M})^2 q^2 \quad (5.82)$$

The Y-Y bonds are deformed only by the four $\vec{r}_i$ displacements, as the displacement of the central ion does not affect them. Observing that, for example, an $\vec{r}_1$ stretch is perpendicular to the $\vec{q}_1$ vector in Fig. 5.8, the deformation produced on the Y-Y bonds by $\vec{r}_1$ can be obtained from Eqs. (5.19) - (5.21) where $\cos\alpha$ has to be interchanged with $\sin\alpha$ such that the above equations become, respectively:

$$\Delta l_{1-2} = q \cdot \cos\alpha = q \sqrt{\frac{2}{3}} \quad (5.83)$$

$$\Delta l_{1-3}^{(1)} = q \cdot \sin\alpha \cdot \cos(45^\circ) = q \frac{1}{2} \sqrt{\frac{2}{3}} \quad (5.84)$$

$$\Delta l_{1-3}^{(2)} = q \cdot \cos \alpha \cdot \cos(60^\circ) = q \frac{1}{2} \sqrt{\frac{2}{3}} \quad (5.85)$$

The total stretch of the 1-3 bond is :

$$\Delta l_{1-3} = \Delta l_{1-3}^{(1)} + \Delta l_{1-3}^{(2)} = q \sqrt{\frac{2}{3}} \quad (5.86)$$

Using the symmetry of the 1-3 and 1-4 bonds with respect to the tetrahedral diagonal plane, the total stretch of bond 1-4 is also given by Eq. (5.86). The “+” sign in front of all the above deformations indicate that all the bonds are stretched by $\bar{r}_1$. Tab. 5.6 summarizes the deformations of the Y-Y bonds produced by the S_{3a} vector.

Stretch vector	Bond 1-2	Bond 1-3	Bond 1-4	Bond 2-3	Bond 2-4	Bond 3-4
$\bar{r}_1$	$q\sqrt{2/3}$	$q\sqrt{2/3}$	$q\sqrt{2/3}$			
$\bar{r}_2$	$q\sqrt{2/3}$			$q\sqrt{2/3}$	$q\sqrt{2/3}$	
$-\bar{r}_3$		$-q\sqrt{2/3}$		$-q\sqrt{2/3}$		$-q\sqrt{2/3}$
$-\bar{r}_4$			$-q\sqrt{2/3}$		$-q\sqrt{2/3}$	$-q\sqrt{2/3}$
Total deformation	$2q\sqrt{2/3}$	0	0	0	0	$-2q\sqrt{2/3}$

Table 5.6 Longitudinal deformations produced on the Y-Y bonds by the components of an S_{3a} anti-symmetric stretch vector.

The contribution to the harmonic potential energy of the Y-Y bonds is obtained by summing the squares of the total deformations given in the last line in Tab. 5.6, and is :

$$V_2 = \frac{k_2}{2} \cdot 2 \cdot \frac{8q^2}{3} = \frac{8k_2q^2}{3} \quad (5.87)$$

Using Eqs. (5.79), (5.82) and (5.87) the Lagrangeian of the system can be written as :

$$\mathcal{L} = T - V_1 - V_2 = 2m(1 + \frac{4m}{3M})\dot{q}^2 - [2k_1(1 + \frac{4m}{3M})^2 + \frac{8k_2}{3}]q^2 \quad (5.88)$$

The equation of motion is given by the Lagrange equation (14) which, combined with Eq. (5.88) gives :

$$\ddot{q} + [\frac{k_1}{m}(1 + \frac{4m}{3M}) + \frac{4k_2}{3m(1 + \frac{4m}{3M})}]q = 0 \quad (5.89)$$

Eq. (5.89) is the equation for a harmonic oscillator with eigenfrequency :

$$\omega^2 = \frac{k_1}{m}(1 + \frac{4m}{3M}) + \frac{4k_2}{3m(1 + \frac{4m}{3M})} \quad (5.90)$$

Eq. (5.90) gives the (angular) frequency of the anti-symmetric stretching mode $\nu_3(T_2)$ as the eigenvalue of the S_{3a} .

4) Anti-symmetric bending mode $\nu_4(T_2)$.

The three S-vectors for the $\nu_4(T_2)$ mode are $[11]$:

$$S_{4a} = \frac{1}{\sqrt{2}}(\alpha_{12} - \alpha_{34}) \quad (5.91)$$

$$S_{4b} = \frac{1}{\sqrt{2}}(\alpha_{14} - \alpha_{23}) \quad (5.92)$$

$$S_{4c} = \frac{1}{\sqrt{2}}(\alpha_{13} - \alpha_{24}) \quad (5.93)$$

As in the previous cases the displacement $\bar{\mathbf{R}}$ of the central ion has to be determined from Eq. (5.2). Figs. 5.8 and 5.9 show that the component of the bending mode vector α_{12} along the 1-2 bond ($q \cdot \sin \alpha$) cancel each other but the

vertical components add up giving a total contribution of $2q \cdot \cos\alpha$. The situation for the $-\alpha_{34}$ mode is the same, such that the total displacement of the four Y ions is $4q \cdot \cos\alpha$. Eq. (5.2) becomes, as projected on the vertical axis Z' (Fig. 5.12) :

$$4qm \cos\alpha + MR = 0 \quad (5.94)$$

with $\cos\alpha$ given by Eq. (5.11). Eq. (5.94) shows that in order to maintain the center of mass at rest, the central ion is displaced downwards, along Z' by :

$$R = -4\sqrt{\frac{2}{3}} \frac{qm}{M} \quad (5.95)$$

Fig. 5.14 shows the ionic displacement for the S_{4a} anti-symmetric bending mode.

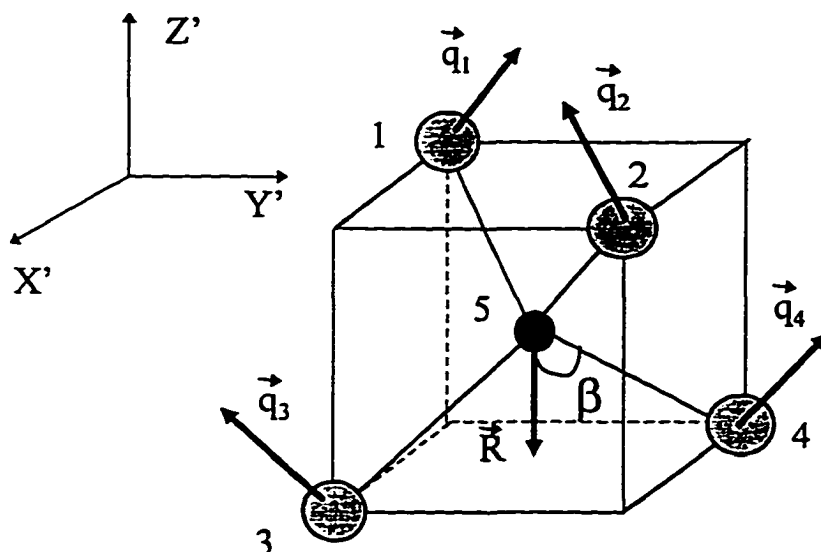


Figure 5.14 Ionic displacement in the $\nu_4(T_2)$ anti-symmetric bending mode described by S_{4a} .

The Cartesian components of the displacements of the four equivalent ions are calculated as shown in Fig. 5.9 by projecting the $\vec{q}_i$ vectors on the $X'Y'Z'$ Cartesian axes shown above. The following Cartesian displacements are obtained:

$$\Delta l^{(1)} = q\left(\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, \sqrt{\frac{2}{3}}\right) \quad (5.96)$$

$$\Delta l^{(2)} = q\left(-\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{6}}, \sqrt{\frac{2}{3}}\right) \quad (5.97)$$

$$\Delta l^{(3)} = q\left(-\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{6}}, \sqrt{\frac{2}{3}}\right) \quad (5.98)$$

$$\Delta l^{(4)} = q\left(\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, \sqrt{\frac{2}{3}}\right) \quad (5.99)$$

The kinetic energy for each of the four Y ions is :

$$T_1 = \frac{m \cdot |\dot{\Delta l}^{(1)}|^2}{2} = \frac{m}{2} \dot{q}^2 \left(\frac{1}{6} + \frac{1}{6} + \frac{2}{3}\right) = \frac{m \dot{q}^2}{2} \quad (5.100)$$

The total kinetic energy is given by Eqs. (5.95) and (5.100) as :

$$T = \frac{M \dot{R}^2}{2} + 4T_1 = \frac{M}{2} 16 \cdot \frac{2}{3} \left(\frac{m}{M}\right)^2 + 4 \cdot \frac{m \dot{q}^2}{2} = 2m \dot{q}^2 \left(1 + \frac{8m}{3M}\right) \quad (5.101)$$

As shown by Fig. 5.14 the projection of $\bar{R}$ on the four X-Y bonds (i.e. the component which gives the potential energy) is $R \cdot \cos\beta$. Using Eq. (5.95), the harmonic potential energy due to the deformation of the X-Y bonds is :

$$V_1 = 4 \cdot \frac{k_1}{2} \cdot \left(4 \sqrt{\frac{2}{3}} \frac{m}{M} \frac{1}{\sqrt{3}} q\right)^2 = \left(\frac{8m}{3M}\right)^2 k_1 q^2 \quad (5.102)$$

In order to obtain the potential energy due to the deformation of the Y-Y bonds, the displacement of the four equivalent ions produced by S_{4a} has to be calculated. The displacement of each ion due to a vector $\bar{q}_i$ is given by Eqs. (5.19), (5.22) and (5.23). As the bending mode vectors are perpendicular to the X-Y bonds, they do not produce a longitudinal deformation, thus do not contribute to the potential energy term. On the other hand the displacement of the central ion given by Eq. (5.95) contributes only to the potential energy of the X-Y bonds. The

longitudinal deformations of the bonds as determined by the S_{4a} vector is given in Tab. 5.6.

Bending mode	q_i	Bond 1-2	Bond 1-3	Bond 1-4	Bond 2-3	Bond 2-4	Bond 3-4
α_{12}	q_1	$-q / \sqrt{3}$	$q / 2\sqrt{3}$	$q / 2\sqrt{3}$			
	q_2	$-q / \sqrt{3}$			$q / 2\sqrt{3}$	$q / 2\sqrt{3}$	
$-\alpha_{34}$	q_1		$-q / 2\sqrt{3}$		$-q / 2\sqrt{3}$		$q / \sqrt{3}$
	q_4			$-q / 2\sqrt{3}$		$-q / 2\sqrt{3}$	$q / \sqrt{3}$
Total deformation		$-2q / \sqrt{3}$	0	0	0	0	$2q / \sqrt{3}$

Table 5.7 Longitudinal deformations (along the bond) produce by the S_{4a} anti-symmetric bending mode vector.

The potential energy due to the deformation of the Y-Y bonds is obtained by summing up the squares of the deformations given in the last line of Tab. 5.7, and leads to :

$$V_2 = \frac{k_2}{2} \cdot 2 \cdot \frac{4q^2}{3} = \frac{4k_2q^2}{3} \quad (5.103)$$

Using Eqs. (5.101) - (5.103) the Lagrangeian of the system can be written as :

$$\mathcal{L} = T - V_1 - V_2 = 2m(1 + \frac{8m}{3M})\dot{q}^2 - [(\frac{8m}{3M})^2 k_1 + \frac{4k_2}{3}]q^2 \quad (5.104)$$

The equation of motion is given by the Lagrange equation (5.14) which, combined with Eq. (5.104) gives :

$$\ddot{q} + \left[\frac{\frac{4k_2}{3} + \left(\frac{8m}{3M}\right)^2 k_1}{2m\left(1 + \frac{8m}{3M}\right)} \right] q = 0 \quad (5.105)$$

Eq. (5.105) is the equation for a harmonic oscillator with eigenfrequency :

$$\omega^2 = \frac{\frac{2k_2}{3} + 2k_1\left(\frac{4m}{3M}\right)^2}{m\left(1 + \frac{8m}{3M}\right)} \quad (5.106)$$

Eq. (5.106) gives the (angular) frequency of the anti-symmetric bending mode $\nu_4(T_2)$ as the eigenvalue of the S_{4a} .

The boxed equations (5.16), (5.48), (5.90) and (5.106) give the frequencies of oscillation of the four tetrahedral internal modes of vibration for an XY_4 molecule in terms of X and Y ionic masses M and m, respectively and in terms of X-Y and Y-Y force constants, k_1 and k_2 , respectively. These four equations, together with the measured values of the local modes given in Tab. 5.3 will provide the value of the force constants in a (CrO_4) tetrahedron and allow the estimation of local effects (changes in terms of force constants) introduced by the impurity ion. The following four mean measured values (determined from Tab. 5.3) for the frequencies of oscillation will be used to calculate the tetrahedral force constants :

$$\nu_1(A_1) = 764 \text{ cm}^{-1} \quad (5.107)$$

$$\nu_2(E) = \frac{498 + 480}{2} \text{ cm}^{-1} = 489 \text{ cm}^{-1} \quad (5.108)$$

$$\nu_3(T_2) = \frac{740 + 690}{2} = 715 \text{ cm}^{-1} \quad (5.109)$$

$$\nu_4(T_2) = \frac{290 + 253}{2} = 272 \text{ cm}^{-1} \quad (5.110)$$

Eqs. (5.16) and (5.48), together with the mean measured values for the corresponding energies, given by Eqs. (5.107) and (5.108), respectively were used for determining the values for the tetrahedral Cr-O and O-O force constants. It should be noted that any two equations, with the corresponding measured values for the energy of oscillation, can be used for determining k_1 and k_2 . Attention has to be paid to the used units and required transformations. As, in SI units :

$$k = m\omega^2 = m(2\pi f)^2 = m(2\pi \frac{c}{\lambda})^2 = 4\pi^2 c^2 m E^2 \quad (5.111)$$

where m is the mass of the oscillator expressed in kg, and E the energy of the mode expressed in units of $1/\lambda$, i.e. $1/m$. By transforming the SI units in the more commonly used atomic scale units m.u. (mass units) for the mass, mdyne/Å units for the force constants and cm^{-1} units for the energy of the mode the following expression is obtained for the force constant :

$$k[\frac{\text{mdyn}}{\text{\AA}}] = 592.76 \cdot 10^{-9} \cdot m[\text{m. u.}] \cdot (E[\text{cm}^{-1}])^2 \quad (5.112)$$

The above equation together with Eqs. (5.48) and (5.108), with $m=16$ m.u., give the value of the O-O force constant in a tetrahedron containing a Cr^{4+} ion as :

$$k_2 = 0.57 \text{ mdyne/\AA} \quad (5.113)$$

Eqs. (5.16), (5.107), (5.112) and the above value for k_2 give the value of the Cr-O force constant in a tetrahedron containing a Cr^{4+} ion as :

$$k_1 = 3.27 \text{ mdyne/\AA} \quad (5.114)$$

Using the above determined values for the force constants, and Eqs. (5.90) and (5.106) with the Cr^{4+} mass $M = 52$ m.u., the computed values of the anti-symmetric modes of vibration are : $\nu_3(\text{T}_2) = 737 \text{ cm}^{-1}$ and $\nu_4(\text{T}_2) = 293 \text{ cm}^{-1}$. These values are in very good agreement with the mean measured values of 715 cm^{-1} and 272 cm^{-1} given by Eqs. (5.109), (5.110), respectively, and confirm the correctness of the mode assignment and calculation.

The local effects introduced by the impurity ion can be estimated by comparing the values of the force constants in a tetrahedron containing a Cr^{4+} ion, given by Eqs. (5.113), (5.114), with the similar values in a SiO_4 tetrahedron given in the rigid-ion model as [10] :

$$k_1(\text{Si}) = 3.75 \text{ mdyn/\AA} \quad (5.115)$$

$$k_2(\text{Si}) = 0.71 \text{ mdyn/\AA} \quad (5.116)$$

The local effects introduced by the impurity ion, in terms of change in the tetrahedral force constants k_1 and k_2 expressed in $\text{mdyn/\AA}$, are summarized in Tab. 5.8. The relative percent change Δk_i is defined as :

$$\Delta k_i = \frac{k_{i(\text{Cr})} - k_{i(\text{Si})}}{k_{i(\text{Si})}} \cdot 100(\%) \quad (5.117)$$

$k_{1\text{Cr-O}}$	$k_{1\text{Si-O}}$	$\Delta k_1 (\%)$	$k_{2\text{O-O (Cr)}}$	$k_{2\text{O-O (Si)}}$	$\Delta k_2 (\%)$
3.27	3.75	-13%	0.57	0.71	-19%

Table 5.8 Comparison between tetrahedral force constants k_1 and k_2 in CrO_4 and SiO_4 tetrahedra, and relative percent change (given by Eq. (5.117)), reflecting local changes introduced by the impurity ion.

The comparison between Eqs. (5.114) and (5.115) and the results presented in Tab. 5.8 indicate a relative percent decrease of $\sim 13\%$ in the X-O ($X = \text{Cr}, \text{Si}$) force constant value in the case when Cr^{4+} replaces a Si^{4+} ion. A decrease of $\sim 19\%$ is obtained when comparing the O-O force constants for CrO_4 and SiO_4 tetrahedra.

The main result of the presented calculations is, besides the local mode assignment in terms of energy and symmetry, the fact that a CrO_4 tetrahedron is looser bound than a SiO_4 tetrahedron, i.e. there is a decrease in both k_1 and k_2

force constants in a CrO_4 molecule if compared to a SiO_4 molecule. The implications and repercussions of this fact are discussed in Chapter 6. The measured energy of vibration of Cr^{4+} local modes also gives a first indication of possible decay routes in nonradiative processes when the energy is transferred from the local modes of the impurity ion into the phonon bands. For example [7], as the breathing local mode ν_1 at 764 cm^{-1} is in a phonon gap, i.e. there are no phonon modes ν_p with the same energy as ν_1 , only a second order process of the type $\nu_1 \rightarrow \nu_{p1} + \nu_{p2}$ allows the energy transfer from the local mode ν_1 into the lattice, through select phonon modes ν_{p1} and ν_{p2} . The most probable, energetic-wise, phonon candidates for the decay route of the 764 cm^{-1} local mode are $\nu_{1p} = 335\text{ cm}^{-1}$ and $\nu_{2p} = 424\text{ cm}^{-1}$ [7].

5.7 References

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Chapter 6

Second neighbor interactions, anharmonic effects and electron-phonon coupling for Cr^{4+} in $\text{Cr:Mg}_2\text{SiO}_4$ probed by low temperature resonance Raman measurements

6.1 Background. Anharmonic effects and electron-phonon interactions

In Chapter 7 it will be shown that during nonradiative processes taking place in an impurity-doped crystal, the energy is transferred from a photoexcited electronic state of the laser impurity ion into its local modes which act as nonradiative decay channels (and also facilitate electronic (bottleneck) transitions). The nonradiative relaxation is completed by the energy transfer from local modes into a select number of daughter phonons which then decay due to interactions with the phonon bath bringing the system back into thermal equilibrium. Thus, from the point of view of nonradiative processes it is important to know how “efficient” are the electronic and the vibrational subsystems coupled, i.e. if electron-phonon interactions facilitating the energy transfer are significant.

Using quantum mechanics it can be shown that only one phonon processes are allowed for a perfect harmonic oscillator, i.e. only the fundamental frequencies of vibration ω_i appear in a Raman spectrum. In order to be able to observe overtones ($2\omega_i$, $3\omega_i$, etc.) or combinations of modes ($\omega_1 + \omega_2 \leftrightarrow \omega_3$, ...) the Hamiltonian of the system has to contain a perturbation. The two most significant types of perturbation terms leading to overtone progressions and combinations of modes are : (1) the consideration of cubic terms in the expansion of the potential accounting for anharmonic effects, and (2) electron-phonon interaction (see Eq. (4.60)). The relevance and consequences of considering these terms are discussed as follows.

The addition of cubic terms to the harmonic potential accounts for coupling between different modes of vibration and energy redistribution in a crystal, and may lead to long overtone progressions. However, if the observed overtone progression for a mode of vibration ω is due to anharmonicity, the energy of the n^{th} overtone is given by [1] :

$$E(n) = \omega(n + \frac{1}{2}) - X(n + \frac{1}{2})^2 + \dots \quad (6.1)$$

where ω is the frequency of the considered mode, and X the anharmonic constant. The first term in Eq. (6.1) is the harmonic contribution due to quadratic terms in the Hamiltonian (describing a harmonic potential - see Eq. (5.9)), while the second term is the anharmonic contribution due to cubic terms. Using Eq. (6.1), the energy difference between two successive overtones n and $n+1$ is obtained as :

$$E(n+1) - E(n) = \omega - 2X(n+1) \quad (6.2)$$

Eq. (6.2) gives the well known result that for a harmonic oscillator ($X = 0$) the spacing between successive overtones is equidistant, given by the frequency of the fundamental vibration ω , but it also shows that for an anharmonic oscillator the overtones are not equidistant any longer. The spacing between successive overtone decreases (if $X > 0$) proportional to X and to the order of the overtone. The value of the anharmonic constant can be determined by plotting the measured energy of the fundamental ($n = 1$) and first n measured overtones $E(n) - E(0)$ as a function of n :

$$\frac{E(n) - E(0)}{n} \equiv (\omega - X) - Xn \quad (6.3)$$

Eq. (6.3) represents a straight line having the y-intercept $(\omega - X)$ and slope $(-X)$, and can be used for determining the two parameters (ω and X) if at least the fundamental ($n = 1$) and the first overtone ($n = 2$) are measured. However, more reliable values for the parameters are obtained if higher order overtones are observed. The value of X (large or small) provides information regarding the

importance of anharmonic terms. Section 6.5 gives the values of the anharmonic constants for the two highest frequency Cr^{4+} local modes as determined from up to fourth order (third overtone) resonance Raman spectra.

Selection rules are different for overtones and combinations but the general criterion given by Eq. (3.29) remains valid (the product of representations describing the initial and final wavefunctions and the moment inducing the transition has to contain the totally symmetric representation). The selection rules for combinations and overtones of nondegenerate modes of vibration (as is the case of Cr^{4+}) are rather straightforward and will be exemplified as follows. It should be noted that special attention has to be paid to combinations and overtones of degenerate modes of vibrations where the symmetry of the final state is given by the symmetrized direct product of the wavefunction for the fundamentals. A complete treatment of this case with several examples can be found in different textbooks [2 - 4].

In order to illustrate the selection rules for a nondegenerate system we will consider the case of Cr^{4+} in $\text{Cr:Mg}_2\text{SiO}_4$ where the site symmetry is C_s and all wavefunctions and operators describing any type of process involving Cr^{4+} ions are either totally symmetric A' or nontotally symmetric A'' (see Appendix A.3). As already discussed in Section 4.2.6 due to the fact that the initial vibrational state is totally symmetric in a Stokes process, the total final state $|\Psi_f\rangle$ has to have the same symmetry as the component of the polarizability inducing the Raman transition. For example, as shown in Tab. 5.1 combinations or overtones whose total final state is totally symmetric A' are obtained in A_g scattering configurations, i.e. in Porto's notation in $s(cc)t$ scattering arrangement where s and t are any of the a , b or c crystal axes. As will be shown in Section 6.3 all A' combinations and overtones for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ were obtained in $b(cc)a$ 90° scattering arrangement. Following the same argument and using again Tab. 5.1, combinations or overtones whose total final state is nontotally symmetric A'' are

obtained in B_{3g} scattering configurations, i.e. in Porto's notation in $s(cb)t$ scattering arrangement where s and t are any of the a , b or c crystal axes. As will be shown in Section 6.3 all A'' combinations and overtones for $Cr^{4+}:Mg_2SiO_4$ were obtained in $a(cb)c$ 90° scattering arrangement.

The symmetry of the total final state for overtones or combinations of nondegenerate modes of vibration is obtained as the product of the representations for the modes of vibration entering the combination or overtone. Considering the multiplication laws for C_s given by Eqs. (4.71), (4.72) and two local modes of vibration ω_1 and ω_2 such that ω_1 is totally symmetric A' and ω_2 is nontotally symmetric A'' , the symmetry of the combination $\omega_1 + \omega_2$ is $A' \times A'' = A''$ and is observed only in a B_{3g} configuration (such as $a(cb)c$). Using the same considerations, the first overtone of ω_2 ($2\omega_2$) has symmetry $A'' \times A'' = A'$ and is observed in an A_g configuration (such as $b(cc)a$), while the third order combination $2\omega_1 + \omega_2$ has symmetry $A' \times A' \times A'' = A''$ and is observed in a B_{3g} configuration (such as $a(cb)c$), etc. Section 6.4 discusses the selection rules applicable to each measured overtone and combination spectrum, together with the mode assignment for the local modes of $Cr^{4+}:Mg_2SiO_4$.

The second term which can be considered as perturbation in the Hamiltonian of a harmonic oscillator, leading to overtones and combinations is the electron-phonon coupling introduced in Chapter 4 (see Eq. (4.60)). Let us consider, as in Section 4.5 an impurity ion which can be described as a harmonic oscillator vibrating with frequency ω along the coordinate Q_a . The Hamiltonian for this mode of vibration if electron-phonon coupling is considered as a perturbation can be written as :

$$H = \frac{P_a^2}{2m} + \frac{m\omega^2 Q_a^2}{2} + \gamma Q_a \quad (6.4)$$

where P_a is the canonical momentum, m the mass of the oscillator and γ the electron-phonon operator, which is a scalar in the one-dimensional case. The

Hamiltonian given by Eq. (6.4) can be rewritten in terms of creation and annihilation operators a^+ and a introduced in Chapter 4 by Eqs. (4.7), (4.8) as :

$$H = \hbar\omega(a^+a + \frac{1}{2}) + \gamma\beta(a + a^+) \quad (6.5)$$

where the coordinate Q_a in the last term in eq. (6.4) was expressed in terms of creation and annihilation operators as [5] :

$$Q_a = \sqrt{\frac{\hbar}{2m\omega}}(a + a^+) \equiv \beta(a + a^+) \quad (6.6)$$

The transition amplitude $A_{n \rightarrow f}$ from an initial vibrational state $|n\rangle$ to a final state $|f\rangle$ due to the electron-phonon coupling is given in first order perturbation theory as :

$$A_{n \rightarrow f} \sim \langle f | \gamma Q_a | n \rangle = \langle f | \gamma \beta (a + a^+) | n \rangle = \gamma\beta\sqrt{n} \langle f | n-1 \rangle + \gamma\beta\sqrt{n+1} \langle f | n+1 \rangle \quad (6.7)$$

where the expression of the perturbation from Eq. (6.6) was used, and the creation and annihilation operators acted on state $|n\rangle$ as shown by Eqs. (4.7), (4.8). Due to the orthonormality of the wavefunctions for the harmonic oscillator :

$$\langle i | j \rangle = \delta_{ij} \quad (6.8)$$

the first term in Eq. (6.7) is nonzero if $|f\rangle = |n-1\rangle$, i.e. if a phonon (vibration) was destroyed and gives the transition amplitude for an anti-Stokes process induced by electron-phonon interactions. The last term in Eq. (6.7) is nonzero if $|f\rangle = |n+1\rangle$, i.e. if a phonon (vibration) was created and gives the transition amplitude for a Stokes process induced by electron-phonon interactions. Eq. (6.7) shows that the transition amplitude for a Raman process induced by electron-phonon interaction is proportional to the electron-phonon coupling γ (the transition probability is proportional to γ^2).

Next it will be shown that the electron-phonon coupling is responsible for overtones, using second order perturbation theory. If the first overtone 2ω is observed (i.e. two vibrational quanta are created in a Stokes process), the final

state of the system is $|n + 2\rangle$. The transition amplitude for the $|n\rangle \rightarrow |n + 2\rangle$ transition in second order perturbation theory is :

$$A_{n \rightarrow n+2} \sim \sum_j \langle n+2 | \gamma \beta (a + a^+) | j \rangle \langle j | \gamma \beta (a + a^+) | n \rangle \quad (6.9)$$

where the summation is over all vibrational states. The energy denominator was omitted from Eq. (6.9). In order for the first overtone to be allowed the transition amplitude given by Eq. (6.9) has to be nonzero. Eq. (6.9) can be rewritten as :

$$A_{n \rightarrow n+2} \sim (\gamma \beta)^2 \sum_j (\sqrt{j} \langle n+2 | j-1 \rangle + \sqrt{j+1} \langle n+2 | j+1 \rangle) (\sqrt{n} \langle j | n-1 \rangle + \sqrt{n+1} \langle j | n+1 \rangle) \quad (6.10)$$

Using the orthonormality given by Eq. (6.8), after taking the products, only the term with $j = n+1$ survives such that the transition amplitude for the overtone 2ω is

$$A_{n \rightarrow n+2} \sim (\gamma \beta)^2 (n+1) \quad (6.11)$$

Eq. (6.11) shows that the observation of an overtone is possible only for modes which display electron-phonon coupling ($\gamma \neq 0$). As Eq. (6.11) was derived in second order perturbation theory it will give rise to modes which are weaker than first order terms (i.e. as the order of the observed spectrum increases its intensity decreases).

Eq. (6.11) proves (and the result can be generalized to the n -th overtone) that the stronger the electron-phonon interaction, the more overtones it give rise to such that the decrease in the intensity of the spectrum for higher order overtones (due to higher order perturbation theory terms) is compensated to some extent by the electron-phonon coupling whose power increases with the order of the spectrum. The correlation between the apparition of overtones and the strength of electron-phonon coupling is schematically suggested by Fig. 4.5 and was mentioned in Section 4.5.

The above discussion shows that the observation of combinations and overtones, especially a long overtone progression indicate that the mode(s) displaying the progression is (are) strongly anharmonic (have large X) and/or that

it is (are) characterized by sizable electron-phonon coupling. Using the measured values of the overtones and Eq. (6.3) the value of the anharmonic constant X can be estimated. If X is small, anharmonic processes can be ruled out as the cause for the progression. In this case one can conclude that electron-phonon coupling is strong for the mode displaying the progression. The overtone progression for the two highest frequency Cr^{4+} local modes in $\text{Cr:Mg}_2\text{SiO}_4$ at 765 and 742 cm^{-1} was measured up to fourth order resonance Raman spectrum and the anharmonic constants were estimated for both modes. As will be shown in Section 6.5 both anharmonic constant values are small indicating relative strong electron-phonon interactions for these modes.

In order to observe combinations and overtones for Cr^{4+} local modes low temperature (77 K) measurements have to be performed. Lowering the temperature usually decreases the background due to thermal noise (phonon coupling). For the same reason (lower phonon occupation number) all features in a low temperature spectrum appear narrower. For example, while at room temperature the high-energy, phonon-aided tail of the $\text{Cr}^{3+}(\text{I})$ emission R-line at 693 nm [6] is sufficiently strong to cover any signal beyond ~ 630 nm, the same high energy emission tail is narrow enough at 77K to allow the measurement of up to the second overtone, 3ω , for the highest frequency tetrahedral breathing mode at 765 cm^{-1} [7]. Under 572 nm resonance excitation, the second overtone of the 765 cm^{-1} breathing local mode, at $3 \times 765 = 2295 \text{ cm}^{-1}$ can be measured in a Stokes spectrum at 658 nm without any interference from the $\text{Cr}^{3+}(\text{I})$ R-line. The lower background together with enhanced absorption conditions at 77 K, allow the observation of weaker, finer structures in the local mode spectrum, such as the A_g local modes in the 340 - 400 cm^{-1} region (Section 6.3), which appear only as a structureless background in room temperature measurements (Fig. 5.2.a).

Sections 6.3 and 6.7 will demonstrate the need to consider second neighbor interactions for the Cr^{4+} ion and will discuss their implication and relevance to the

problem of nonradiative processes. It should be mentioned that although previously reported, second neighbor interactions were detected only by IR measurements and only for cases when the impurity ion is lighter than the ion it substitutes [8].

6.2 Experimental setup and experimental method

Low temperature (4K - liquid He and 77K - liquid N₂) resonance and off-resonance Raman measurements were performed on two Cr:Mg₂SiO₄ oriented single crystals with low doping levels, $\sim 3 \times 10^{18}$ ions/cm³ and $\sim 4 \times 10^{18}$ ions/cm³ free of any visible inhomogeneities such as cracks, bubbles, inclusions or discolorations [7]. All Stokes- Raman spectra were obtained using linearly polarized along the *c*-crystallographic axis excitation.

The experimental setup is the same as the one used for room temperature resonance Raman measurements, with the exception of the sample compartment. The setup is presented in detail in Section 2.7, and is briefly described as follows. It consists of a CW mode-locked Nd:YAG laser with 82 MHz repetition rate and 7W output power at 1.064 μ m, which has a KTP frequency doubling crystal attached to its output head. The average power of the frequency doubled 532 nm pulses is 1.3 W. The frequency doubled Nd:YAG laser synchronously pumps a Rh-6G dye laser tunable over the 570 - 630 nm spectral range. Stokes Raman spectra were obtained using three different wavelengths : (a) 572 nm, 50 mW linearly polarized along the *c*-crystallographic axis pulses, corresponding to the maximum of absorption of the $^3B_2(^3T_1)$ Cr⁴⁺ band (Fig. 3.11), were used to obtain first through third order resonance Raman spectra; (b) 582 nm, 100 mW linearly polarized along the *c*-crystallographic axis pulses were used to obtain off-resonance Raman spectra. The off-resonance spectra were normalized at the same excitation level and exposure time as the on-resonance spectra (see Section 6.3);

(c) 532 nm, 1.3 W linearly polarized along the *c*-crystallographic axis pulses, corresponding to the high energy phonon-aided tail of the ${}^3B_2({}^3T_1)$ Cr^{4+} absorption band (Fig. 3.11), were used to obtain third and fourth order resonance Raman spectra (Section 6.3). Appropriate narrow band filters were used for each wavelength, such that the intensity of the excitation beam was further reduced by $\sim 50\%$. A 12 cm lens was used for focusing the beam into the sample down to ~ 40 μm .

As measurements were performed at low temperature (4K and 77K) the sample was placed in a Dewar (see Fig. 2.8). The Dewar had quartz windows on each of the four vertical walls which allow the sample to be irradiated. A mirror tilted at 45° was introduced inside the Dewar such that the excitation beam was directed along the vertical axis inside the sample (see Fig. 2.8) and was, at the same time, parallel to (along) the entrance slit of the spectrometer (90° vertical illumination). The advantages of this type of excitation geometry were discussed in Section 2.3. The scattering geometry is given for all spectra presented in Section 6.3 in Porto's notation (see Section 2.6). In order to minimize the absorption of the scattered radiation, the sample was illuminated close to the plane facing the spectrometer. The temperature was monitored throughout the experiments with a temperature controller.

The scattered signal was collected by a triplemate SPEX spectrograph. using the highest resolution grating (#5) with 1800 grooves/mm. The following combination of slits was used : $S_1 = 200$ μm , $S_2 = 5$ cm and $S_3 = 200$ μm , leading to a spectral resolution of ~ 5 cm^{-1} [7]. The scattered signal was collected by a system of two lenses : a camera lens placed 2 cm (at its focal distance) away from the sample, and a 20 cm focal lens, placed at its focal distance away from the spectrometer's entrance slit (and close to the camera lens in order to minimize losses). The notable performance of the photon counting image acquisition system (PIAS, Hamamatsu, model C1815) allows weak signals (as those obtained in high

order resonance spectra) to be collected and analyzed. The Raman spectra were further processed, analyzed and saved (as images, and in ASCII format) using two PCs, together with the specifically designed software (described in Appendix A.1, A.2).

6.3 Experimental results

Although Stokes Raman spectra were measured both at 4K and 77K, no differences were observed for the two temperatures. Consequently, all spectra presented in this section were measured at 77K. It should also be noted that although two Cr:Mg₂SiO₄ samples were used, the obtained Stokes Raman spectra were identical for both samples. Consequently, all spectra presented in this section were measured using the 10x8x6 mm³ oriented single crystal with doping level $\sim 3 \times 10^{18}$ ions/cm³ (0.02 at%) [7]. The scattering geometries are given throughout this chapter in Porto's notation, in terms of crystal axes expressed in the *Pnma* notation (see Section 2.6). As Cr⁴⁺ ions are excited in the ³B₂(³T₁) band, the incident excitation is polarized along the *c*-crystallographic axis. All resonance modes are boxed. Highlighted resonance modes were not observed in room temperature spectra [9]. Phonon modes are not boxed.

The experiments performed at 77K, under 572 nm resonant excitation, allow the observation of first through third order resonance enhanced spectra (Figs. 6.1 - 6.3). Observation of higher order resonance spectra obtained under 572 nm excitation is not possible because of the strong high energy, phonon aided tail of the Cr³⁺(I) emission R-line at 693 nm [6]. Figs. 6.1.a - 6.1.c present the first order resonance Raman spectra (boxed modes) for different mode symmetries covering the 180 - 1000 cm⁻¹ spectral range (upper spectra - thick line). Each figure also contains Stokes Raman spectra obtained under 582 nm off resonance excitation (lower spectra - thin line). The off resonance spectra are used as reference, and

identify the phonon modes as those modes who do not change their intensity under the two excitation conditions (572 and 582 nm). These modes are not boxed. On the other hand, modes which appear only under 572 nm excitation, or significantly decrease their intensity under off-resonance conditions are identified as local modes. The position of the measured Cr^{4+} local modes is: 253, 288, 346, 361, 390, 499, 691 and 765 cm^{-1} for A_g symmetry (Fig. 6.1.a); 408, 420, 477, 526 and 742 cm^{-1} for B_{3g} symmetry (Fig. 6.1.b); and 468, 691, 765 and 820 cm^{-1} for B_{2g} symmetry (Fig. 6.1.c). The local modes at 346, 361, 390, 408, 420, 468, 526 and 820 cm^{-1} (highlighted) were not observed in similar spectra taken at room temperature [9]. As was already mentioned, the “appearance” of additional local modes in low temperature spectra is attributed to an overall lower background and to an ≈ 2 fold increase in the Cr^{4+} absorption coefficient at 572 nm at 77K, supported by a relative larger intensity of all resonance enhanced modes at 77K, if compared to room temperature data [9]. The increase in the Cr^{4+} absorption coefficient can account for the enhancement of all previously reported, in room temperature measurements, local modes (boxed unhighlighted), as well as for the appearance of new local modes (boxed highlighted), too weak to be resolved at room temperature. The intensity of the spectrum in the 720 - 1000 cm^{-1} range, in A_g symmetry was reduced 5 times. The intensity of the spectrum in the 700 - 900 cm^{-1} range, in B_{3g} symmetry was reduced 4 times. The estimated experimental accuracy for the modes in the first order spectra was $\approx \pm 1.5 \text{ cm}^{-1}$. The relevance of the behavior of RE modes under the two excitation wavelengths (resonant 572 nm and off-resonance 582 nm) is discussed in section 6.6.

Figs. 6.2.a and 6.2.b present second order RE Raman spectra, obtained under resonant 572 nm resonant excitation, in two different symmetries corresponding to A_g and B_{3g} modes, covering the 990 - 1600 cm^{-1} spectral range.

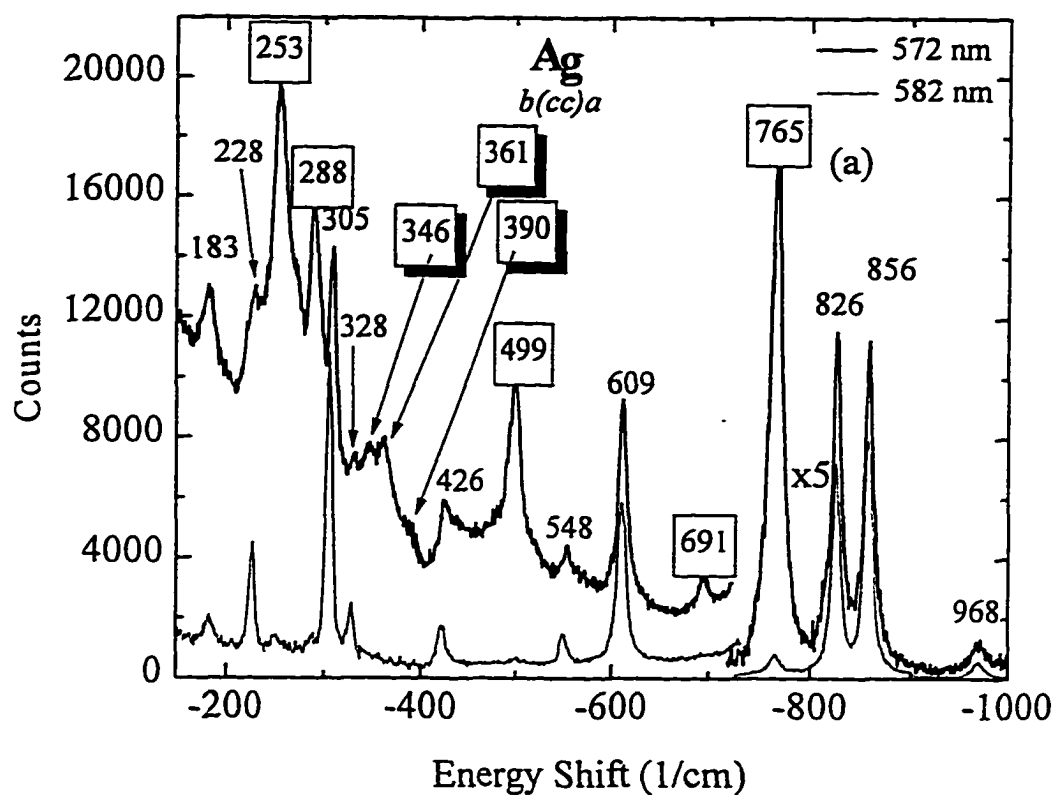
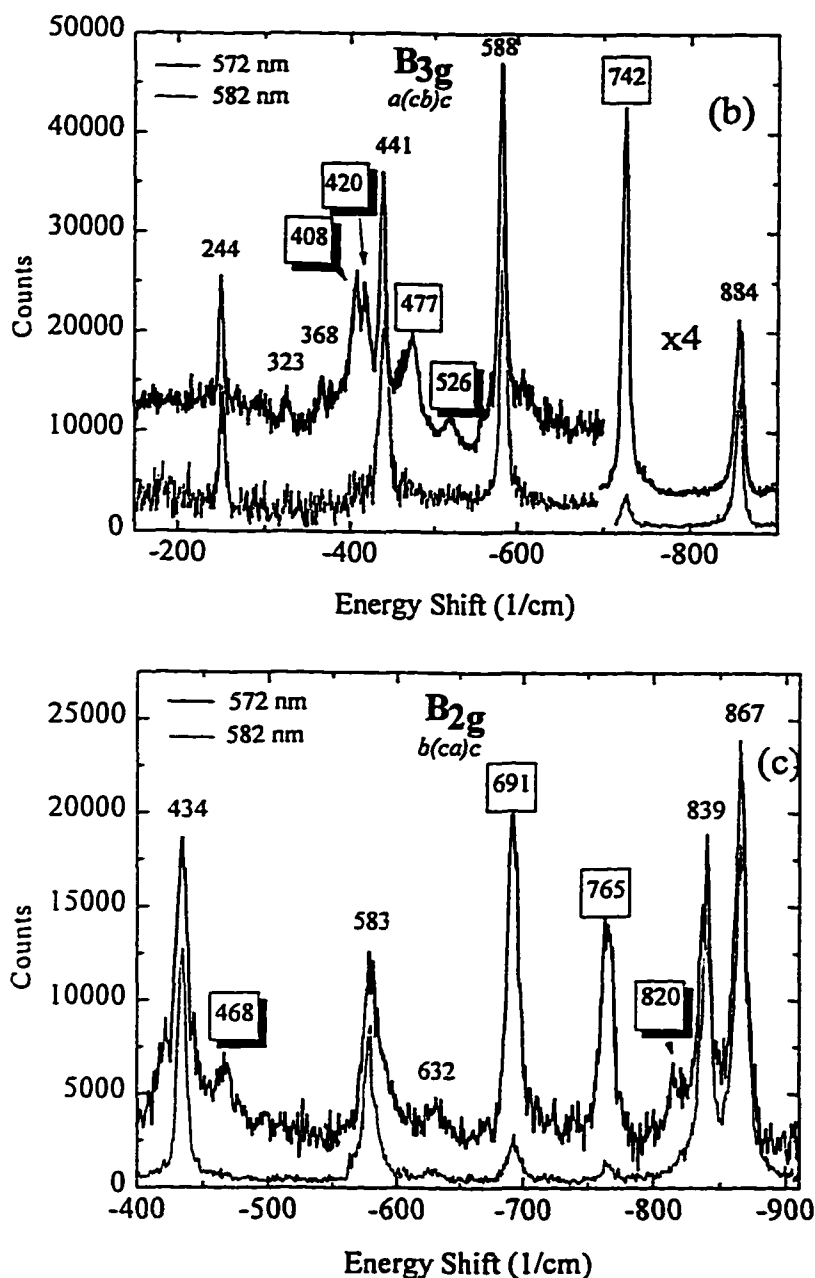


Figure 6.1 (a) First order A_g resonance Stokes Raman spectra (boxed modes) for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ obtained under resonant 572 nm (thick line) and off-resonance 582 nm (thin line) excitation at 77K. The scattering configuration is $b(cc)a$. Local modes are boxed. Highlighted local modes were not observed in room temperature spectra.



Figs. 6.1 (b), (c) First order B_{3g} and B_{2g} , respectively, resonance Stokes Raman spectra (boxed modes) for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ obtained under resonant 572 nm (thick line) and off-resonant 582 nm (thin line) excitation at 77K. The corresponding scattering configurations are $a(cb)c$ and $b(ca)c$ for B_{3g} and B_{2g} modes, respectively. Local modes are boxed. Highlighted local modes were not observed in room temperature spectra.

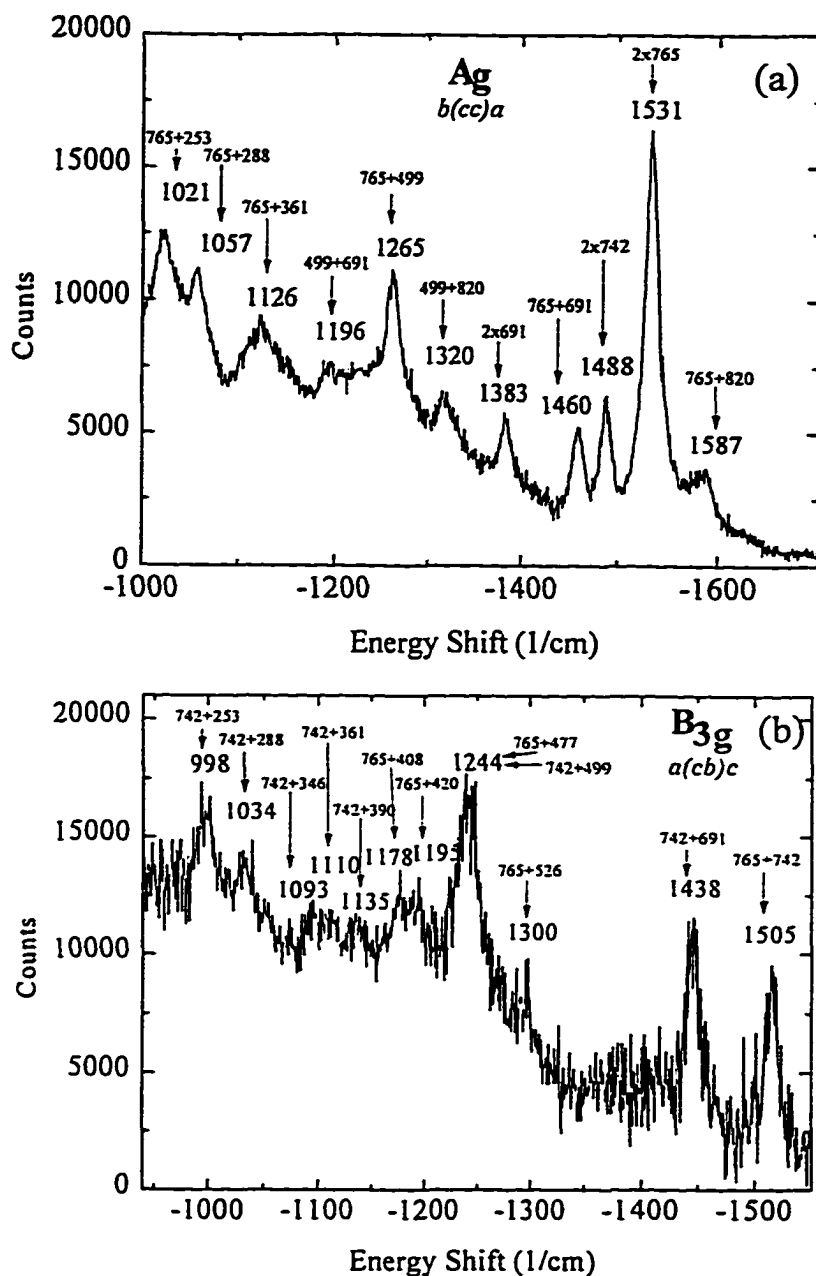


Figure 6.2 (a), (b) Second order resonance Raman spectra for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ obtained under resonant 572 nm excitation at 77K for Ag (in $b(cc)a$ configuration) and B_{3g} (in $a(cb)c$ configuration) symmetry, respectively. The modes assigned for each combination and overtone are indicated above each measured value.

In section 6.4 it will be shown that the A_g and B_{3g} scattering configurations are sufficient for determining all the combinations and overtones. As the Raman phonon spectrum for Mg_2SiO_4 extends between $140 - 980\text{ cm}^{-1}$ [10], no phonon modes are present in the $990 - 1600\text{ cm}^{-1}$ range. The position of the combinations and overtones of first order local modes is : $1021, 1057, 1126, 1196, 1265, 1320, 1383, 1460, 1488, 1531$ and 1587 cm^{-1} for A_g symmetry (Fig. 6.2.a) and $998, 1034, 1093, 1110, 1135, 1178, 1195, 1244, 1300, 1438$ and 1505 cm^{-1} for B_{3g} symmetry (Fig. 6.2.b). The estimated experimental accuracy for the second order spectra was $\approx \pm 2.5\text{ cm}^{-1}$. The combination or overtone assigned to each mode is indicated above the measured values.

Figs. 6.3.a and 6.3.b present the third order resonance Raman spectra, obtained under resonant 572 nm resonant excitation, for A_g and B_{3g} mode symmetries, covering the $1700 - 2300\text{ cm}^{-1}$ spectral range.

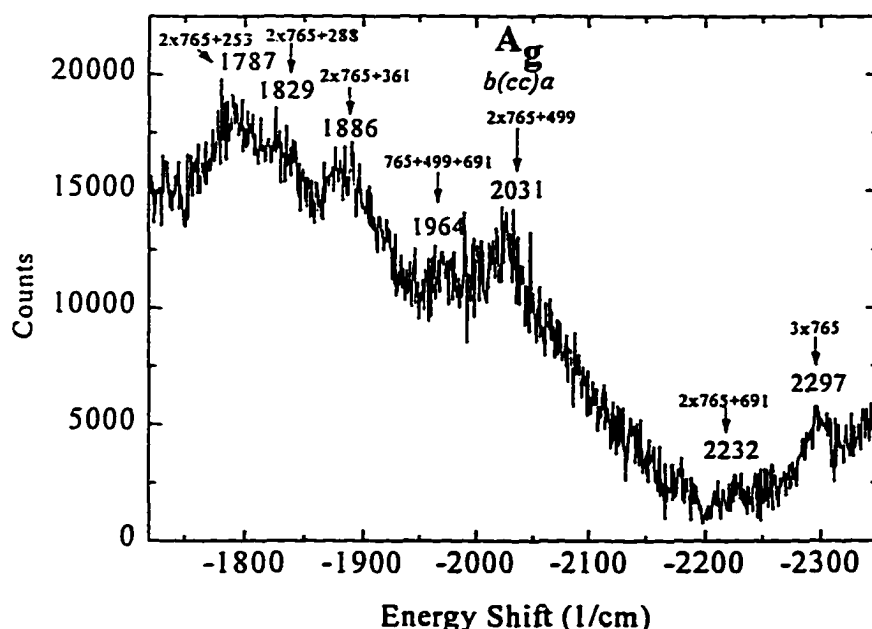


Figure 6.3 (a) Third order resonance Raman spectrum for $Cr^{4+}:Mg_2SiO_4$ obtained under resonant 572 nm excitation at 77K for A_g symmetry in $b(cc)a$ scattering configuration. The modes assigned for each combination and overtone are indicated above each measured value.

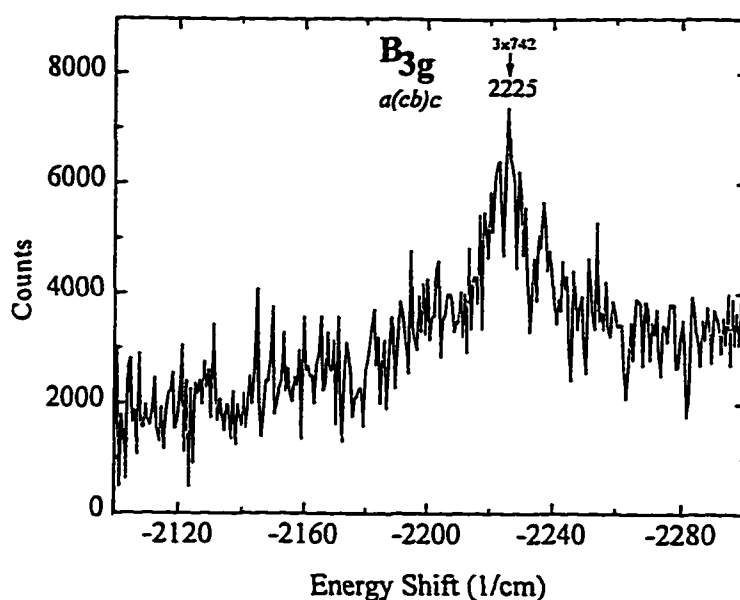


Figure 6.3 (b) Third order resonance Raman spectrum for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ obtained under resonant 572 nm excitation at 77K for B_{3g} symmetry in $a(cb)c$ scattering configuration. The modes assigned for each combination and overtone are indicated above each measured value.

No phonon modes are present in the $1700 - 2300 \text{ cm}^{-1}$ range [10]. The position of combinations and overtones of local modes is : 1787, 1829, 1886, 1964, 2031, 2232 and 2297 cm^{-1} for A_g symmetry (Fig. 6.3.a) and 2225 cm^{-1} for B_{3g} symmetry (Fig. 6.3.b). The estimated experimental accuracy for the third order spectra was $\approx \pm 3 \text{ cm}^{-1}$. The combinations or overtones assigned to each mode are indicated above the measured values.

Fig. 6.4 presents third and forth order A_g resonance Raman spectra of $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ at 77K, obtained under 532 nm excitation, corresponding to the high energy phonon-aided tail of the ${}^3B_2({}^3T_1)$ Cr^{4+} absorption band (Fig. 3.11), covering the $2150 - 3200 \text{ cm}^{-1}$ spectral range. No phonon modes are present in this range [10]. Although Cr^{4+} absorption is weaker at 532 nm than at 572 nm, this fact is partly compensated by a ~ 10 times increase in the excitation power.

Due to their relative large spectral width, the 532 nm pulses are not desirable for obtaining high quality first order resonance spectra. However, this factor does not influence the quality of higher order, broader, resonance spectra, such as third or fourth order.

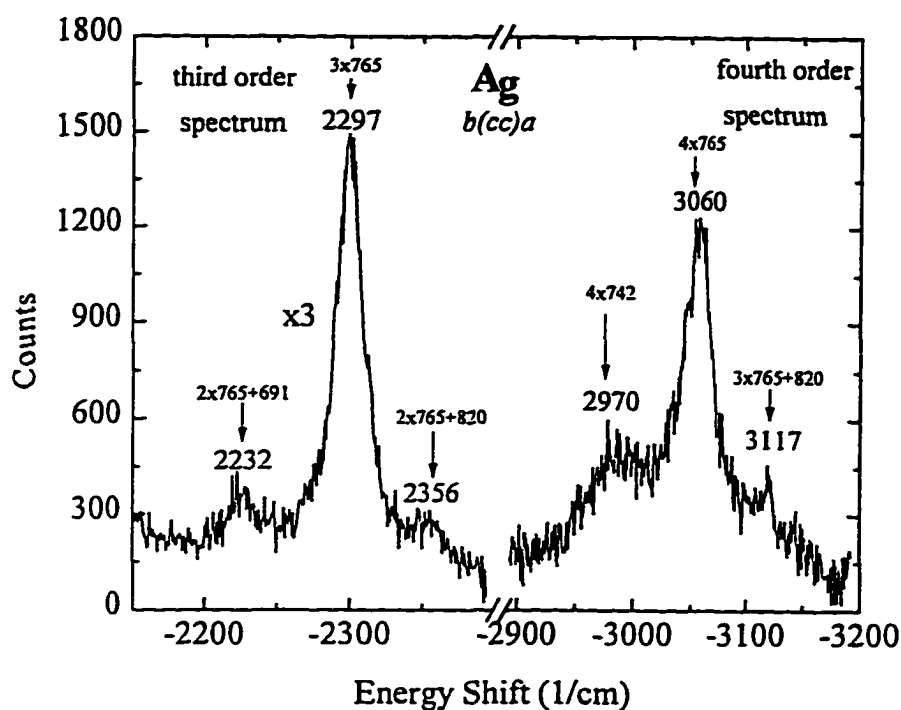


Figure 6.4 Third and fourth order resonance Raman spectra for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ obtained under resonant 532 nm excitation at 77K in the 2150 - 3200 cm^{-1} range. The modes assigned for each combination and overtone are indicated above each measured value. The scattering configurations was $b(cc)a$, Ag symmetry.

The main advantage of the 532 nm excitation is its blue shift with respect to the maximum of Cr^{4+} absorption at 572 nm, and the possibility to investigate higher order spectra. For example, the third harmonic (4ω) of the 765 cm^{-1} breathing mode at 3060 cm^{-1} is situated in a Stokes Raman spectrum at 693 nm if 572 nm excitation is used, and is totally covered by the $\text{Cr}^{3+}(\text{I})$ R-line. On the other hand, the same overtone is situated at 635 nm if 532 nm excitation is used

and is not affected by the R-line. The measured position of combinations and overtones of local modes is : 2232, 2297 and 2356 cm^{-1} for third order spectra and 2970, 3060 and 3117 cm^{-1} for fourth order spectra. The estimated experimental accuracy was $\approx \pm 3 \text{ cm}^{-1}$ and $\approx \pm 5 \text{ cm}^{-1}$ for the third and fourth order spectra, respectively. The modes assigned for each combination and overtone are indicated above each measured value. The intensity of the third order spectrum was reduced 3 times.

6.4 Selection rules. Combination and overtone assignment

The selection rules for the combinations and overtones for the Cr^{4+} local modes presented in Figs. 6.1 - 6.4 were discussed in Section 6.1 and are detailed as follows. Selection rules are obtained by taking into account the site symmetry of the ion of interest, i.e. C_s for Cr^{4+} . As shown by its table of characters (Appendix A.3) the C_s group has two types of representations, A' and A'' , with the following multiplication rules (Eqs. (4.71), (4.72)) :

$$A' \times A' = A' \quad (6.12)$$

$$A' \times A'' = A'' \times A' = A'' \quad (6.13)$$

$$A'' \times A'' = A' \quad (6.14)$$

or, more general :

$$(A')^n = A' \quad (6.15)$$

$$(A'')^{2n+1} = A'' \quad (6.16)$$

$$(A'')^{2n} = A', \quad n \in \mathbb{N} \quad (6.17)$$

Tab. 5.1 gives the space group (crystal) symmetry corresponding to each C_s representation and shows, for example, that A' modes are obtained in any of the A_g or B_{2g} scattering configurations. As, in general, modes corresponding to totally symmetric configurations have higher scattering cross sections and give rise to more intense signals, the A_g configuration will be the choice for investigating

A' local modes. On the other hand, B_{3g} configurations give information on A'' local modes.

Eqs. (6.12) - (6.17), together with Tab. 5.1 give the selection rules and appropriate scattering geometries for obtaining combinations and overtones of local modes. For example, they show that a combination involving two A' or two A'' modes is observable in an A_g scattering configuration, while a combination involving two modes of different symmetry (A' + A'') is observable in a B_{3g} scattering configuration. A more general statement is that a combination or overtone which involves an odd number of A'' modes is observable in a B_{3g} scattering configuration, while a combination or overtone which involves an even number of A'' modes is observable in an A_g scattering configuration.

An observation can be made regarding the intensity of higher order spectra (expected to be, in general, much weaker than a first order spectrum). Room temperature resonance Raman spectra [9] have shown that, according to Albrecht's theory, the strongest local mode is the tetrahedral breathing mode. In consequence, the strongest (most intense) features in higher order resonance enhanced spectra, should involve the breathing mode at 765 cm⁻¹. The assignment of the modes presented in Figs. 6.1 - 6.4 is presented as follows.

a) First order Cr⁴⁺ resonance enhanced modes.

The energies of the fifteen observed first order Cr⁴⁺ local modes and their symmetry, obtained from spectra presented in Figs. 6.1.a - 6.1.c are summarized in Tab. 6.1. As mentioned before [9], B_{2g} spectra should contain depolarized A_g resonance modes. However, the B_{2g} modes at 468 cm⁻¹ and 820 cm⁻¹ are not observed in the A_g spectrum probably because they are overlapping with other strong A_g modes (and thus are not resolved in Fig. 6.1.a).

Symmetry	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
A_g	253	288	346	361	390	499	691	765
B_{3g}	408	420	477	526	742			
B_{2g}	468	820						

Table 6.1 First order Cr^{4+} resonance enhanced modes. The mode energy is given in cm^{-1} .

b) Second order Cr^{4+} resonance enhanced modes.

Figs. 6.2.a, b present second order Cr^{4+} combinations and overtones of first order modes obtained under resonant 572 nm excitation. As previously mentioned, Fig. 6.2.a (A_g modes) contains combinations between two A' or between two A'' modes. As the 765 cm^{-1} mode is the strongest in intensity and the only totally symmetric Cr^{4+} local mode in T_d symmetry, it is expected to give the strongest contribution in the second order Raman spectra, in combinations with other modes. This fact is reflected in Tab. 6.2 and Fig. 6.2.a. The 765 cm^{-1} mode gives combinations with all A_g modes. The strongest line in the second order A_g spectrum is the overtone of the 765 cm^{-1} mode at 1531 cm^{-1} . The wide band at 1126 cm^{-1} is probably due to the overlap of the $765 + 346\text{ cm}^{-1}$, $765 + 361\text{ cm}^{-1}$ and $765 + 390\text{ cm}^{-1}$ mode combinations. The only four lines which can not be assigned to any combinations with the 765 cm^{-1} mode are combinations of the 499 cm^{-1} mode (the second strongest in intensity A_g mode) with each of the 691 and 820 cm^{-1} modes, the overtone of 691 cm^{-1} and the only overtone of a A'' mode, 742 cm^{-1} (which is the strongest B_{3g} resonance enhanced mode - Fig. 6.1.b). The assignment of combinations and overtones are given in Tab. 6.2.

Combinations ($\omega_1 + \omega_2$) and overtones ($2\omega_1$)

ω_1	ω_2	Calculated $\omega_1 + \omega_2$	Measured $\omega_1 + \omega_2$
765	253	1018	1021
765	288	1053	1057
765	361	1126	1126
765	499	1264	1265
765	691	1456	1460
765	820	1585	1587
499	691	1190	1196
499	820	1310	1320
691	691	1382	1383
742	742	1484	1488
765	765	1530	1531

Table 6.2 Assignment of combinations ($\omega_1 + \omega_2$) and overtones ($2\omega_1$) observed in the second order A_g resonance Raman spectrum (Fig. 6.2.a). All frequencies are given in cm^{-1} .

Fig. 6.2.b (B_{3g} A'' modes) contains combinations between one A' and one A'' mode. The B_{3g} second order spectrum is expected to contain combinations of the 765 cm^{-1} mode (strongest A' mode) with A'' (B_{3g}) modes as well as combinations of the 742 cm^{-1} mode (strongest A'' mode) with A' (A_g) modes. The combination assignment presented in Tab. 6.3 shows that the 765 cm^{-1} mode gives combinations with all first order A'' modes and that the 742 cm^{-1} mode gives combinations with all first order A' modes (except for the 820 cm^{-1} mode). It is worth mentioning that the combination between the 742 cm^{-1} mode and each of

the 346, 361 and 390 cm^{-1} modes is individually resolved at 1093, 1110 and 1135 cm^{-1} in the B_{3g} spectrum (Fig. 6.2.b) while the combination between these modes with the 765 cm^{-1} mode appears as a broad band centered at 1126 cm^{-1} in the A_g spectrum (Fig. 6.2.a).

Combinations ($\omega_1 + \omega_2$)

ω_1	ω_2	Calculated $\omega_1 + \omega_2$	Measured $\omega_1 + \omega_2$
765	408	1173	1178
765	420	1185	1195
765	477	1242	1244
765	526	1291	1300
765	742	1507	1505
742	253	995	998
742	288	1030	1034
742	346	1088	1093
742	361	1103	1110
742	390	1132	1135
742	499	1241	1244
742	691	1433	1438

Table 6.3 Assignment of combinations ($\omega_1 + \omega_2$) measured in second order B_{3g} Raman spectrum (Fig. 6.2.b). All frequencies are given in cm^{-1} .

c) Third and fourth order Cr^{4+} resonance enhanced modes.

Figs. 6.3 a, b present third order Cr^{4+} resonance Raman spectra (combinations and overtones) obtained under 572 nm excitation. Fig. 6.3.a (A_g

modes) contains combinations and overtones between three A' modes. As the overtone of the 765 cm^{-1} mode (at 1531 cm^{-1}) is the strongest line in the second order spectrum, we expect most of the third order modes to be given by combinations with the 1531 cm^{-1} overtone. Only one combination (at 1964 cm^{-1}) doesn't contain the first overtone of the 765 cm^{-1} mode. Instead, the 1964 cm^{-1} line is assigned to the 691 cm^{-1} mode in combination with the $765 + 499\text{ cm}^{-1}$ mode which is the second strongest line in the second order A_g spectrum (Fig. 6.2.a). Fig. 6.3.b (B_{3g} modes) contains the only resonance mode observed in the third order B_{3g} spectrum, measured at 2225 cm^{-1} . This mode is assigned as the second overtone of the strongest B_{3g} A'' first order RE mode at 742 cm^{-1} . Higher order resonance spectra obtained under 572 nm excitation cannot be observed because of the strong fluorescence from the $\text{Cr}^{3+}(\text{I})$ R-line. Third and fourth order A_g resonance spectra were obtained under excitation with 532 nm and are shown in Fig. 6.4. Higher order RE spectra obtained under 532 nm are covered by the $\text{Cr}^{3+}(\text{I})$ R-line and cannot be observed. It is interesting to note that the second overtone of 765 cm^{-1} measured at 2297 cm^{-1} appears much weaker in Fig. 6.3.a, under 572 nm excitation, than in Fig. 6.4 under 532 nm excitation, due to an increasing background from the Cr^{3+} fluorescence. For the same reason the weak combination at 2356 cm^{-1} assigned to $2 \times 765 + 820\text{ cm}^{-1}$ is observed only under excitation with 532 nm (Fig. 6.4). The assignment of combinations and overtones in the third order resonance spectra is given in Tab. 6.4.

Combinations ($\omega_1 + \omega_2 + \omega_3$) and overtones ($3\omega_1$)

Symmetry	ω_1	ω_2	ω_3	Calculated $\omega_1 + \omega_2 + \omega_3$	Measured $\omega_1 + \omega_2 + \omega_3$
A_g	765	765	253	1783	1787
A_g	765	765	288	1818	1829
A_g	765	765	361	1891	1886
A_g	765	765	499	2029	2031
A_g	765	765	691	2221	2232
A_g	765	765	820	2350	2356
A_g	765	499	691	1955	1964
A_g	765	765	765	2295	2297
B_{3g}	742	742	742	2226	2225

Table 6.4 Assignment of combinations ($\omega_1 + \omega_2 + \omega_3$) and overtones ($3\omega_1$) measured in third order resonance Raman spectra (Fig. 6.3.a, 6.3.b and 6.4). All frequencies are given in cm^{-1} .

In addition to the third order resonance spectrum, Fig. 6.4 presents the fourth order A_g resonance spectrum obtained under 532 nm excitation. The strongest (most intense line) is, as in all other high order Raman spectra, the overtone (third) of 765 cm^{-1} measured at 3060 cm^{-1} . The band peaking at 2970 cm^{-1} was assigned to the third overtone of the A'' 742 cm^{-1} local mode but it might also contain the combination between the second overtone of 765 cm^{-1} and the 691 cm^{-1} mode. The assignment of combinations and overtones observed in the fourth order A_g Raman spectrum is given in Tab. 6.5.

Combinations ($\omega_1 + \omega_2 + \omega_3 + \omega_4$) and overtones ($4\omega_1$)

ω_1	ω_2	ω_3	ω_4	Calculated $\omega_1 + \omega_2 + \omega_3 + \omega_4$	Measured $\omega_1 + \omega_2 + \omega_3 + \omega_4$
765	765	765	820	3115	3117
742	742	742	742	2968	2970
765	765	765	765	3060	3060

Table 6.5 Assignment of combinations ($\omega_1 + \omega_2 + \omega_3 + \omega_4$) and overtones ($4\omega_1$) measured in fourth order resonance Raman spectrum (Fig. 6.4). All frequencies are given in cm^{-1} .

6.5 Anharmonic constants for Cr^{4+} local modes

Using Eq. (6.3) and plotting $\frac{E(n) - E(0)}{n}$ as a function of n , where $E(n)$ is the frequency of the n -th overtone ($n=1$ gives the fundamental), $E(0) = 0$ is the reference energy, and $n = 1, 2, 3, \dots$ gives the order of the overtone, the values for the local mode frequency ω and the anharmonic constant X can be obtained from a linear fit. Using the fundamental (first order) for the 765 cm^{-1} mode (Tab. 6.1) and the three overtones measured at 1531 cm^{-1} (Tab. 6.2), 2297 cm^{-1} (Tab. 6.4), and 3060 cm^{-1} (Tab. 6.5) the values for ω and X were estimated to be $\omega_{765} \approx 765.23 \text{ cm}^{-1}$ and $X_{765} \approx -0.02 \text{ cm}^{-1}$. Using the fundamental (first order) for the 742 cm^{-1} mode (Tab. 6.1) and the three overtones measured at 1488 cm^{-1} (Tab. 6.2), 2225 cm^{-1} (Tab. 6.4) and 2970 cm^{-1} (Tab. 6.5), the values for ω and X were estimated to be $\omega_{742} \approx 742.97 \text{ cm}^{-1}$ and $X_{742} \approx 0.08 \text{ cm}^{-1}$.

The small values for the anharmonic constants for both the 765 and 742 cm^{-1} Cr^{4+} local modes rule out anharmonic processes as the cause for the long observed overtone progression. As already discussed in section 6.1, this fact leads to the conclusion that electron-phonon interactions are strong for these two particular local modes and that it is most likely that these modes are the ones facilitating energy transfer from the electronic states of the photoexcited impurity ion (Cr^{4+}) into the vibrational system during nonradiative processes. Indeed, in Chapter 7 it will be shown that the measured dynamics of the 765 cm^{-1} local mode confirms that the electronic energy is transferred into this local mode which displays a time dependent local mode population. The energy transfer between the electronic state and the 765 cm^{-1} mode takes ~ 3 ps (time needed for the electronic system to make the ${}^3\text{B}_2({}^3\text{T}_1) - {}^1\text{E}$ transition). No direct information is available for the dynamics of the 742 cm^{-1} local mode due to its weakness in the anti-Stokes spectrum (used for time resolved measurements). Nevertheless, using group theory arguments it can be shown that this mode has the appropriate symmetry for coupling the ${}^3\text{B}_2 - {}^1\text{E}$ states. The coupling between this local mode and the electronic states appears to be sizable due to the strong resonance enhancement and the long observed overtone progression which indicate once more that the 742 cm^{-1} plays an active role during nonradiative deexcitation of Cr^{4+} ions.

6.6 Possible explanations for the higher than expected (15) number of local modes

As shown in Section 6.3 and summarized in Tab. 6.1, low temperature resonance Raman measurements reveal a surprisingly high number of Cr^{4+} local modes : 15 instead of the maximum expected 9 internal vibrations (see Section 5.1). The possible explanations considered to account for the higher than expected number of local modes are :

- a) Some of the 15 local modes are sample dependent (due to accidental contamination of the sample with different agents).
- b) Not all 15 local modes reported in Tab. 5.1 are first order local modes.
- c) Some of the measured local modes are due to clustering effects.
- d) Some of the measured local modes are due to Cr^{3+} ions.
- e) Some of the 15 local modes appear due to the presence of different Cr^{4+} isotopes in the crystal.
- f) Some local modes can be associated to rotations and/or translations of the CrO_4 molecule in the rigid cage of its neighbors.
- g) The additional local modes are due to second neighbor interactions.

Each of the above possible explanations for the anomalous number of measured local modes is considered and discussed as follows.

- a) Some of the 15 local modes are sample dependent (due to accidental contamination of the sample with different agents).

This hypothesis was excluded by repeating the resonance Raman measurements on a different $\text{Cr:Mg}_2\text{SiO}_4$ sample, with the doping level $\sim 4 \times 10^{18}$ ions/ cm^3 (see Section 6.2). Identical resonance spectra to those presented in Figs. 6.1 were obtained for the second sample. This proved that the 15 measured first order local modes are not due to some accidental contamination, and are not sample dependent.

- b) Not all 15 local modes reported in Tab. 5.1 are first order local modes.

By analyzing the frequencies of the local modes shown in Figs. 6.1 and summarized in Tab. 6.1, one can notice that the only possible combination or overtone assignment among the first order modes is 691 cm^{-1} , which could be attributed to the overtone of the 346 cm^{-1} ($2 \times 346 = 692 \text{ cm}^{-1}$). One argument against 691 cm^{-1} belonging to the second order spectrum is that it was observed in room temperature measurements [9]. The second argument is based on the relative

intensities of the 691 and 346 cm^{-1} local modes. Fig. 6.1.a shows that the intensity of the 691 cm^{-1} “overtone” is higher than that of the 346 cm^{-1} “fundamental”. But as a general rule, the strongest (most intense) spectrum is the first order. Thus, it would be surprising for a second order mode to be more intense than the fundamental. On the other hand, for the crystal under investigation, comparing the relative intensities of different order spectra (ex : Fig. 6.1.a, Fig. 6.2.a and Fig. 6.3.a), it was noticed that the intensity I decreases ~ 10 times when the order of the spectrum is increased by 1, i.e. $I_n/I_{n+1} \sim 10$. At the same time, modes within the same order have comparable intensities. All these arguments show that all the 15 measured local modes given in Tab. 6.1 belong to the first order spectrum.

c) Some of the measured local modes are due to clustering effects.

This hypothesis can be eliminated based on the low doping level of the sample ($\sim 3 \times 10^{18}$ ions/ cm^3) such that only one in ~ 1100 unit cells contains an impurity [7]. Based on statistical arguments the presence of clustering is negligible, as the crystal appears to be optically homogeneous (no changes in coloration intensity, no opacity...). The spectra have been repeatedly taken over a period of more than three months, such that different regions were probed inside the sample. No differences were observed between the spectra. Under these circumstances, clustering effects are discarded as being improbable.

d) Some of the measured local modes are due to Cr^{3+} ions.

This hypothesis is very likely, taking into account the fact that the sample contains both Cr^{3+} and Cr^{4+} ions. In order to differentiate the eventual contributions of the two types of ions in a resonance Raman spectrum, information from site selective excitation spectra is used [6]. The site selective excitation spectra for Cr^{4+} shows a decrease of ≈ 10

times in the absorption coefficient when the wavelength is varied from 572 nm to 582 nm, while the absorption coefficient for Cr^{3+} remains almost constant in the same spectral domain [6]. Thus, any local modes belonging to Cr^{3+} should have approximately the same intensity under the two excitation wavelengths (572 and 582 nm) while local modes associated to Cr^{4+} should significantly decrease their intensity (or disappear).

As shown in Figs. 6.1.a - 6.1.c, where first order resonance Raman spectra obtained under 572 nm excitation (thick line) and off-resonance Raman spectra obtained under 582 nm excitation (thin line) are presented, all 15 first order local modes (boxed) drastically decrease their intensity or vanish under 582 nm excitation. Only the strongest resonance modes (253 cm^{-1} , 765 cm^{-1} in A_g symmetry, 742 cm^{-1} in B_{3g} symmetry and 691 cm^{-1} and 765 cm^{-1} in B_{2g} symmetry) are still observable under off-resonance 582 cm^{-1} excitation, while all other local modes disappeared under off-resonance conditions. This dependence of the intensity of the local modes on the excitation wavelength indicates that all 15 first order local modes are associated to Cr^{4+} ions only. All other modes (non-boxed), which are lattice modes, exhibit practically constant intensity under the two excitation wavelengths which shows, as expected, that no resonance effects are present for the lattice modes. Therefore, the potential mechanism involving resonant enhancement of Cr^{3+} modes is eliminated.

- e) Some of the 15 local modes appear due to the presence of different Cr^{4+} isotopes in the crystal.

As discussed in section 3.3, Cr has four natural isotopes with the following relative abundance [11] : Cr_{24}^{50} - 4.35%, Cr_{24}^{52} - 83.79%, Cr_{24}^{53}

- 9.5%, Cr_{24}^{54} - 2.36%. Using Eqs. (5.16), (5.48), it can be shown that in the tetrahedral approximation neither the A_1 , nor the E modes change their energy for an isotopic substitution for the central ion. (It should be reminded that an isotopic substitution changes only the mass of the ion, not the values of the force constants). Using Eqs. (5.90) and (5.106), which give the expressions for the frequencies of the nontotally symmetric modes, with $k_1 = 3.27 \text{ mdyn/\AA}$ (Eq. 5.114) and $k_2 = 0.57 \text{ mdyn/\AA}$ (Eq. 5.113), $M = 53 \text{ m.u.}$ (the mass of the second most abundant Cr isotope), the following values are obtained for the frequencies of the two T_2 modes : $\nu_3(T_2) = 735 \text{ cm}^{-1}$ (to be compared to 737 cm^{-1} obtained with $M = 52 \text{ m.u.}$), and $\nu_4(T_2) = 290 \text{ cm}^{-1}$ (to be compared to 293 cm^{-1} obtained with $M = 52 \text{ m.u.}$). These calculations show that isotopic substitutions introduce small shifts (within the experimental resolution) and can not account for the larger than predicted observed number of local modes.

- f) Some local modes can be associated to rotations or translations of the CrO_4 molecule in the rigid cage of its neighbors.

Although this case is unlikely, in the situation of Mn:KClO_4 [12], additional to the 9 tetrahedral internal modes of vibration were observed and assigned as localized translations and rotations of the molecule containing the impurity Mn ion, in the rigid cage formed by the surrounding neighbors.

In Mn:KClO_4 , Mn substitutes for Cl which occupies a position with C_s site symmetry, forming a tetrahedral MnO_4 molecule. Taking into account the D_{2h} space group symmetry of the host, this makes the situation identical to that of $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$. Consequently, a MnO_4^- molecule has 9 internal vibrations, given in terms of tetrahedral

symmetry by Eq. (3.25), and measured at [12] : $\nu_1(A_1) = 850.8 \text{ cm}^{-1}$, $\nu_2(E) = 354.2$ and 360.3 cm^{-1} , $\nu_3(T_2) = 915, 920$ and 940 cm^{-1} , and $\nu_4(T_2) = 393.4, 396$ and 406.4 cm^{-1} . Using the same results for an XY_4 tetrahedral molecule, derived in Chapter 5.6 and the mean measured values of the above modes, the following result are obtained. From Eq. (5.48) and the mean measured value of the symmetric bending E mode at 357.3 cm^{-1} ($= (354.2 + 360.3)/2 \text{ cm}^{-1}$), and $m = 16 \text{ m.u.}$, the mass of O^{2-} ions, the value of the tetrahedral O-O force constant k_2 is $k_2 = 0.303 \text{ mdyn/\AA}$. Using Eq. (5.16) and the measured value of the breathing mode at 850.8 cm^{-1} , together with k_2 and $M = 55 \text{ m.u.}$ as the Mn mass, the Mn-O force constant is $k_1 = 5.655 \text{ mdyn/\AA}$. Eqs. (5.90) and (5.106) for the nontotally symmetric modes T_2 , together with the previously determined values for k_1 and k_2 allow the calculation of the remaining two frequencies as : $\nu_3(T_2) = 926.4 \text{ cm}^{-1}$ (to be compared with the mean measured value of 925 cm^{-1}), and $\nu_4(T_2) = 336 \text{ cm}^{-1}$ (to be compared with the mean measured value of 398.6 cm^{-1}). These comparisons show a fair agreement between the calculated and measured values and verify the correctness of the mode assignment.

In addition to the previously measured 9 internal vibrations, 4 additional local modes, all at lower frequencies than the internal vibrations, have been reported at 160, 143.5, 127.9 and 60 cm^{-1} . They are attributed to translational and rotational motions of the molecule containing the impurity, in the cage formed by its surrounding ions [12]. However, this explanation is not valid for forsterite for the following reasons. In Mg_2SiO_4 the force constant between the Mg ions which surround the SiO_4 ($Cr^{4+}O_4$) tetrahedra (and would form the cage) is negligible [10] or of lesser value [13] than the force constant between the tetrahedron itself and the surrounding Mg ions [13], ruling out the

existence of a rigid cage formed of Mg ions around the Cr^{4+}O_4 tetrahedron. In addition, in the case of a heavier impurity substituting an ion in a lattice, as is the case for both $\text{Cr} \rightarrow \text{Si}$ and $\text{Mn} \rightarrow \text{Cl}$ substitutions, the 3 translational modes associated with the impurity shift towards lower frequencies, if compared to similar host translational modes, and are well separated from the impurity's internal vibrations. This is exactly the case presented by [12], where, for example, the translational local mode at 60 cm^{-1} has lower frequency than any phonon mode. On the other hand, in Mg_2SiO_4 the highest and the lowest SiO_4 translational modes were assigned at 305 and 192 cm^{-1} , respectively (see [10] and Tab. 3.9). Therefore the three CrO_4 translational modes should be positioned at energies lower than, at least, 305 cm^{-1} . The lowest possible CrO_4 local mode that can be assigned to translations is measured at 346 cm^{-1} (the 253 and 288 cm^{-1} local modes belong to the split $\nu_4(\text{T}_2)$ internal vibration [9]) indicating that none of the observed 15 local modes can be consistently assigned to localized translations.

g) The additional local modes are due to second neighbor interactions.

The only explanation left to account for the 15 measured local modes is to consider second neighbor interactions for Cr^{4+} ions, i.e. an “extended” molecule which would include Mg^{2+} . This case will be discussed in detail in the next section.

6.7 Second neighbor interactions for Cr^{4+} in $\text{Cr:Mg}_2\text{SiO}_4$. Delocalization of T_d breathing modes

To explain the 15 observed Cr^{4+} resonance enhanced local modes, the Cr^{4+} associated molecule was considered to contain more than 5 (Cr^{4+}O_4) atoms, by including the next to the O ions neighbors (Mg ions). This is in part motivated

by the force constant estimates obtained in Section 5.6, where it was shown that when Cr^{4+} substitutes for Si^{4+} the $\text{Cr}^{4+}\text{-O}$ force constant decreases by 13% compared to the Si-O force constant. This makes the Mg-O interaction relatively stronger for the CrO_4 than for the SiO_4 tetrahedron introducing the necessity of considering second neighbor interactions for Cr^{4+} .

Second neighbor interactions were previously proposed to explain the density of states for combination modes obtained from the infrared absorption spectrum for NCO :KBr [8]. However, it was pointed out that additional to molecular internal vibrations have never been observed in cases in which the impurity is heavier than the ion it replaces [14]. In our case Cr^{4+} is two times heavier than Si^{4+} which is substituted. Thus, to the best of our knowledge, this is the first time when second neighbor interactions are detected using resonance Raman spectroscopy, and also the first time when interactions extending beyond - the first neighbor sphere are present in a molecule where the mass of the impurity ion is larger than the mass of the ion it substitutes.

In the second neighbor approximation a model tetrahedral undistorted structure is considered, of the form $\text{Cr}^{4+}\text{O}_4\text{Y}_4$, where Y represents the neighboring Mg^{2+} ions. (As will be shown shortly, the model is further refined by considering the structure of the Y -complex as given by Refs. [13, 15]. Such a molecule is schematically depicted in Fig. 6.5.

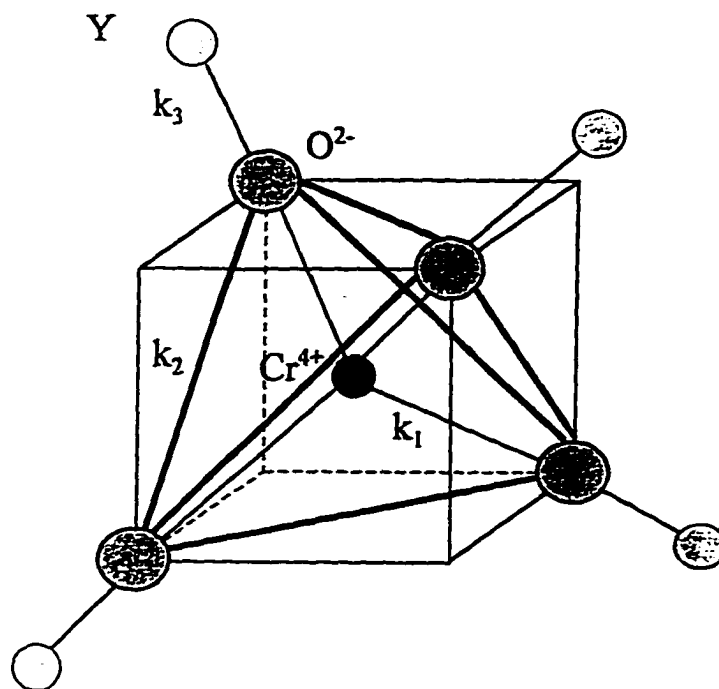


Figure 6.5 Model tetrahedral configuration for the CrO_4Y_4 (where Y stands for the neighboring Mg^{2+} ions), used for modeling second neighbor interaction effects. k_1 is the Cr-O force constant, k_2 is the O-O force constant and k_3 is the Mg-O force constant.

A molecule like the one depicted in Fig. 6.5 contains 9 ions and has a total of $9 \times 3 = 27$ modes of vibration, out of which $27 - 6 = 21$ are internal modes of vibration, most likely to be resonance enhanced. Applying the results given by Eqs. (3.5) - (3.18) and the method described in Section 3.2.2.5, the symmetry of the 27 modes of vibration can be calculated in tetrahedral approximation. The characters describing the 27 modes of vibration of the CrO_4Y_4 tetrahedral molecule are given by Tab. 6.6, and were obtained as follows. The character of the identity operation E is $3N$ (Eq. 3.5), where N is the total number of ions contained in the molecule, i.e. $\chi(E) = 3 \times 9 = 27$. Eq. (3.8) shows that the

character of C_3 is $\chi(C_3) = 0$. Eq. (3.9) shows that the character of C_2 is $-p$, where p is the number of ions on a c_2 axis of rotation. As the c_2 axes pass through the center of the tetrahedron (Fig. 3.2), there is only one ion on such an axis, the impurity ion, i.e. $p = 1$ and $\chi(C_2) = -1$. The exact same argument applies for $\chi(S_4)$ (see also Fig. 3.3). Finally, $\chi(\Sigma_d)$ is given by Eq. (3.14) as being equal to p . But this time the number of ions on a diagonal plane is $p = 5$ (the central ion, two O^{2-} and two Y ions). These results are summarized in Tab. 6.6.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\Sigma_d$
Γ_{tot}	27	0	-1	-1	5

Table 6.6 Characters describing the 27 modes of vibration of the tetrahedral CrO_4Y_4 molecule.

The representation describing the 27 modes of vibration of a CrO_4Mg_4 molecule is decomposed in the irreducible representations of T_d using Eqs. (3.16) - (3.17) and leads to :

$$\Gamma_{tot} = 2A_1 + 2E + 2T_1 + 5T_2 \quad (6.18)$$

The 3 rotations (T_1) and 3 translations (T_2) are eliminated using the table of characters for a tetrahedral group (Appendix A.3). The remaining representations describe the internal vibrations of the CrO_4Mg_4 molecule as [16] :

$$\Gamma_{int}^{Td} = 2A_1 + 2E + T_1 + 4T_2 \quad (6.19)$$

where the triple degenerate T_1 representation is the only Raman inactive mode. Taking into account the C_s site symmetry the degeneracy is completely lifted and the irreducible representation for the internal modes of vibration for a $Cr^{4+}O_4Y_4$ molecule modes becomes [16] :

$$\Gamma_{\text{int}}^{\text{Cs}} = 13A' + 8A'' \quad (6.20)$$

Such a structure can account for the fifteen experimentally observed local modes (10A' and 5A''). By comparing $\Gamma_{\text{int}}^{\text{Cs}}$ with the experimentally observed number of modes it can be noted that 6 modes are missing. A possible explanation for the absence of the 6 modes could be weak electron-phonon coupling leading to weak scattering cross sections for these modes.

Seven Cr^{4+} resonance enhanced local modes were previously assigned in terms of symmetry to tetrahedral internal vibrations in the first neighbor approximation [9], with the 765 cm^{-1} mode as the only totally symmetric stretching T_d mode, A_1 (Eq. 3.25). In the second neighbor approximation another totally symmetric breathing mode, A_1 , is expected, according to Eq. (6.19). The theory of resonance Raman effect predicts that the strongest resonance enhanced modes are the totally symmetric ones. Accordingly, the strongest, yet unassigned totally symmetric mode in Fig. 6.1.a, at 361 cm^{-1} (A_g symmetry) will be identified as the second A_1 mode, in second neighbor approximation. The frequencies of the two A_1 modes given by Eq. (6.19) (ω_1 and ω_2) are calculated using the molecular configuration given by [13, 15] as follows.

As in the case of an XY_4 molecule, the A_1 modes represent the breathing modes of the CrO_4Y_4 molecule. From symmetry considerations and from the analogy with an XY_4 molecule it can be shown that the central ion does not move in a breathing mode, while the O and Y ions oscillate along the tetrahedron's main diagonals. One of the two A_1 modes in Eq. (6.19) corresponds to "in phase" motion of O^{2-} and Mg^{2+} ions (analog to acoustic modes in a one-dimensional two atoms per unit cell lattice), while the second A_1 mode corresponds to 180° "out of phase" motion of O^{2-} and Mg^{2+} ions (analog to optic modes in a one-dimensional two atoms per unit cell lattice). The molecular structure presented in Fig. 6.5 can be further refined by considering the more accurate ionic arrangement, as given by

$$CD = \frac{2}{3} CM = \frac{2}{3} \cdot \frac{\sqrt{3}}{2} CA = 1.805 \text{ \AA} \quad (6.24)$$

From the COD triangle :

$$\sin(\hat{C\hat{O}D}) = \frac{CD}{CO} = \frac{1.805}{3.13} = 0.855, \text{ and } \hat{C\hat{O}D} \sim 60^\circ \quad (6.25)$$

Eq. (6.25) shows that the angle between a k_1 and k_3 bond is 60° (see Fig. 6.6). The following notations are used : m is the mass of O^{2-} ions, m_2 is the effective mass of Mg^{2+} ions, k_1 is the Cr-O force constant, k_2 is the O-O force constant, k_3 is the Mg-O force constant, x_1 is the displacement of an O^{2-} ion along the tetrahedral diagonal and x_2 is the displacement of an Mg^{2+} ion along the Mg-O bond. A special note should be made regarding the value of the effective mass m_2 . As shown in Fig. 6.6 each O ion is connected to 3 Mg ions, but taking the fundamental formula of the unit cell into account (Mg_2SiO_4) each for each O in the unit cell there is only $\frac{1}{2}$ a Mg ion (i.e. for each 16 m.u. of O there are $12 = 24/2$ m.u. of Mg, where the mass of a Mg ion is 24 m.u.). This proportionality has to be reflected by the effective mass, such that $3m_2 = 12$ m.u., (or $m_2 = 4$ m.u.). Consequently, the effective mass m_2 will be taken as $m_2 = 4$ m.u.

As was shown in Section 5.6, in order to calculate the frequencies of the two breathing modes, the Lagrangeian of the system has to be constructed. The kinetic energy of the system is easily obtained as the sum of the kinetic energies of the 4 O^{2-} and 12 Mg^{2+} ions of effective mass m_2 :

$$T = 4 \cdot \frac{m\dot{x}_1^2}{2} + 12 \cdot \frac{m_2\dot{x}_2^2}{2} = 2m\dot{x}_1^2 + 6m_2\dot{x}_2^2 \quad (6.26)$$

As shown in Fig. 6.6, the deformations of the Cr-O and O-O bonds produced by the displacement x_1 are identical to the deformations produced by the tetrahedral breathing mode in first neighbor approximation (see Fig. 5.5). As a result, the harmonic potential energy of the Cr-O bond is given by Eq. (5.10), and is (using the x_1 deformation) :

$$V_1 = 4 \cdot \frac{kx_1^2}{2} = 2k_1x_1^2 \quad (6.27)$$

In a similar way, the harmonic potential energy for the six O-O bonds is given by Eq. (5.12), and is (using the x_1 deformation) :

$$V_2 = 8k_2x_1^2 \quad (6.28)$$

as the projection of x_1 along each Mg-O bond is $x_1 \cdot \cos(60^\circ)$ (see Fig. 6.6), the deformation of the 3 x 4 Mg-O bonds is, $x_2 - x_1/2$, such that the harmonic potential energy for the k_3 bonds is :

$$V_3 = 12 \cdot \frac{k_3(x_2 - \frac{x_1}{2})^2}{2} = 6k_3(x_2 - \frac{x_1}{2})^2 \quad (6.29)$$

Using Eqs. (6.26) - (6.29) the Lagrangeian of the system can be written as :

$$\mathcal{L} = T - V_1 - V_2 - V_3 = 2m\dot{x}_1^2 + 6m_2\dot{x}_2^2 - 2k_1x_1^2 - 8k_2x_1^2 - 6k_3(x_2 - \frac{x_1}{2})^2 \quad (6.30)$$

Eq. (6.30) and the Lagrange equation (5.14) give the equations of motion as :

$$\begin{cases} m\ddot{x}_1 + (k_1 + 4k_2 + \frac{3}{4}k_3)x_1 - \frac{3}{2}k_3x_2 = 0 \\ 3m_2\ddot{x}_2 - \frac{3}{2}k_3x_1 + 3k_3x_2 = 0 \end{cases} \quad (6.31)$$

The above system of coupled differential equations can be solved by writing it in matrix form, and solving the secular equation for the eigenfrequencies ω for a harmonic oscillator :

$$\hat{\mathbf{K}} - \hat{\mathbf{M}}\omega^2 = 0 \quad (6.32)$$

with

$$\hat{\mathbf{K}} = \begin{pmatrix} k_1 + 4k_2 + \frac{3}{4}k_3 & -\frac{3}{2}k_3 \\ -\frac{3}{2}k_3 & 3k_3 \end{pmatrix} \quad (6.33)$$

and

$$\hat{\mathbf{M}}\omega^2 = \begin{pmatrix} m\omega^2 & 0 \\ 0 & 3m_2\omega^2 \end{pmatrix} \quad (6.34)$$

The eigenfrequencies ω are given by the condition that the determinant of Eq. (6.32) is zero, i.e. :

$$\begin{vmatrix} k_1 + 4k_2 + \frac{3}{4}k_3 - m\omega^2 & -\frac{3}{2}k_3 \\ -\frac{3}{2}k_3 & 3k_3 - 3m_2\omega^2 \end{vmatrix} = 0 \quad (6.35)$$

The solutions of Eq. (6.35) are :

$$\omega_{1,2}^2 = \frac{mk_3 + m_2(k_1 + 4k_2 + 0.75k_3)}{2mm_2} \pm \frac{\sqrt{[mk_3 + m_2(k_1 + 4k_2 + 0.75k_3)]^2 - 4mm_2k_3(k_1 + 4k_2)}}{2mm_2} \quad (6.36)$$

where k_1 , k_2 and k_3 are the Cr^{4+} -O, intratetrahedral O-O, and Mg-O force constants, respectively, m the O mass, and m_2 the effective mass of Mg (second neighbor). Using $k_1 = 3.27$ mdyn/ Å (Eq. (5.114)), $k_2 = 0.57$ mdyn/ Å (Eq. (5.113)) [16], $k_3 = 0.25$ mdyn/ Å [13], $m = 16$ m.u. (mass units), $m_2 = 4$ m.u. ($3m_2 = 12$ m.u.) and Eq. (6.34), the frequencies of the two A_1 modes were calculated at $\omega_1 = 780$ cm^{-1} (in good agreement with the measured value at 765 cm^{-1}) and $\omega_2 = 320$ cm^{-1} (in reasonable agreement with the measured value at 361 cm^{-1}) The difference between the calculated and measured values are due to the fact that no C_s distortions have been taken into account, and that other interactions such as intertetrahedral O-O and Cr^{4+} -Mg have been neglected in deriving Eq. (6.34).

ω_1 and ω_2 have been plotted using Mathematica (Appendix A.6), Eq.(6.34) and the appropriate unit transformations given in Eq. (5.112) , as functions of

second neighbor parameters k_3 and $3m_2$. Their dependence on second neighbor parameters are shown in Figs. 6.7 (a) and 6.7 (b).

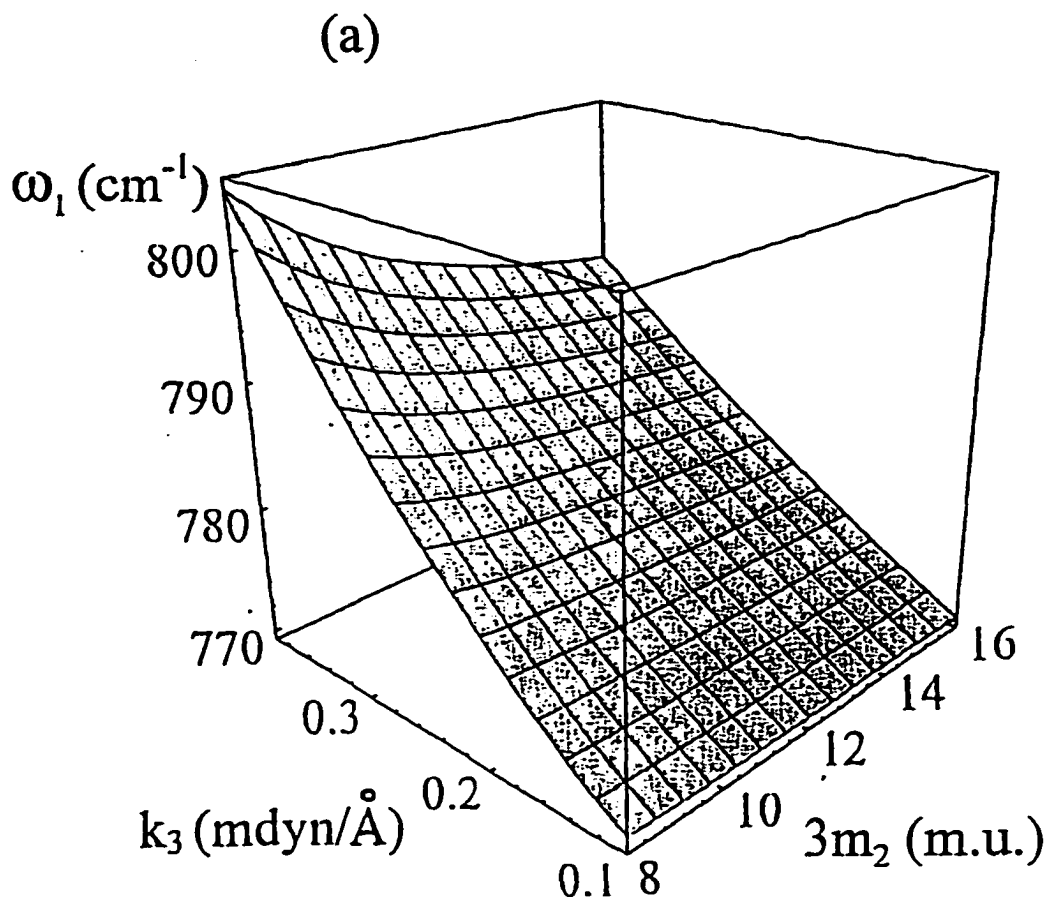


Figure 6.7 (a) Dependence of the frequency of the high energy, ω_1 tetrahedral stretching mode on second neighbor parameters : $3m_2$ - Mg effective mass and k_3 - Mg-O force constant.

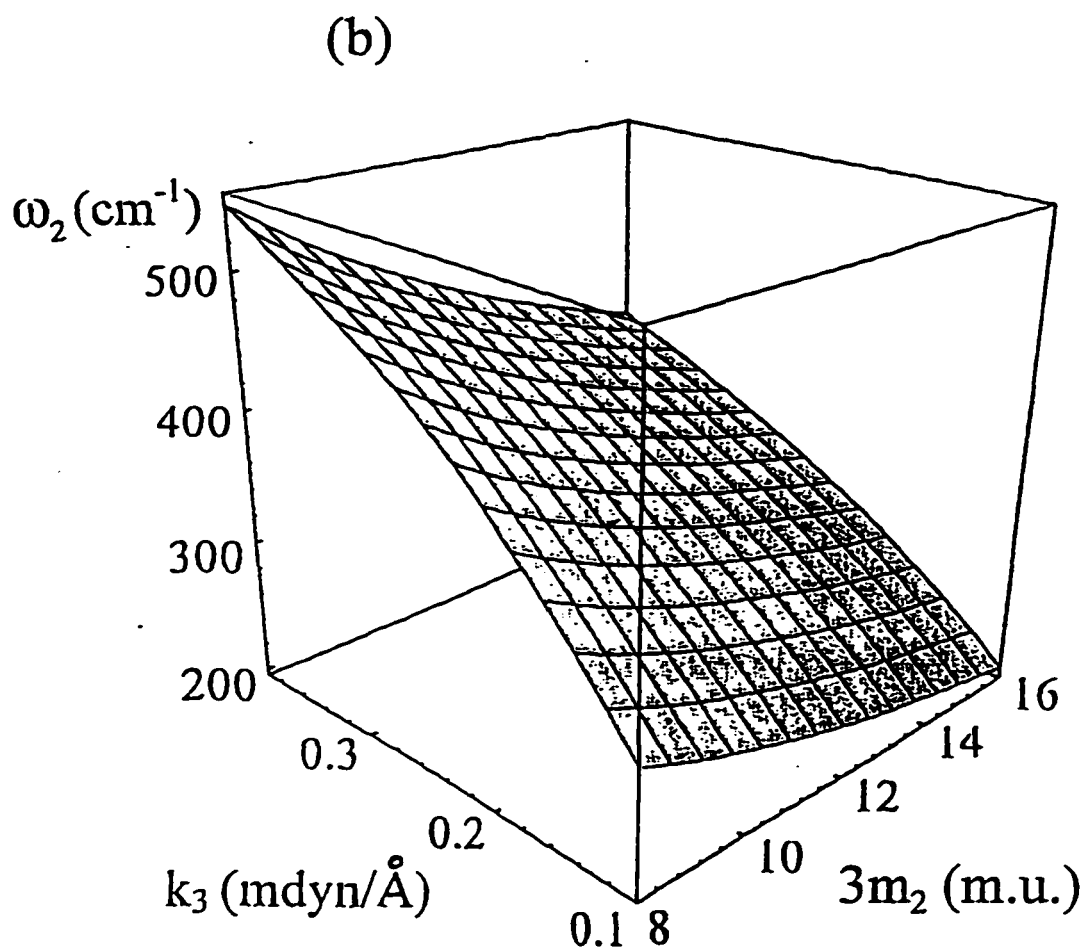


Figure 6.7 (b) Dependence of the frequency of the low energy, ω_2 tetrahedral stretching mode on second neighbor parameters : $3m_2$ - Mg effective mass and k_3 - Mg-O force constant.

The most interesting result displayed by these plots is that ω_1 varies moderately from (770 - 810) cm^{-1} , i.e. changing its frequency by $\sim 7\%$ when $k_3 \in [0.1, 0.4]$ $\text{mdyn}/\text{\AA}$ and $3m_2 \in [8, 16]$ m.u., while ω_2 varies significantly, from (200 - 550) cm^{-1} , changing its frequency by $\sim 78\%$ for the same ranges for k_3 and $3m_2$. These dependencies show that ω_1 is rather insensitive to changes occurring outside the first neighbor tetrahedron (Cr^{4+}O_4) indicating that it is mostly localized at the tetrahedron site and may be labeled as “intrinsic” tetrahedral mode. On the other hand ω_2 strongly depends on changes occurring outside the first neighbor

tetrahedron, indicating a higher degree of delocalization for this mode and reflecting interactions which extend beyond the first nearest neighbors, into the lattice. If the high frequency mode is normally expected to participate in nonradiative processes due to its high energy (it is more efficient for the system to discharge a larger quanta of energy, in one step, than to release the same energy in several steps, through several lower frequency local modes), Fig. 6.7.b suggests that the lower frequency local mode at 346 cm^{-1} is also a promoter of nonradiative processes due to its delocalization, i.e. “deeper” spread into the lattice. It is interesting to note that the 370 cm^{-1} phonon (closest to ω_2) was shown to participate in nonradiative processes [17].

In conclusion an anomalous number of 15 local modes (instead of the expected 9) was measured for $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$. All 15 local modes are expected to participate to nonradiative processes, leading to relatively strong nonradiative decay, supported by the increased number of decay channels. Among the 15 local modes two of them (the 742 and 765 cm^{-1}) display long overtone progressions. The small anharmonic constants for both modes indicate that strong electron-phonon interactions occur for these modes, suggesting that they are responsible for the energy transfer from the electronic into the vibrational system. The larger than expected number of measured local modes was explained by considering second neighbor interactions. This assumption is supported in part by a decrease in the Cr-O force constant, if compared to the Si-O force constant, which leads to an increase in the relative strength of the Mg-O (second neighbor) force constant. Modeling the behavior of the two tetrahedral breathing modes A_1 measured at 765 and 361 cm^{-1} as a function of second neighbor parameters (effective mass and force constant), it was shown that the high frequency local mode behaves like an intrinsic tetrahedral mode, and is quite insensitive to changes occurring in the second neighbor sphere. On the other hand, the low frequency breathing mode at 361 cm^{-1} is more delocalized and extends further into the lattice.

6.8 References

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Chapter 7

Dynamics of Cr^{4+} local modes and their interaction with the electronic system and phonon modes during nonradiative processes probed by time resolved resonance Raman measurements

7.1 Nonradiative processes. Background

Following the photoexcitation induced by a photon of energy $h\nu_0$, an impurity laser ion embedded in a lattice host has two available, competing decay routes for returning to the ground state (see Fig. 7.1) : (a) radiative decay and (b) nonradiative decay.

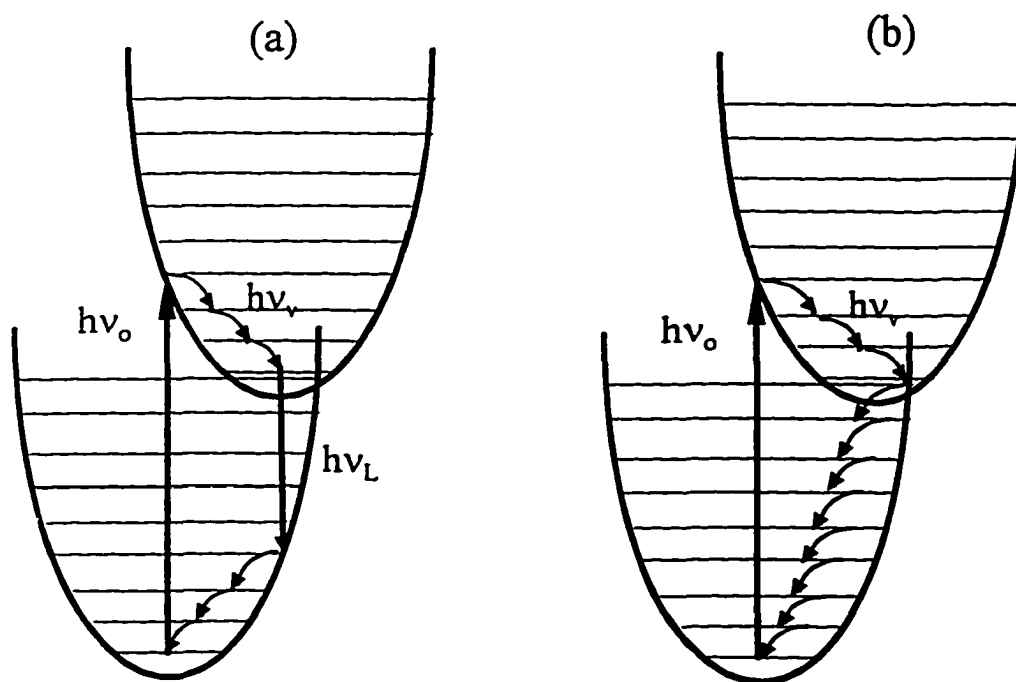


Figure 7.1 Relaxation pathways for a photoexcited impurity ion : (a) radiative decay, and (b) nonradiative decay.

In a radiative decay process (Fig. 7.1 (a)) the photoexcited ion returns to the ground state by emitting a red-shifted photon of energy $h\nu_L < h\nu_0$. The energy difference between the absorbed and emitted photons $h\nu_0 - h\nu_L$ is dissipated nonradiatively in the crystal via crystal vibrations of energy $h\nu_v$. Fig. 7.1 (a) schematically depicts a radiative decay process and, at the same time, the energetic configuration of a four-level laser, typical for IR-tunable solid state lasers, as is the case of $\text{Cr:Mg}_2\text{SiO}_4$. If population inversion is achieved, i.e. if the upper electronic state is a metastable level, the radiative decay route leads to lasing at energy $h\nu_L$.

Besides the radiative decay route, the system can also deexcite via a nonradiative route, depicted in Fig. 7.1 (b). In a nonradiative pathway, instead of deexciting in “one step” by emitting a photon of energy $h\nu_L$, the ion relaxes in a step-like process, such that its excessive energy is transferred into the lattice via vibrations (ultimately phonons) of energy $h\nu_v$. From the point of view of lasing, the energy released into the lattice nonradiatively is practically lost. As nonradiative processes represent an alternative decay route for the laser ion, the increase in the nonradiative deexcitation probability leads to a decrease in the lifetime of the metastable level. Being intimately connected to phonons which obey the Bose-Einstein distribution law, nonradiative processes become more intense as the temperature of the surrounding increases, affecting the laser properties of an impurity doped system operating at room temperature. In extreme cases nonradiative processes completely overcome the radiative channel and destroy lasing.

One of the first empirical laws inferred for the nonradiative decay was the “exponential energy gap” law [1] which states that the nonradiative decay rate decreases proportional with the energy difference between the two purely electronic levels between which the deexcitation occurs, i.e. :

$$\ln\left(\frac{1}{\tau_{\text{nonrad}}}\right) \sim -\Delta E \quad (7.1)$$

or,

$$\tau_{\text{nonrad}} \sim e^{\Delta E} \quad (7.2)$$

where τ_{nonrad} is the lifetime of the nonradiative decay, and ΔE is the energy difference (gap) between the two purely electronic states. Eq. (7.2) shows that the larger the gap, the larger the lifetime of the nonradiative decay, i.e. the smaller the nonradiative transition probability $1/\tau_{\text{nonrad}}$, thus, the weaker the nonradiative decay. The relevant consequence of this fact is that NIR (near infrared) lasers, as is the case of Cr:Mg₂SiO₄, are more likely to be affected by nonradiative processes if compared to other types of lasers (e.g. UV lasers) due to the relative low energy gap between the metastable and the ground state, $\Delta E \sim 10000 \text{ cm}^{-1}$, while for UV lasers $\Delta E \sim 30000 \text{ cm}^{-1}$.

As previously discussed, IR tunable solid state lasers operating at room temperature are expected to be severely affected by nonradiative processes. This fact is well illustrated by the comparison between the low temperature and room temperature fluorescence lifetimes for the first Cr⁴⁺-based tunable solid state laser, Cr:Mg₂SiO₄. In general, the “potential” as lasing center of an impurity ion is given by the fluorescence lifetime of the metastable level measured at low temperature (77 K), while the actual laser performance depends on the fluorescence lifetime measured at room temperature, which is shortened by nonradiative processes. For example, in Cr:Mg₂SiO₄ the lifetime of the Cr⁴⁺ ³A₂(³T₂) metastable level situated at 9150 cm⁻¹, is 25 μs at 77K, but decreases to 2.7 μs at 300K due to strong nonradiative processes [2, 3], such that the quantum efficiency of this laser crystal is only ~ 10%.

Although, as previously discussed, nonradiative relaxation processes largely affect the overall properties of solid state tunable laser materials and represent the

major competing channel to lasing, many aspects of nonradiative processes such as the role of local modes (impurity associated) in the nonradiative decay, the conditions and physical parameters which influence the nonradiative relaxation, the presence of select decay routes promoting nonradiative relaxation are not yet completely understood and need further investigation.

This chapter presents the first results regarding the direct involvement and dynamics of local modes during nonradiative relaxation taking place in a laser crystal, obtained using time resolved resonance Raman scattering in Cr:Mg₂SiO₄ [4]. In order to explain what the expected processes are, a short review of nonradiative relaxation follows.

Seitz [5] was the first one to make a breakthrough towards studying the problem of an impurity in a solid. He used separate coordinate spaces (independent harmonic oscillators) to depict each electronic state as a potential (parabolic) surface. The nonradiative decay is interpreted as a downward motion on such a potential surface (Fig. 7.2). The question concerning the excess energy released by the impurity ion was first addressed by Gouterman [6] who showed that the energy lost during the descent on the electronic manifold is balanced by the energy gained by the lattice via phonon modes. As shown in Fig. 7.2, following photoexcitation (Fig. 7.2 (b)), the impurity ion relaxes descending on the electronic parabola by decreasing its local mode population (vibrations associated to the impurity ion) $n_L(t)$. As suggested by Gouterman, the energy released by the impurity ion (via local modes) is transferred into the lattice and absorbed by phonons. Thus, a nonradiative process implies **changes in both local ($n_L(t)$) and phonon ($n_p(t)$) mode populations** (Fig. 7.2 (c)). As the system finally returns to equilibrium (Fig. 7.2 (d)), the local and phonon mode populations return to their equilibrium values. A measurement with temporal resolution performed during the brief time ($\sim$ ps) it takes the impurity ion to deexcite should be able to detect the non-equilibrium local and phonon mode populations ($n_L(t)$ and $n_p(t)$),

respectively), created during the non-equilibrium relaxation, and characterize the dynamics of the nonradiative relaxation.

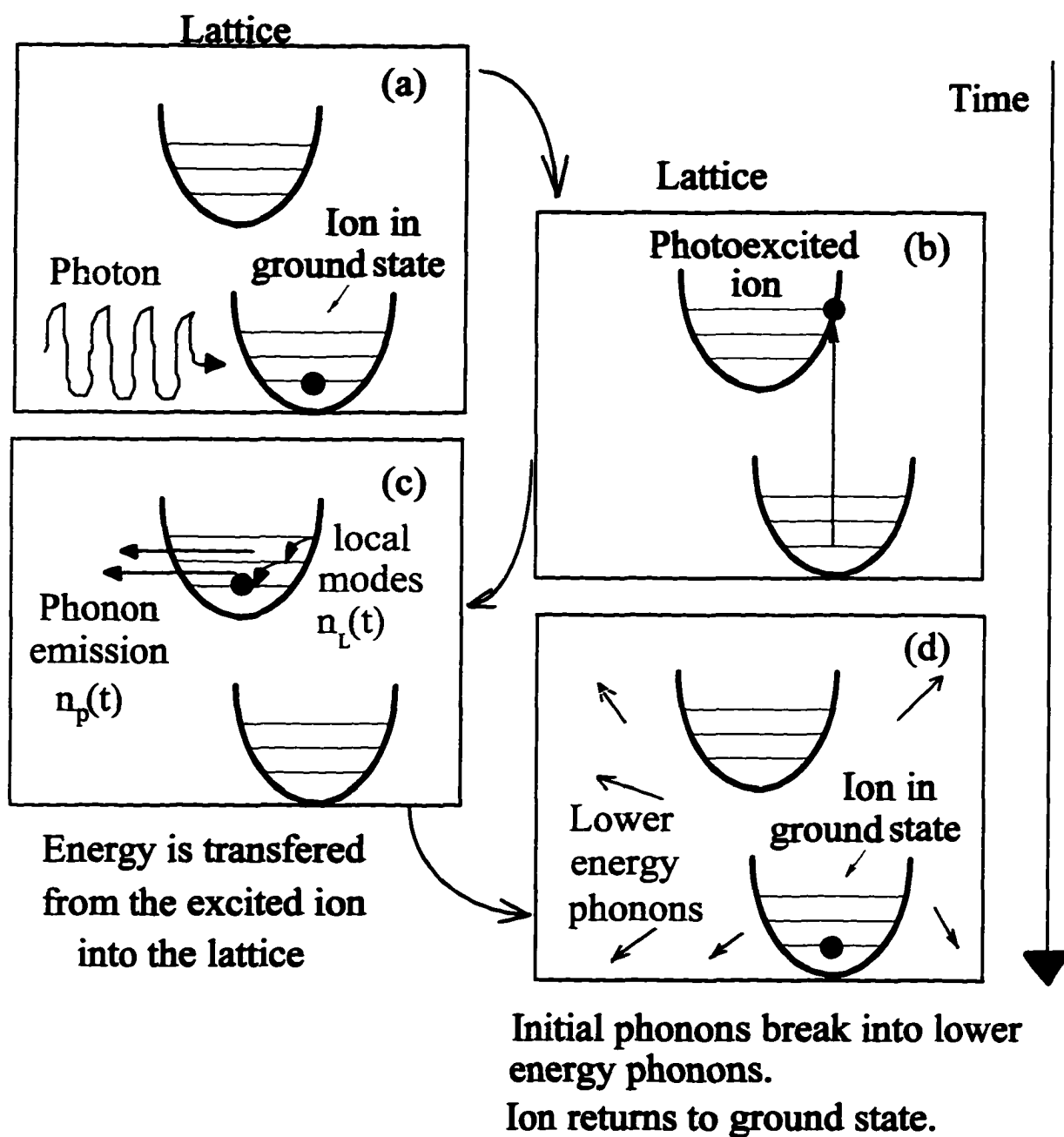


Figure 7.2 Time diagram depicting nonradiative processes in an ion-doped crystal.

Following photoexcitation, an impurity ion generally changes both the electronic state and the local mode occupation number (see Fig. 7.2 (b)). As a consequence, during the nonradiative deexcitation two types of processes occur : (a) during the time when the ion “slides down” the same electronic state only the local mode occupation number changes (decreases). Such a process is called **vibronic transition** as it implies only the change (decrease) in the quantum vibrational number and occurs on a fast time scale (~ 100 fs/step). The second type of process (b) occurs when the ion reaches the bottom of the electronic state and in order to continue its nonradiative deexcitation has to tunnel to a lower lying electronic state, i.e it has to change the electronic state. Such a process is called **electronic-vibronic transition** as it implies the change in both electronic state and in the vibrational quantum number (see Fig. 7.3).

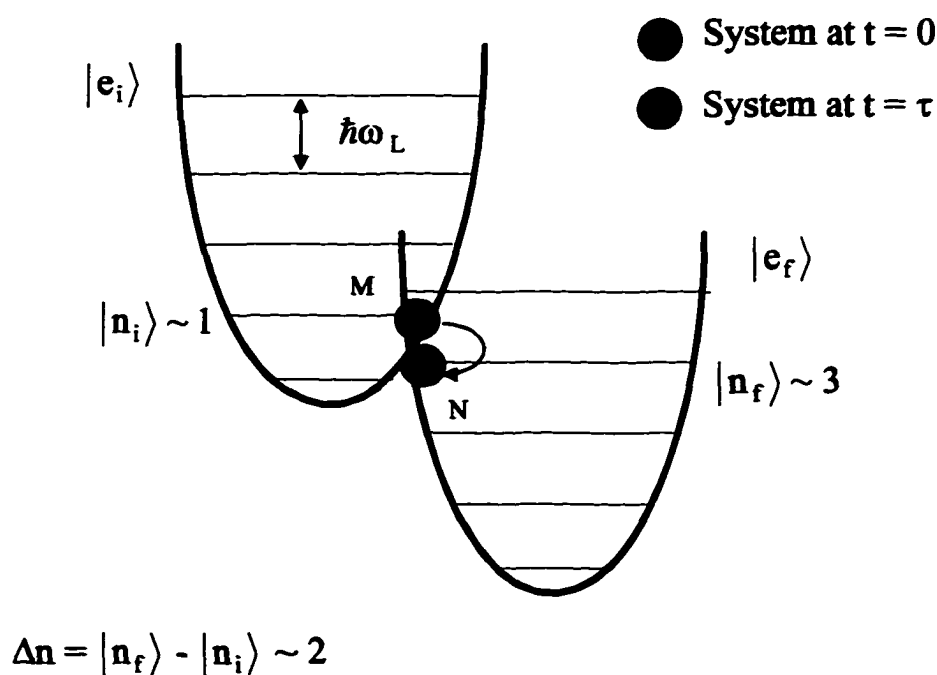


Figure 7.3 Schematic electronic-vibronic transition, with increase ($\Delta n > 0$) in the occupation number for mode ω_L .

An electronic-vibronic transition towards a lower lying electronic state is usually accompanied by an increase in the occupation number for the local modes, as shown by Fig. 7.3. Assuming that at $t = 0$ the system is near the bottom of the initial electronic state $|e_i\rangle$, with the occupation number of the depicted local mode $|n_i\rangle = 1$ (at point M), in order for the deexcitation to proceed nonradiatively, the ion has to make a transition towards the lower lying electronic state $|e_f\rangle$ (in N), such that the final occupation number is $|n_f\rangle > |n_i\rangle$ ($|n_f\rangle = 3$ in Fig. 7.3). An electronic-vibronic transition is a slower process occurring on the $\sim$ ps - μ s time scale. If τ is the time needed for the system to cross between the two electronic states, the local mode population is expected to increase during this time.

The transition between two different electronic states is facilitated by several factors, such as : (1) spin-orbit coupling, (2) corrections to Born-Oppenheimer approximation, and (3) electron-phonon interactions [1]. It is important to stress that electron-phonon interactions are usually significant in the case of d-electrons, as is the case of Cr ions, and appear to be the main factor facilitating electronic-vibronic transitions in transition-metal ions. The transition time between two different electronic states is also affected by the spin multiplicity of the initial and final electronic states [1]. If the spin multiplicity is conserved, the transition is expected to be faster than in the case when the spin changes during the electronic transition (e.g. transition from a triplet to a singlet state).

7.2 Time resolved techniques

Time resolved techniques are based on the pump - probe ultrafast approach and involve the same basic principle : an ultrashort light pulse (pump) excites the system on a specific state $|s\rangle$. After a time delay τ_p the probe (ultrashort light

pulse) monitors the momentary population in state $|s\rangle$. The change in one of the physical parameters of the system under investigation measured by the probe, such as absorption coefficient, scattering cross section, etc. as a function of τ_p gives information on the dynamics of state $|s\rangle$. Depending on the population type to be studied different excitation and probing processes are used. Two main phenomena are involved in pump - probe techniques : a) absorption, and b) scattering. The most important categories of ultrafast techniques used for probing the dynamics of a given state $|s\rangle$ are reviewed as follows.

7.2.1 Pump-probe absorption experiments

A strong pump pulse of energy $h\nu_0$ excites the system from the ground state to a well defined excited state $|e_f\rangle$, of energy $E_f = h\nu_0$. The absorption of a (weak) time delayed probe pulse is measured as a function of delay time τ_p . Depending on the energy of the probe pulse $h\nu_p$, several cases can be distinguished :

- a) if $h\nu_p = h\nu_0$ and no matching upper state is available to generate a second absorption, the probe will monitor the repopulation of the ground state (Fig. 7.4 (a));
- b) if $E' > E_f$ (where E' is an electronic state of the system) and $h\nu_p = E' - E_f$ (Fig. 6.4 (b)) the absorption initiated by the probe decreases with τ_p indicating the rate of depopulation of E_f ;
- c) if $E' < E_f$ and $h\nu_p = E'$ (Fig. 7.4 (c)), the probe monitors the population (decrease of absorption) of E' , and finally,
- d) if $E' < E_f$ and the system has another state E_1 (usually $E_1 > E_f$) such that $h\nu_p = E_1 - E'$ the probe monitors the population (i.e. rise in absorption) of state E' (Fig. 7.4 (d)).

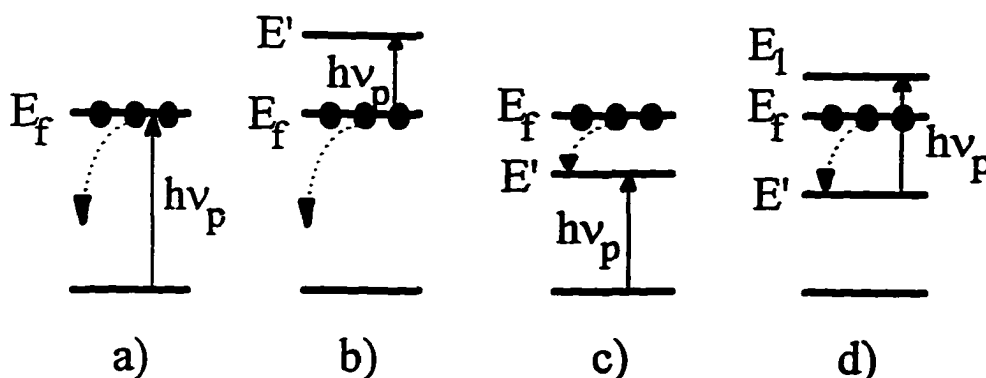


Figure 7.4 (a) - (d) Pump-probe electronic absorption schemes. The system is excited by the pump on the electronic level E_f . The decay of level E_f (.....) is monitored by the probe $h\nu_p$ (—→).

Pump-probe absorption is widely used to investigate and characterize ultrafast processes in impurity doped solids. For example, a b-type scheme was used by von der Linde [8] to measure the lifetime of the $^2T_2$ state in $\text{Cu}^{2+}:\text{LiTaO}_3$. Bradford [9] and Williams [10, 11] used a d-type scheme to study formation and stability of F-centers in KCl, NaCl and NaBr using $E_1 = E_f$. It should be noted that an alternative way of probing the dynamics of an electronic state is by measuring the fluorescence (i.e. population at time τ_p) from an electronic state by a gating technique.

7.2.2 Pump-probe scattering experiments

A second method of pumping and/or probing a system is by light scattering. Two main trends have developed in this field : a) coherent scattering (SRS and CARS) and b) incoherent scattering (Raman).

SRS (Stimulated Raman Scattering) was developed by Alfano and Shapiro [12, 13], and Laubereau [14] and von der Linde [15]. SRS is used to measure the dephasing relaxation rates of excited vibrational levels in the ground electronic state. A strong laser pulse (ω_0) gets scattered (Raman) leaving the system in the excited vibrational state ω_v . The scattered pulse has frequency $\omega_0 - \omega_v$ (Stokes) and the vibrational mode ω_v is coherent with the exciting pump pulse. A time delayed probe pulse ω_p , almost parallel to ω_0 is scattered by the molecules in state ω_v . The anti-Stokes signal at $\omega_p + \omega_v$ is monitored in the direction $\mathbf{k}_{AS} = \mathbf{k}_p + \mathbf{k}_v$ (near forward direction, phase matched) (see Fig. 7.5).

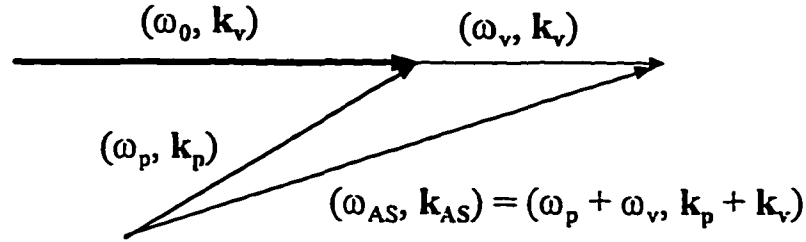


Figure 7.5 Schematic configuration for Stimulated Raman Scattering experiments.

The intensity of the anti-Stokes signal is a measure of the coherence τ_c (i.e. dephasing relaxation rate) of ω_v . If, on the other hand, the anti-Stokes signal is observed in an arbitrary direction (ex. perpendicular to $\mathbf{k}_p$), one measures the depopulation rate (τ_v) of ω_v . It should be noted that τ_c and τ_v can differ by more than one order of magnitude [16]. The advantage of this technique is that it can be applied using any laser frequency ω_0 .

CARS (Coherent Anti-Stokes Raman Scattering) is used to coherently generate and monitor the coherence dephasing time in solids [17] and liquids [18]. Two exciting laser beams of frequencies ω_1 and ω_2 and wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are chosen to coherently drive a phonon mode $\omega_v = \omega_1 - \omega_2$ of wave vector $\mathbf{k}_v = \mathbf{k}_1 - \mathbf{k}_2$ (in III-V semiconductors such a mode is, in general, unique). The coherent

anti-Stokes signal obtained from a time delayed probe pulse (ω_p, k_p) at $\omega_{AS} = \omega_v + \omega_p$ and $k_{AS} = k_v + k_p$ monitors the loss in coherence for ω_v as a function of delay time.

Incoherent Raman scattering is used to monitor the time evolution of incoherent optical phonons in solids [19, 20, 21]. A pump pulse ω_0 photoexcites the system (e.g. impurity ion) on an electronic state. During the nonradiative deexcitation, while sliding down on the electronic manifold, the excess energy is passed into the lattice generating a surplus of phonon population (see Fig. 7.2 (c)). The nonequilibrium phonon population is created throughout the time it takes the system to deexcite. A time delayed probe pulse ω_p probes the system at different times τ_p following photoexcitation, by scattering off the generated nonequilibrium phonons. The changes in the anti-Stokes signal of the probe reflect the evolution of the nonequilibrium phonon population. The pump and the probe pulses may have the same frequency, but have to have different intensities.

Although both Stokes and anti-Stokes signals carry information on the generated nonequilibrium phonon population, the anti-Stokes spectrum is more sensitive to changes in the phonon occupation number, as will be shown shortly, and is the signal of choice to be measured among the two for monitoring the dynamics of the phonon population. A Stokes process implies the creation of a vibration (phonon, local mode) of energy ω , such that the Stokes signal is observed at an energy $\omega_{Stokes} = \omega_0 - \omega$, where ω_0 is the frequency of the excitation laser beam. Using the creation operator a^+ acting on a population $|n\rangle$, a Stokes process can be written as (Eq. (4.7)) :

$$a^+|n\rangle = \sqrt{n+1}|n+1\rangle \quad (7.3)$$

Eq. (7.3) shows that the system started in a state with $|n\rangle$ vibrations and ended up with $|n+1\rangle$ vibrations (Stokes process). The intensity of a Stokes line I_{Stokes} is proportional to the square of Eq. (7.3), i.e ;

$$I_{\text{Stokes}} = A \cdot (n + 1) \quad (7.4)$$

where A is a constant (which depends on energy) and, for the system in thermal equilibrium n is the Bose -Einstein factor for the considered mode of vibration, given by :

$$n \equiv n(\omega, T) = \frac{1}{\exp(\frac{h\omega}{kT}) - 1} \quad (7.5)$$

where h is Planck's constant, $h = 6.6 \times 10^{-34}$ J-s , k is Boltzmann's constant, $k = 1.38 \times 10^{-23}$ J-K⁻¹ and T is the temperature of the crystal (surrounding).

On the other hand, an anti-Stokes process implies the destruction of a vibration (phonon, local mode) of energy ω , such that the anti-Stokes signal is observed at an energy $\omega_{\text{anti-Stokes}} = \omega_0 + \omega$. Using the annihilation operator a acting on a population $|n\rangle$, an anti-Stokes process can be written as (Eq. (4.8)):

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad (7.6)$$

Eq. (7.6) shows that the system started in a state with $|n\rangle$ vibrations and ended up with $|n-1\rangle$ vibrations (anti-Stokes process). The intensity of an anti-Stokes line $I_{\text{anti-Stokes}}$ is proportional to the square of Eq. (7.6), i.e ;

$$I_{\text{anti-Stokes}} = B \cdot n \quad (7.7)$$

where B is a constant (which depends on energy).

Let us assume that we are monitoring the changes in the nonequilibrium population for a mode of vibration of energy $\omega = 765 \text{ cm}^{-1}$, whose occupation number changes due to the nonradiative decay by 10% τ_p ps after photoexcitation. The changes in both Stokes and anti-Stokes signal intensities can be estimated using Eqs (7.4), (7.5), (7.7). The equilibrium value for the Stokes signal (obtained, for example just before the arrival of the pump, i.e at $t = 0$) is given by Eqs. (7.4), (7.5) and is $I_{\text{Stokes}}(0) = A \cdot 1.026$. An increase of 10% in the population of this vibration leads to a nonequilibrium Stokes signal $I_{\text{Stokes}}(\tau_p) = A \cdot 1.0286$. The

relative percent change in the Stokes signal produced by the 10% increase in the vibrational population is :

$$\frac{I_{\text{Stokes}}(\tau_p) - I_{\text{Stokes}}(0)}{I_{\text{Stokes}}(0)} \cdot 100\% = \frac{1.0286 - 1.026}{1.026} = 0.25\% \quad (7.8)$$

Eq. (7.8) shows that the observation of the change in the Stokes signal due to the nonradiative relaxation would be practical impossible.

On the other hand, for the anti-Stokes signal, the equilibrium value is given by Eqs. (7.4), (7.7) and is $I_{\text{anti-Stokes}}(0) = B \cdot 0.026$. An increase of 10% in the population of this vibration leads to a nonequilibrium anti-Stokes signal $I_{\text{anti-Stokes}}(\tau_p) = B \cdot 0.0286$. The relative percent change in the anti-Stokes signal produced by the 10% increase in the vibrational population is :

$$\frac{I_{\text{anti-Stokes}}(\tau_p) - I_{\text{anti-Stokes}}(0)}{I_{\text{anti-Stokes}}(0)} \cdot 100\% = \frac{0.0286 - 0.026}{0.026} = 10\% \quad (7.9)$$

Eq. (7.9) shows that the change in the anti-Stokes signal is equal to the change in the nonequilibrium population. This makes the Raman anti-Stokes scattering the primary tool for measuring the dynamics of vibrational populations (changes in the spectral intensity due to nonequilibrium populations). Of course, the disadvantage of measuring an anti-Stokes spectrum is its weakness if compared to the intensity of a Stokes spectrum (their ratio is given by the Boltzmann factor, $\exp(-\frac{h\omega}{kT})$).

7.3 Time resolved resonance Raman technique. Experimental method.

Particularities for the Cr:Mg₂SiO₄ case

In order to study the role and dynamics of Cr⁴⁺ local modes in Cr:Mg₂SiO₄ during nonradiative processes, incoherent time resolved resonance Raman technique was used for monitoring the changes in the nonequilibrium local mode population created following photoexcitation of Cr⁴⁺ ions. As shown in

Figs. 7.2 and 7.3, following photoexcitation, Cr^{4+} ions start relaxing nonradiatively. During this process we expect changes in the local mode population which can be monitored using incoherent Raman scattering, as discussed in Section 7.2, by observing the anti-Stokes signal at different time delays between the pump and probe pulses. The eventual observed differences in the intensity of the anti-Stokes signal as a function of pump-probe delay time describe the nonequilibrium local mode population created during the nonradiative relaxation. The particularities of the material under investigation and of the laser system determine the types of processes, in terms of energy and temporal characteristics, to be monitored, and are discussed as follows.

Taking into account the capabilities of the laser system (see Chapter 2 and Section 7.4) the following temporal limits apply to the types of detectable processes : (a) as the repetition rate of the laser system is 82 MHz, the upper limit for the duration of the detectable processes is $1/82 \text{ MHz} \sim 12 \text{ ps}$. The upper limit rules out observation of processes involving an electronic state with a lifetime longer than 12 ps; (b) as the duration of the laser pulses is $\sim 500 \text{ fs}$, the lower temporal limit for the observed processes is $\sim 0.5 - 1 \text{ ps}$. This limit rules out the observation of fast vibrational deexcitations (see Section 7.1) but enables the observation of electronic-vibronic transitions occurring on the ps time scale.

A desirable electronic-vibronic transition of the type depicted in Fig. 7.3 which leads to observable changes in the local mode population would be best described by the situation where the spin multiplicity is not conserved during the electronic transition, which ensures a longer tunneling time between the two electronic states (see Section 7.1). Another useful feature of the electronic crossing, from the point of view of nonradiative deexcitation would be a reduced, or absence of luminescence which signals a weak, or even closed radiative decay channel, leaving only a strong nonradiative route open for the deexcitation. The two above features (change in spin and absence of luminescence) describe the case

of the ${}^3B_2({}^3T_1)$ - ${}^1E$ Cr^{4+} electronic crossing at ~ 600 nm which will be investigated by time resolved incoherent resonance Raman scattering.

If, in general, one of the advantages of incoherent Raman scattering is that it can be observed at any wavelength (see Section 7.2), certain restrictions apply to the case of resonance Raman processes which enable the observation of local modes only for particular excitation wavelengths (under resonance conditions - see Chapters 3 and 4). The excitation wavelength has to be such as to excite the Cr^{4+} ions near the zero-phonon line of the ${}^3B_2({}^3T_1)$ state. Although the maximum of site selective absorption for this level occurs at 575 nm, its zero-phonon line lies in the 590 - 620 nm region [22] suggesting that the ${}^3B_2({}^3T_1)$ level is Stokes shifted (in coordinate space) with respect to the ${}^3A_2({}^3T_2)$ ground state (see Figs. 4.5 and 7.1). As no radiative emission occurs from the ${}^3B_2({}^3T_1)$ electronic state, the exact position of its zero-phonon line can not be determined exactly. The above considerations give the effective range for the excitation pulses to be used in time resolved resonance Raman experiments between 590 - 620 nm.

On the other hand, up-converted hot luminescence experiments [19] which take advantage of a two-step excitation of Cr^{4+} ions to upper electronic states have shown that the 580 - 630 nm spectral region is characterized by a relatively stronger emission indicating the presence of an electronic bottleneck where nonradiative processes slow down, probably due to the ${}^3B_2({}^3T_1)$ - ${}^1E$ spin-forbidden inter-crossing. Thus, up-converted hot luminescence experiments suggest as effective range for the excitation pulses to be used in time resolved resonance Raman experiments for probing the transition in the ${}^3B_2({}^3T_1)$ - ${}^1E$ electronic bottleneck, wavelengths in the 580 - 630 nm range.

Finally, the condition which “fine-tunes” the desirable range of excitation wavelengths to be used for time resolved resonance Raman experiments is the resonance condition. As already mentioned, the intensity of local modes varies with the excitation wavelength, giving rise to “excitation profiles”. As anti-Stokes

spectra will be monitored for changes in the local mode population, it is desirable to choose a local mode with relatively high intensity which will allow observations of changes in its intensity. Thus, from the high scattering cross section's point of view, the totally symmetric A' Cr^{4+} local mode at 765 cm^{-1} was chosen to be observed in time resolved measurements. The second, but as important reason for choosing to observe this mode is its significant electron-phonon coupling (see Chapter 6) which makes it probably the best candidate for probing the energy transfer from the electronic states into the vibrational system during nonradiative processes. Yet another advantage of this local mode is that it does not overlap with any phonon modes, such that any changes in intensity can be attributed exclusively to this local mode. It should be mentioned that the only other local mode which offers the same advantage (except for a moderate scattering cross section), the 745 cm^{-1} A'' mode (see Chapter 6), is too weak to be observed in an anti-Stokes spectrum. All the other 5 local modes observed at room temperature in the Stokes spectrum overlap with phonon modes and are much weaker (sometimes apparently absent) from the anti-Stokes spectrum, thus can not be monitored during time resolved experiments.

Anti-Stokes excitation profiles for the 765 cm^{-1} A' Cr^{4+} local mode were and taken at room temperature by varying the excitation wavelength between 575 and 613 nm. Fig. 7.6 shows the A_g anti-Stokes spectra for $\text{Cr:Mg}_2\text{SiO}_4$ obtained under various excitations in the above mentioned range, in the $700 - 1000\text{ cm}^{-1}$ spectral region using an $a(cc)a$ scattering arrangement. As expected, the intensity of the three phonon modes at 826, 856 and 966 cm^{-1} is constant under different excitation wavelengths, but the intensity of the local mode at 765 cm^{-1} (boxed) changes due to different resonance conditions (see Chapter 4).

The excitation profile for the 765 cm^{-1} local mode represented as the normalized ratio between the intensity of the 765 cm^{-1} local mode and the 826 cm^{-1} (constant) phonon mode, obtained for different excitation wavelengths

varying between 575 and 607 nm is shown in Fig. 7.7. The excitation profile was obtained using the setup presented in Chapter 6 and Section 2.7, with the only difference that the anti-Stokes signal was measured, and the excitation wavelength was changed in the 575 - 607 nm spectral range. For excitation wavelengths higher than 607 nm the 765 cm^{-1} local mode practically disappears.

Anti-Stokes A_g excitation profiles

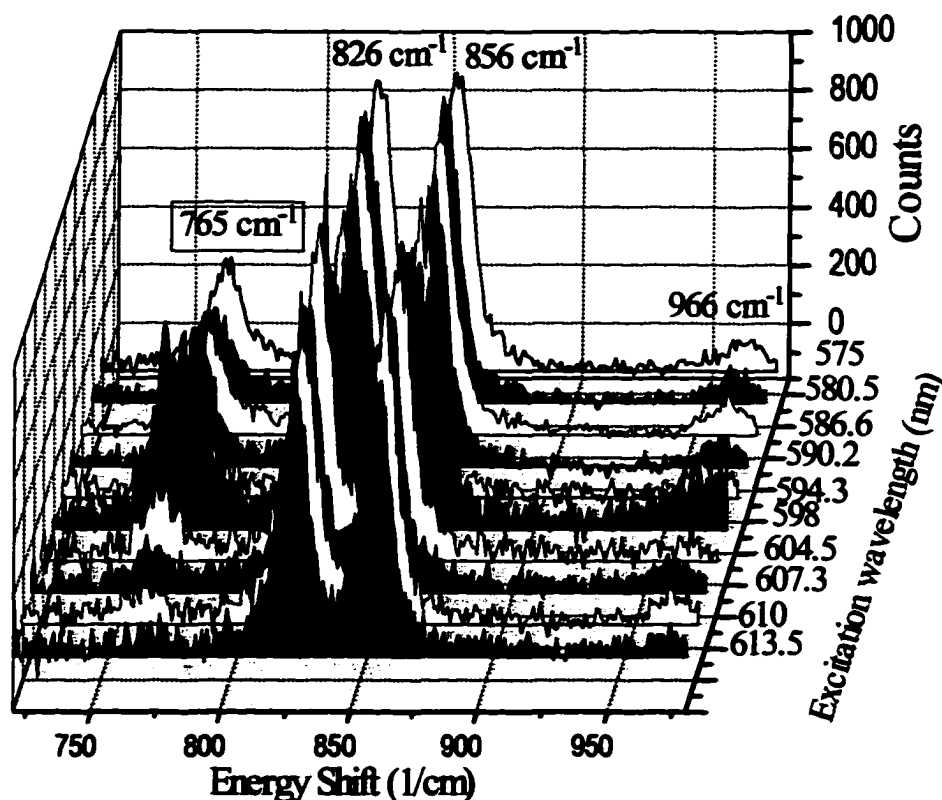


Figure 7.6 Anti-Stokes A_g spectra for $\text{Cr:Mg}_2\text{SiO}_4$ obtained under various excitations in the 575 - 613 nm range, at room temperature, in an $a(cc)a$ scattering configuration. The 765 cm^{-1} local mode is boxed. All other modes are phonons.

As the 765 cm^{-1} local mode is totally symmetric, it appears in scattering configurations corresponding to A_g modes (see Tab. 5.1). An $a(cc)a$ back-

scattering arrangement (identical to the one used for time resolved measurements - see Chapter 2 and Section 7.4) was used for obtaining the excitation profile shown in Fig. 7.7.

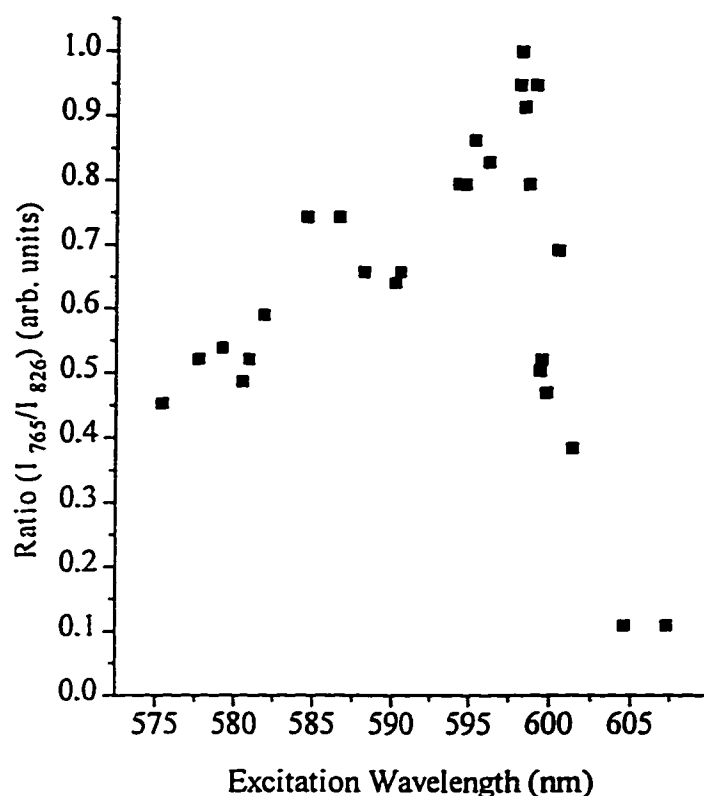


Figure 7.7 Anti-Stokes excitation profile for Cr:Mg₂SiO₄ obtained at room temperature for the 765 cm⁻¹ local mode. The intensity of the 826 cm⁻¹ A_g phonon mode was taken as reference.

Fig. 7.7 shows that using excitation wavelengths higher than 607 nm would make the observation of any changes in the intensity of the 765 cm⁻¹ local mode impossible due to the weakness of the local mode itself. On the other hand, the most desirable excitation wavelength to be used is 597 - 600 nm. Time resolved resonance Raman measurements performed for monitoring the dynamics of the 765 cm⁻¹ Cr⁴⁺ local mode during the electronic-vibronic transition between the

${}^3B_2({}^3T_1)$ - ${}^1E$ states used 598 nm excitation pulses, corresponding to the maximum anti-Stokes enhancement for the local mode under investigation.

Both pump and probe pulses used in time resolved resonance Raman experiments had the same wavelength (598 nm), and the same polarization, determined by the resonance condition for the 765 cm^{-1} local mode, i.e. they were polarized parallel to the c -crystal axis, but had intensity ratio 2/1, respectively. As previously mentioned, time resolved measurements were performed in an $a(cc)a$ back-scattering arrangement. The experimental set-up used for time resolved resonance Raman measurements was presented in Chapter 2 and is summarized as follows.

7.4 Experimental setup

Time resolved resonance Raman scattering measurement were performed on a $10 \times 8 \times 6$ mm oriented $\text{Cr:Mg}_2\text{SiO}_4$ single crystal free of any visible inhomogeneities such as bubbles, cracks or inclusions, with doping level $\sim 3 \times 10^{18}$ ions/ cm^3 . All spectra were obtained at room temperature.

The $1.064\text{ }\mu\text{m}$, 90 ps, 7.5 W output pulses of a mode-locked Nd:YAG laser operating at 82MHz repetition rate, are compressed in an optical fiber pulse compressor (see Section 2.2.2) down to 4 ps, and frequency doubled by a KTP crystal to 532 nm, 750 mW. This system synchronously pumps a Rh-6G tunable over the 575 - 630 nm spectral region dye laser which provides 500 fs, 200 mW pulses. Time resolved resonance Raman experiments used 598 nm pulses, linearly polarized along the c -crystallographic axis of the sample, which photoexcite Cr^{4+} ions near the zero-phonon line of the ${}^3B_2({}^3T_1)$ state and correspond to the maximum anti-Stokes resonance enhancement for the highest frequency, highest scattering cross section 765 cm^{-1} Cr^{4+} local mode (Section 7.3). A narrow band filter is used to minimize any residual background due to the wide laser pulses.

The 35 cm^{-1} excitation pulses are split by a beam splitter (see Fig. 2.9) into a pump and a probe pulse with intensity ratio 2/1, respectively. The weaker probe pulse enters an adjustable time delay unit where it was retarded by a variable time Δt with respect to the pump pulse. The pump and probe are then recombined and focused into the sample in a backscattering geometry, using a 2 cm microscope objective such that the incident power at the sample site is $\sim 30\text{ mW}$. The estimated diameter of the focused beam is $\sim 7\text{ }\mu\text{m}$. The back-scattered signal was collected and focused into the triple spectrometer by a 30 cm lens. The entrance slits of the triple spectrometer were opened at : $S_1 = 300\text{ }\mu\text{m}$, $S_2 = 5\text{ cm}$, $S_3 = 400\text{ }\mu\text{m}$. Grating #5 (1800 grooves/mm) was used for all spectra such that the spectral resolution was $\sim 10\text{ cm}^{-1}$. The relatively low resolution does not affect the quality of the spectra as the width of the excitation pulses was 35 cm^{-1} . The typical level of the measured anti-Stokes signal was $\sim 120\text{ counts/sec}$ and each spectrum was collected for $\sim 30\text{ min}$.

Polarized anti-Stokes spectra corresponding to totally symmetric A_g modes were collected for different pump-probe time delays Δt , in an $a(cc)a$ scattering configuration given in Porto's notation (see Section 2.6). The change in the intensity of the $765\text{ cm}^{-1}\text{ Cr}^{4+}$ local mode, indicating the transient presence of nonequilibrium local mode population following photoexcitation of Cr^{4+} ions was monitored for different pump-probe time delays. The 609 and $826 - 856\text{ cm}^{-1}$ phonon modes were selected as reference since they are not involved in the nonradiative relaxation process [20]. The experimental results obtained using the above described setup and method are presented in the next section.

7.5 Experimental results

Anti-Stokes resonance Raman spectra obtained under the experimental conditions described above were measured for pump-probe time delays Δt varying between 0 and 40 ps. The changes in the intensity of the 765 cm^{-1} were monitored by taking as reference the constant intensities of the 609 cm^{-1} and 826 - 856 cm^{-1} phonon modes. Fig. 7.8 shows two anti-Stokes spectra obtained for $\Delta t = 3$ ps (continuous line) and $\Delta t = 35$ ps (dashed line) time delays, in the 500 - 900 cm^{-1} spectral range. The increased intensity of the 765 cm^{-1} Cr^{4+} local mode 3 ps after photoexcitation indicates the transient presence of nonequilibrium local mode population. The insert in Fig. 7.8 shows the anti-Stokes spectrum in the 500 - 900 cm^{-1} spectral region obtained under 598 nm excitation for the Mg_2SiO_4 undoped crystal (dashed line) containing only the 609, 826 and 856 cm^{-1} phonon modes, while the similar spectrum for the Cr doped crystal contains the additional Cr^{4+} resonance enhanced local mode at 765 cm^{-1} (boxed).

The normalized relative change in the integrated (over 26 cm^{-1}) intensity of the 765 cm^{-1} local mode, taking as reference the 609 cm^{-1} integrated (over 26 cm^{-1}) constant phonon mode intensity, for different pump-probe time delays Δt is shown in Fig. 7.9. The measured dynamics of the 765 cm^{-1} local mode indicates that the nonequilibrium local mode population builds up during the initial 3 - 4 ps following photoexcitation and then gradually decays. A model explaining the dynamics shown in Fig. 7.9 and the calculated characteristic parameters for the nonradiative decay are presented in the next section.

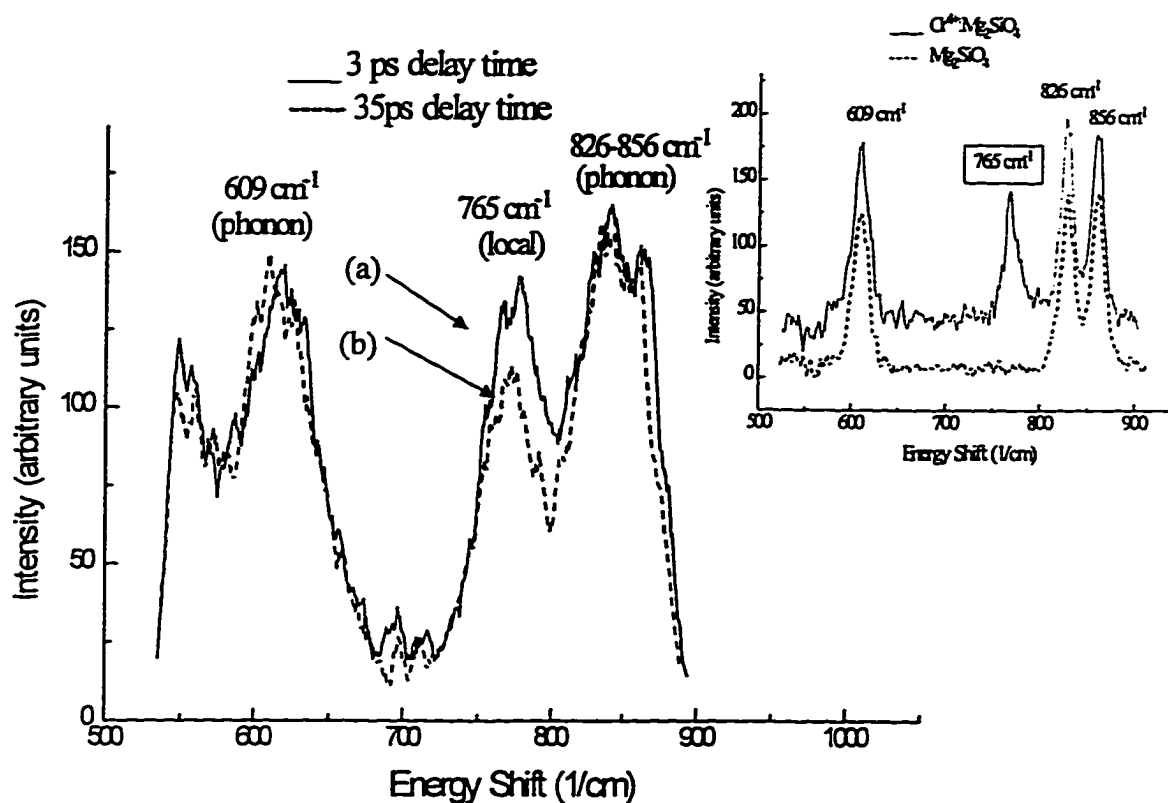


Figure 7.8 Time resolved $\text{Cr:Mg}_2\text{SiO}_4$ anti-Stokes A_g spectra obtained at room temperature under 598 nm excitation wavelength, in $a(cc)a$ scattering configuration for : (a) $\Delta t = 3$ ps (continuous line) and (b) $\Delta t = 35$ ps (dash line) pump-probe delay time, in the 500 - 900 cm^{-1} spectral region. The insert shows anti-Stokes resonance Raman (continuous line) and Raman (dash line) A_g spectra, for $\text{Cr}^{4+}:\text{MgSiO}_4$ and Mg_2SiO_4 , respectively, obtained under 598 nm excitation wavelength, in the 500 - 900 nm spectral range. The 765 cm^{-1} local mode is

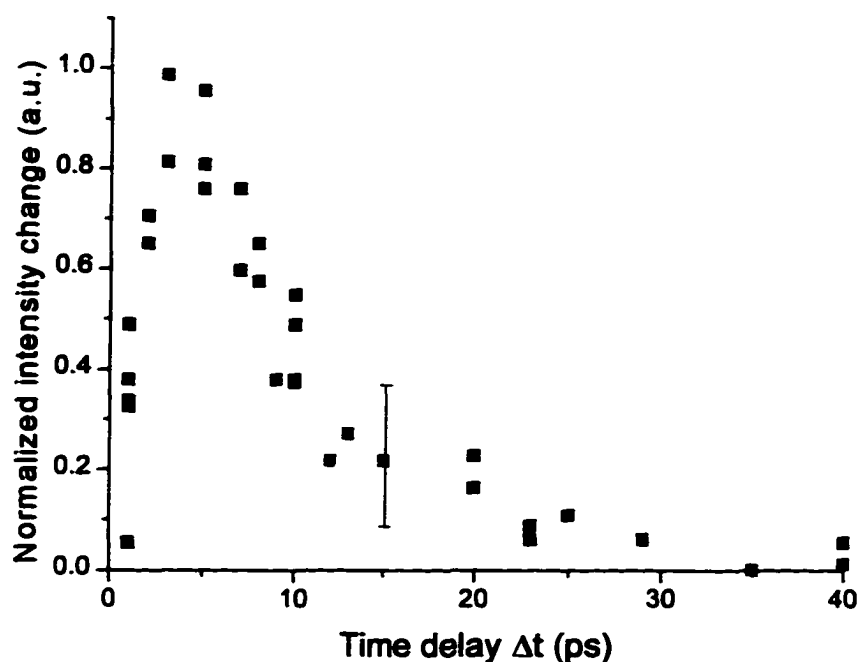


Figure 7.9 Normalized measured dynamics for the nonequilibrium $765\text{ cm}^{-1}\text{ Cr}^{4+}$ local mode population in $\text{Cr:Mg}_2\text{SiO}_4$ during the electronic-vibronic ${}^3\text{B}_2({}^3\text{T}_1) - {}^1\text{E}$ nonradiative transition.

7.6 Proposed model and derived parameters for the nonradiative decay

In order to explain the experimental results shown in Fig. 7.9 and to estimate the characteristic lifetimes of the subsystems involved in the nonradiative decay process, the following model, schematically depicted in Fig. 7.10, was developed.

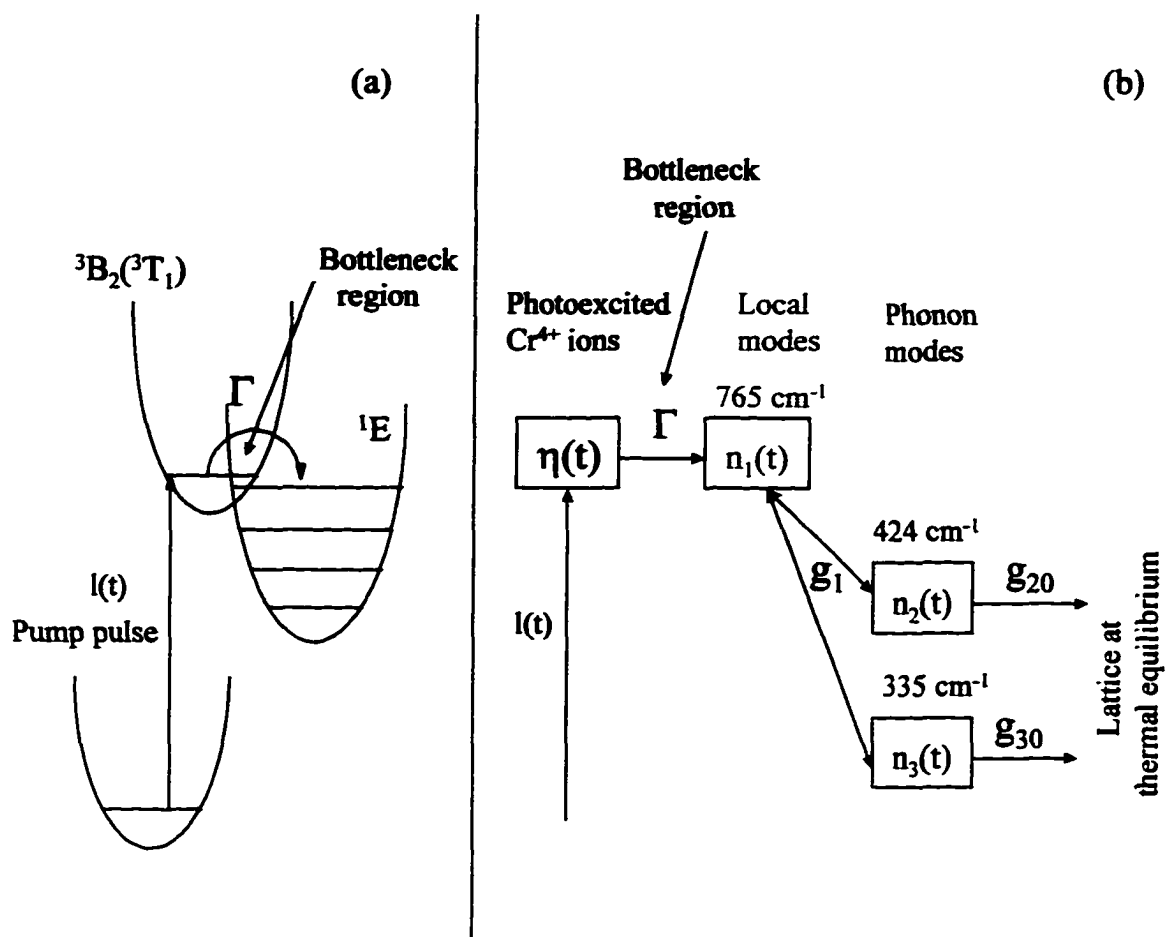


Figure 7.10 (a) Schematic diagram showing the increase in the local mode population following the crossing of the ${}^3B_2({}^3T_1)$ - ${}^1E$ electronic bottleneck; (b) Intermolecular nonradiative relaxation pathway for the 765 cm^{-1} local mode and characteristic decay rates.

The 598 nm pump pulse photoexcites Cr^{4+} ions near the zero-phonon line of the ${}^3B_2({}^3T_1)$ state, creating an excited state population $\eta(t)$. The lack of emission from the ${}^3B_2({}^3T_1)$ state suggests that Cr^{4+} ions relax nonradiatively towards the metastable level at 9150 nm , by making a transition to the lower lying ${}^1E$ state. As the above mentioned transition is spin-forbidden, the system requires a longer tunneling time Γ^{-1} , giving rise to an electronic bottleneck (Γ is the transition rate of the system through the electronic bottleneck). The presence of

the $^3B_2(^3T_1) - ^1E$ bottleneck was first reported using up-converted hot luminescence technique and its lifetime was measured to be $\Gamma^{-1} < 10$ ps [19]. As shown in Fig. 7.3 and previously discussed, the electronic-vibronic transition is accompanied by an increase in the occupation number for local modes. As a consequence, it is expected that the nonequilibrium local mode population rises during the time needed to cross the electronic bottleneck, Γ^{-1} .

Following the transition through the electronic bottleneck, the local mode population decays nonradiatively. The energy of the nonequilibrium local mode population can be transferred nonradiatively into the lattice by one of the following processes : the local mode interacts with the lattice represented by a continuum of phonon modes and distributes the excess energy into the reservoir (discrete-to-continuum energy transfer), and/or the local mode interacts with a very restricted number of vibrations (daughters) which take over the excess energy and display a transient, “time-shifted” (from the driving local mode) nonequilibrium population (discrete-to-discrete energy transfer). The most likely energetic-wise daughter decay channels for the investigated 765 cm^{-1} local mode are :

- (a) decay into two phonon modes $\omega_{1P} + \omega_{2P}$ (**intermolecular decay**), such that $765\text{ cm}^{-1} \rightarrow \omega_{1P} + \omega_{2P}$ with $\omega_{1P} = 335\text{ cm}^{-1}$ and $\omega_{2P} = 424\text{ cm}^{-1}$;
or
- (b) decay into two local modes $\omega_{1L} + \omega_{2L}$ (**intramolecular decay**), such that $765\text{ cm}^{-1} \rightarrow \omega_{1L} + \omega_{2L}$ with $\omega_{1L} = 346\text{ cm}^{-1}$ and $\omega_{2L} = 420\text{ cm}^{-1}$.

The nonequilibrium local mode population transfers into nonequilibrium phonon mode population (for both cases a) and b)). As the nonequilibrium mother local mode population decreases, the nonequilibrium daughter phonon modes which are driven by this particular decay route increase. The nonequilibrium daughter phonon mode population decays by interactions with the phonon continuum allowing the system to return to thermal equilibrium.

It should be mentioned that the insert in Fig. 7.8 shows that there are no phonon or local modes in resonance with the 765 cm^{-1} local mode, indicating that resonance nonradiative processes can not occur for this local mode. Discrete-to-discrete energy decay pathways were first investigated in liquids [13] where it was shown that intermolecular resonance processes are possible [24].

Previous measurements [20] have shown that the 335 cm^{-1} daughter phonon is created following the photoexcitation of Cr^{4+} ions to the ${}^3\text{B}_2({}^3\text{T}_1)$ state, indicating the presence of an intermolecular discrete-to-discrete decay pathway. It should be noted that no information can be obtained on the dynamics of the 424 cm^{-1} daughter phonon mode which is too weak to be resolved in an anti-Stokes Raman spectrum.

Using selection rules it can be shown that the intermolecular decay pathway case a) is allowed but the intramolecular pathway, case b) is forbidden. A certain phonon decay pathway is allowed if the product of the wavefunctions of the vibrational modes involved in this particular route is equal to, or contains the totally symmetric representation (i.e. the representation which is invariant under all the operations of the group) [25] (and Eq. (3.29)). In Chapter 6 it was shown that the symmetry of the local modes involved in the intramolecular pathway is, expressed in terms of the site symmetry C_s the following : 765 and 346 cm^{-1} are totally symmetric (A') while 420 cm^{-1} is nontotally symmetric (A''). Using the orthogonality of the two representations of the C_s group, the following multiplication laws apply (Eqs. (4.71), (4.72)) :

$$A' \times A' = A'' \times A'' = A' \quad (7.10)$$

$$A' \times A'' = A'' \times A' = A'' \quad (7.11)$$

Using the above equations it can be shown that the product of wavefunctions for the intramolecular pathway is :

$$A' \times A' \times A'' = A'' \quad (7.12)$$

i.e. nontotally symmetric, which means that the intramolecular decay route is forbidden. On the other hand, in Tab. 5.1 it was shown that all phonon modes which appear in an A_g spectrum originate only in totally symmetric A' , C_s representations. As a consequence the wavefunctions of the 424 and 335 cm^{-1} A_g phonon modes (see Fig. 3.5) involved in the intermolecular pathway, are totally symmetric, A' . Using Eqs. (7.10), (7.11) the product of the wavefunctions of the modes involved in the intermolecular decay pathway is :

$$A' \times A' \times A' = A' \quad (7.13)$$

i.e. totally symmetric, which means that the intermolecular decay route is allowed (as shown in Fig. 7.10 (b)). Finally, the 335 and 424 cm^{-1} daughter phonons created during the intermolecular decay route transfer their energy into the lattice which acts as reservoir allowing the system to return to equilibrium.

The intermolecular allowed nonradiative decay pathway is modeled using the scheme depicted in Fig. 7.10 (b), as follows. The rate of change in the photoexcited population $\eta(t)$ is given by two terms : (a) the laser pulse $I(t)$, which acts as a source (increases $\eta(t)$) and (b) the decay of this population due to the transition through the electronic bottleneck. If Γ is the transition rate through the bottleneck, the equation for $\eta(t)$ can be written as :

$$\dot{\eta}(t) = I(t) - \Gamma\eta(t) \quad (7.14)$$

Eq. (14) has to be solved with the initial condition :

$$\eta(0) = 0 \quad (7.15)$$

i.e., initially the upper electronic level is not populated.

The equations describing the dynamics of the local and phonon modes is written as a system of coupled differential equations, which can be uncoupled using the relaxation time approximation. This procedure is shown as follows. Let $N_1(t)$, $N_2(t)$ and $N_3(t)$ be the populations of the 765, 424 and 335 cm^{-1} modes of vibration, at time t following photoexcitation. Let g_{23} be the transition rate for transferring energy between the 765 cm^{-1} mother local and two daughter phonon

modes. Let g be the transition rate for populating the mother local mode following the transition through the electronic bottleneck. Finally let g_{20} and g_{30} be the transition rates between the daughter phonon modes at 424 and 335 cm^{-1} , respectively and the phonon bath.

The terms determining the rate of change in the mother and daughter populations are schematically depicted in Fig. 7.11, where the notations introduced above were used.

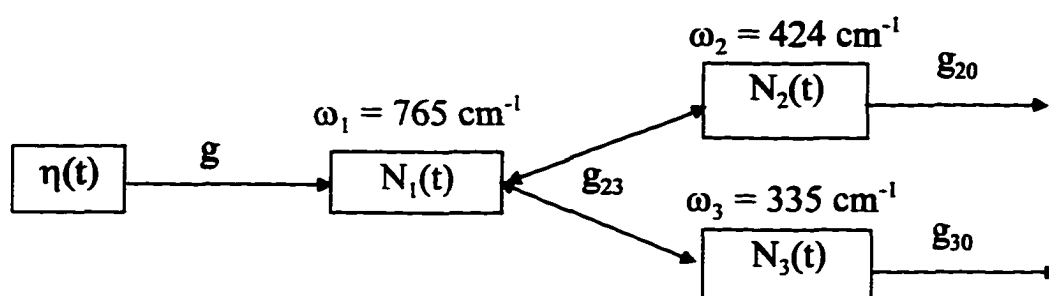


Figure 7.11 Schematic diagram used for deriving the equations describing the dynamics of the intermolecular decay route.

As shown in the above diagram, the rate of change of the local mode N_1 is determined by the following terms :

- N_1 increases due to the depopulation of $\eta(t)$, with a transition rate g ,
- N_1 decreases due to its decay in the two daughter phonons, i.e due to processes of the type : $\omega_1 \rightarrow \omega_2 + \omega_3$, with transition rate g_{23} , and
- N_1 increases due to interactions with the two daughter phonons, i.e due to processes of the type : $\omega_2 + \omega_3 \rightarrow \omega_1$ with transition rate g_{23} .

The (a) term gives the following contribution to the rate of change in N_1 :

$$\dot{N}_1(t) = g\eta(t) + \dots \quad (7.16)$$

In order to calculate the contribution to $\dot{N}_1$ of the (b) term, the probability of the $\omega_1 \rightarrow \omega_2 + \omega_3$ process is determined as the amplitude squared ($|A|^2$) of the decay, as :

$$A = \langle \Psi_f | \hat{O} | \Psi_i \rangle \quad (7.17)$$

where $|\Psi_i\rangle$ and $|\Psi_f\rangle$ are the initial and final, respectively wavefunctions for the system and $\hat{O}$ is the operator inducing the transition. For the (b)-type process :

$$|\Psi_i\rangle = |N_1, N_2, N_3\rangle \quad (7.18)$$

i.e. the system starts with N_1 local modes and N_2 and N_3 phonons, and ends up in the state

$$|\Psi_f\rangle = |N_1 - 1, N_2 + 1, N_3 + 1\rangle \quad (7.19)$$

i.e. a quanta ω_1 has been destroyed, but a quanta each of ω_2 and ω_3 have been created. The operator responsible for this decay consists of a destruction operator for N_1 (a_{N_1}), and a creation operator for each N_2 and N_3 ($a_{N_2}^+, a_{N_3}^+$), such that (see Eqs. (7.3), (7.6)) :

$$\hat{O} = a_{N_3}^+ a_{N_2}^+ a_{N_1} \quad (7.20)$$

Plugging Eqs. (7.18) - (7.20) into Eq. (7.17) and making use of Eqs. (7.3), (7.6) the probability for a (b)-type process is :

$$|A|^2 = N_1(N_2 + 1)(N_3 + 1) \quad (7.21)$$

Taking the transition rate g_{23} into account, the contribution to the rate of change of N_1 due to a (b)-type process is, using Eq. (7.21) :

$$\dot{N}_1(t) = \dots - g_{23} N_1(N_2 + 1)(N_3 + 1) + \dots \quad (7.22)$$

The “-” sign in Eq. (7.22) shows that a $\omega_1 \rightarrow \omega_2 + \omega_3$ process leads to a decrease in the population N_1 .

Finally, using the same type of derivation as above, a (c)-type process which involves the creation of an ω_1 quanta and the destruction of each of an ω_2 and ω_3 quanta contributes to the rate of change of N_1 as :

$$\dot{N}_1(t) = \dots + g_{23}(N_1 + 1)N_2N_3 + \dots \quad (7.23)$$

The total rate of change of the N_1 population is obtained by adding the contributions of the (a), (b) and (c) terms given by Eqs. (7.16), (7.22) and (7.23) giving ;

$$\dot{N}_1(t) = g\eta(t) - g_{23}[N_1(t)(1 + N_2(t) + N_3(t)) - N_2(t)N_3(t)] \quad (7.24)$$

The rate of change for the daughter phonon modes are written using the above observations and Fig. 7.11. For example, the rate of change of N_2 is determined by the (b) and (c)-type processes described above (but with changes sign, as when N_1 loses energy, N_2 gains it, and the other way around), plus an additional term which reflects the interactions with the reservoir. The rate of change for the N_2 population can be written as :

$$\dot{N}_2(t) = g_{23}[N_1(t)(1 + N_2(t) + N_3(t)) - N_2(t)N_3(t)] - g_{20}(N_2(t) - N_{20}) \quad (7.25)$$

N_{20} in the above equation is the equilibrium value of the population of mode ω_2 . The last term in Eq. (7.25) shows that if N_2 is above the equilibrium value, the reservoir will absorb the excess energy with a transition rate g_{20} .

A similar equation to Eq. (7.25) can be written for the dynamics of the 335 cm^{-1} phonon mode as :

$$\dot{N}_3(t) = g_{23}[N_1(t)(1 + N_2(t) + N_3(t)) - N_2(t)N_3(t)] - g_{30}(N_3(t) - N_{30}) \quad (7.26)$$

where N_{30} is the equilibrium value of the population of mode ω_3 .

The system of coupled differential equations (7.14), (7.24) (7.25) and (7.26) describe the dynamics of the mother and daughter modes during and following the electronic-vibronic transition. In order to solve it the following approximations are made. The last term in Eq. (7.24) which represents the decay of the mother local mode is treated in the relaxation time approximation as :

$$g_{23}[N_1(t)(1 + N_2(t) + N_3(t)) - N_2(t)N_3(t)] \approx g_1(N_1(t) - N_{10}) \quad (7.27)$$

where g_1 is the transition rate for the process coupling the mother and daughter phonon modes and N_{10} is the equilibrium value of the population N_1 . Eq. (7.27) shows that as long as the instantaneous population $N_1(t)$ is above the equilibrium value, the daughter modes act like a sink taking over the excess energy.

A new variable, $n_i(t)$ representing the nonequilibrium population of a mode of vibration N_i is introduced as the difference between the instantaneous population of the considered mode and its equilibrium value :

$$n_i(t) \equiv N_i(t) - N_{i0}, \quad i = 1 \div 3 \quad (7.28)$$

Using the fact that N_{i0} has a constant value for a given mode, the derivative of Eq. (7.28) with respect to time gives :

$$\dot{n}_i(t) = \dot{N}_i(t) \quad (7.29)$$

Eqs. (7.14), (7.24), (7.25) and (7.26) describing the dynamics of the system can be rewritten using Eqs. (7.27) - (7.29) as :

$$\dot{\eta}(t) = l(t) - \Gamma\eta(t) \quad (7.14)$$

$$\dot{n}_1(t) = g\eta(t) - g_1n_1(t) \quad (7.30)$$

$$\dot{n}_2(t) = g_1n_1(t) - g_{20}n_2(t) \quad (7.31)$$

$$\dot{n}_3(t) = g_1n_1(t) - g_{30}n_3(t) \quad (7.32)$$

Eqs. (7.14), (7.30) and (7.32) will be solved as follows. By fitting them to the measured dynamics of the 765 cm^{-1} local mode presented in Fig. 7.9 and to the measured dynamics of the 335 cm^{-1} phonon mode [20] the transition time through the electronic bottleneck Γ^{-1} , the local mode lifetime g_1^{-1} and the phonon mode lifetime g_{30}^{-1} will be determined. It should be reminded that although no information is available on the dynamics of the 424 cm^{-1} phonon mode described by Eq. (7.31), this does not affect in any way the determination of the previously mentioned parameters, which do not depend on Eq. (7.31).

The homogeneous part of Eq. (7.14) :

$$\dot{\eta}(t) = -\Gamma\eta(t) \quad (7.33)$$

can be rewritten as ;

$$d\eta(t) = -\Gamma\eta(t)dt \quad (7.34)$$

and solved by separating the variables, with the solution :

$$\eta(t) = ce^{-\Gamma t} \quad (7.35)$$

The solution for the inhomogeneous part is obtained by considering the constant c in Eq. (7.35) as a function of time. By equating the temporal derivative of Eq. (7.35) with the right-hand side of Eq. (7.14) one obtains the Eq. for c as :

$$dc = l(t)e^{\Gamma t} dt \quad (7.36)$$

which gives upon integration from $t = 0$ (initial condition) to an arbitrary time t :

$$c = c_0 + \int_0^t l(t')e^{\Gamma t'} dt' \quad (7.37)$$

Plugging Eq. (7.37) into Eq. (7.35) gives :

$$\eta(t) = c_0 e^{-\Gamma t} + e^{-\Gamma t} \int_0^t l(t')e^{\Gamma t'} dt' \quad (7.38)$$

c_0 is determined from the initial condition that at $t = 0$ the electronic state is not populated, given by Eq. (7.15), i.e. :

$$\eta(0) = c_0 = 0 \quad (7.39)$$

The solution of Eq. (7.14) is :

$$\eta(t) = e^{-\Gamma t} \int_0^t l(t')e^{\Gamma t'} dt' \quad (7.40)$$

Eq. (7.40) can be solved exactly for a δ -shape laser pulse, i.e for :

$$l(t) = k\delta(t) \quad (7.41)$$

where k is a constant which gives the intensity of the laser pulse.

Using Eq. (7.41), Eq. (7.40) becomes :

$$\eta(t) = ke^{-\Gamma t} \quad (7.42)$$

Eq. (7.42) shows that following the δ -type photoexcitation, the population $\eta(t)$ decays exponentially, as the laser pulse is its only source.

Eq. (7.30) is solved in the same manner as Eq. (7.14), by first considering its homogeneous part :

$$\dot{n}_1(t) = -g_1 n_1(t) \quad (7.43)$$

with the solution

$$n_1(t) = ce^{-g_1 t} \quad (7.44)$$

The inhomogeneous equation is solved by considering c as a function of time $c(t)$ and by equating the time derivative of Eq. (7.44) with the right-hand side of Eq. (7.30). The integration of the obtained equation yields :

$$c = c_0 + \int_0^t g\eta(t')e^{g_1 t'} dt' \quad (7.45)$$

Plugging Eq. (7.45) into Eq. (7.44) gives :

$$n_1(t) = c_0 e^{-g_1 t} + ge^{-g_1 t} \int_0^t \eta(t')e^{g_1 t'} dt' \quad (7.46)$$

c_0 is determined from the initial condition that at $t = 0$ the local mode is at equilibrium, i.e. $n_1(0) = 0$, which, together with Eq. (7.46), leads to :

$$n_1(0) = c_0 = 0 \quad (7.47)$$

The solution of Eq. (7.30) becomes :

$$n_1(t) = ge^{-g_1 t} \int_0^t \eta(t')e^{g_1 t'} dt' \quad (7.48)$$

The general solution for the dynamics of the local mode can be solved exactly using Eq. (7.42) and gives :

$$n_1(t) = \frac{B}{g_1 - \Gamma} (e^{-\Gamma t} - e^{-g_1 t}) \quad (7.49)$$

where $B = g \cdot k$ is a constant. B can be eliminated by normalizing the expression for the nonequilibrium local mode population, such that its maximum value is equal to 1. In fact this is exactly the way the relative change $n_1(t)$ was plotted in Fig. 7.9. Using Eq. (7.49) it can be shown that the function $n_1(t)$ reaches its maximum at :

$$t_{\max} = \frac{1}{g_1 - \Gamma} \ln\left(\frac{g_1}{\Gamma}\right) \quad (7.50)$$

and the normalization condition $n_1(t_{\max}) = 1$ gives :

$$B = \Gamma \left(\frac{g_1}{\Gamma}\right)^{\frac{g_1}{g_1 - \Gamma}} \quad (7.51)$$

Eqs. (7.49) and (7.51) give the normalized nonequilibrium population for the local mode as :

$$n_1(t) = \frac{\Gamma}{g_1 - \Gamma} \left(\frac{g_1}{\Gamma}\right)^{\frac{g_1}{g_1 - \Gamma}} (e^{-\Gamma t} - e^{-g_1 t}) \quad (7.52)$$

The above equation is used for fitting the data shown in Fig. 7.9 and yields the values for the parameters Γ and g_1 . The best fits were obtained using the nonlinear least-square fitting routine in Origin (commercially available plotting and fitting program package) and lead to : electronic bottleneck transition time $\Gamma^{-1} = 2.8 \pm 0.3$ ps, and local mode lifetime $g_1^{-1} = 5.1 \pm 0.5$ ps. The best fit, together with the measured dynamics of the local mode are presented in Fig. 7.12.

Eq. (7.32) which gives the dynamics of the 335 cm^{-1} daughter phonon mode has the same formal solution as Eq. (7.30) where the quantities $n_1(t)$, $\eta(t)$, g and g_1 in Eq. (7.30) are replaced by $n_3(t)$, $n_1(t)$, g_1 and g_{30} , respectively for the solution of Eq. (7.32). Making these changes in Eq. (7.48), the solution of Eq. (7.32) can be written as :

$$n_3(t) = g_1 e^{-g_{30}t} \int_0^t n_1(t') e^{g_{30}t'} dt' \quad (7.53)$$

Using the expression for $n_1(t)$ given by Eq. (7.52) in Eq. (7.53), the dynamics of the nonequilibrium daughter 335 cm^{-1} phonon mode population can be written as ;

$$n_3(t) = C \left[\frac{e^{-g_1 t} - e^{-g_{30} t}}{g_{30} - g_1} - \frac{e^{-\Gamma t} - e^{-g_{30} t}}{g_{30} - \Gamma} \right] \quad (7.54)$$

where C is a normalization constant. Using the previously determined values for Γ and g_1 and the measured dynamics of the nonequilibrium population of the 335 cm^{-1} phonon mode [20], the best fit for Eq. (7.54) was obtained for a phonon lifetime $g_{30}^{-1} = 5 \pm 0.5\text{ ps}$ and $C = 1.1$.

Fig. 7.12 shows the measured and calculated dynamics for the 765 cm^{-1} local and for the 335 cm^{-1} daughter phonon modes involved in the intermolecular nonradiative decay route of Cr^{4+} ions. The measured dynamics for the 765 cm^{-1} mother and the 335 cm^{-1} daughter modes show that the nonequilibrium local mode population reaches its maximum $\sim 3\text{ ps}$ following photoexcitation, and then starts decaying. Meanwhile, the daughter phonon modes which “absorb” the energy released by the local modes display a time-shifted dynamics reaching their maximum $\sim 8\text{ ps}$ following photoexcitation, and then start decaying. As previously mentioned, the best fit for the dynamics of the local mode was obtained using Eq. (7.52), with $\Gamma^{-1} = 2.8\text{ ps}$, and $g_1^{-1} = 5.1\text{ ps}$ and is depicted with continuous line in Fig. 7.12. The best fit for the dynamics of the 335 cm^{-1} phonon mode was obtained using Eq. (7.54), with $g_{30}^{-1} = 5 \pm 0.5\text{ ps}$ and $C = 1.1$ and is depicted with dash line in Fig. 7.12. It should be mentioned that more realistic laser pulse shapes do not lead to significant changes in these characteristic relaxation lifetimes.

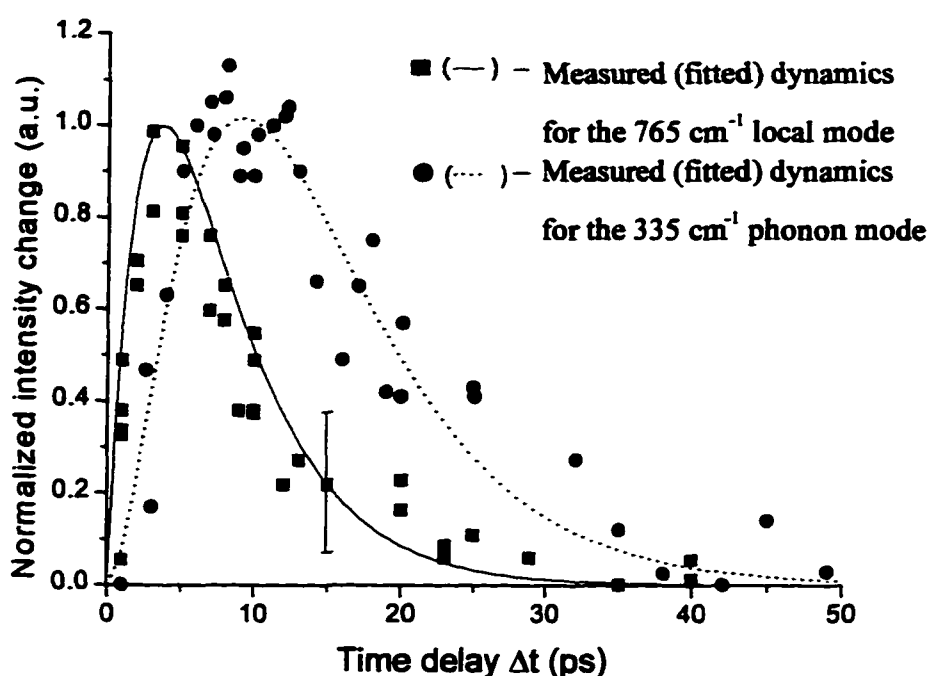


Figure 7.12 Normalized measured (■, ●) and fitted (—, ...) dynamics for the 765 cm^{-1} (local) and 335 cm^{-1} (phonon) modes, respectively. Best fits were obtained using the following parameters for the intermolecular relaxation pathway : electronic bottleneck transition time $\Gamma^{-1} = 2.8\text{ ps}$, local mode lifetime $g_1^{-1} = 5.1\text{ ps}$, and phonon mode lifetime $g_{30}^{-1} = 5\text{ ps}$.

In conclusion, the dynamics of local modes during the electronic-vibronic nonradiative relaxation of a photoexcited laser impurity ion was measured for the first time, proving the active participation of local modes, as a distinctive step from the phonon modes, in nonradiative relaxation processes. It was shown that the nonequilibrium local mode population builds up during the transition through an electronic bottleneck and decays by interaction with a restricted number of phonon modes (discrete-to-discrete energy transfer). This leads to a time-shifted temporal profile for the nonequilibrium daughter phonons with respect to the

dynamics of the nonequilibrium mother local mode (Fig. 7.12) such that the daughters peak at $\sim \Gamma^{-1} + g_1^{-1} \approx 8\text{ps}$. The following key parameters were determined for the system under investigation (Cr^{4+} in $\text{Cr:Mg}_2\text{SiO}_4$) : $^3\text{B}_2(^3\text{T}_1) - ^1\text{E}$ electronic bottleneck transition time 2.8 ± 0.3 ps, local mode lifetime (due only to an intermolecular anharmonic decay channel) 5.1 ± 0.5 ps, birth time of daughter phonons 7.9 ± 0.6 ps, and lifetime of daughter phonons (due to interaction with the continuum of phonons) 5 ± 0.5 ps. It is interesting to note that the local mode at 765 cm^{-1} which takes over the energy from the electronic level and displays a transient increased nonequilibrium population is the mode with the strongest electron-phonon coupling (see Chapter 6), and appears to be the best candidate for facilitating the energy transfer from the electronic to the vibrational system (i.e. the nonradiative relaxation) due to electron-phonon interactions.

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Chapter 8

Conclusions and proposed future experiments

8.1 Conclusions

This thesis was focused on the identification and characterization in terms of energy and symmetry of Cr^{4+} local modes in the $\text{Cr:Mg}_2\text{SiO}_4$ tunable solid state laser, and in establishing for the first time their role and dynamics during nonradiative processes, using steady state and time resolved resonance Raman measurements.

Mg_2SiO_4 belongs to the olivine family and has D_{2h} space group symmetry with the following lattice parameters given in standard *Pnma* notation : $a = 10.22$ Å, $b = 5.99$ Å and $c = 4.73$ Å. Cr^{4+} is the lasing ion in $\text{Cr: Mg}_2\text{SiO}_4$ and substitutes for Si^{4+} in a tetrahedral coordination given by four Oxygen ions, distorted due to the crystal field such that the site symmetry of Cr^{4+} is C_s . The quantum efficiency for this laser crystal is $\sim 10\%$ due to sizable nonradiative processes which cause the lifetime of the metastable level to decrease from 25 μs at 77K to 2.7 μs at room temperature. The relative strong nonradiative processes make $\text{Cr:Mg}_2\text{SiO}_4$ a good candidate for studying the role of local modes in the nonradiative decay.

The local modes of Cr^{4+} were identified in terms of energy and symmetry using polarized steady state resonance Raman scattering corresponding to the ${}^3A_2 \rightarrow {}^3B_2({}^3T_1)$ Cr^{4+} transition [1]. Seven (out of the expected nine) Cr^{4+} local modes were identified in room temperature resonance Raman spectra having the following energy and symmetry, given in both the site C_s and the undistorted T_d (in parenthesis) symmetries : 765 cm^{-1} - $A'(A_1)$, 740 cm^{-1} - $A''(T_2)$, 690 cm^{-1} - $A'(T_2)$, 498 cm^{-1} - $A'(E)$, 480 cm^{-1} - $A''(E)$, 290 cm^{-1} - $A'(T_2)$, 253 cm^{-1} -

A'(T₂). Force constant calculations show a decrease of 13 - 19% in the intra-tetrahedral force constants for a CrO₄ molecule if compared to a SiO₄ molecule indicating that the former is looser bound than the latter.

Low temperature resonance Raman measurements which offer improved resonance conditions and allow the observation of up to fourth order resonance enhanced spectra, reveal two interesting features [2] : (i) an anomalous number of first order local modes (15 instead of the expected 9) and (ii) a very rich combination and overtone spectrum whose most distinctive characteristic is a long overtone progression for two high frequency local modes at 765 and 742 cm⁻¹.

The 15 measured local modes were [2] : 10 totally symmetric A' modes at 253, 288, 346, 361, 390, 468, 499, 691, 765 and 820 cm⁻¹ and 5 nontotally symmetric A'' modes at 408, 420, 477, 526 and 742 cm⁻¹. After eliminating several possible explanations it was concluded that the anomalous number of local modes is due to second neighbor interactions. The second neighbor interaction hypothesis is also supported by the decrease in intra-tetrahedral force constants for molecules containing Cr⁴⁺ ions, suggesting the necessity of considering an extended molecule. It should be noted that this was the first report of second neighbor interactions detected by resonance Raman scattering [3]. As local modes act as decay channels during nonradiative processes transferring the energy from the electronic states into the vibrational system, the increased number of observed local modes indicates an increased number of decay channels conducive to strong nonradiative processes. Model calculations have also shown that different local modes have different degrees of delocalization, and the ones extending further into the lattice (i.e. those which are sensitive to changes in second neighbor parameters) have the potential to couple more efficient with phonon modes and transfer the excess energy towards the phonon bath facilitating nonradiative processes.

The long overtone progression for the 765 and 742 cm⁻¹ local modes indicates either sizable electron-phonon interactions or/and relative strong

anharmonic effects. As the calculated anharmonic constants are small for both modes (-0.02 and 0.08 cm^{-1} , respectively), it follows that the overtone progression is due to electron-phonon coupling suggesting that these two local modes couple effectively with the electronic states and are able to eventually take over the excessive energy (the mode at 765 cm^{-1}) and to facilitate electronic crossing (the mode at 742 cm^{-1}). Both these properties enable the energy transfer from the photoexcited ion into the lattice and (potentially) lead to enhanced nonradiative processes.

Finally the dynamics of the 765 cm^{-1} local mode was measured during the ${}^3\text{B}_2({}^3\text{T}_1) - {}^1\text{E}$ bottleneck crossing using time resolved resonance Raman measurements performed with 500 fs pulses [4]. It was shown that, as indicated by higher order resonance Raman spectra, the local mode at 765 cm^{-1} is coupled to the ${}^3\text{B}_2({}^3\text{T}_1)$ electronic state (by electron-phonon coupling) and takes over the excessive electronic energy during the nonradiative relaxation. The dynamics of the 765 cm^{-1} mode shows that during the nonradiative relaxation the energy is transferred from the nonequilibrium local mode population created following the bottleneck transition into a select number of daughter phonon modes. The daughter phonons decay due to anharmonic interactions with the phonon bath and the system returns to thermal equilibrium. The following parameters characterizing the nonradiative decay were estimated from time-resolved measurements : bottleneck transition time $\sim 2.8 \text{ ps}$, local mode lifetime $\sim 5.1 \text{ ps}$, phonon mode lifetime $\sim 5 \text{ ps}$. This was the first report on the dynamics of a laser ion's local modes during the nonradiative relaxation in an impurity-doped laser crystal.

8.2 Proposed future experiments

Based on the conclusions of this research two new general criteria (besides the local-phonon mode energy resonance [5]) which may determine the strength of nonradiative processes are proposed :

- (i) as local modes act as nonradiative decay channels, systems which display a large number of local modes are more likely to be significantly affected by nonradiative processes. According to this criterion, crystals which display second neighbor interactions and have an anomalous large number of local modes (decay channels) should be affected more by nonradiative processes than impurity-doped crystals exhibiting a reduced number of local modes. Thus the first proposed criterion can be stated as : “The total number of local modes in a resonance Raman spectrum is correlated to the strength of nonradiative processes”.
- (ii) the second criterion refers to the “efficiency” of the coupling between the electronic system (starting point for nonradiative relaxation) and the vibrational system (“receiver” of the excessive energy made available during an electronic transition) determined by the strength of electron-phonon coupling (which is in general different for different modes). As suggested in Chapter 6, local modes displaying relatively strong electron-phonon coupling act as intermediary between the electronic and vibrational system and facilitate the energy transfer from the former to the latter during nonradiative relaxation. The strength of the electron-phonon coupling can be assessed from the presence of long overtone sequences for some modes. Thus the second proposed criterion can be stated as : “The higher the number of local modes displaying long overtone progressions and small anharmonic constants (i.e. sizable electron-phonon interactions), the more intense the nonradiative processes”.

In order to test the validity of the proposed criteria the following set of measurements is suggested (preferable to be performed on an analog series of hosts doped with the same ion, e.g. $\text{Cr}^{4+}:\text{A}_2\text{BO}_4$, with $\text{A} = \text{Mg, Ca, ..}$ and $\text{B} = \text{Ge, Si}$) :

- a) Low temperature and room temperature fluorescence lifetime measurements performed on the doped host. The low temperature fluorescence lifetime gives the “potential” of the material as laser crystal, i.e. the lifetime in the absence of nonradiative processes. The room temperature fluorescence lifetime gives the “real” behavior of the material as laser material operating at room temperature. The ratio between the two lifetimes gives the quantum efficiency and the strength of nonradiative processes. For example, for both $\text{Cr}:\text{Mg}_2\text{SiO}_4$ and $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$ (Cunyite), a newly developed Cr^{4+} -based laser material [6] the low temperature fluorescence lifetimes for the metastable levels is 25 μs , but the room temperature fluorescence lifetime is 2.7 μs for the former and $\sim 15 \mu\text{s}$ for the latter, indicating weaker nonradiative processes in Cunyite.
- b) The room temperature polarized Raman spectrum of the undoped host identifies the phonon spectrum (“reference”). The polarized off-resonance spectrum of the doped host may serve the same purpose, as it contains only phonon modes (with the observation that for higher impurity concentrations, some phonon modes may be shifted in the doped sample if compared to the undoped host). The phonon spectrum is identified in terms of energy and symmetry.
- c) The room temperature polarized resonance Raman spectrum identifies the laser ion’s local modes (which appear in addition to phonon modes) in terms of energy and symmetry.
- d) The low temperature polarized resonance Raman spectrum contains information regarding the two proposed criteria : (i) the eventual presence of an anomalous number of local modes in the first order spectrum signals second

neighbor interactions, and (ii) the eventual presence of long overtone sequences for certain local modes indicates sizable electron-phonon coupling. Both the large number of local modes and the presence of sizable electron-phonon interactions are expected to promote nonradiative processes.

- e) Finally, time resolved measurements give information on the dynamics of the local and phonon modes involved in the nonradiative relaxation.

The correlation between the results obtained in section a) with information contained in sections b) - e) will verify the connection between second neighbor interactions, electron-phonon coupling and nonradiative processes taking place in impurity doped crystals.

It may be worth mentioning that preliminary resonance Raman measurements reveal only three local modes in Cunyite [6], if compared to 15 in Cr:Mg₂SiO₄ where nonradiative processes are ~ 5 times stronger. This result is especially interesting due to the fact that the strongest resonance enhanced, breathing mode in Cunyite at 733 cm⁻¹ is in resonance with a phonon mode. According to the criterion of local-phonon mode energy resonance this pair should promote strong nonradiative relaxation. But at this point it seems that the energy resonance can not make up for the very low number of local modes which may, in its turn, be due to weak electron-phonon interactions. Further study is needed to shed more light on the correlation between the proposed criteria and nonradiative processes.

8.3 References

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Appendix A.1 Code for program DANA2

```

10  DIM P(515)
20  INPUT "Grating no. : ", GRX
30  INPUT "Central wavelength (nm) : ", PX
40  INPUT "Laser wavelength (nm) : ", FX
50  P(513) = GRX
60  P(514) = PX
70  P(515) = FX
80  GOPEN
90  GCLR
100 INPUT "Upper line : ", A
110 INPUT "Lower line : ", B
120 WOPEN ,X, A, B
130 INPUT "Change position (y/n) ", A$
140 IF A$ = "y" THEN GOTO 90
150 WSUM
160 FOR I = 1 TO 512
170 P(I) = WD1(I-1)
180 NEXT I
190 WCLOSE
210 FOR I = 1 TO 512
220 IF P(I) > 31000 THEN P(I) = 31000
230 NEXT I
240 PRINT : PRINT : INPUT "Do you want to send data to PC ? (y/n) : ", QA$
250 IF QA$ = "y" THEN GOTO 270
260 IF QA$ = "n" THEN GOTO 350 ELSE GOTO 240
270 PRINT : INPUT "Press 'Enter' when you are ready : ", K$
280 PRINT "TRANSMISSION STARTED"
290 FOR I = 1 TO 515
300 RSPRINT P(I)
320 NEXT I
330 RSPRINT 0
340 CLOSE
350 END

```

Appendix A.2 Code for program DANA8

```

DECLARE SUB y ()
DECLARE SUB createfile ()
DECLARE SUB display (a, q, w, r, t, y, u, i, o, p, s, a$, m)
DECLARE SUB modif ()
DECLARE SUB plot ()
DECLARE SUB plotprelim (ar())
DECLARE SUB finalplot (ar())
DECLARE SUB border (p, a, b, c, d, e, f, g, h, i, j)
DECLARE SUB lincol (a, b, lin, col)
DECLARE SUB graph (ar(), n, colo, d(), l, m, o, e, f, g, h)
DECLARE SUB title (ti$, li)
DECLARE SUB arrow (a(), n, d(), l, m, p)
DECLARE SUB transfer ()
DECLARE SUB helpa (a, s, g, h)
DECLARE SUB adddata ()
DECLARE SUB moddata ()
10 CLS : SCREEN 9: COLOR 15, 1: LOCATE 3, 15: PRINT "M A I N  M E N U"
   LOCATE 5, 5: PRINT "1 - Transfer data file from Hamamatsu"
   LOCATE 7, 5: PRINT "2 - Type data files"
   LOCATE 9, 5: PRINT "3 - View / Modify data file"
   LOCATE 11, 5: PRINT "4 - Plot"
   LOCATE 13, 5: PRINT "5 - Add data for calibration"
   LOCATE 15, 5: PRINT "6 - Modify data calibration"
   LOCATE 17, 5: PRINT "7 - End"
   LOCATE 19, 5: INPUT "Option : ", mac
   SELECT CASE mac
   CASE 1
     CALL transfer
   CASE 2
     CALL createfile
   CASE 3
     CALL modif
   CASE 4
     CALL plot
   CASE 5
     CALL adddata
   CASE 6
     CALL moddata
   CASE 7
     END
   END SELECT
   GOTO 10

```

```

SUB adddata
  OPEN "r", #1, "c:\fors\calib", 16
  FIELD #1, 8 AS n$, 4 AS lc$, 4 AS ll$
  CLS
  GET #1, 300: n = CVS(lc$) + 1
  LOCATE 3, 5: PRINT "There are "; n - 1; " data"
  LOCATE 5, 5: INPUT "Name of data file : ", f$
  LSET n$ = f$
  LOCATE 7, 5: INPUT "Central wavelength : ", a
  f$ = MKS$(a): LSET lc$ = f$
  LOCATE 9, 5: INPUT "Laser wavelength : ", l
  f$ = MKS$(l): LSET ll$ = f$
  PUT #1, n
  d$ = MKS$(n): LSET lc$ = d$: PUT #1, 300
  CLOSE
END SUB

```

```

SUB arrow (ar(), n, d(), lin, inf, opti)
'moves arrow in graph. ar is the data array, n no.of channels to smooth on
'd: d(1)=ax,d(2)=xl,d(3)=xmin,d4=xmax,d9=llaser
' d5=ay,d6=yu,d7=ymin,d8=ymax,lin=line where to write title and n
REDIM n(512), x(512), xx(512), yy(512), y1(512), a(40), inty(20)
intp = 1: mui = 1
j1 = (n + 1) / 2
mag = 1242375
FOR i = 1 TO 512
  n(i) = ar(i)
NEXT i
j1 = (n + 1) / 2
mag = 1242375: llaser = d(9)
ymax = d(8): ymin = d(7): ay = d(5): b1 = ay / (ymax - ymin)
y56 = d(5) + d(6)
xmax = d(4): xmin = d(3): ax = d(1): xl = d(2)
ste = (xmax - xmin) / 511
FOR i = 1 TO 512
  x(i) = xmin + (i - 1) * ste 'x in wavelength
NEXT i
SELECT CASE opti
CASE 1
  FOR i = 1 TO 512
    x(i) = mag / x(i)
  NEXT i
  FOR i = 1 TO 256
    SWAP x(i), x(513 - i)
    SWAP n(i), n(513 - i)

```

```

NEXT i
CASE 3
  FOR i = 1 TO 512
    x(i) = 10000000 * (1 / x(i) - 1 / llaser)
  NEXT i
  IF ((x(1) <= 0) AND (x(512) <= 0)) THEN
    FOR i = 1 TO 256
      SWAP n(i), n(513 - i)
    NEXT i
  END IF
  FOR i = 1 TO 256
    SWAP n(i), n(513 - i)
  NEXT i
END SELECT
  FOR i = j1 TO 513 - j1
    s = 0
    FOR k = i - j1 + 1 TO i - j1 + n
      s = s + n(k)
    NEXT k
    y1(i) = CINT(s / n)
  NEXT i
ERASE n
xmin = x(1): xmax = x(512)
a1 = ax / (xmax - xmin)
FOR i = j1 TO 513 - j1
  xx(i) = x1 + (x(i) - xmin) * a1
  yy(i) = y56 - (y1(i) - ymin) * b1
  IF yy(i) < d(6) THEN
    yy(i) = d(6)
  ELSEIF yy(i) > y56 THEN
    yy(i) = y56
  END IF
NEXT i
ck = 2: lk = 5
COLOR 4: PSET (lk, ck): DRAW "D7 L3 R7 G1 L5 F1 R3 L1 D1"
GET (lk - 4, ck - 1)-(lk + 5, ck + 10), a
PUT (lk - 4, ck - 1), a, XOR
PUT (xx(j1) - 4, yy(j1) - 17), a, XOR
FOR i = j1 TO 513 - j1
  IF y1(i) < 0 THEN
    y1(i) = 0
  END IF
NEXT i
SELECT CASE opti
CASE 1

```

```

LOCATE inf + 1, 54: PRINT "1/l (1/cm) : ";
PRINT USING "#####.#"; 10000000 * x(j1) / mag
LOCATE inf, 57: PRINT "E (meV) : ";
PRINT USING "#####.#"; x(j1)
LOCATE inf + 3, 57: PRINT "Channel : "; 512 - j1
CASE 2
  LOCATE inf, 57: PRINT "          "
  LOCATE inf + 1, 58: PRINT "l (nm) : ";
  PRINT USING "#####.#"; x(j1)
  LOCATE inf + 3, 57: PRINT "Channel : "; j1 - 1
CASE 3
  LOCATE inf, 57: PRINT "          "
  LOCATE inf + 1, 52: PRINT "Shift (1/cm) : ";
  PRINT USING "+#####.#"; x(j1)
  LOCATE inf + 3, 57: PRINT "Channel : "; j1 - 1
END SELECT
LOCATE inf + 2, 54: PRINT "No. counts : "; CINT(y1(j1))
LOCATE inf + 4, 59: PRINT "Integ : "
pis = j1
50 IF INKEY$ = "6" THEN
  PUT (xx(pis) - 4, yy(pis) - 17), a, XOR
  pis = pis + 1
  IF pis > 513 - j1 THEN pis = 513 - j1
  PUT (xx(pis) - 4, yy(pis) - 17), a, XOR
  mao = x(pis)
  CALL helpa((opti), (mao), (pis), (inf))
  LOCATE inf + 2, 67: PRINT INT(y1(pis)); "    "
ELSEIF INKEY$ = "4" THEN
  PUT (xx(pis) - 4, yy(pis) - 17), a, XOR
  pis = pis - 1
  IF pis <= j1 THEN pis = j1
  PUT (xx(pis) - 4, yy(pis) - 17), a, XOR
  mao = x(pis)
  CALL helpa((opti), (mao), (pis), (inf))
  LOCATE inf + 2, 67: PRINT INT(y1(pis)); "    "
ELSEIF INKEY$ = "n" THEN
  GOTO 52
ELSEIF INKEY$ = "i" THEN
  LOCATE inf + 4, 67: PRINT intp
  inty(mui) = pis
  IF (intp = 2) THEN
    axa1 = inty(mui - 1): axa2 = inty(mui)
    LINE (xx(axa1), yy(axa1))-(xx(axa2), yy(axa2)), 2
  END IF
  CIRCLE (xx(pis), yy(pis)), 2, 2

```



```

        PAINT (xx(pis), yy(pis)), 2
        intp = (intp MOD 2) + 1: mui = mui + 1
    ELSE
        GOTO 50
    END IF
    GOTO 50
52 CLS
    muimax = mui - 1: COLOR 7
    LOCATE 3, 8: PRINT "The selected integral values are : "
    IF (muimax MOD 2 <> 0) THEN muimax = muimax - 1
    wer = muimax / 2: PRINT
    FOR i = 1 TO wer
        a = 2 * i - 1: PRINT
        PRINT "    xmin = ";
        PRINT USING "#####.##"; x(inty(a));
        SELECT CASE opti
        CASE 1
            PRINT " meV    xmax = ";
        CASE 2
            PRINT " nm    xmax = ";
        CASE 3
            PRINT " 1/cm    xmax = ";
        END SELECT
        PRINT USING "#####.##"; x(inty(a + 1));
        SELECT CASE opti
        CASE 1
            PRINT " meV"
        CASE 2
            PRINT " nm"
        CASE 3
            PRINT " 1/cm"
        END SELECT
        PRINT "    Integral value = ";
        s = 0
        FOR k = inty(a) TO inty(a + 1)
            s = s + y1(k)
        NEXT k
        PRINT s
    NEXT i
    PRINT : CALL y
    CLS : PRINT : PRINT
    PRINT "    Want to store data in ASCII file ? (y/n)"
245 IF INKEY$ = "y" THEN
    PRINT : INPUT "    Name of data file : ", x$
    x$ = x$ + ".dat"

```

```

OPEN x$ FOR OUTPUT AS #1
FOR i = j1 TO 513 - j1
  WRITE #1, x(i), CINT(y1(i))
NEXT i
CLOSE : GOTO 247
ELSEIF INKEY$ = "n" THEN
  GOTO 247
END IF
GOTO 245
247 CLS : LOCATE 5, 2
  CALL y
  ERASE x, xx, yy, a, y1, inty
END SUB

```

```

SUB border (spec, xl, xr, yu, yd, xmin, xmax, ymin, ymax, opti, llaser)
' plots border of scaled graph in color spec
CLS : COLOR 7, 0
ax = 620 - xl - xr: ay = 350 - yu - yd
a = 350 - yd: mag = 1242375
SELECT CASE opti
CASE 1
  mi = mag / xmax: ma = mag / xmin: xmin = mi: xmax = ma
CASE 3
  mi = 10000000 * (1 / xmin - 1 / llaser)
  ma = 10000000 * (1 / xmax - 1 / llaser)
  xmin = mi: xmax = ma
  IF ((mi >= 0) AND (ma >= 0)) THEN 'AS spectra
    SWAP xmin, xmax
  END IF
END SELECT
CALL lincol(xl, a, l1, c1)
LOCATE l1, c1: PRINT USING "+#####"; xmin: PSET (xl, a): DRAW "D4"
CALL lincol(ax + xl, a, l1, c2)
LOCATE l1, c2: PRINT USING "+#####"; xmax: PSET (ax + xl, a): DRAW "D4"
CALL lincol(xl + ax / 2, a, l1, c3)
LOCATE l1, c3: PRINT USING "+#####"; (xmin + xmax) / 2: PSET (xl + ax / 2, a):
DRAW "D4"
c = INT((c3 - c2 - 15) / 2)
SELECT CASE opti
CASE 1
  LOCATE l1, c2 + c + 4: PRINT "Energy (meV)"
CASE 2
  LOCATE l1, c2 + c + 3: PRINT "Wavelength (nm)"
CASE 3
  LOCATE l1, c2 + c: PRINT "Energy shift (1/cm)"

```

```

END SELECT
CALL lincol(xl, yu, ll, cl): cl = cl - 2
IF cl < 1 THEN cl = 1
ll = ll - 1
LOCATE ll, cl: PRINT CINT(yu): PSET (xl, yu): DRAW "L4"
CALL lincol(xl, yu + ay / 2, ll, cl): cl = cl - 2
IF cl < 1 THEN cl = 1
ll = ll - 1
LOCATE ll, cl: PRINT CINT((yu + yd) / 2): PSET (xl, yu + ay / 2): DRAW "L4"
CALL lincol(xl, 350 - yd, ll, cl)
SELECT CASE yd
  CASE 10 TO 99
    cl = cl - 1
  CASE 0 TO 9
    cl = cl
  CASE ELSE
    cl = cl - 2
END SELECT
IF cl < 1 THEN cl = 1
ll = ll - 1
LOCATE ll, cl: PRINT CINT(yd): PSET (xl, 350 - yd): DRAW "L4"
LINE (xl, yd)-(xl, 350 - yd): LINE (xl, 350 - yd)-(620 - xr, 350 - yd)
END SUB

```

```

SUB createfile
'creates data file
  REDIM ar(20)
  CLS : LOCATE 4, 8: INPUT "Name of data file : ", b$
  c$ = b$ + ".dat"
  OPEN "r", #1, c$, 2
  FIELD #1, 2 AS x$
  CLS : LOCATE 5, 8: INPUT "Grating no. : ", gr
  a$ = MKIS(gr): LSET x$ = a$: PUT #1, 513
  LOCATE 7, 8: INPUT "Central wavelength (nm) : ", p
  a$ = MKIS(p): LSET x$ = a$: PUT #1, 514
  LOCATE 9, 8: INPUT "Laser wavelength (nm) : ", f
  a$ = MKIS(f): LSET x$ = a$: PUT #1, 515
  FOR j = 1 TO 25
    CLS
    FOR i = 1 TO 20
      n = (j - 1) * 20 + i
      LOCATE i, 5: PRINT "Data no. "; n
      LOCATE i, 25: INPUT "Data : ", ar(i)
    NEXT i
  FOR i = 1 TO 20

```

```

n = (j - 1) * 20 + i: a$ = MKIS(ar(i)): LSET x$ = a$: PUT #1, n
NEXT i
NEXT j
CLS
FOR i = 1 TO 12
LOCATE i, 5: PRINT "Data no. "; 500 + i
LOCATE i, 25: INPUT "Data : ", ar(i)
NEXT i
FOR i = 1 TO 12
a$ = MKIS(ar(i)): LSET x$ = a$: PUT #1, 500 + i
NEXT i
CLOSE : CLS : ERASE ar
END SUB

```

```

SUB display (lprobe, gr, xmin, xmax, xl, xr, yu, yd, opti, lin, inf, titl$, llaser)
CLS
LOCATE 5, 5: INPUT "Use calibration (1) or program values (2) :", ed
SELECT CASE ed
CASE 1
LOCATE 7, 5: INPUT "Data file name used in `calib` file (NO DIRECTORY !) : ",
ghf$
OPEN "r", #3, "c:\fors\calib", 16
FIELD #3, 8 AS n$, 4 AS lc$, 4 AS ll$
GET #3, 300: n = CVS(lc$)
FOR i = 1 TO n
GET #3, i
df = 8 - LEN(ghf$)
FOR j = 1 TO df
ghf$ = ghf$ + " "
NEXT j
IF n$ = ghf$ THEN
lprobe = CVS(lc$): llaser = CVS(ll$): GOTO 146
END IF
NEXT i
146 CLOSE #3
LOCATE 10, 5: PRINT "Central wavelength : "; lprobe
LOCATE 12, 5: PRINT "Laser wavelength : "; llaser
LOCATE 18, 5: CALL y: CLS
END SELECT
LOCATE 5, 8: PRINT "Display graph : "
LOCATE 7, 10: PRINT "1 - Linear in energy (meV)"
LOCATE 9, 10: PRINT "2 - Linear in wavelength (nm)"
LOCATE 11, 10: PRINT "3 - Raman spectra (1/cm)"
33 LOCATE 15, 8: INPUT "Option : ", opti
IF ((opti = 1) OR (opti = 2) OR (opti = 3)) THEN

```

```

    GOTO 41
ELSE
    GOTO 33
END IF
41 IF ((opti = 3) AND (ed <> 1)) THEN
    CLS : LOCATE 5, 5: INPUT "Laser wavelength : ", llaser
    END IF
38 CLS : LOCATE 3, 5: PRINT "The screen has coordinates :"
    LOCATE 5, 8: PRINT "1) X0 left = 45"
    LOCATE 6, 8: PRINT "2) X0 right = 20"
    LOCATE 7, 8: PRINT "3) Y0 up = 25"
    LOCATE 8, 8: PRINT "4) Y0 down = 48"
    xl = 45: xr = 20: yu = 25: yd = 48
35 LOCATE 10, 5: INPUT "Change coordinates ? (y/n) ", d$
    IF d$ = "y" THEN
        LOCATE 11, 8: PRINT "Press 'Enter' after each coordinate"
        LOCATE 12, 8: PRINT "Input new coordinates as : "
        LOCATE 13, 10: PRINT "( X0l, X0r, Y0u, Y0d)"
        LOCATE 15, 10: PRINT "(" ;
        INPUT "", xl
        LOCATE 15, 15: PRINT ", ";
        INPUT "", xr
        LOCATE 15, 20: PRINT ", ";
        INPUT "", yu
        LOCATE 15, 25: PRINT ", ";
        INPUT "", yd
        LOCATE 15, 30: PRINT ")"
    ELSEIF d$ <> "n" THEN
        LOCATE 10, 32: PRINT "          "
        GOTO 35
    END IF
    LOCATE 17, 10: INPUT "Title : ", titl$
44 LOCATE 19, 10: INPUT "Line where you want to write title (1-10) : ", lin
    IF lin > 10 OR lin < 1 THEN 44
49 LOCATE 21, 10: INPUT "Line where you want to write information (1 - 10) : ", inf
    IF ((inf > 10) OR (inf < 1)) THEN 49
    SELECT CASE gr
    CASE 3
        IF ed <> 1 THEN
            lprobe = lprobe - 3.7
        END IF
        xmin = lprobe - 23.8: xmax = lprobe + 23.8
    CASE 4
        IF ed <> 1 THEN
            lprobe = lprobe - 1.8

```

```

    END IF
    xmin = lprobe - 12: xmax = lprobe + 12
CASE 5
    IF ed <> 1 THEN
        lprobe = lprobe - .6
    END IF
    xmin = lprobe - 7.64: xmax = lprobe + 7.64
END SELECT
END SUB

SUB finalplot (ar())
    REDIM d(9)
    mag = 1242375: oblique = 0
    CLS : LOCATE 5, 8: PRINT "n is ODD !"
    LOCATE 3, 8: INPUT "Input no. of channels that you will smooth on : ", n
    n = 2 * INT((n + 1) / 2) - 1
    LOCATE 7, 8: PRINT "You can move the arrow in the graph with:"
    LOCATE 8, 12: PRINT "a) 6 to the right"
    LOCATE 10, 12: PRINT "b) 4 to the left"
    LOCATE 12, 12: PRINT "c) 'n' to exit"
    LOCATE 14, 12: PRINT "d) 'p' to select a data to be printed"
    LOCATE 16, 12: PRINT "e) 'i' to select integration interval"
    LOCATE 18, 8
    CALL y
    lprobe = ar(514): gr = ar(513)
    CALL display(lprobe, (gr), xmin, xmax, xl, xr, yu, yd, opti, lin, inf, titl$, llaser)
    ax = 620 - xl - xr: ay = 350 - yu - yd
    j1 = (n + 1) / 2
    ymin = ar(1): ymax = ar(1)
    teddy = 1
    FOR i = j1 TO 513 - j1
        s = 0
        FOR k = i - j1 + 1 TO i - j1 + n
            s = s + ar(k)
        NEXT k
        ye = CINT(s / n)
        IF ye > ymax THEN
            ymax = ye
        ELSEIF ye < ymin THEN
            ymin = ye
        END IF
    NEXT i
    d(1) = ax: d(2) = xl: d(3) = xmin: d(4) = xmax
    d(5) = ay: d(6) = yu: d(7) = ymin: d(8) = ymax: d(9) = llaser

```

```

58 CALL border(15, (xl), (xr), (yu), (yd), (xmin), (xmax), (ymin), (ymax), (opti),
(llaser))
CALL title(titl$, (lin))
CALL graph(ar(), n, 15, d(), lin, opti, oblique, 0, 0, 0, 0)
SELECT CASE teddy
CASE 1
GOTO 66
CASE 2
GOTO 56
END SELECT
66 LOCATE 3, 10: COLOR 2: PRINT "Want to change ymax , ymin , rescale "
LOCATE 4, 10: PRINT "and/or subtract background ? (y/n)"
51 IF INKEY$ = "y" THEN
LOCATE 5, 10: INPUT "Change ymin (1), ymax (2), rescale (3) or background
(4) : ", dori
LOCATE 7, 10
SELECT CASE dori
CASE 1
INPUT "ymin = ", ymin: d(7) = ymin
CASE 2
INPUT "ymax = ", ymax: d(8) = ymax
CASE 3
ym = ymin: yma = ymax
PRINT "ymin is "; ymin; " . Change it ? (y/n)"
222 IF INKEY$ = "y" THEN
LOCATE 8, 10: INPUT "New value of ymin will be : ", ym
ELSEIF INKEY$ = "n" THEN
GOTO 225
ELSE
GOTO 222
END IF
225 LOCATE 9, 10: PRINT "ymax is "; ymax; " . Change it ? (y/n)"
228 IF INKEY$ = "y" THEN
LOCATE 10, 10: INPUT "New value of ymax will be : ", yma
ELSEIF INKEY$ = "n" THEN
GOTO 226
ELSE
GOTO 228
END IF
226 sc = ymin * (yma - ym) / (ymax - ymin)
FOR i = 1 TO 512
ar(i) = ar(i) * (yma - ym) / (ymax - ymin) + (ym - sc)
NEXT i
ymax = yma: d(8) = ymax: ymin = ym: d(7) = ymin
CASE 4

```

```

x1 = xl: y1 = yu + ay: x2 = xl + ax: y2 = yu + ay
123   CLS
      CALL border(15, (xl), (xr), (yu), (yd), (xmin), (xmax), (ymin), (ymax), (opti),
(laser))
      CALL graph(ar(), n, 15, d(), lin, opti, oblique, 0, 0, 0, 0)
      CALL title(titl$, (lin))
      LINE (x1, y1)-(x2, y2), 4
      tempo = 1
125   IF INKEY$ = "l" THEN
140       IF INKEY$ = "4" THEN
          LOCATE 1, 20: PRINT tempo
          x1 = x1 - 1: tempo = tempo + 1
          IF x1 < xl THEN
              x1 = xl: tempo = tempo - 1
          END IF
          LINE (x1, y1)-(x2, y2), 4
        ELSEIF INKEY$ = "6" THEN
          LOCATE 1, 20: PRINT tempo
          x1 = x1 + 1: tempo = tempo + 1
          IF x1 > xl + ax THEN
              x1 = xl + ax: tempo = tempo - 1
          END IF
          LINE (x1, y1)-(x2, y2), 4
        ELSEIF INKEY$ = "2" THEN
          LOCATE 1, 20: PRINT tempo
          y1 = y1 + 1: tempo = tempo + 1
          IF y1 > yu + ay THEN
              y1 = yu + ay: tempo = tempo - 1
          END IF
          LINE (x1, y1)-(x2, y2), 4
        ELSEIF INKEY$ = "8" THEN
          LOCATE 1, 20: PRINT tempo
          y1 = y1 - 1: tempo = tempo + 1
          IF y1 < yu THEN
              y1 = yu: tempo = tempo - 1
          END IF
          LINE (x1, y1)-(x2, y2), 4
        ELSEIF INKEY$ = "n" THEN
          GOTO 123
        ELSE GOTO 140
        END IF
        GOTO 140
      ELSEIF INKEY$ = "r" THEN
150       IF INKEY$ = "4" THEN
          LOCATE 1, 20: PRINT tempo

```



```

    x2 = x2 - 1: tempo = tempo + 1
    IF x2 < x1 THEN
        x2 = x1: tempo = tempo - 1
    END IF
    LINE (x1, y1)-(x2, y2), 4
ELSEIF INKEY$ = "6" THEN
    LOCATE 1, 20: PRINT tempo
    x2 = x2 + 1: tempo = tempo + 1
    IF x2 > x1 + ax THEN
        x2 = x1 + ax: tempo = tempo - 1
    END IF
    LINE (x1, y1)-(x2, y2), 4
ELSEIF INKEY$ = "2" THEN
    LOCATE 1, 20: PRINT tempo
    y2 = y2 + 1: tempo = tempo + 1
    IF y2 > yu + ay THEN
        y2 = yu + ay: tempo = tempo - 1
    END IF
    LINE (x1, y1)-(x2, y2), 4
ELSEIF INKEY$ = "8" THEN
    LOCATE 1, 20: PRINT tempo
    y2 = y2 - 1: tempo = tempo + 1
    IF y2 < yu THEN
        y2 = yu: tempo = tempo - 1
    END IF
    LINE (x1, y1)-(x2, y2), 4
ELSEIF INKEY$ = "n" THEN
    GOTO 123
ELSE GOTO 150
END IF
GOTO 150
ELSEIF INKEY$ = "n" THEN
    oblique = 100
    CALL graph(ar(), n, 15, d(), lin, opti, oblique, x1, y1, x2, y2)
    oblique = 0
    GOTO 235
ELSE GOTO 125
END IF
GOTO 125
235  END SELECT
    teddy = 1
    ELSEIF INKEY$ = "n" THEN
        teddy = 2
    ELSE
        GOTO 51

```

```

END IF
CLS : GOTO 58
56 CALL arrow(ar(), n, d(), lin, inf, opti)
  ERASE d
END SUB

SUB graph (ar(), n, colo, d(), lin, opti, oblique, x1, y1, x2, y2)
' plots the graph smoothed on "n" channels, in color "colo"
REDIM x(512), y1(512), n(512)
COLOR colo
FOR i = 1 TO 512
  n(i) = ar(i)
NEXT i
j1 = (n + 1) / 2
mag = 1242375: llaser = d(9)
ymax = d(8): ymin = d(7): ay = d(5): b1 = ay / (ymax - ymin)
y56 = d(5) + d(6)
xmax = d(4): xmin = d(3): ax = d(1): x1 = d(2)
ste = (xmax - xmin) / 511
FOR i = 1 TO 512
  x(i) = xmin + (i - 1) * ste 'x in wavelength
NEXT i
SELECT CASE opti
CASE 1
  FOR i = 1 TO 512
    x(i) = mag / x(i)
  NEXT i
  FOR i = 1 TO 256
    SWAP x(i), x(513 - i)
    SWAP n(i), n(513 - i)
  NEXT i
CASE 3
  FOR i = 1 TO 512
    x(i) = 10000000 * (1 / x(i) - 1 / llaser)
  NEXT i
  IF ((x(1) <= 0) AND (x(512) <= 0)) THEN
    FOR i = 1 TO 256
      SWAP n(i), n(513 - i)
    NEXT i
  END IF
  FOR i = 1 TO 256
    SWAP n(i), n(513 - i)
  NEXT i
END SELECT
FOR i = j1 TO 513 - j1

```

```

      s = 0
      FOR k = i - j1 + 1 TO i - j1 + n
        s = s + n(k)
      NEXT k
      y1(i) = CINT(s / n)
    NEXT i
    xmin = x(1): xmax = x(512)
    a1 = ax / (xmax - xmin)
    IF oblique = 100 THEN
      xp1 = (x1 - xl) / a1 + xmin
      xp2 = (x2 - xl) / a1 + xmin
      yp1 = (y56 - y1) / b1 + ymin
      yp2 = (y56 - y2) / b1 + ymin
      ms = (yp2 - yp1) / (xp2 - xp1): ns = yp1 - ms * xp1
      coun = 1
305  IF ((x(coun) <= xp1) AND (x(coun + 1) >= xp1)) THEN
      aj1 = coun: GOTO 300
    ELSE
      coun = coun + 1
    END IF
    GOTO 305
300  coun = 1
303  IF ((x(coun) <= xp2) AND (x(coun + 1) >= xp2)) THEN
      aj2 = coun: GOTO 302
    ELSE
      coun = coun + 1
    END IF
    GOTO 303
302  FOR i = aj1 TO aj2
    y1(i) = y1(i) - (ms * x(i) + ns)
  NEXT i
  FOR i = 1 TO 512
    ar(i) = y1(i)
    IF ar(i) < 0 THEN
      ar(i) = 0: y1(i) = 0
    END IF
  NEXT i
  ymin = ar(1): ymax = ar(1)
  FOR i = 2 TO 512
    IF ar(i) < ymin THEN
      ymin = ar(i)
    ELSEIF ar(i) > ymax THEN
      ymax = ar(i)
    END IF
  NEXT i

```

```

d(8) = ymax: d(7) = ymin: b1 = ay / (ymax - ymin)
SELECT CASE opti
CASE 1, 3
  FOR i = 1 TO 256
    SWAP ar(i), ar(513 - i)
  NEXT i
END SELECT
n = 1
GOTO 234
END IF
x1 = x1 + (x(j1) - xmin) * a1
y1 = y56 - (y1(j1) - ymin) * b1
IF y1 < d(6) THEN
  y1 = d(6)
ELSEIF y1 > y56 THEN
  y1 = y56
END IF
PSET (x1, y1)
FOR i = j1 + 1 TO 513 - j1
  x2 = x1 + (x(i) - xmin) * a1
  y2 = y56 - (y1(i) - ymin) * b1
  IF y2 < d(6) THEN
    y2 = d(6)
  ELSEIF y2 > y56 THEN
    y2 = y56
  END IF
  LINE -(x2, y2)
  x1 = x2: y1 = y2
NEXT i
LOCATE lin, 60: PRINT "n = "; n
234 ERASE x, y1, n
END SUB

SUB helpa (o, m, pis, i)
mag = 1242375
SELECT CASE o
CASE 1
  LOCATE i + 1, 67
  PRINT USING "#####.#"; 10000000 * m / mag
  LOCATE i, 67: PRINT USING "#####.#"; m
  LOCATE i + 3, 68: PRINT USING "####"; 512 - pis
CASE 2
  LOCATE i + 1, 67: PRINT USING "#####.#"; m
  LOCATE i + 3, 68: PRINT USING "####"; pis - 1
CASE 3

```

```

        LOCATE i + 1, 67: PRINT USING "+####.#"; m
        LOCATE i + 3, 68: PRINT USING "###"; pis - 1
    END SELECT
END SUB

```

```

SUB lincol (a, b, lin, col)
' Computes the line and col where to print a message
lin = INT(b / 15) + 3
IF lin > 23 THEN lin = 23
col = INT(a / 8) - 1
IF col > 76 THEN col = 76
IF col < 1 THEN col = 1
END SUB

```

```

SUB moddata
    OPEN "r", #1, "c:\fors\calib", 16
    FIELD #1, 8 AS n$, 4 AS lc$, 4 AS ll$
    CLS
    GET #1, 300: n = CVS(lc$)
    LOCATE 3, 5: PRINT "There are "; n; " data"
    LOCATE 5, 5: INPUT "Name of data file to modify : ", f$
    FOR i = 1 TO n
        GET #1, i
        df = 8 - LEN(f$)
        FOR j = 1 TO df
            f$ = f$ + " "
        NEXT j
        IF n$ = f$ THEN
            lprobe = CVS(lc$): llaser = CVS(ll$): numy = i: GOTO 158
        END IF
    NEXT i
158 LOCATE 7, 5: PRINT "Central wavelength = "; lprobe
    LOCATE 8, 10: PRINT "Want to modify it ? (y/n)"
227 IF INKEY$ = "y" THEN
    GOTO 223
    ELSEIF INKEY$ = "n" THEN
    GOTO 232
    END IF
    GOTO 227
223 LOCATE 9, 5: INPUT "Central wavelength : ", lprobe
    v$ = MKS$(lprobe): LSET lc$ = v$: PUT #1, numy
232 LOCATE 11, 5: PRINT "Laser wavelength = "; llaser
    LOCATE 12, 10: PRINT "Want to modify it ? (y/n)"
248 IF INKEY$ = "y" THEN
    GOTO 334

```

```

ELSEIF INKEY$ = "n" THEN
    GOTO 336
END IF
GOTO 248
334 LOCATE 9, 5: INPUT "Laser wavelength : ", llaser
    v$ = MKS$(llaser): LSET ll$ = v$: PUT #1, numy
336 CLOSE
END SUB

SUB modif
'prints and modifies data in data file
CLS : LOCATE 4, 8: INPUT "Name of data file : ", b$
c$ = b$ + ".dat"
OPEN "r", #1, c$, 2
FIELD #1, 2 AS x$
GET #1, 513: gr = CVI(x$)
LOCATE 7, 8: PRINT "Current no. grating : "; gr
LOCATE 8, 8: INPUT "Do you want to correct no.grating ? (y/n) : ", d$
IF d$ = "y" THEN
    LOCATE 9, 8: INPUT "Grating no. : ", g
    a$ = MKIS(g): LSET x$ = a$: PUT #1, 513
END IF
GET #1, 514: p = CVI(x$)
LOCATE 11, 8: PRINT "Current central wavelength (nm) : "; p
LOCATE 12, 8: INPUT "Do you want to correct wavelength ? (y/n) : ", d$
IF d$ = "y" THEN
    LOCATE 13, 8: INPUT "Central wavelength (nm) : ", p1
    a$ = MKIS(p1): LSET x$ = a$: PUT #1, 514
END IF
GET #1, 515: f = CVI(x$)
LOCATE 15, 8: PRINT "Current laser wavelength (nm) : "; f
LOCATE 16, 8: INPUT "Do you want to correct wavelength ? (y/n) : ", d$
IF d$ = "y" THEN
    LOCATE 17, 8: INPUT "Laser wavelength (nm) : ", f1
    a$ = MKIS(f1): LSET x$ = a$: PUT #1, 515
END IF
FOR i = 1 TO 5
    CLS
    FOR k = 1 TO 5
        LOCATE 1, 4 + 15 * (k - 1): PRINT "No"
        LOCATE 1, 10 + 15 * (k - 1): PRINT "Data"
        LINE (124 + 120 * (k - 1), 1)-(124 + 120 * (k - 1), 293)
    NEXT k
    LINE (12, 12)-(602, 12)
    FOR k = 1 TO 5

```

```

FOR j = 1 TO 20
n = 100 * (i - 1) + 20 * (k - 1) + j
LOCATE j + 1, 3 + 15 * (k - 1): PRINT n
LOCATE j + 1, 9 + 15 * (k - 1): GET #1, n: a = CVI(x$): PRINT a
NEXT j
NEXT k
23 LOCATE 22, 2: INPUT "Do you want to correct any data ? (y/n) ", d$
IF d$ = "y" THEN
LOCATE 23, 2: INPUT "Data number to correct : ", dn
p = dn MOD 100: IF p = 0 THEN p = 100
l = (p MOD 20) + 1: IF l = 1 THEN l = 21
IF l > 21 THEN
c = p \ 20
ELSE c = p \ 20 - 1
END IF
LOCATE l, 10 + 15 * c: PRINT "    "
LOCATE l, 10 + 15 * c: INPUT "", dat
LOCATE 23, 2: PRINT "                "
LOCATE 22, 2: PRINT "                "
a$ = MKIS$(dat): LSET x$ = a$: PUT #1, dn
ELSEIF d$ = "n" THEN GOTO 21
END IF
GOTO 23
21 NEXT i
CLS
LOCATE 1, 4: PRINT "No": LOCATE 1, 10: PRINT "Data"
LINE (124, 1)-(124, 178)
LINE (12, 12)-(123, 12)
FOR k = 1 TO 12
LOCATE k + 1, 3: PRINT 500 + k
LOCATE k + 1, 9: GET #1, 500 + k: a = CVI(x$): PRINT a
NEXT k
27 LOCATE 22, 2: INPUT "Do you want to correct any data ? (y/n) ", d$
IF d$ = "y" THEN
LOCATE 23, 2: INPUT "Data number to correct : ", dn
p = dn - 500: LOCATE p + 1, 9: PRINT "    "
LOCATE p + 1, 9: INPUT "", dat
a$ = MKIS$(dat): LSET x$ = a$: PUT #1, dn
LOCATE 22, 2: PRINT "                "
LOCATE 23, 2: PRINT "                "
ELSEIF d$ = "n" THEN GOTO 25
END IF
GOTO 27
25 CLOSE : CLS
END SUB

```

```

SUB plot
  REDIM ar(515)
  CLS : LOCATE 4, 8: INPUT "Name of data file : ", b$
  c$ = b$ + ".dat"
  OPEN "r", #1, c$, 2
  FIELD #1, 2 AS x$
  FOR i = 1 TO 515
    GET #1, i: ar(i) = CVI(x$)
  NEXT i
  CLOSE #1
31 CLS : COLOR 15, 1: LOCATE 3, 15: PRINT "P L O T  M E N U"
  LOCATE 5, 5: PRINT "1 - Preliminary plot"
  LOCATE 7, 5: PRINT "2 - Final plot"
  LOCATE 9, 5: PRINT "3 - Exit"
  LOCATE 15, 5: INPUT "Option : ", mpl
  SELECT CASE mpl
  CASE 1
    CALL plotprelim(ar())
  CASE 2
    CALL finalplot(ar())
  CASE 3
    GOTO 30
  END SELECT
  GOTO 31
30 ERASE ar
END SUB

SUB plotprelim (ar())
  REDIM d(9)
  mag = 1242375: oblique = 0
  CLS : LOCATE 3, 8: PRINT "The initial data will be plotted. (white)"
  LOCATE 4, 8: PRINT "The data will be smoothed on 'n' channels and plotted "
  LOCATE 6, 12: PRINT " by preserving the counts. ";
  LOCATE 8, 8: PRINT "The program is continued by pressing 'y'."
  LOCATE 9, 8: PRINT "The program is interrupted by pressing 'n'"
  LOCATE 11, 8: PRINT "The top of the screen will show the current 'n'."
  LOCATE 18, 8: CALL y
  lprobe = ar(514): gr = ar(513)
  CALL display(lprobe, (gr), xmin, xmax, xl, xr, yu, yd, opti, lin, inf, titl$, llaser)
  ax = 620 - xl - xr: ay = 350 - yu - yd
  ymin = ar(1): ymax = ar(1)
  FOR i = 2 TO 512
    IF ar(i) > ymax THEN
      ymax = ar(i)
    
```



```

ELSEIF ar(i) < ymin THEN
    ymin = ar(i)
END IF
NEXT i
d(1) = ax: d(2) = xl: d(3) = xmin: d(4) = xmax
d(5) = ay: d(6) = yu: d(7) = ymin: d(8) = ymax: d(9) = llaser
mes$ = "y": n = 1: teddy = 1
WHILE mes$ <> "n"
    CALL border(15, (xl), (xr), (yu), (yd), (xmin), (xmax), (ymin), (ymax), (opti),
(llaser))
    CALL title(titl$, lin)
    CALL graph(ar(), n, 15, d(), lin, opti, oblique, 0, 0, 0, 0)
36 IF INKEY$ = "y" THEN
    GOTO 39
ELSEIF INKEY$ = "n" THEN
    mes$ = "n"
    GOTO 98
END IF
GOTO 36
39 LOCATE 3, 10: COLOR 2: PRINT "Want to change ymax , ymin ? (y/n)"
90 IF INKEY$ = "y" THEN
    teddy = 0
    LOCATE 5, 10: INPUT "Change ymin (1) or ymax (2) : ", dori
    LOCATE 7, 10
    SELECT CASE dori
        CASE 1
            INPUT "ymin = ", ymin: d(7) = ymin
        CASE 2
            INPUT "ymax = ", ymax: d(8) = ymax
    END SELECT
ELSEIF INKEY$ = "n" THEN
    teddy = 1
ELSE
    GOTO 90
END IF
93 CLS
IF teddy = 1 THEN
    n = n + 2
END IF
WEND
98 COLOR 15, 1: ERASE d
END SUB

SUB title (a$, li)
    a = LEN(a$): c = INT((60 - a) / 2)

```

```

    LOCATE li, c + 2: PRINT a$
END SUB

```

```

SUB transfer
CLS
OPEN "com2:9600,n,8,1,asc" FOR INPUT AS #1
LOCATE 4, 5
INPUT "Name of file where you want to store data : ", c$
f$ = c$ + ".dat"
OPEN "r", #2, f$, 2
FIELD #2, 2 AS z$
FOR i = 1 TO 515
INPUT #1, x, qe
d$ = MKI$(x): LSET z$ = d$: PUT #2, i
PRINT i, x
NEXT i
CLOSE
END SUB

```

```

SUB y
PRINT "      Press `y` to continue"
99 IF INKEY$ <> "y" THEN 99
END SUB

```

Appendix A.3 Point-group character tables

1. C_i group ($N = 2$)

C_i	E	I	Basis	
A_g	+1	+1	R_x, R_y, R_z	$x^2, xy, xz, ..$
A_u	+1	-1	x, y, z	

2. C_s group ($N = 2$)

C_s	E	Σ_h	Basis	
A'	+1	+1	x, y, R_z	x^2, y^2, z^2, xy
A''	+1	-1	z, R_x, R_y	xz, yz

3. D_{2h} group ($N = 8$)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	I	$\Sigma(xy)$	$\Sigma(zx)$	$\Sigma(yz)$	Basis	
A_g	+1	+1	+1	+1	+1	+1	+1	+1		x^2, y^2, z^2
B_{1g}	+1	+1	-1	-1	+1	+1	-1	-1	R_z	xy
B_{2g}	+1	-1	+1	-1	+1	-1	+1	-1	R_y	xz
B_{3g}	+1	-1	-1	+1	+1	-1	-1	+1	R_x	yz
A_u	+1	+1	+1	+1	-1	-1	-1	-1		
B_{1u}	+1	+1	-1	-1	-1	-1	+1	+1	z	
B_{2u}	+1	-1	+1	-1	-1	+1	-1	+1	y	
B_{3u}	+1	-1	-1	+1	-1	+1	+1	-1	x	

4. T_d group ($N = 24$)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\Sigma_d$	Basis	
A_1	+1	+1	+1	+1	+1		$x^2+y^2+z^2$
A_2	+1	+1	+1	-1	-1		
E	+2	-1	+2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	+3	0	-1	+1	-1	(R_x, R_y, R_z)	
T_2	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)

5. O group ($N = 24$)

O	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	Basis	
A_1	+1	+1	+1	+1	+1		$x^2+y^2+z^2$
A_2	+1	+1	-1	-1	+1		
E	+2	-1	0	0	+2		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	+3	0	-1	+1	-1	(R_x, R_y, R_z)	
T_2	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)

6. O_h group ($N = 48$)

O_h	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	I	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$	Basis
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
E_g	2	-1	2	0	0	2	-1	2	0	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1	(xy, yz, zx)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	
E_u	2	-1	2	0	0	-2	1	-2	0	0	
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	(x, y, z)
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1	

7. C_{2v} group ($N = 4$)

C_{2v}	E	C_2	$\sigma_v(zx)$	$\sigma_v(zy)$	Basis	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Appendix A.4 Notations used for group theory

1. Elements of symmetry (lower case)

c_n - axis of rotation of order n (rotation of angle $2\pi/n$).

$\sigma_{h,v,d}$ - plane of reflection (horizontal, vertical, diagonal, respectively).

i - inversion center.

s_n - improper axis of rotation of order n (axis of rotation of angle $2\pi/n$ followed by a reflection in a plane perpendicular to the axis of rotation).

2. Operations of symmetry (upper case)

C_n - rotation of order n (rotation of angle $2\pi/n$).

$\Sigma_{h,v,d}$ - reflection in a horizontal, vertical, diagonal plane, respectively.

I - inversion.

S_n - improper rotation of order n (rotation of angle $2\pi/n$ followed by a reflection in a plane perpendicular to the axis of rotation).

E - identity operation (leaves the object unchanged).

3. Other notations

χ - character (trace of the matrix of transformation).

Γ_X - total representation of object (molecule, ...) X .

4. Representations

a. Dimensionality

A , B - uni-dimensional representations (their character under E is 1, i.e.

$\chi_A(E) = 1$, $\chi_B(E) = 1$; their basis are one-dimensional vectors, ex. :

x, y, z). Note : A is symmetric with respect to C_n ($\chi_A(C_n) = 1$), B is anti-symmetric with respect to C_n ($\chi_B(C_n) = -1$).

E - bi-dimensional representations ($\chi_E(E) = 2$; their basis are two-dimensional vectors, ex. : $(x, y), (z, x), \dots$).

T (or F) - tri-dimensional representations ($\chi_T(E) = 3$; their basis are three-dimensional vectors : (x, y, z)).

b. Superscripts

' - the representation is symmetric with respect to reflections in a horizontal plane (ex. : $\chi_{B'}(\Sigma_h) = 1$).

" - the representation is anti-symmetric with respect to reflections in a horizontal plane (ex. : $\chi_{B''}(\Sigma_h) = -1$).

c. Subscripts

g - the representation is even ("gerade") with respect to inversion (ex. : $\chi_{A_g}(I) = 1$).

u - the representation is odd ("umgerade") with respect to inversion (ex. : $\chi_{A_u}(I) = -1$).

Note : "g" and "u" appear only for groups which have an inversion center.

1 (for A and B) - the representation is symmetric with respect to C_2 (c_2 is an axis of order 2 perpendicular on c_n), or is symmetric with respect to Σ_v (ex. : $\chi_{A_1}(C_2) = 1, \chi_{B_1}(\Sigma_v) = 1$).

2 (for A and B) - the representation is anti-symmetric with respect to C_2 (c_2 is an axis of order 2 perpendicular on c_n), or is anti-symmetric with respect to Σ_v (ex. : $\chi_{A_2}(C_2) = -1, \chi_{B_2}(\Sigma_v) = -1$).

1 (for E and T) - the representation is symmetric with respect to C_n (ex. : $\chi_{E_1}(C_n) = 1$).

2 (for E and T) - the representation is anti-symmetric with respect to C_n (ex. :

$$\chi_{T_2}(C_n) = -1).$$

5. Group notations

C_i - the group has only an inversion center (c_i); i.e. the group has only two elements of symmetry : E (identity operator) and I (inversion).

C_s - the group has only a reflection plane (σ_h); i.e. the group has only two elements of symmetry : E (identity operator) and Σ_h (reflection).

C_n - the group has only an axis of rotation of order n, c_n .

C_{nv} - the group has c_n and n vertical planes passing through c_n , σ_v .

C_{nh} - the group has c_n , σ_h and s_n .

$D_{nh,v}$ - the group has c_n , diagonal planes of reflection σ_d and/or n c_2 axes perpendicular on c_n .

S_n - the group has s_n , $c_{n/2}$ and (eventually) i.

T, T_d , T_h , O, O_h - cubic groups.

I, I_h - icosahedral groups.

6. Symmetry of different transition operators $\hat{O}$

Operator	Notation	Symmetry
Electric dipole (absorption, emission, IR-active phonons)	$\hat{P}$	x, y, z
Translations	$\hat{T}$	x, y, z
Raman tensor (Raman active phonons)	$\hat{R}$	$x^2, xy, yz, \dots$
Electric quadrupole	$\hat{Q}$	$x^2, xy, yz, \dots$
Rotations	$\hat{R}$	R_x, R_y, R_z
Magnetic dipole	$\hat{M}$	R_x, R_y, R_z

Appendix A.5 Code for program calculating the B, C and Dq crystal field parameters - "Tanabe"

```

DIM w(11): DIM e(11)
20 CLS : sum = 10 ^ 12: unu = 0: doi = 0: trei = 0
INPUT "Dq (Dq positive) =", dq      'Input value given by the measured
                                     'energy of the  $^3T_2(^3F)$  state divided by 10 - see Eq. (3.84)
INPUT "B =", b                      'Input the B value for the free ion;
                                     'for  $Cr^{4+}$  B = 1039 cm-1
INPUT "C =", c                      'Input the C value for the free ion;
                                     'for  $Cr^{4+}$  C = 4238 cm-1
INPUT "Measured energy of the  $^3T_2(^3F)$  level (in cm-1) =", w1
                                     'For  $Cr^{4+}:Mg_2SiO_4$  w1 = 10140
INPUT "Measured energy of the  $^3T_1(^3F)$  level (in cm-1) =", w2
                                     'For  $Cr^{4+}:Mg_2SiO_4$  w2 = 15610
INPUT "Measured energy of the  $^1E(^1D)$  level (in cm-1) =", w3
                                     'For  $Cr^{4+}:Mg_2SiO_4$  w3 = 15875
INPUT "Measured energy of the  $^3T_1(^3P)$  level (in cm-1) =", w4
                                     'For  $Cr^{4+}:Mg_2SiO_4$  w4 = 26810
INPUT "Measured energy of the  $^1T_1(^1G)$  level (in cm-1) =", w5
                                     'For  $Cr^{4+}:Mg_2SiO_4$  w5 = 28735

FOR i = dq - 200 TO dq + 200 STEP 5
FOR j = b - 200 TO b + 200 STEP 5
FOR k = c - 200 TO c + 200 STEP 5
w(1) = -8 * j + 10 * i              'Eq. (3.81) for the ground state  $^3A_2(^3F)$ 
w(2) = -8 * j                      'Eq. (3.78) for  $^3T_2(^3F)$ 
e(2) = w(2) - w(1)                 'Energy of the  $^3T_2(^3F)$  state
w(3) = (-10 * i - j - SQR(100 * i * i + 180 * j * i + 225 * j * j)) / 2
                                     'Eq. (3.71) for  $^3T_1(^3F)$ 
e(3) = w(3) - w(1)                 'Energy of the  $^3T_1(^3F)$  state
w(4) = (4 * k + j - SQR(400 * i * i + 49 * j * j - 40 * j * i)) / 2
                                     'Eq. (3.63) for  $^1E(^1D)$ 
e(4) = w(4) - w(1)                 'Energy of the  $^1E(^1D)$  state
w(5) = (-10 * i - j + SQR(100 * i * i + 180 * j * i + 225 * j * j)) / 2
                                     'Eq. (3.72) for  $^3T(^3P)$ 
e(5) = w(5) - w(1)                 'Energy of the  $^3T(^3P)$  state
w(6) = 4 * j + 2 * k                'Eq. (3.75) for  $^1T_1(^1G)$ 
e(8) = w(8) - w(1)                 'Energy of the  $^1T_1(^1G)$  state
s = (e(2) - w1) ^ 2 + (e(3) - w2) ^ 2 + (e(4) - w3) ^ 2 + (e(5) - w4) ^ 2 + (e(6) - w5)
^ 2
IF s < sum THEN
    sum = s: unu = i: doi = j: trei = k

```

```
    PRINT sum, "dq="; unu, "b="; doi, "c="; trei
END IF
NEXT k
NEXT j
NEXT i
PRINT : PRINT sum, "dq="; unu, "b="; doi, "c="; trei
END
```

Appendix A.6 Mathematica program used for obtaining Figs. 6.7 a,b

'This program uses the dependencies of the two tetrahedral breathing modes A_1 on second neighbor parameters given by Eq. (6.34) and plots the results as shown by Figs. 6.7 a, b.

```
m=16; a=3.27; b=.57          'm = mass of Oxygen (in m.u.), a = k1, b = k2
                                (in mdyn/Å)
be[t_,c_]:=t/3*(a+4*b+0.75*c)+m*c;    't = 3m2 = 1/2 Mg mass, c = k3
ce[c_]:=c*(a+4*b);
ae[t_]:=m*t          ' the previously defined ae, be, ce are the coefficients
                      of Eq. (6.34) written as ae*ω4 + be*ω2 + ce = 0
f[t_,c_]:=((be[t,c]+(be[t,c]^2-4*ae[t]*ce[c])^0.5)/
(2*ae[t])/1.67*10^29)^0.5/6/Pi/10^10;    'f[t,c] is ω (in cm-1) in Eq. (6.34)
g1=Plot3D[f[t,c],{t,8,16},{c,0.1,0.39},ViewPoint->{-2.09,-2,1.24},BoxRatios->
{1,1,1}]
```

Note : The expression for the low frequency mode ω_2 is obtained using the same program, where the a “-“ sign is used in the expression for f[t_,c_] such that :

```
f[t_,c_]:=((be[t,c]-(be[t,c]^2-4*ae[t]*ce[c])^0.5)/
(2*ae[t])/1.67*10^29)^0.5/6/Pi/10^10
```

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