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**LASER BRILLOUIN AND RAMAN SCATTERING INVESTIGATION OF THE
MELTING TRANSITION IN THE MOLECULAR CRYSTAL SALOL**

City University of New York

Ph.D. 1984

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LASER BRILLOUIN AND RAMAN SCATTERING INVESTIGATION OF
THE MELTING TRANSITION
IN THE MOLECULAR CRYSTAL SALOL $C_{13}H_{10}O_3$

BY
MUHAMMAD ABDUL AWAL

A dissertation submitted to the Graduate Faculty in
Physics in partial fulfillment of the requirements for the
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York, New York.

1983

This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

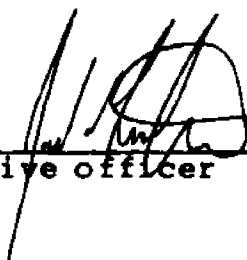
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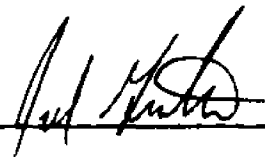
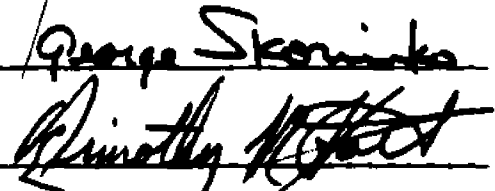
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Abstract

LASER BRILLOUIN AND RAMAN SCATTERING INVESTIGATION OF THE MELTING TRANSITION IN THE MOLECULAR CRYSTAL SALOL $C_{13}H_{10}O_3$

by

Muhammad Abdul Awal

Advisor: Professor Herman Z. Cummins

Light scattering studies of the melting transition in phenyl salicylic acid commonly known as salol have been performed. Using a $5145\text{\AA}$ argon ion laser, both Brillouin and Raman scattering experiments on salol were performed very close to the melting point and down to room temperature. In the Brillouin scattering measurements, the velocity and attenuation of the acoustic modes have been determined to within 0.01°C of the melting point ($T_m \sim 41.0^\circ\text{C}$). Single-pass and triple-pass interferometers were used which yielded a working finesse of 50 and 70 respectively. The Brillouin spectra were analysed by a

non-linear least squares fitting program with eighteen parameters in order to determine the Brillouin shift and the deconvoluted Brillouin linewidth accurately.

Deconvoluted Brillouin linewidths were determined by fitting each observed Brillouin component to a Voigt profile which reduces to a Lorentzian and a Gaussian at its two extrema. Within 0.01°C of T_m both a decrease of Brillouin shift and an increase in linewidth were observed in all three Brillouin modes of salol. The observed sound velocity decreased to 80% of its room temperature value near T_m . Though Born's melting criterion could not be completely tested, the observed continuous decrease of sound velocity was attributed qualitatively to the effect of defects generated near T_m .

The most prominent result was the observation of a rapid increase of Brillouin linewidth near T_m . This result was interpreted by a simple dislocation model, in which the concentration of thermally activated dislocations was assumed proportional to the observed hypersonic attenuation. By taking the temperature dependent dislocation density as $\rho_D(T) \sim e^{-\frac{E_D(T)}{k_B T}}$, the temperature dependence of the dislocation formation energy $E_D(T)$ was extracted from the measured temperature dependence of the Brillouin linewidths for different background linewidths

which had no effect on the temperature dependent behavior of $E_D(T)$. The formation energy continuously decreased towards T_m and showed upto 60% decrease from its room temperature value near T_m indicating the onset of rapid growth (faster than exponential) of dislocations near T as predicted by the dislocation theory of melting. The linewidth on the liquid side cannot be predicted by this model.

Through room temperature Brillouin scattering measurements on six different samples, the complete set of elastic and elasto-optic coefficients of salol was determined for the first time. Poekel's coefficients were calibrated with quartz via benzene. The complete set of Brillouin Scattering tensors for all necessary phonon wavevector directions q was also calculated for both isotropic and anisotropic (n_x, n_y, n_z being different) considerations. A second set of elastic coefficient tensors of salol was also determined experimentally utilizing anisotropic considerations. The determined refractive indices at $\lambda = 5145\text{\AA}$ were:

$$n_x = 1.5473 \pm 0.0265, \quad n_y = 1.812 \pm 0.0233 \quad \text{and} \\ n_z = 1.6513 \pm 0.0145.$$

Raman scattering experiments showed $\sim 5\%$ softening of some salol optical phonons near T_m . The observed change in relative intensities of the Raman modes suggested molecular rotation during melting. The observation of up to eight new modes near T_m which were present in neither the room temperature crystal nor in the liquid spectra at T_m , were attributed to activation by thermally generated defects near T_m which further strengthens the dislocation theory interpretation of the melting phenomenon. One experiment was carried out with melt-grown succinonitrile which also showed a decrease of Brillouin frequency and broadening of linewidth in its longitudinal acoustic mode. Melting experiments were carried out on various solution-grown and melt-grown (zone refined) salol samples which were grown by the author. The lack of a fully structured theory of melting limited the interpretation of the results of this experiment to qualitative and semiquantitative analyses.

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I express my gratitude to Professor Herman Cummins for his patient guidance and continued support during the research for and writing of this thesis.

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Moreover, I express a special affection to my high school teacher Sheik Ataul Hoque who inspired me to study physics at the age of 14. I am also thankful to Professor Gunar Berg and Professor Frederick Froelich of the University of Halle in Germany whose friendship and understanding also contributed to making this achievement possible.

DEDICATION

I dedicate this effort, and
the good it represents, to
my mother and father with
love and prayer.

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CHAPTER I

INTRODUCTION

The melting transition is one of the most fundamental of all phase transitions and has been extensively investigated both theoretically and experimentally for many decades. Faraday in 1850 devised various elegant demonstrations to show that increased pressure lowered the melting point of ice. Measurements with reasonable precision of the heat changes accompanying melting came fairly late in the development of calorimetry. Bunsen's ice calorimeter gave close correlation between the volume change and the latent heat[1].

Although the gross features of the melting transition are generally understood, there is still no microscopic picture of exactly what happens when a crystal melts[2]. Since melting involves a drastic change of symmetry in that the essentially infinite long range order of the crystal disappears completely in the liquid state, the development of a complete theory will undoubtedly be extremely difficult.

The most fundamental unanswered question about melting concerns the underlying dynamical mechanism of the

transition. The usual assumption is that melting is entirely a first order phenomenon in which two distinct phases, liquid and solid, attain the same free energy at the melting temperature T_m where the transformation from solid to liquid occurs discontinuously, driven by random thermodynamic fluctuations. This interpretation is consistent with the usually large entropy of melting and with the observed discontinuous change at the melting transition in a number of physical properties including volume, specific heat, conductivity, viscosity and diffusion coefficients of most crystals.

On the other hand, there are several theories and some experimental evidence in favor of a dynamical process involving a quasi continuous change. Of these, the most important are Born's [3] proposal of a continuous decrease of the shear rigidity to zero at T_m , Lindemann's conjecture that increasing vibrational motion destabilizes the lattice[10], and the possibility of a drastic increase of the defect concentration at or near T_m , known as the defect theory of melting [4,5,6].

As we review the experimental studies of the melting transition in chapter II we shall see how little consistent experimental evidence about melting has been reported so far. A major reason for this lack of experimental information lies in the difficulty of

performing any type of experiment during melting. Among the various experimental techniques applied so far in melting experiments are neutron scattering, ultrasonic measurements and thermodynamic measurements. Very few experiments have employed light scattering spectroscopy. As in the case of ultrasonic measurements, one can also deduce information on sound velocities and attenuation in solids through Brillouin scattering spectroscopy.

The present thesis research involved an experimental investigation of the melting transition in salol by Brillouin and Raman scattering spectroscopy techniques, with the goal of testing the Born postulate and the defect theory of melting. From the measurements of temperature dependent Brillouin shifts, I determined the variation of the shear rigidity near T_m and from the measurement of Brillouin linewidths, the defect formation energy was calculated by a simple dislocation model of melting assuming the concentration of generated dislocations to be proportional to the hypersonic attenuation to see if the formation energy approaches zero near T_m , as predicted by the dislocation theory of melting[6]. In a recent experiment, Catlow et al [9] showed by Brillouin scattering experiments that in fluorite crystals the generation of disorder at the critical temperature for sublattice melting associated

with ionic conductivity causes a large decrease in C_{11} . But a change in linewidth or attenuation in sound velocity due to defect generation has not been reported yet either by laser scattering technique or by ultrasonic measurement. In that respect, the present work is the first to report both a continuous decrease in shear rigidity and significant increase in ultrasonic attenuation as the crystal was gradually brought to the melting temperature T_m . Previous reports on the changes in the elastic coefficients at T_m will be reviewed in chapter II.

In chapter II an experimental and theoretical review of the history of the melting transition is given. Chapter III presents a brief review of light scattering theory with emphasis on Brillouin and Raman scattering. The structure, properties and growth mechanism of the materials used (salol and succinonitrile) in the experiments are described in chapter IV. In Chapter V the Brillouin scattering tensors required to determine the complete set of elastic coefficients and Pockel's coefficients of salol are derived. Chapter VI discusses the experimental apparatus and considerations particular to this experiment including a brief description of the computer programs and how they control various aspects of the experiment including interferometer alignment and data collection. A brief

description of all the melting and room temperature experiments on different samples is given in chapter VII. Part I of chapter VIII describes the data analysis, and the results of the experiments are summarized in part II. A pronounced temperature dependence of elastic coefficients and Brillouin linewidth was found which provides strong evidence in favor of the defect theory of melting.

Chapter IX is the concluding chapter which discusses and interprets the results of this thesis on the basis of current theories and presents some considerations relevant to future experimentation. The growing importance of large high quality single crystals for semiconductor and optical devices requires an improved understanding and management of the underlying melting mechanisms. That requirement was a major motivation for applying one of the most powerful contemporary experimental techniques (laser light scattering) to obtain some clear experimental information about melting phenomena.

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CHAPTER I I

HISTORY OF THE MELTING TRANSITION: A THEORETICAL AND EXPERIMENTAL REVIEW

A. Introduction

The crystalline and liquid states of condensed matter are so familiar that it is surprising how little we know about the relationship between them. A crystal melts when its temperature reaches a certain value, but just what happens at the atomic level remains a mystery, although the gross features of the melting transition are understood.

One reason for our lack of knowledge about the microscopic picture of melting is its inaccessibility to experiment. The obvious approach, therefore, is to make observations on the solid and liquid states as close as possible to the melting point, and look for any changes in the physical parameters of the system. The macroscopic parameters which are known to show anomalies through the melting transition are: density, latent heat, thermal and electrical resistivity, the solid-liquid interfacial energy, diffusion constant, shear modulus, sound velocity and attenuation, and viscosity[1].

Another difficulty in forming a unified theory of melting is the lack of understanding of the liquid state. If we had an acceptably detailed picture of liquids, the melting transition would probably be less puzzling. The most important experimental technique in the study of liquids are diffraction of electrons, x-rays or neutrons which provide some structural and dynamical information. But with unavoidable spatial and temporal integration, such experiments produce only an average picture[2].

At the macroscopic level, thermodynamics provides an adequate guide. It tells us for example, that the free energies of a crystal and the corresponding liquid are equal at the melting point. But it tells nothing about how to calculate the free energy of a liquid. The atoms in a crystal are deployed in an orderly fashion, and apart from occasional diffusive hops, they merely vibrate about fixed sites. A liquid lacks the symmetrical pattern of the crystal, but its structure is not entirely devoid of order. In addition, the atoms in a liquid appear to translate and vibrate simultaneously. The transverse acoustic waves present in a crystal disappear in the liquid since a liquid can't resist against shear, but the longitudinal waves are still present.

Melting of the crystalline state of matter is

classically understood to be a first order phase transition involving an absorbtion of heat. In the opinion of a number of experimentalists, melting is a heterogeneous process that occurs by nucleation and subsequent growth through the movement of a solid-liquid interface.

In the next section, I shall review several theoretical pictures of melting phenomena with emphasis on Born's theory of melting and the dislocation theory of melting. Previous experiments on melting will be discussed in section C. Section D will briefly review previous experiments on salol, including melting experiments.

B. Theories of Melting

During the past seventy years, a number of melting theories have been proposed, and they have ranged from modest attempts to explain some of the obvious features of the phenomenon, to more ambitious efforts in which the changes of several parameters across the transition have been quantitatively accounted for, but only a very few of them actually attempted to give a detailed description of atomic motions involved in the transition. Two of the better known theories are due to Lindemann[3] and

Born[4]; a third more modern one is the defect theory of melting proposed by several authors [5,6,7,8,9].

Following is a description of each of those three theories.

1. Lindemann's Theory

The first and simplest dynamical explanation of melting was suggested by F.A. Lindemann in 1910. He suggested that a solid should melt when the root mean square amplitude of thermal vibrations of the constituent atoms reaches a certain value r_{rms} given by:

$$r_{rms} = (9h^2 T / 4\pi^2 M k_B \theta_D^2 r_s^2)^{1/2} \quad (3-1)$$

where T is the temperature, M the atomic mass, θ_D the Debye temperature and r_s the Goldschmidt atomic radius. It has been found that for all elements having a mutually common crystal structure, r_{rms} is approximately constant. Many experiments have been interpreted on the basis of Lindemann's postulate by many authors, and several theoretical modifications have been proposed [10,11,12,13]. McLachlan et al [13] have reconsidered Lindemann's theory and have managed to calculate reasonable values for a number of metals, working essentially from first principles. A recent work by Pietronero [12] suggested that the melting instability in simple ionic compounds is dominated by the dynamics of

the larger ion. He found the variation of T_m with pressure was due to change of the force constants between ions. Surprisingly, Lindemann's theory is the only microscopic theory of melting till today. In section C I shall enumerate some recent experiments on the measurement of lattice parameters through the melting transition which can be explained by Lindemann's theory.

2. Born's theory of melting:

In 1939, Born considered the problem of melting as part of the general theory of the stability of crystal lattices. From the difference between a solid and a liquid, the former with elastic resistance against shearing stresses and the latter without, he formulated this theory from an investigation of the stability of a lattice under shearing stress. He derived the general conditions for stability of a bcc lattice, and suggested that melting would occur when the shear modulus (elastic constant) C_{44} becomes zero, which would constitute a violation of the conditions of stability. Voluminous theoretical and experimental work followed Born's ideas of the melting transition.

The temperature dependence of elastic constants was calculated in the quasi-harmonic approximation by Liebfried [15], who found C_{11} decreasing faster than

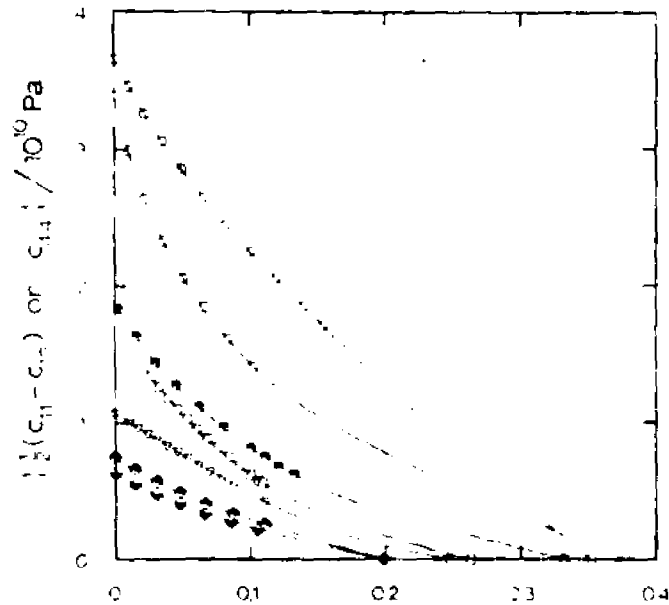


Fig. 2-1: The shear modulus $1/2 (C_{11} - C_{12})$ as a function of true dilation in the solid and in the melt. The modulus appears to fall continuously to zero at the dilatation of the melt at the melting point. $\square$ KCl, $\circ$ NaCl, $\triangle$ NaF, $\blacksquare$ denotes CsBr and $\blacklozenge$ denotes CsI and for these two salts the modulus is C_{44} .
(From: Tallon and Robinson [17])

temperature T_I with the lattice instability very close to T_m . Jackson and Liebermann [20] calculated stability criteria for alkali halides with the CsCl structure, and by comparing with ultrasonic data of C_{ij} as a function of P and T , showed a close connection between shear instability and melting.

3. Dislocation Theory of Melting

Most modern theories of melting invoke defects (or dislocations) as the fundamental source for destroying the crystal structure. The origins of the dislocation model of melting goes back to Boltzman [21] in 1896, who suggested that melting occurs because atoms acquire enough energy and free volume to slip past one another. We now know that slip in crystals proceeds through the motion of dislocations. Another early theory that emphasized the possible importance of defects in melting was formulated by Mott and Gurney in 1930. They pictured a liquid as resembling a polycrystal with an average grain diameter spanning just a few atoms. Because grain boundaries are formally equivalent to arrays of dislocations, the Mott-Gurney model is related to the dislocation theory of melting which has been prominent in the last four decades. In 1952, Schockley accounted for the fluidity of a liquid by assuming it to be equivalent

to a crystal with a high density of moving dislocations.

The dislocation theory of melting in its present form first emerged in simultaneous, but independent studies by Mizushima [9] and Ookawa in 1960, the crucial feature being a cooperative factor which lowers the dislocation formation energy as the dislocation concentration increases. By making reasonable assumptions about the entropy of a dislocation array, they showed that there must be a temperature at which the free energies of a perfect crystal and one saturated with dislocations are equal, and this was identified with the melting point. Melting, in this model, therefore corresponds to a rapid and catastrophic increase in the concentration of dislocations. This suggestion was further elaborated by Nabarro [5] who assumed that the local structure of a liquid close to its freezing point is similar to that of a solid, but in its equilibrium configuration there is some concentration of dislocations which can move to the surface under the influence of an arbitrarily small shear stress and so produce viscous flow. In the solid state, there are no free dislocations in equilibrium, and so the system is rigid.

Edwards [7] recently showed that an important term was missing from these earlier analysis. Each dislocation that is generated increases the overall

volume, and when this factor is included, the free energy varies with dislocation concentration in a way predicted by Landau for a first order transition. There are two different hypotheses about how dislocations are generated. Kuhlman-Wilsdorf suggested that they would be generated in the form of dipoles. Siol proposed that the dislocations would be of shear type and form closed loops. Another dislocation model was proposed by Ninomiya [8] who calculated several melting characteristics which were in close agreement with computer simulation results. The details of computer simulation results will be presented later.

4. 2-D theories of melting

With the development of experimental techniques for studying two-dimensional phenomenon, the 2-D melting problem became one of the growth fields in condensed matter physics. The first 2-D melting model was proposed by Kosterlitz and Thouless [22], who suggested that melting would occur when thermally activated dislocation pairs dissociate at sufficiently high temperature. The dynamics of melting in two dimensions was later studied by Zippelius, Halperin and Nelson [23] assuming that solids melt into liquids via a sequence of dislocation and disclination unbinding transitions. Unlike three

dimensional solids, dislocations are pointlike imperfections in two dimension, which are much simpler to study. A more recent 2-D melting model was proposed by Greif [24], who calculated a critical temperature consistent with the melting point as suggested by the Kosterlitz-Thouless-Nelson -Halperin-Young model. A calculation was also made by Kagan[25] to determine the effect of defect-phonon interactions on sound attenuation in 2-D.

5. Molecular dynamic theories: computer simulation model.

The recent advent of fast electronic digital computers with large memory capacities has spurred the development of the technique of molecular dynamics. With this technique the motions of individual atoms under the influence of known forces can be studied. It is possible to follow the temporal evolution of an assembly of atoms and to observe directly the response of such a system to mechanical and thermal stimuli.

From the computer simulation study of melting by Cotterill [1], a microscopic picture emerges. He finds the driving force for melting arising from the fact that above a certain temperature the disordered state of the liquid has a lower free energy than that of the ordered crystalline solid. The transition from order to disorder

is then accomplished by the sudden proliferation of dislocations, and it is completed when the dislocation density is so high that the dislocation cores are contiguous, whereupon all long range order has disappeared. In his work Cotteril shows that the introduction of these dislocations accounts for the changes in volume, entropy, diffusion constant, viscosity and the ability to support shear stress, while the latent heat is simply the energy required to generate the dislocations. More recent computer simulation studies of melting can be found in [26,27].

6. Miscellaneous melting theories

There are other theories of melting referred to less frequently such as the vacancy theory of melting first propounded by Frenkel in 1927, in which vacancies played a central role in the melting process. The first melting theory based on interstitials was put forward by Lennard-Jones and Devonshire [28] who proposed melting as the transition from order to disorder due to formation of interstitials. Instability of a particle under the action of its neighbors (Rashevsky 1927), and instability of vibration of two rigid sublattices against each other [Braunbeck, 1926] have also been suggested to cause melting. The reader should consult the recent

(1978) melting reviews of Ubbelohde [29] for other thermodynamic theories of melting.

C. Review of experimental studies on melting

Unfortunately, the melting transition is not particularly accessible to experiment. The best approach is to make observations on the solid and liquid as close to the transition as possible, and this strategy has already yielded a considerable body of experimental data during the past three decades on thermodynamic, mechanical, electrical, optical and microscopic properties, against which various theories can be tested. In the first section of this review of past experimental studies of the melting transition, I shall describe the results of various experimental techniques applied in the study of the melting transition. A number of light scattering experiments on the melting transition have followed the above approach and have added considerably to the literature of this field a comprehensive review of which I shall present in section 2. Section 3 will briefly summarize the past experiments on salol and succinonitrile, which were the materials used in this experimental work.

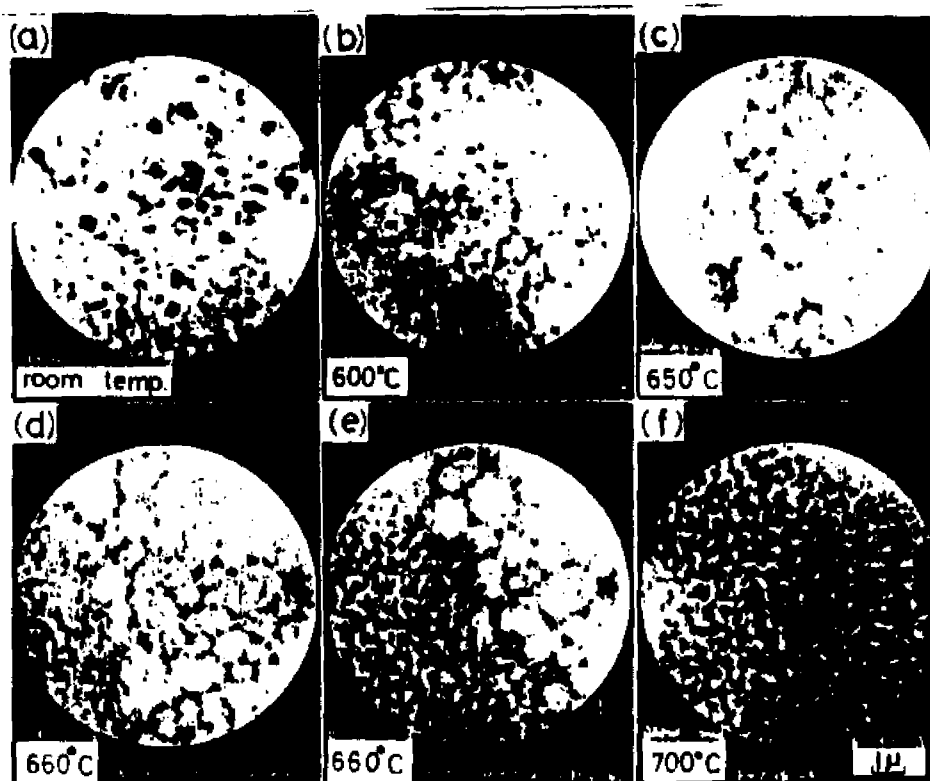
(1) Miscellaneous Experimental Studies on Melting

(a) High Voltage Electron Microscope

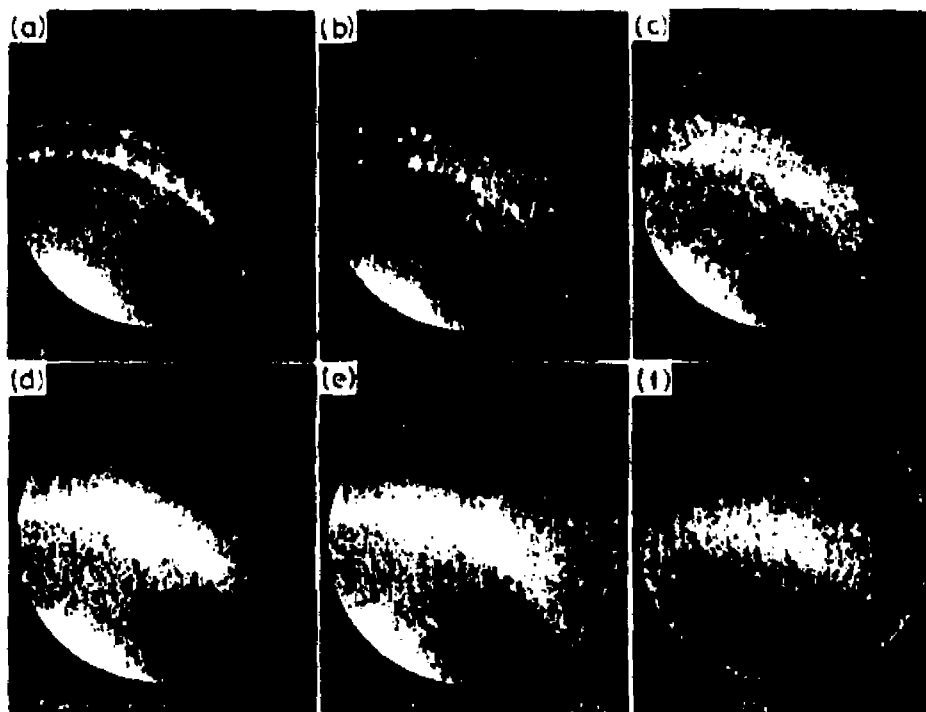
The HVEM is the only technique where one can directly visualize the successive stages of the melting transition and detect changes in microscopic parameters. One such direct observation was made by Fujita et al [30] with an electron microscope. They examined the behavior of dislocations in solid aluminium in successive stages of melting, and recorded by video-tape recording (see fig. 2-2). Evidence for the growth of dislocation in silicon near T_m was also obtained by Narayan and Young [31] by transmission electron microscopy.

(b) Ultrasonic Measurement

The ultrasonic method had been the only technique to probe the elastic properties of solids near the melting point. Hunter [32] in 1942 was the first to test the Born criteria of melting by measuring the elastic constants of NaCl by ultrasonic techniques. By ultrasonic measurements through the melting transition in molecular crystal, Konev and Koshkin [33,34] reported a drastic decrease in sound velocities and a large increase in sound attenuation near T_m . For benzene,



Successive stages of melting process of an aluminum foil in a carbon-capsule. These micrographs were taken at 0.85 MV by a video-tape recording



Video-tape recording of changing the diffraction patterns during melting in an aluminum foil. Extra rings at both sides of a halo-ring in (f) are due to oxides. These patterns were taken at 0.85 MV.

FIG. 2-2 (From Fujita et al [30])

they reported that the shear modulus decreased from 7×10^9 dynes/cm² at -6°C to 4×10^6 dynes/cm² at -1.9°C corresponding to a decrease in velocity from 840 m/sec to 20 m/sec [$T_m = 5.5^\circ\text{C}$].

In contrast to these results, Varshni [35] showed that for six FCC metals the elastic constant C_{44} at T_m is close to 0.55 times its value at 0°C , and argued against Born's conjecture that $C_{44} \rightarrow 0$ at T_m . The relationship between melting and shear instability of a crystal was further determined by Jackson [20], through ultrasonic measurements of temperature and pressure dependence of the elastic constants. For ultrasonic measurements one needs a big single crystal, and it becomes very difficult to maintain a bond between transducer and crystal close to melting. That's why Brillouin scattering measurements of the same parameters (C_{ij} and α) are more accurate and reliable. Y. Hiki [36] showed in the measurement of sound attenuation through the melting transition that the dislocation density fluctuates severely near T_m .

(c) Neutron scattering measurement

The most important experimental technique in the study of liquids is diffraction. In addition to structural information, neutron scattering data can also

provide information about the atomic motions since the energy of thermal neutrons is comparable to the atomic translational energy in the solid and liquid phases. Some recent neutron scattering experiments [37] have also been able to study defects in Silicon. Thomas [53] could determine the concentration of interstitials in fluorite crystals at high temperature by neutron diffraction experiments. R.K. Crawford [38] investigated the neutron scattering of rubidium near the melting transition. His results showed no change in the transverse acoustic modes at T_m except for that due to thermal expansion. Similarly, the neutron scattering studies of aluminium and lead near their melting transitions by Klaestrip-Kristensen [39] also ruled out any elastic anomalies near T_m . Other neutron scattering experiments [40] failed to establish any relation between lattice instability and melting. The most recent neutron scattering study of the melting transition in ^3He surface-layers was reported by Feile [41]. Through a simple model assuming the melting transition to be driven by thermally created lattice defects, they could explain the changes in nearest neighbor distance and peak intensity.

(d) X-ray studies

Scattering of beams of x-rays from a crystal near the melting transition provides information about the gradual changes in the structure of the solid. Chickawa and Sato [42] could directly view the melting and growth process in Silicon crystals by x-ray topography. They observed high mobility of dislocations just at T_m which may have reduced the solid-liquid interfacial energy. Tohji and Murata [43] observed the melting and premelting process of benzene using an energy dispersive x-ray diffractometer. They related the observed intensity changes of Bragg peaks to the changes in the molecular arrangements. They also found the molecular structure of the solid just below T_m to be similar to that of the liquid. Further x-ray studies of crystals through the melting transition are reviewed in [44,45].

(e) NMR measurements

Measurements of relaxation times by NMR techniques have been reported by many authors. Hwang et al [46] could study the defect properties of a crystal by NMR experiments. Thermal behavior studied by the NMR technique was reported in [47].

(f) IR measurements

Very few melting experiments by IR emission and absorption have been reported so far. Mead and Wilkonson [48] observed a decrease in emissivity (at low frequencies) for alkali halides through the melting transition. An IR absorption measurement on salol was reported by Ansari [49].

(g) Defect concentration measurements

It has been established by many melting experiments that thermally activated defects disrupt the long range crystalline structure producing the melt. But it has been very difficult to monitor the increase of defect concentration through the melting process. The measurement of dislocation density from the shrinkage of carbonyl nickel powder during sintering was reported by Taskinin [50]. Galkin [51] observed the pressure dependence of dislocation density at the initial stages of plastic deformation. Changes in the dislocation density was inferred by Sinvani [52] from the measurement of electrical resistance of films. Determination of defect density by a neutron scattering study was already described in [53].

(h) Measurements of lattice parameters.

Since Lindemann's postulate in 1910, many melting

experiments reported on the measurement of atomic parameters. A drastic decrease in the lattice parameters of alkali halides was observed by Kotelnikov[10]. A very precise lattice parameter measurement by Adlhart [54] using a neutron double crystal back-scattering device showed a decrease in the lattice parameters of highly pure sodium single crystal near the melting transition. Zhaanov [55] in the melting study of anisotropic crystals related the observed changes in the lattice parameters to the shear instability.

(i) Thermodynamic measurements

Changes in volume, entropy and specific heat on melting are well known. These parameters describe melting as a purely first order transition. Levanyuk [56] studied the influence of defects on thermodynamic properties during melting. In a recent work, A.R. Ruffa [18] related the thermodynamic potential and mechanical instability to the melting entropy. A similar study of the instability of the shear modulus relates it to the changes in heat capacity of the solid.

(j) Measurements of mechanical, electrical and optical properties

Since the instability criterion of Born was put

forward as a possible theory of melting, measurements of shear rigidity became one of the main techniques for melting experiments. No melting experiment revealed a continuous decrease of shear modulus from solid to liquid. Until the advent of the laser, elastic constants were primarily determined by ultrasonic measurements. Now they can also be determined by Brillouin scattering spectroscopy. Most of the measurements show a discontinuous drop of shear modulus from solid to liquid[57].

The most dramatic change through the melting transition is observed in fluidity. It increases approximately by a factor of 10^{19} . Most other properties show a relatively subtle change. The volume change ΔV is usually positive and on the order of a few percent. The diffusion constant is typically about 10^{-9} cm²/sec in a crystal just below T_m and 10^{-5} cm²/sec in a liquid just above T_m . A continuous increase of the diffusion constant in In was observed by Eckert and Drickamer [58]. The change in electrical resistivity on melting has been measured for several metals, and it is frequently less than a factor of two. Frisch observed a volume expansion, anomalies in thermal and electrical conductivities and sound velocities of Na [59] very close to T_m . Variations in thermal expansion

and compressibility were observed by Pruzan [60] in solid ammonia through the melting transition.

Fernandez [61] reports dielectric and optical measurements of a crystal from room temperature to the melting point, and found anomalies in the refractive index. McFarlane, Courtens and Bischofberger [62] studied the refractive index n of succinonitrile near T_m , and found a discontinuous drop in n for a pure crystal whereas a downward bending was observed in n with small residual impurity concentrations present.

(k) 2-D melting experiments

Many experiments have been performed on the melting of thin films. Damodara and Jayaprakash [63] report a melting experiment on thin film silicon. They suggest a decrease of defect density with increase of substrate temperature in the growth and nucleation process of those thin films. An experimental observation of continuous melting of thin films into the hexatic phase was recently reported by Rosenbaum [64]. 2-D melting experiments have become more common because of the existence of a microscopic theory.

(2) Light scattering experiments on the melting transition

As mentioned earlier, the advent of the laser has made it very easy to measure many properties of solids during the melting transition. The measurement of velocity and attenuation of hypersonic waves inside solids through the melting transition has been the main objective of this current experimental project. Despite their high accuracy, ultrasonic studies of melting suffer from two basic limitations: First an ultrasonic measurement requires a relatively large single crystal and measures sound velocities which are averaged over the sample. Secondly, it is technically difficult to maintain an appropriate bond between the transducer and the crystal as the crystal melts. Laser scattering, in contrast, requires no mechanical contact and can probe very small regions of a sample in the range of 0.001 mm^3 or less. In the following I shall enumerate the past melting experiments using Brillouin and Raman scattering technique.

(a) Brillouin scattering studies of the melting transition

In the past, numerous ultrasonic studies of crystals near the melting point have been reported, which have

sometimes shown large modifications of both the velocity and attenuation of sound close to T_m [33].

Brillouin scattering studies of fluorite crystals were reported by Catlow [65]. He showed that the generation of disorder in the anion lattice sites at T_m resulted in a large decrease in C_{11} , a much smaller change in C_{44} and C_{12} and caused a heat anomaly just before melting. In a subsequent work, he calculated the change in defect concentration, and computed the contribution of both anharmonicity and defect generation in decreasing C_{11} as the temperature was increased. His measured changes in elastic constants are shown in figure 2-3. [My own results for salol, to be discussed in ch. IX. closely resemble those of Catlow]

Brillouin scattering studies of polymer films through the melting transition were reported by Kruger et al [66] who observed a continuous decrease in sound velocity. They claimed the existence of a new mesomorphic ordered state in the melt from an isotropic state at room temperature. Melting studies of the plastic crystal succinonitrile by Brillouin scattering technique were made by Bird, Jackson and Pentecost [67] and by Boyer, Vacher, Adam and Cecchi [68] in 1971. Boyer et al found a discontinuous drop of about 30% in the velocity of the longitudinal mode [the tranverse mode was not seen] with

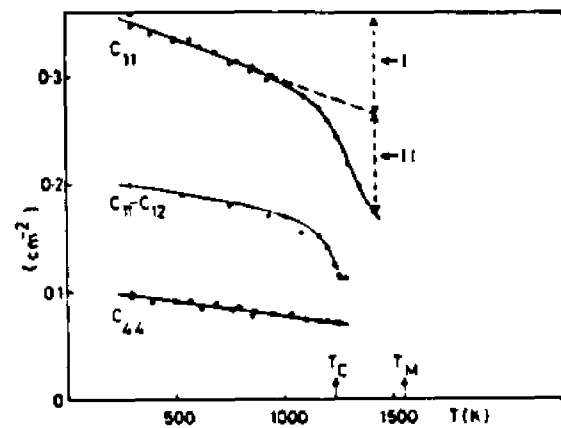


Fig. 2-3: Temperature dependence of elastic constants C_{11} , $(C_{11}-C_{12})$ and C_{44} of BaF_2 (see text for discussion of ordinates). Contributions of anharmonicity (I) and defects (II) to changes in C_{11} are indicated.
(From: Catlow et al [65])

a comparable increase in attenuation. At T_m they observed the solid and liquid Brillouin components simultaneously in the spectrum, indicating that solid and liquid coexisted within the scattering volume [the same effect was found by the author, see fig. 8-14].

In 1974, Levy-Mannheim, et al [69] performed Brillouin scattering experiments on carbon tetrachloride in the range of -54°C to 20°C . They observed a discontinuous drop in the longitudinal Brillouin shift and an increase in the linewidth at T_m . Tekippe and Abbels [70] reported Brillouin scattering measurements on carbon tetrabromide through the liquid plastic crystal transition at 92°C . These authors found no pretransitional softening of either the longitudinal or tranverse Brillouin components.

Brillouin scattering studies of supercooled water down to -9°C were performed by Rouch, Lai and Chen [71]. As the temperature was lowered from T_m , they found an increasing attenuation with decreasing velocity. They interpreted their results in terms of critical behavior, both ν and α showing a power law dependence on $(T-T_g)$, with evidence of a thermodynamic singularity at $T_g \sim 228^{\circ}\text{K}$.

Recently Dutta, Mudare and Jackson [72] performed Brillouin scattering studies on KCN doped with 6×10^{19}

cm^{-3} of CN^- ions at various temperatures down to 4.2°K . They interpreted the frequency shifts as due to a defect-phonon interaction modeled by Walton [73].

From the above review, one can see how little experimental work on the melting transition by light scattering methods has been done so far. The present work is the first report of a melting experiment on salol by Brillouin and Raman scattering techniques. The analysis of the anomalies in Brillouin shift and linewidth near T_m with a dislocation model of melting is also presented for the first time, and may be one of the first experiments on the melting transition that supports the dislocation theory of melting. The changes in sound velocity near T_m were interpreted here qualitatively by a defect-phonon interaction model.

(b) Raman scattering studies of the melting transition

In contrast to the small number of Brillouin scattering experiments through the melting transition, more investigators have reported the study of Raman spectra of various crystals in the region of the melting transition. In distinction to Brillouin scattering experiments which probe a macroscopic property of the crystal (ie the elastic constants), Raman scattering

probes the atomic or molecular movements within the crystal and is thus more closely related to microscopic changes associated with melting. For molecular crystals, the Raman spectra exhibit three important classes of features [74]: (1) internal vibrations corresponding to intramolecular motions which are nearly identical in the solid and liquid, (2) external vibrations corresponding to translational motion of the molecule as a whole which have zero frequency in the liquid, and (3) torsional modes corresponding to molecular twisting motion which also have zero frequency in the liquid.

Shinoda [75] observed the external lattice modes in the Raman spectrum of crystalline 1,2-dibromomethane during melting and found a general decrease in the intensity of these features as the crystal slowly transformed into a fluid. In the analysis of a Raman scattering melting experiment in naphthalene, Secharev et al [76], considered both the usual anharmonic damping and renormalization effects, and the presence of orientational defects which modify the positions and widths of the external vibrations.

Fleury [77] studied the second order Raman spectra of argon, krypton and xenon near their melting transitions and found that the solid spectrum transforms in an essentially continuous way into the liquid spectrum. [My

own results on the first order Raman spectra of salol, discussed in Ch. 9 show similar behavior for the internal modes].

In a Raman scattering study of a molecular crystal at melting, Prasad and Kopelman [74] measured the temperature dependence of the frequency and linewidth of the pseudo-internal modes. The frequency shift of 10-20% was interpreted as due to anharmonic interactions. Elliot et al [78] reported an investigation of the effect of disorder on the Raman modes in the fluorite crystal. The most recent (1983) Raman scattering studies of ionic and molecular transitions in AlCl_3 near the melting point are reviewed in [79].

The Raman scattering results of the author on salol through its melting transition are discussed in details in ch. 9.

(c) Photon Correlation studies of the melting transition

There are very few reports on melting studies by photon correlation spectroscopy. A preliminary investigation of both the intensity and photon correlation function of light scattered by NaCl was reported by Pike and Vaughan [80]. They found that the total scattered intensity decreases with increasing

temperature in NaCl, presumably because the radius of the charge cloud (to which the light couples) surrounding the dominant anion vacancy decreases with temperatures faster than the vacancy concentration increases.

Mesquita and Neal, of our laboratory in their study of the dynamics of the crystal-melt interface of salol by photon correlation spectroscopy found clear evidence of the existence of screw dislocations at the solid-liquid interface.

(C) Previous melting experiments on salol and succinonitrile

Very few experimental studies on salol have been reported so far. The reasons for choosing salol in this experiment were its convenient melting temperature ($T_m = 41.0^\circ\text{C}$), easy growth of large pure single crystals and high optical quality. In the past, salol has been widely employed in studies of the crystallization process [81,82].

Light scattering studies on liquid salol were reported by a number of groups [83,84,85], as described in chapter 4. An IR absorption measurement on salol was reported by Ansari [49]. In 1974, Obrutski and Podolinski [86] reported the results of a study of the kinetics of the growth of salol crystals from the molten

state. They determined the threshold of supercooling at which growth began. They interpreted the distortions in the growth process as the result of the formation of defects. The details of salol growth from the melt along the b-face can be found in the work of Alias Gan et al [17]. Raju and Subba [87] reported an ultrasonic relaxation study in salol in 1970, and Raman scattering of salol was reported by Poulet [88] in 1977.

The refractive index study of succinonitrile by McFarlane [62] indicated a pretransitional rounding which was found to gradually disappear on repeated zone refining of the crystal, suggested a similar behavior in the velocity of hypersound. This prompted us to undertake a Brillouin scattering study of succinonitrile samples, with various zone refined orders of purity. The results, discussed in detail in ch. IX, did not show any dependence on crystal purity [see fig. 8-15] except for a small softening of the longitudinal acoustic mode near T_m .

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CHAPTER III

THEORY OF LIGHT SCATTERING

A. Introduction

Since the beginning of this century, it has been known [1,2] that when light traverses a transparent material some light is scattered by the dielectric inhomogenities produced by thermal fluctuations in the sample. In this chapter I shall briefly review the theory of light scattering [3,4,5] which will be utilized in the subsequent chapters of this thesis. I shall present a general introduction to the theory and practice of spontaneous (linear) light scattering spectroscopy (due to natural thermal excitation of the scattering substance). I shall concentrate on Raman and Brillouin Scattering in crystals which will be limited to lattice vibrations (phonons).

Most light scattering experiments are designed to measure the spectrum of the scattered light $I_s(\omega)$. I will discuss the theory of $I_s(\omega)$ from both the classical and quantum mechanical points of view.

B. Normal mode analysis

The analysis of normal modes in a crystal with Ns atoms, N being the number of unit cells and s the number of atoms in a unit cell, begins with the construction of a potential energy function expressed as a power series in the displacements of the nuclei from their equilibrium positions. If all terms in the potential energy are ignored except for the quadratic ones, we obtain the familiar harmonic approximation which readily gives a set of $3sN$ equations of motion indicating the presence of $3sN$ vibrational modes[9].

By utilizing the translational symmetry property of the crystal, one obtains $3s$ coupled equations of motion for each value of $\vec{q}$ whose solutions yield $3s$ eigenvalues of the frequency. Each eigenvalue has a corresponding eigenvector which is a linear superposition of the $3s$ cartesian displacements of the atoms in the unit cell. Each such solution is called a normal mode.

When the equations of motion are solved for different values of $\vec{q}$ all of which are parallel, one obtains a set of dispersion curve ($\omega_{\vec{q}}$ vs $\vec{q}$). A typical set of dispersion curves is shown in fig. 3-1. Three of the branches always exhibit $\omega_{\vec{q}} \rightarrow 0$ (for $\vec{q} \rightarrow 0$) behavior. Examination of the eigenvectors shows that these three branches correspond to all the atoms in a unit cell

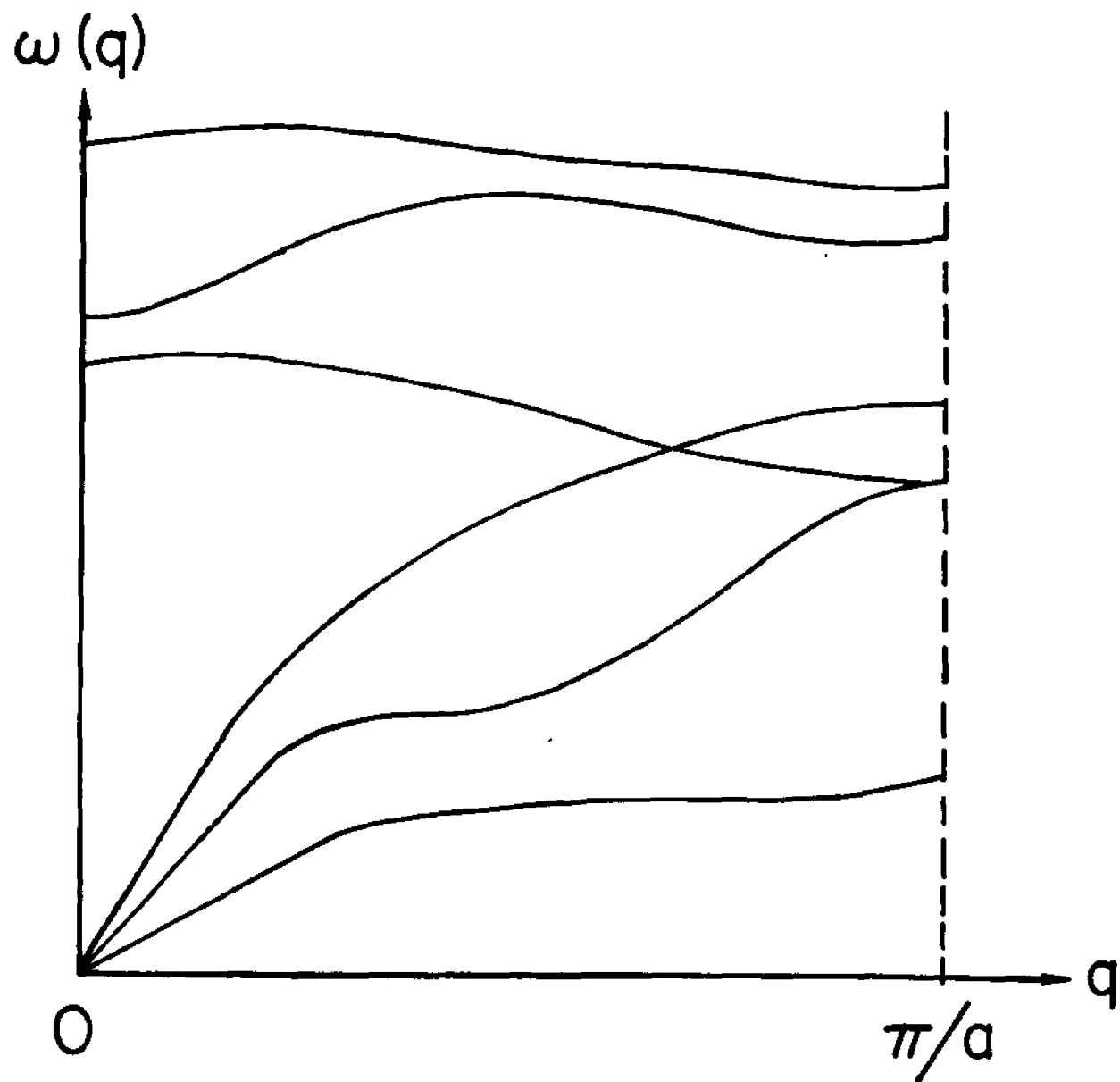


Fig. 3-1: Schematic dispersion curves for the lattice vibrations of a crystal with two atoms per unit cell showing three acoustic and three optical branches.

moving in unison. They are therefore identical to macroscopic sound waves, and are called acoustic branches. In Brillouin scattering, we consider the scattering of incident photons by these acoustic phonons, which I shall describe in section III-(D). A complete calculation of all possible acoustic eigenvalues and eigenvectors for six different $\vec{q}$'s in salol is presented in chapter V.

The remaining 3s-3 branches have nonzero intercepts ($\omega_{\vec{q}} \neq 0$ at $\vec{q}=0$) and correspond to relative motions of atoms within a unit cell. The modes on those branches (which are related to molecular vibrations) are responsible for infrared absorption by crystals and are called optic modes. These modes can also be studied by Raman scattering spectroscopy. In salol $C_{13}H_{10}O_3$ where each unit cell contains 12 formula units (each formula unit consisting of 26 atoms), one may expect up to 933 optic modes. In my Raman experiment, I could observe up to 36 different Raman modes (See Fig. 8-50). The reason for this discrepancy may result from some mode degeneracy (particularly for $\vec{q}$ in a high symmetry direction of the crystal). Also, not all optic modes are expected to be Raman active. Nobody has yet analyzed the atomic motions and eigen-frequencies for all the normal modes of salol.

The range of $\vec{q}$ in the dispersion curves of fig. 3-1 spans the first Brillouin zone - $\pi/a \leq q \leq \pi/a$ where a is the repeat distance of the crystal. Typically $\vec{q}$ ranges from 0 to 10^8 cm^{-1} . Since light scattering only interacts with modes whose wavelength is comparable to the wave length of light, we only observe modes for $\vec{q} \leq 10^5 \text{ cm}^{-1}$ so that in first order light scattering experiments we can only investigate the modes lying very close to the zone center ($\vec{q}_f \rightarrow 0$). Investigations of other modes for q up to 10^8 cm^{-1} can be made by neutron scattering or two phonon Raman scattering experiments.

C. General Theory of Light Scattering.

(1) Classical approach

The interatomic spacing in solids and liquids is so small compared to the wavelength of light that we can consider the medium optically as a uniform anisotropic dielectric continuum, and characterize the optical properties by a dielectric constant ϵ (more properly a second-rank symmetric tensor). We consider a plane monochromatic light wave:

$$\vec{E}_i(\vec{r}, t) = E \exp[i(\vec{k} \cdot \vec{r} - \omega_0 t)] \quad (3-1)$$

incident on a volume V of the crystal. The material within the volume sustains various thermal fluctuations which perturb the dielectric constant. Classically we imagine that each lattice vibration with wave vector $\vec{q}$ and eigenfrequency ω_q perturbs the dielectric constant $\epsilon(\vec{r}, t)$ so that:

$$\epsilon(\vec{r}, t) = \epsilon_0 + \delta\epsilon = \epsilon_0 + \sum_{\vec{q}, \omega_q} \Delta\epsilon_{q, \omega} e^{i(\vec{q} \cdot \vec{r} - \omega_q t)} \quad (3-2)$$

where each $(\vec{q}, \omega_q)$ term should be read as the sum of two terms, one with both 'plus' signs and one with both 'minus' signs. This dielectric fluctuation together with the incident field produces an excess polarization $\delta\vec{P} = E\delta\epsilon/4\pi$ in the medium and will radiate a scattered field $\vec{E}_s(\vec{r}, t)$. This scattered field is found to be of the form[3]:

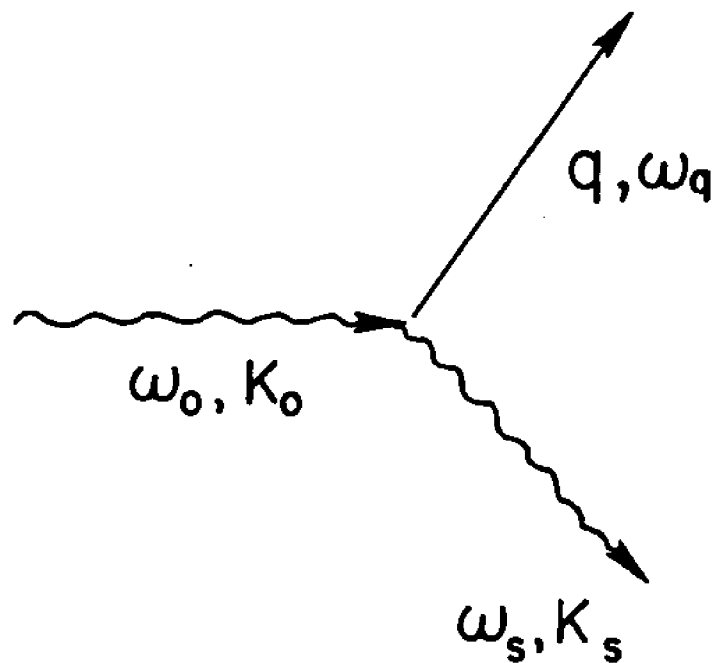
$$\vec{E}_s(\vec{r}, t) \sim \sum_{\vec{q}, \omega_q} e^{i[\vec{k}_s \cdot \vec{r} - (\omega_0 \pm \omega_q)t]} \int_V e^{i(\vec{k}_0 \pm \vec{q} - \vec{k}_s) \cdot \vec{r}'} dV' \quad (3-3)$$

The volume integral in (3-3) gives a δ -function in $(\vec{k}_i \pm \vec{q} - \vec{k}_s)$ which imposes wave vector or momentum conservation. Thus of the 3Ns normal modes in a crystal, kinematically only 3s of them can produce scattering of

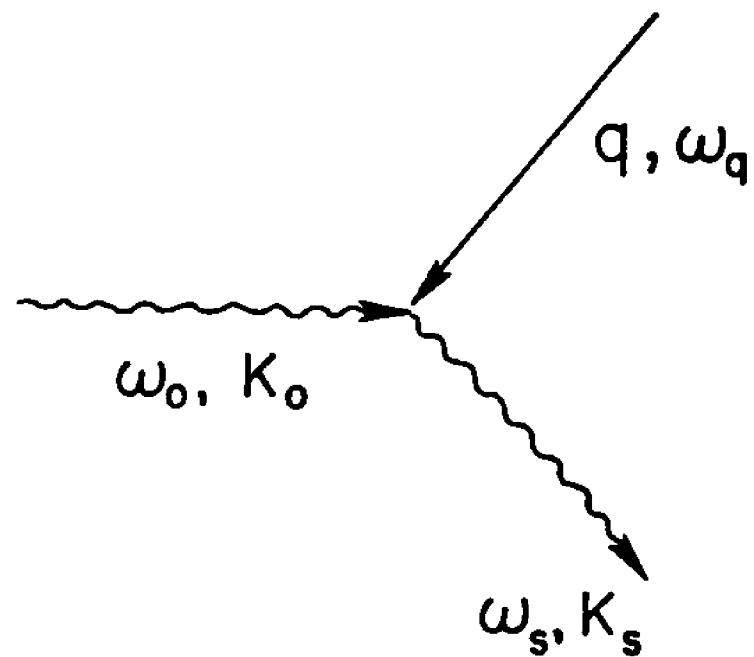
light with frequency $\omega_0 \pm \omega_q$ in any given direction characterized by the scattering angle θ , although not all 3s are necessarily allowed by selection rules. The scattered field will thus consist of components at $\omega_0 \pm \omega_q$ where the ω_q are the 3s frequencies at which a vertical line $q = |\vec{k}_s - \vec{k}_0|$ intersects each of the 3s branches of the dispersion curve (fig 3-1) for a particular mode. The scattering cross section for the entire sample is then given by [3]:

$$\frac{d\sigma}{d\Omega} = \frac{\omega_s^4 V^2}{16\pi^2 c^4} \langle (\Delta \epsilon_{q\omega})^2 \rangle \quad (3-4)$$

where $\langle (\Delta \epsilon_{q\omega})^2 \rangle$ can be taken as either a time or ensemble average. The spectral lineshape of the scattered light $\frac{d^2\sigma}{d\Omega d\omega_s}$ will be derived in section III(D). Since ω_q is usually very small compared to ω_0 , and ω_s, ω_0 being approximately equal, one can say that $|\vec{k}_s| \approx |\vec{k}_i|$. Therefore the condition $\vec{k}_i + \vec{q} - \vec{k}_s = 0$ establishes a simple geometry indicated in figure (3-2). In fact, $\vec{k}_s$ and $\vec{k}_i$ may have different lengths due to anisotropy of the crystal (see the calculation of ch. V) in which case the polarization selection of incident and scattered light determines the magnitude of a particular $\vec{q}$.



PHONON CREATION
(STOKES EVENT)



PHONON ANNIHILATION
(ANTI STOKES EVENT)

Fig. 3-2: First order photon-phonon scattering diagrams

If we assume $|\vec{k}_s| \approx |\vec{k}_i|$, then by simple geometry we can show that

$$q = 2k_0 \sin(\theta/2) \quad (3-5)$$

Equation (3-5) is analogous to the Bragg condition for x-ray scattering as will be shown below. Since the long wavelength acoustic modes involve in-phase motion of all the atoms in the unit cell, the atomic displacements are nearly constant over distances on the order of 100 unit cells, so that one may discuss these modes in terms of an elastic continuum model. Let a, b, c represent three different wavefronts of the propagating elastic wave in the crystal with wave vector $\vec{q}$ and frequency ω_q as shown in fig. 3-3. These wave fronts may be considered as lattice planes from which electromagnetic radiation can be scattered by satisfying the Bragg condition:

$$\frac{\lambda}{2} = d \sin(\theta/2) \quad (3-6)$$

where d , the distance between two such lattice planes is equal to the wavelength of the elastic waves, and θ is the angle between $\vec{k}_i$ and $\vec{k}_s$. With $d = \Lambda$, and $q = \frac{2\pi}{\Lambda}$, one can readily show that:

$$q = 2k_0 \sin(\theta/2) \quad (3-7)$$

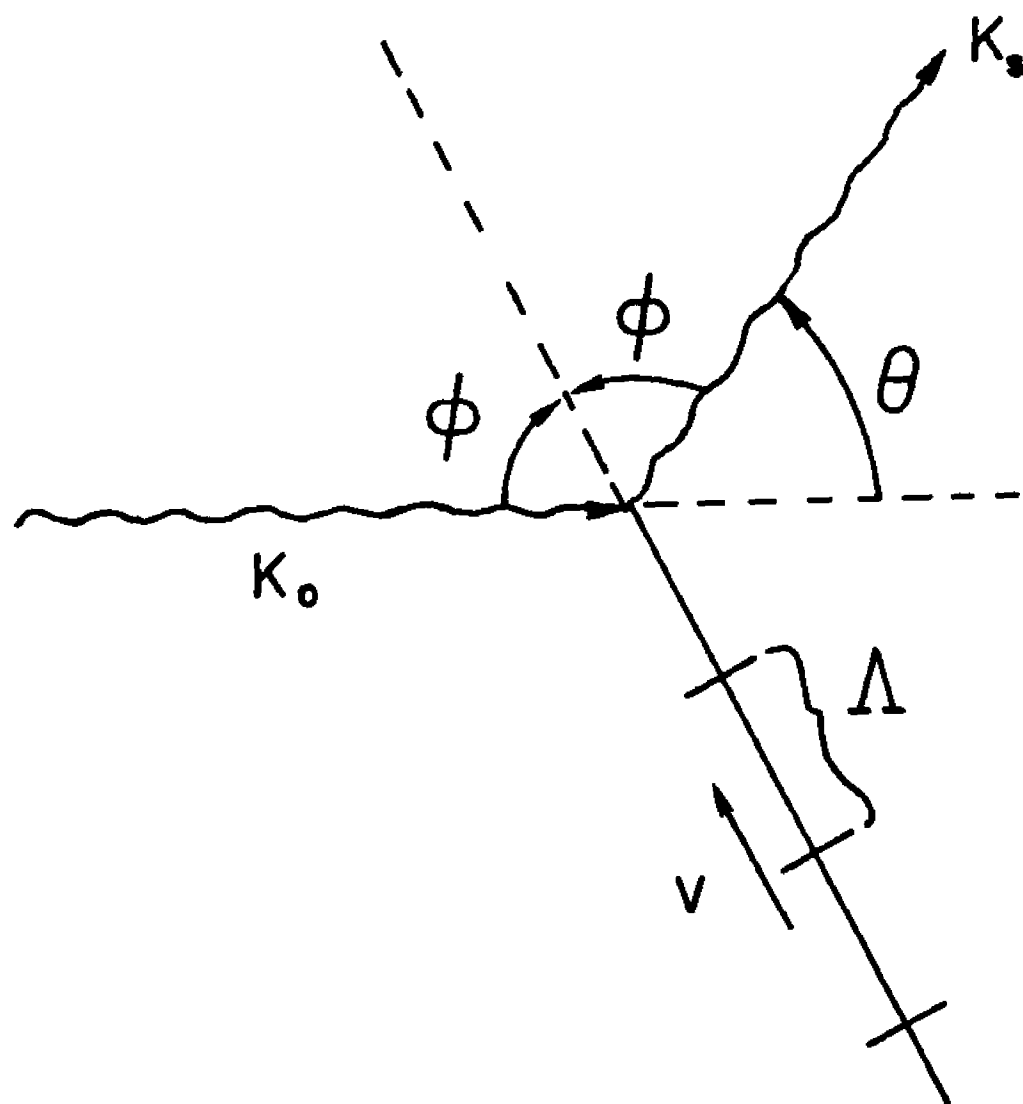


Fig. 3-3: Brillouin scattering geometry choice of the incident wave vector K_0 and the scattering angle θ selects those thermally excited acoustic modes which satisfy the Bragg scattering condition.

which is identical to the equation (3-5) derived earlier.

(2) Quantum Mechanical Approach

The same results can also be obtained from the second quantized theory of lattice dynamics. Each normal mode $(\vec{q}, \omega_q)$ is described in terms of a number of quasi-particles (phonons) of energy $\hbar\omega_q$ and crystal momentum $\hbar\vec{q}$. We begin by quantizing each normal mode of the system, and consider the n -th energy eigenstate of a mode to mean that there are n quasi-particles in the mode.

The scattering diagrams of fig. 3-2 now can be interpreted as "scattering events" in which a quasi-particle or phonon is either created (Stokes line) or annihilated (anti-Stokes line). Conservation of energy and momentum between the photons and phonons yields:

$$\begin{aligned}\omega_s &= \omega_o - \omega_q \\ \vec{k}_s &= \vec{k}_o - \vec{q}\end{aligned}\tag{3-8a}$$

$$\begin{aligned}\omega_s &= \omega_o + \omega_q \\ \vec{k}_s &= \vec{k}_o + \vec{q}\end{aligned}\tag{3-8b}$$

The momentum conservation is not absolute because the Hamiltonian of the crystal is not invariant under all

translations, but only under translations through discrete crystal vectors. In the scattering diagrams, for photons and phonons alike, a line terminating at the vertex implies annihilation of the particle while a line originating at the vertex implies creation.

Approximating $|\vec{k}_g| = |\vec{k}_i|$ one can also derive the earlier equations (3-5) and (3-7). Unfortunately, the scattering diagrams in fig. 3-2 cannot be used to calculate the cross-sections since they leave out the basic nature of the photon-phonon interaction. The true vertices are not as simple as shown in the figure, since the interaction occurs in an order of perturbation theory higher than the first.

(D) Brillouin scattering in crystals

As mentioned earlier, the scattering of photons by acoustic modes is called Brillouin scattering. In 1922, Brillouin predicted that there would be components in the spectrum of light scattered by liquids and solids whose frequencies would be shifted from that of the incident light by interaction with thermally excited soundwaves in the scattering medium [2]. Since the accessible $\vec{q}$ values are small, these components due to the acoustic modes occur at frequency shifts ω_q very much smaller than

those due to optic modes. Thus the Brillouin spectrum is restricted to a very small spectral region. And since for long wavelength acoustic modes $\omega_q = vq$, the scattered frequency ω_s can be written as (using $\vec{q}$ from equation (3-7)) :

$$\omega_s = \omega_o \pm 2 \frac{v\omega_o}{n/c} \sin \frac{1}{2}\theta \quad (3-9a)$$

The shifted frequencies can thus be given by:

$$\omega_s - \omega_o = \pm \omega_q \quad (3-9b)$$

Rewriting (3-9b) in standard form, the Brillouin shift $\nu_B = (\omega_s - \omega_o)/2\pi$ can be express as:

$$\nu_B = \pm \frac{2\pi v}{\lambda_o} \sin \frac{1}{2}\theta \quad (3-10)$$

where n is the reflective index and λ_o is the vacuum wavelength of the incident light. Egn. (3-10) will be frequently used to calculate the sound velocity v :

$$v = \frac{\lambda_o \nu_B}{2\pi \sin \frac{1}{2}\theta} \quad (3-11)$$

The polarizations and frequencies of the three acoustic modes for any particular $\vec{q}$ chosen by a scattering configuration both with isotropic and anisotropic consideration will be discussed in detail in chapter 5.

As derived earlier, the scattering cross section is given by equation (3-4) as

$$\frac{d\sigma}{d\Omega} = \frac{\omega_s^4 V^2}{16\pi^2 c^4} \langle (\Delta\epsilon_{\vec{q}\omega}^{ij})^2 \rangle \quad (3-4)$$

where $\langle (\Delta\epsilon_{\vec{q}\omega}^{ij})^2 \rangle$ is the time or ensemble average of the fluctuations in the dielectric constant $\epsilon(\vec{r}, t)$. Since these fluctuations arise from the atomic motions (lattice vibration) of the system, we can expand the fluctuations in terms of A_k for the k -th normal mode represented by (A_k, ω_k, q_k) where A_k, ω_k and q_k are respectively the amplitude, frequency and wave vector of the k -th normal mode:

$$\Delta\epsilon_{ij} = \sum_{k=1}^{35} \frac{\partial \epsilon_{ij}}{\partial A_k} A_k \quad (3-12)$$

The above sum can be broken into two sums:

$$\Delta \epsilon_{ij} = \sum_{k=1}^3 \frac{\partial \epsilon_{ij}}{\partial A_k} A_k + \sum_{k=3+1}^{3s-3} \frac{\partial \epsilon_{ij}}{\partial A_k} A_k \quad (3-13)$$

Here the first sum corresponds to the 3 acoustic modes with a given $\vec{q}$ studied by Brillouin scattering and the second sum corresponds to the $3s-3$ optic modes of vibration, which are studied by first order Raman scattering at the zone center.

The normal coordinates $A_k(t)$ are related to the strain produced in the crystal by the elastic waves by:

$$A_k = \sum_{l,m} b_{lkm} \chi_{lkm}(t) \quad (3-14a)$$

where:

$$\chi_{lkm}(t) = \frac{1}{2} \left(\frac{\partial u_l}{\partial r_m} + \frac{\partial u_m}{\partial r_l} \right) \quad (3-15a)$$

u_l being the local displacement of the atoms.

Considering the distortion in ϵ by local strain through the elasto optic effect one can easily calculate the $\langle (\Delta \epsilon_{ij})^2 \rangle$ in terms of the Brillouin scattering tensor

T, and given by [see chapter 5(C)] :

$$\langle (\Delta \epsilon_{ij})^2 \rangle = \epsilon_i^2 \epsilon_j^2 [\hat{e}_j \cdot T \cdot \hat{e}_i]^2 q^2 \langle A_K^2(\omega) \rangle \quad (3-16)$$

The fluctuation $\langle (A_K(\omega))^2 \rangle$ can be calculated by applying the fluctuation-dissipation theory to a harmonic oscillator model.

The atoms are considered to be simple oscillator with natural frequency ω_0 and damping coefficient Γ whose response function $X(\omega)$ due to an external perturbation $f(\omega)$ is given by:

$$X(\omega) = \frac{A(\omega)}{f(\omega)} \quad (3-17)$$

For this familiar damped harmonic oscillator equation one can readily derive:

$$X(\omega) = \frac{\omega_0^2 - \omega^2 + i \Gamma \omega}{(\omega_0^2 - \omega^2)^2 + (\Gamma \omega)^2} \quad (3-18)$$

The fluctuation-dissipation theory relates $\langle (A_e(\omega))^2 \rangle$ to $\chi(\omega)$ by:

$$\langle A_e^2(\omega) \rangle = \text{Im} \chi(\omega) \frac{k_B T}{\pi \omega} \quad (3-19)$$

which gives the final expression for the power spectrum for the scattering process as:

$$\frac{d^2 S}{d\Omega d\omega} = \frac{\omega_s^4 k_B T \epsilon_i^2 \epsilon_j^2 n_s}{16 \pi^3 c^4 g v^2 n_o} \frac{\Gamma}{(\omega_o^2 - \omega^2)^2 + (\Gamma \omega)^2} [\hat{e}_j \cdot \tau \cdot \hat{e}_i]^2 \quad (3-20)$$

Equation (3-20) can be simplified by approximation $\omega_o + \omega \approx 2\omega$ and rewritten as:

$$\frac{d^2 S}{d\Omega d\omega} = \frac{\omega_s^4 k_B T \epsilon_i^2 \epsilon_j^2 n_s}{32 \pi^3 g v^2 n_o} \frac{\Gamma}{(\omega_o^2 - \omega^2)^2 + \Gamma^2} [\hat{e}_j \cdot \tau \cdot \hat{e}_i]^2 \quad (3-21)$$

which is the familiar Lorentzian functional form. The observed Brillouin spectrum shown in fig. 8-1(a) can be described by the equation (3-21).

(E) Raman Scattering in Crystals

First order Raman scattering arises from scattering of photons by optic phonons at the zone center $\vec{q} \approx 0$. It is clear from the normal mode analysis in section III(B) and equation (3-13), that $3s-3$ optic modes exist, some of which may couple to the incident field if $(\partial E / \partial A) \neq 0$. The complete description of the Raman scattering process requires a quantum mechanical treatment [4,6]. However, to obtain the frequency relations in the Raman effect, a classical treatment of the optical field and crystal can be employed[7].

We consider a unit cell with s atoms, with a polarizability α , and with each atom connected to its nearest neighbor by a spring which represents the electron clouds separating them. A plane monochromatic wave $E_0 \cos \omega_0 t$ is incident on the system and induces a dipole moment because of its interaction with the electron cloud. Allowing for the tensor properties of the system, the induced dipole moment in the i ($i = \hat{x}, \hat{y}$ or $\hat{z}$) direction resulting from the field polarized in the j -direction is:

$$P_i = \alpha_{ij} E_j \quad (3-22)$$

If Ω_k and A_k are the frequency and amplitude of one of the 3s-3 optic modes, then the displacement of the atoms in a unit cell from the equilibrium position, $\Delta x(t) = (x - x_0)$ can be written as a linear combination of the normal coordinates A_k by:

$$\Delta x(t) = \sum_{k=1}^{3s-3} A_k \cos \Omega_k t \quad (3-23)$$

Expanding the polarizability α about the equilibrium position x_0 , the induced dipole moment has the form:

$$P_i = \alpha_{ij}(x_0) \cos \omega_0 t + \sum_{k=1}^{3s-3} \left(\frac{\partial \alpha_{ij}}{\partial A_k} \right)_{A_k=0} (A_k E_j) / 2 \left[\cos(\omega_0 + \Omega_k)t + \cos(\omega_0 - \Omega_k)t \right] \quad (3-24)$$

The intensity of the Raman spectrum is proportional to P_i^2 . The first term in equation (3-24) gives the light scattered at the incident frequency, and the second term gives two components of the scattered light for each

normal vibration at frequencies:

$$\begin{aligned}\omega_s &= \omega_0 - \Omega_k && \text{Stokes event} \\ \omega_s &= \omega_0 + \Omega_k && \text{anti-Stokes event} \quad (3-25)\end{aligned}$$

where $k = 1, 2, 3, \dots, s-3$ includes all degenerate and distinct frequencies.

From a quantum mechanical point of view, the Stokes radiation results from the creation of a phonon and anti-Stokes radiation results from the annihilation of a phonon.

In order to observe a Raman mode, it must couple to the incident field. Considering the frequency shifted scattered light, we rewrite equation (3-24):

$$P_i = \sum_{k=1}^{3s-3} \alpha_{ij}^k E_j^k \quad (3-26a)$$

where

$$\alpha_{ij}^k = \frac{1}{2} \left(\frac{\partial \alpha_{ij}}{\partial A_k} \right)_{A_k=0} A_k \quad (3-26b)$$

and

$$E_j^k = E_j [\cos(\omega_0 + \Omega_k)t + \cos(\omega_0 - \Omega_k)t] \quad (3-26c)$$

The mode is Raman active if $\alpha_{ij}^k \neq 0$ and the mode is Raman inactive if $\alpha_{ij}^k = 0$ which is called the selection rule. From symmetry consideration, one can show that [8], $\alpha_{ij}^k \neq 0$ only if α_{ij} and A_k transform according to the same irreducible representation of the crystal point group.

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CHAPTER IV

STRUCTURE, PROPERTIES AND PREPARATION OF CRYSTALS

A. Introduction

In this chapter I shall describe the materials which have been used in this work. Initially, the experiment was started with succinonitrile, and later on switched to salol. Both these crystals were grown in our laboratory; details of the growth will be described in sections C and D of this chapter. The reasons for choosing salol were (I) its low melting temperature ($T_m = 41^\circ\text{C}$), (II) easy growth and (III) excellent optical quality. In this section, I shall assemble all the relevant information on these crystals and review the previous light scattering experiments on them. Since salol was used in the main part of the experiment, I shall emphasize salol, its structure and other properties.

B. Salol

(1) General description

Because of the ease with which large single crystals

of salol can be grown, it has frequently been employed in studies of the crystallization process [1,2]. Light scattering in liquid and supercooled salol has also been studied by a number of groups since its depolarized Brillouin spectrum exhibits "shear wave" structure, and its viscosity can be varied by ten orders of magnitude by changing the temperature from -48°C to $+120^{\circ}\text{C}$ [3,4,5,6].

Phenyl Salicylate with chemical formula $\text{C}_{13}\text{H}_{10}\text{O}_3$ is commonly known as salol [see figure 4-1 for the chemical structure]. It is synthesized by condensation of salicylic acid with phenol. It is one of the three ester derivatives of salicylic acid. Salol was first used in the 19th Century as an intestinal antiseptic. It is now widely used as a coating for pills and tablets, and in protective "sunscreen" creams because of its ultraviolet absorption.

(2) Structure

The structure of salol was determined recently by a Swiss group [7] by X-ray diffraction measurements. The structure was refined by full matrix least-squares analysis using the x-ray system [8]. The final R factor was 0.030, with anisotropic vibration parameters for Carbon and Oxygen, isotropic for Hydrogen. Cell dimensions recorded at -80°C are:

$$a=11.258\text{\AA}, b=23.402\text{\AA} \text{ and } c=7.961\text{\AA}$$

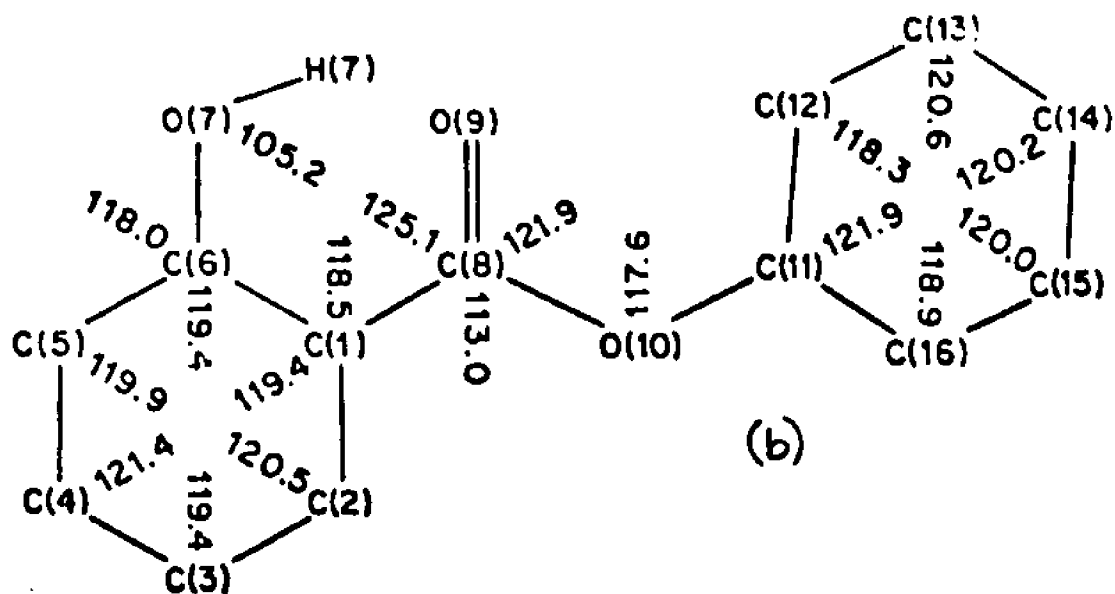
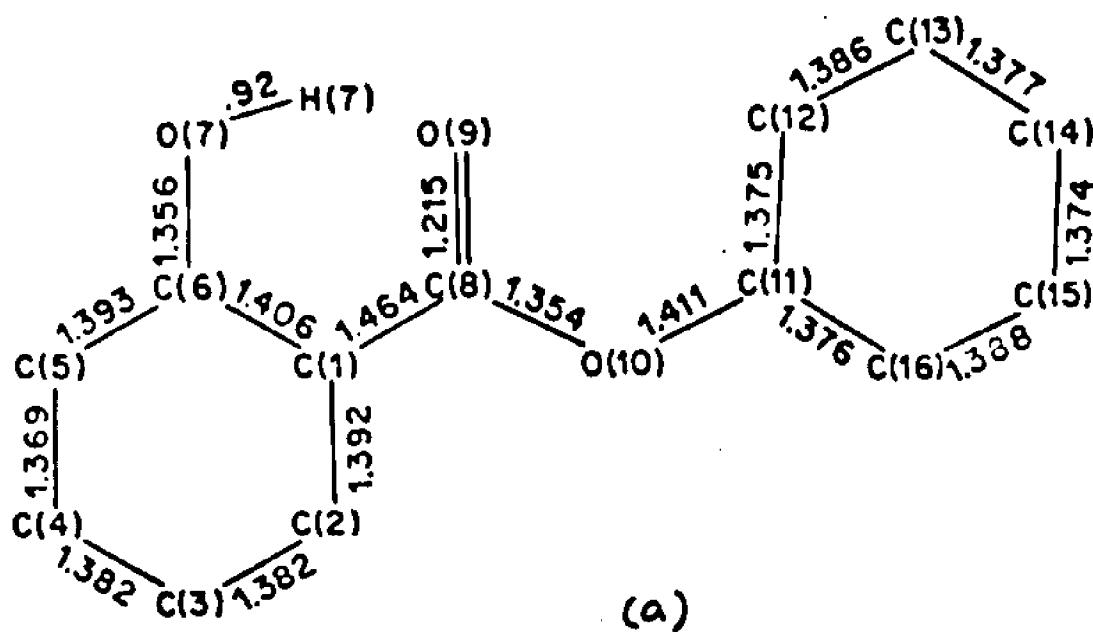


Fig. 4-1: One salol molecule $C_{13}H_{10}D_3$ showing (a) the bond distances (in Å) and (b) bond angles. (Bilgram, 1980[7])

with e.s.d.'s of about 0.05%. An earlier measurements (1957) of the lattice constants can be found in [9]. Bond lengths and bond angles calculated from the final atomic coordinates are shown in fig. 4-1 (a) and (b) respectively.

(3) Symmetry properties

Crystalline salol is orthorhombic (dipyramidal) with point group $mmm=D_{2h}$ containing eight symmetry elements ($E, C_2', C_2'', I, C_V, C_V', C_V'',$) which includes three mutually perpendicular two-fold rotation or inversion axes parallel to the x,y or z-axis and three mutually perpendicular mirror planes (planes xy, yz and zx), each perpendicular to one of the three 2-fold rotation axes, and each containing two rotation axes. The space group of salol is D_{2h}^{15} (Pbca) and each unit cell (see fig. 4-2) consists of 12 formula units [10]. The other important parameters of salol are [11]:

Molecular weight M.W.=214.2

Density: $\rho = 1.2784 \text{ g/cm}^3$

(determined in our laboratory, see chapter VII)

Solubility: 80g/100g in benzol

0.015g/100g in water

and highly soluble in ethanol and

methanol

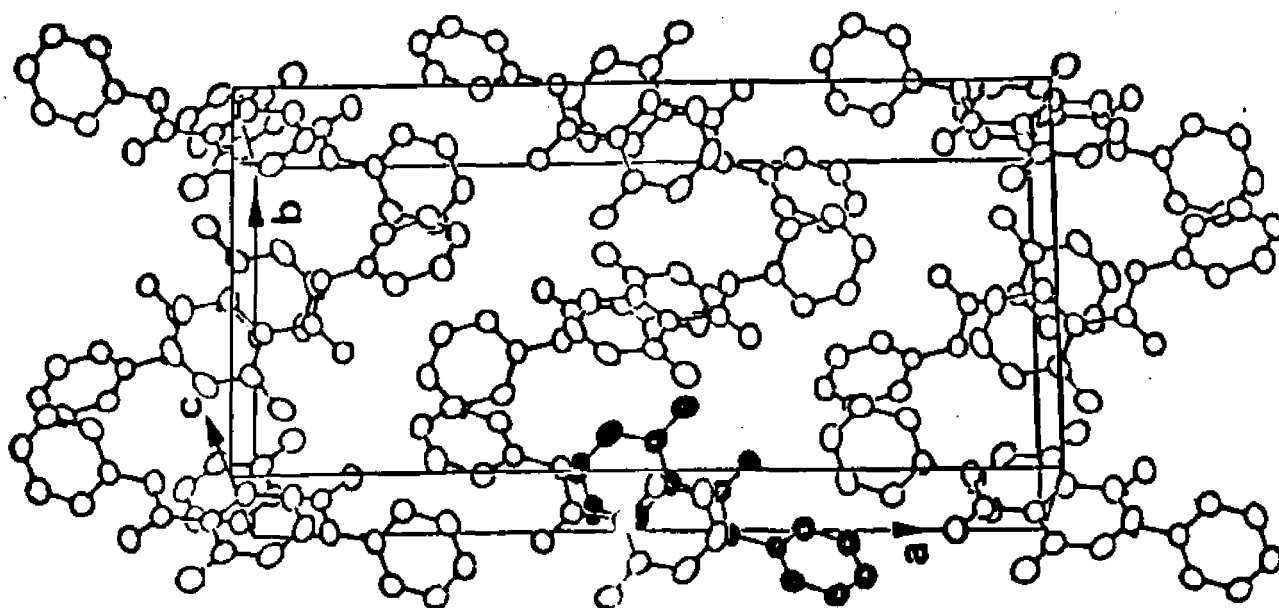
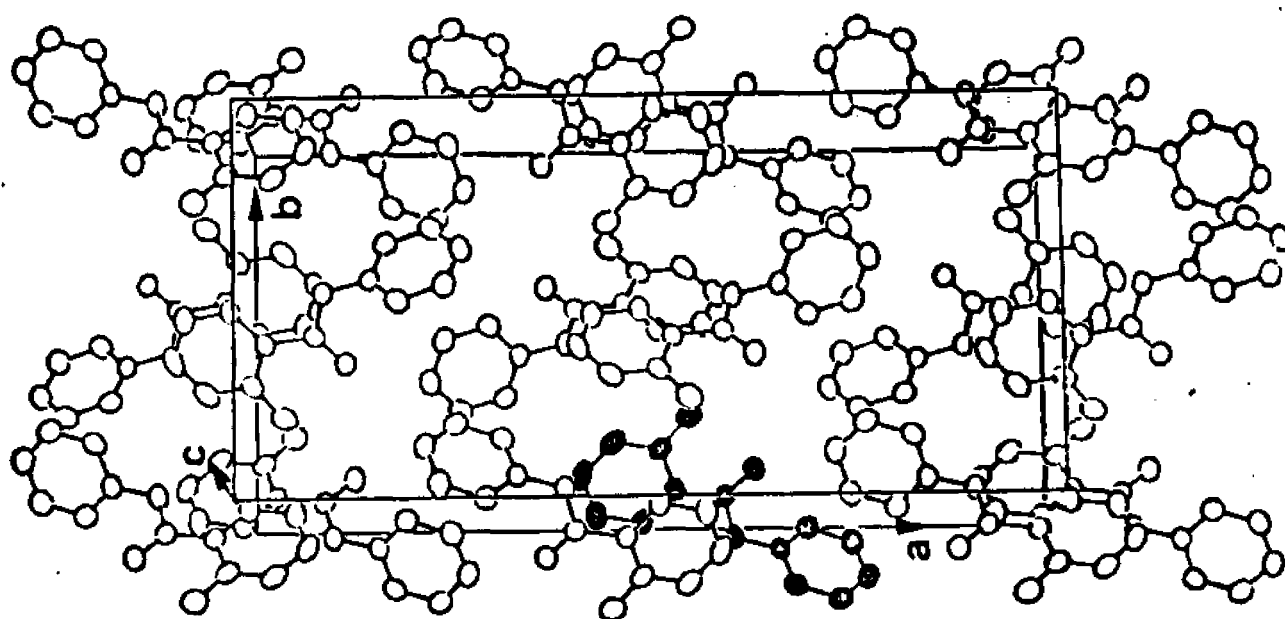


Fig. 4-2: Stereoscopic view of the packing in the unit cell of a salol crystal consisting of twelve formula units. On standard molecule is blackened. (Bilgram, 1980 [7])

Melting Temp: $T_m = 41.0^{\circ}\text{C}$ (solution grown)
 41.2°C (melt grown)

(4) Mechanical, Optical and Electrical properties

Crystalline salol is highly brittle. It is very sensitive to thermal shock and has to be handled very carefully. It was often observed to crack easily simply from thermal gradients produced by touching, or during removing crystals from solution (from ethanol to air).

The elastic stiffness constants of salol are not yet known; their determination is one part of this thesis. Similarly, electrical properties of salol have not been studied so far.

The crystalline seeds display excellent optical quality. Strong anisotropy is observed in the refractive indices which have also been measured in the course of the experiments (see chapt. VII). Salol is a biaxial crystal, with two optical axes. Its refractive indices are:

$$n_x = 1.547 \pm 0.0265$$

$$n_y = 1.812 \pm 0.0233$$

$$n_z = 1.651 \pm 0.0145$$

Other useful information, like the temperature dependence of refractive indices, volume expansion and electrical conductivity have not yet been reported. The results in chapter VIII will add some new information

about salol e.g. the temperature dependence of polarizability, sound velocity and attenuation. A complete set of elastic coefficients and Pockel's coefficients obtained from this experimental work will be given in chapter VIII, section II. Brillouin scattering tensors for salol will be calculated in chapter V.

C. Salol growth and preparation

(1) Solution method

Salol in powder form was bought from Eastman Kodak Co. It could be vacuum distilled before making a solution for growth. Salol crystals were grown from saturated ethanol solution by continuously lowering the temperature $1/5^{\circ}\text{C}$ per day, starting from 25.5°C . Small salol seeds were suspended in the solution to start the growth process. Good crystals grew from small suspended seeds in about six days. A short description of various steps of the growth process is described below. The schematic diagram of the solution method is shown in fig. 4-3.

(a) Growing the starting salol seeds

Supersaturated salol-ethanol solution (in a hot water bath at 40°C) was made (25gm salol in 100ml ethanol), and the solution was poured into a glass dish. The dish was kept in a quiet environment with a loose cover for about 24 hours. The natural decrease of the

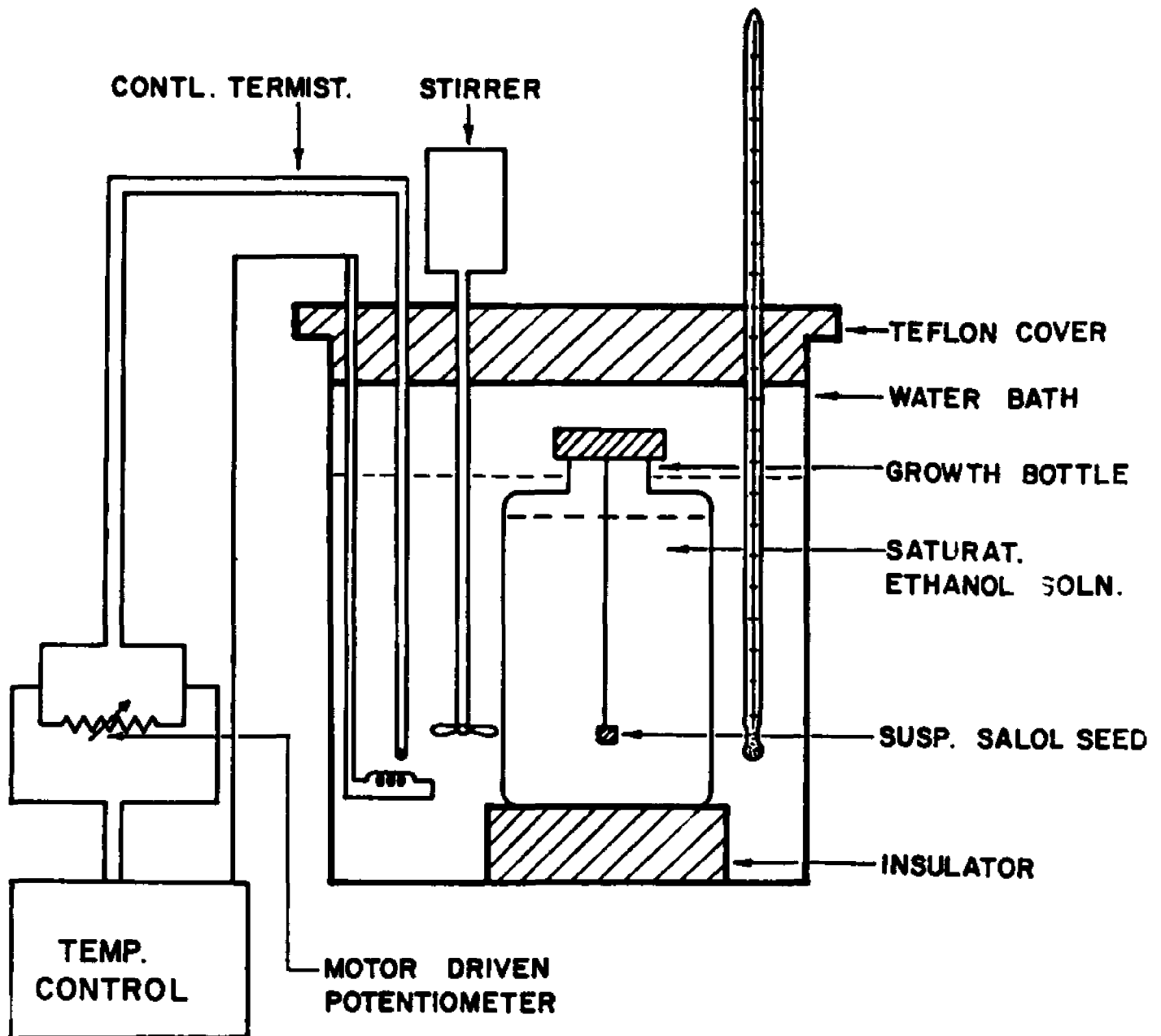


FIG. 4-3 SCHEMATIC DIAGRAM SHOWING APPARATUS FOR CRYSTAL GROWTH FROM SOLUTION

dish temperature was sufficient to let very small salol seeds grow on the bottom which were excellent starting seeds. Seeds also formed during the preparation of the final salol-ethanol solution.

(b) Preparing exactly saturated salol-ethanol solution

500 grams of salol powder was dissolved in 1000 ml of ethanol (98% pure) in a glass bottle, and stirred under hot water (45°C) which flowed around the bottle until all of the salol dissolved. The most important initial step was to prepare an exactly saturated solution of salol in ethanol.

The temperature controlled water bath was kept at 25.5°C . When the supersaturated salol solution was kept in the bath at 25.5°C for 24h, all the excess salol precipitated at the bottom, leaving a perfectly saturated solution above. The saturated solution was carefully transferred to another clean bottle leaving the solid salol precipitate behind. This precipitated salol also contained many nice seeds which could occasionally be used for experiments as well as for starting seeds.

The new bottle with apparently saturated solution was again allowed to stay for 48 hours at the same bath temperature ($T=25.5^{\circ}\text{C}$), this time with a small piece of solid salol dropped at its bottom to check whether the solution is exactly saturated. The size of the dropped seed will remain unchanged even after 48h if the solution

is exactly saturated. Any increase or decrease in its size indicates that the solution is supersaturated or undersaturated. If the seed starts to grow, one must wait for 2-3 days in order to allow deposition of excess salol on to the seed to make the solution exactly saturated.

When the solution is exactly saturated, the seed is then taken out carefully. Care must be taken during removal of the seed or transfer of the solution, since evaporation of highly volatile ethanol may cause supersaturation. These steps must be done very fast. A seed is tied to a thread and suspended in the bottle while the solution bottle is inside the water bath. A hard round cardboard disc fitting tightly inside the screw cap of the bottle is punched with a hole through which passes the thread that holds the seed suspended in solution.

At first the suspended seed is kept overnight (24h) at the same temperature. If the solution is still exactly saturated nothing will happen to the seed. Then it is useful to increase the controlled temperature by 0.1°C to 25.6°C and watch continuously for the moment when the seed starts to dissolve (the surrounding thread looks loosely bound). When a little decay of the seed is observed, we decrease the temperature by 0.2°C and after waiting 2h start the cooling process. Starting the cooling process just after observing a slight decay in

the seed was a crucial step to obtain excellent optical quality single crystals.

On the other hand the suspended seed may disappear or small seeds may start to grow on the bottom depending on whether the solution has become undersaturated or supersaturated. If that is observed, one has to repeat all the previous steps again to get an exactly saturated solution. After the seed is properly in place, one can start the cooling process.

(c) Temperature lowering

One of the most vital point for getting very good quality crystals is to control the rate of cooling. Slower cooling will of course produce better quality crystals than those obtained from faster cooling. The principle of cooling was based on the continuous decrease of resistance of one leg of the control bridge connected to the control thermistor, which was achieved by parallel connection with the thermistor of a 200Ω potentiometer driven by a motor (one revolution per day). The continuous decrease of resistance was calibrated with temperature decrease of the bath in such a way that I could decrease about 0.2°C per day.

(d) Morphology and Orientation

In five to seven days one could get a large single salol crystal, typically of the shape shown in figure

4-4. Our crystals always grew in the form of tablets with large parallel hexagonal top and bottom surfaces. From the measured angles and the known lattice parameters we inferred that the hexagonal basal planes are b-faces (010) with two a edges (100) bounded by the 126° angles and four (101) edges. This assignment agrees with Flaschbart's observation of tabular development on (010) and was also supported by the polarization selection rules for Brillouin scattering as well as by X-ray diffraction.

(e) Sample preparation: cutting and polishing

All crystal cutting was oriented to the well-formed growth faces shown in figure 4-4. Samples were cut with a string saw wet with ethanol. Crystals were attached to an aluminium stud by molten salol (this proved to be the best adhesive and could be removed very easily later on). The aluminium stud was subsequently rotated by 90° to make the other two cuts.

Since the x and y faces were very well defined, the first two cuts were made perpendicular to the z-axis. The final two cuts were perpendicular to the x-axis. The angle between the string and the z-axis was checked to be $90^{\circ} + 2^{\circ}$ both by protractor and eye. Samples of typical size 8mm x 9mm x 12mm which fit snugly inside the cell holder were obtained in this process. Many of the

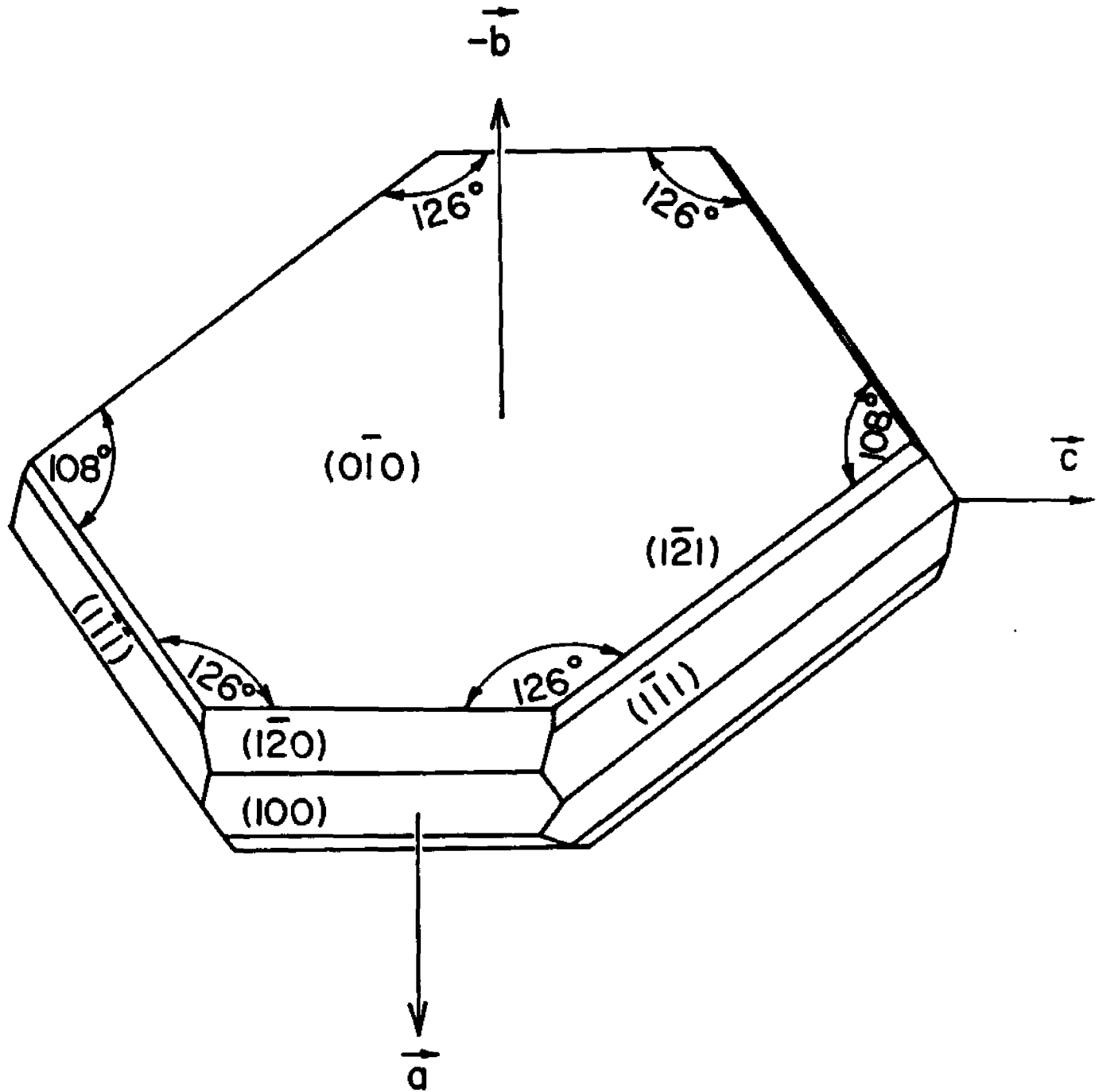


Fig. 4-4

Morphology of a typical salol crystal grown from solution. Showing prominent growth faces.

later cuts were made by a diamond saw blade. For these the crystal was mounted on a goniometer, glued in place by molten salol. Angular measurements with respect to the z or x-axis was more accurate ($90^{\circ} \pm 1^{\circ}$). The goniometer was held magnetically against the cutting table of the diamond saw. Diamond blade cuts were much faster than string saw cuts. Besides, samples with face normals at 45° from principal axis (e.g. 101, 011 etc.) were more accurately cut by the diamond blade.

It was expected that the diamond blade might crack the crystal or that samples cut by the diamond saw would have poor optical quality. Neither was true.

Much care was required during polishing of the samples, because salol crystals are very soft and extremely sensitive to thermal and mechanical shock. Initial polishing was done very gently on an extremely fine sand paper using paraffin oil as the polishing fluid. Final polishing was carried out on a polishing pad from Geoscience Co., style Polytex Supreme 125m42 wet with paraffin oil. The quality of the polished surface was checked on a microscope and the orientation on a polariscope. Very soft dry kleenex was finally used to clean the surfaces of oil. Slight misorientation of the sample could be corrected during rough polishing on the oil soaked sandpaper surface.

(2) High quality salol growth from the melt

Since elastic scattering often becomes very strong near the onset of melting and masks the Brillouin components, it was essential to use samples with very little elastic scattering. The room temperature strength of the elastic component was found to be at least 5 times stronger than the Brillouin components for solution grown samples whereas it was found to be three times weaker than any of the Brillouin components for melt grown samples. The melting experiment results on salol 18 which was grown from the melt with 2 zone refining passes, will be reported in chapter VIII. Following is a brief description of how such highly pure single salol crystals were grown from the melt with several zone refining passes [7].

Figure 4-5 is a schematic diagram of the melt growing setup for salol. Two temperature regions are created inside the glass jar: (1) the upper part filled with paraffin oil is maintained at 46°C by a metallic heater and a control thermistor through the Fisher proportional temperature controller, (2) the lower part is filled with water at room temperature. A cylindrical uniform growth tube of glass is inserted through the metallic cover plate and can be raised or lowered easily by a string attached to a motor which determines the speed with which the growth tube will move downward.

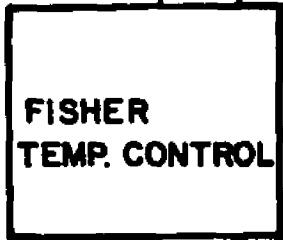


FIG.4—5EXP. SET. UP FOR SALOL GROWTH
FROM MELT (ZONE REFINED)

(a) Distillation

To obtain very pure crystals, the raw salol powder was usually vacuum distilled twice at 110°C . Once the salol started to vaporize, one could collect 100 grams of distilled salol in 4 hours. The distillation process was repeated several times. The distilled salol was transferred to the growth tube after a properly oriented salol seed was seated in the tube.

(b) Mounting the seed

One of the crucial step of the melt growing technique is to mount a seed in the lower end of the growth tube so that the b axis of the seed is exactly parallel to the cylindrical axis of the tube. This allows the growth direction to be along the crystal b-axis.

The circular seed was cut from a large solution-grown tablet-shaped crystal on a lathe turning at low speed. Its diameter was smoothed to produce a snug fit in the 8 mm growth tube.

The b face of the seed was aligned with the axis of the lathe by a He-Ne alignment laser after the seed was glued on a goniometer mounted on the lathe. Starting from a 14 mm (in diameter) seed, the radius was decreased by 1/8 mm at each step, until the seed fit into the glass tube. Initially two scratches were marked on the b-face indicating the x and z axes of the crystal (see figure 4-4). The seed was then carefully placed at the end of

the growth tube with its b-axis parallel to the cylinder axis.

(C) Growth process

Once the seed was mounted inside the tube, the tube was filled with distilled salol. It was lowered far enough in the glass jar to prevent melting of the seed. When kept for 2-3 h at a fixed height one gets a steady state solid-liquid interface, clearly visible from outside. The tube is raised a very small step and kept for 2-4 hours to equilibrate properly. It may take several (2-3) days until the interface is brought exactly to the top of the b face of the mounted seed. The main purpose of raising the tube very slowly was to avoid melting or displacing the mounted seed which would force a restart.

With several preliminary trials the best growth velocity was determined. The tube was lowered at a speed of $0.04 \mu\text{m}/\text{sec}$ or $0.34 \text{ cm}/\text{day}$ [which is therefore the growth velocity of the crystal] by a motor with $1/30\text{th}$ RPD (revolution per day) speed and having a 3.17 cm diameter pulley. After starting the motor I could harvest a 3 cm long cylindrical crystal in about 8 days. I also let the tube go through a second pass to improve the crystal purity. At the end of each pass one could clearly observe the yellowish liquid containing impurities that collected on top of the melt.

The next step was to take out the crystal carefully.

To avoid thermal shock, the temperature controller was turned off about two hours before the tube was to be taken out. Keeping the top of the tube open, the bottom of the tube was broken and the tube was warmed very gently in an upside down position until the whole cylinder of salol slipped out of the tube. The top face was then the b-face of the original seed, with the x and z axes already marked. I could prepare samples cut along principal axis or at 45° to them. salol 18 was cut with faces along (101), (101) and (010). Polishing and cutting was done as described above.

(D) Succinonitrile

Succinonitrile ($\text{NCCH}_2\text{CH}_2\text{CN}$) was the first crystal used in my experiment. It exists in a plastic crystalline phase at room temperature. Since I did not carry out any intensive experiments with it, I shall only discuss briefly its structure, properties and growth mechanism.

(1) Structure and properties

Succinonitrile is in a plastic crystal phase from -37°C to $+58^\circ\text{C}$ (T_M). X-ray investigation [15] has shown that the crystal belongs to the $m3m$ class of the cubic system with a body-centered lattice with one molecule per unit cell. Many of the properties of this crystal have already been studied, for example IR absorption [17], dielectric absorption [18], light

scattering [19] and NMR [20]. Some of the known parameters of succinonitrile are:

Density $\rho = 1.0316 \text{ g/cm}^3$
 Thermal expansion $\alpha = 1.9 \times 10^{-4} / \text{K}$
 Elastic constants $C_{11} = 5.07 \times 10^{10} \text{ dynes/cm}^2$

[21]

$C_{12} = 3.54 \times 10^{10} \text{ dynes/cm}^2$

$C_{44} = 0.65 \times 10^{10} \text{ dynes/cm}^2$

refractive index $n = 1.410$ (4880 Å) [22]

(2) Growth and sample preparation

Succinonitrile powder was purchased from Eastman Kodak Co. Single crystals were grown by the Bridgeman-Stockbarger method. The powder was melted and poured into glass growth tubes 1.7 cm in diameter by 25 cm long with tight fitting screw caps and long pointed conical tips. The tube was suspended from a clock motor and was lowered at $0.177 \mu\text{m/sec}$ (1.53 cm/day) through a thin layer of oil maintained at 63°C floating on water at 36°C . On subsequent passes the tube was started with its tip in the cool water to provide a seed for regrowth. After each pass, a small amount of liquid that collected at the top of the tube was poured off. Using distilled starting material, succinonitrile single crystals with up to 10 zone refined passes were grown.

We were unable to determine the orientation of the

crystallographic axes of succinonitrile without taking the crystal out of the container. Melting experiments were conducted with the sample in the growth tube. The absence of any T-mode in the Brillouin spectrum illustrated the isotropic nature of the material. Samples with identification SUCC D5, SUCC D3, SUCC ED1 were used in the experiments.

(E) Other Materials

The two other crystals used in these experiments were quartz (for calibration to determine Pockel's coefficient) and Ammonium bisulphate (NH_4HSO_4). Following is a short description of them.

(1) Quartz

Quartz, SiO_2 is a member of the trigonal crystal system with point symmetry 32. The known parameters of quartz are[12]:

Molecular weight =60.09

Density ρ =2.65 g/cm³

Lattice constants : a=4.9128Å

 c=5.4042Å

Refractive indices:

n_o =1.5428

n_e =1.5519

Rotatory power 18.48°/mm (at 6368Å)

Elastic and Pockel's coefficients (see appendix A)

Characteristic properties : piezoelectric and optically active.

(2) Ammonium-bi-sulphate

Attempts were made between the succinonitrile and salol experiments to grow and use NH_4HSO_4 in the melting experiment. Single crystal NH_4HSO_4 was successfully grown in collaboration with Dr. M. Copic by very slow cooling of Ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ dissolved in concentrated sulphuric acid. Transparent, colorless single crystals NH_4HSO_4 with cleavage planes along (001) were obtained. A better quality of NH_4HSO_4 single crystal was later grown by slow hydrolysis of chloroacetate-amide in dilute H_2SO_4 .

NH_4HSO_4 has a monoclinic structure at room temperature with point group 2/m and space group C_{2h}^5 [14]. Its melting temperature $T_M = 147^\circ\text{C}$. Other parameters are [11]

Lattice const : $a = 24.66\text{\AA}$, $b = 4.60\text{\AA}$, $c = 14.80\text{\AA}$

$$\beta = 89.87^\circ$$

Refractive index : $n_x = 1.463$, $n_y = 1.473$,

$$n_z = 1.510$$

Solubility : 100% in water.

Samples were prepared in the same way as salol samples described above, cut on a string saw wet with water. All efforts to observe Brillouin scattering components failed. The strong elastic scattering, even from optically very transparent samples prevented observation of any Brillouin modes. Ultimately the experiment with NH_4HSO_4 was abandoned in favor of salol.

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CHAPTER V

CALCULATION OF BRILLOUIN SCATTERING TENSORS

A. Introduction

The determination of the elastic and Pockel's coefficients of salol by Brillouin spectroscopy was also a part of this thesis project. In order to determine the complete set of elastic and elasto optic coefficients, I had to choose phonon wave vectors along six different directions. This led me to prepare six different samples for 90° scattering experiments with the phonon wave vector directions $\hat{q} = (100)$, (001) , (010) , $\frac{1}{\sqrt{2}}(1\bar{1}0)$, $\frac{1}{\sqrt{2}}(10\bar{1})$ and $\frac{1}{\sqrt{2}}(0\bar{1}1)$. In this chapter, I shall calculate the relationship between elastic coefficients and sound velocities for each of those phonon wave vectors. Each $\hat{q}$ -vector is associated with three different phonons which may be longitudinal, transverse, quasi-longitudinal or quasi-transverse modes. Calculations will also be carried out to obtain Brillouin scattering tensors for all phonon modes associated with each of the six wave vectors given above. These tensors determine the incident and scattered polarizations for which this particular mode may be observed.

Since the components of the Brillouin scattering tensor are proportional to the square root of the scattering cross section, Rockels coefficients (contained in the components of a Brillouin scattering tensor) could then be calculated by experimentally determining the integrated intensity of that mode.

Since salol is a highly birefringent crystal, one section of this chapter will carry out the calculations considering salol to be an anisotropic crystal in which case the incident and scattered polarization directions as well as the propagation directions of incident and scattered light will determine the phonon wave vector. All the results will be presented in tables for easy comparison.

B. Brillouin scattering tensors and elastic coefficients.

The calculation of Brillouin scattering tensors for salol in this section was based on the general procedures described in [1]. As was shown in chapter III, eqn.3-10, the velocity of sound in a solid can be found from the frequency shift measurements in Brillouin scattering experiments. The velocity of sound in turn is related to the elastic properties of the medium. Thus by means of Brillouin scattering we are able to study the elastic properties of solids at a higher frequency than with ultrasonic techniques ($\sim 10^{10}$ Hz).

In the following I shall first develop a general relationship between sound velocities and the elastic coefficients, and then turn to salol.

(1) Elastic properties of solids

The properties of long wavelength acoustic modes of a crystal can be derived by considering the crystal as an elastic continuum and applying the classical theory of elasticity [2]. The generalized Hook's law relating the stress and strain tensors is:

$$\sigma_{ij} = c_{ijkl} u_{kl} \quad (5-1)$$

where σ_{ij} is the stress (force per unit area along j direction, on the i -face of the crystal), u_{kl} is the strain and c_{ijkl} are elastic stiffness constants (summation over repeated indices is implied). If we utilize the symmetry properties of the elastic constants [4]:

$$c_{ijkl} = c_{jikl} = c_{klji}$$

and use the reduced Voigt notation we can rewrite eqn. (5-1) as:

$$\sigma_m = c_{mn} x_n \quad (5-2)$$

For each crystal system, the elastic constants C_{mn} are restricted by symmetry and some vanish identically. In appendix A, the elastic constants for salol are displayed in matrix form.

The components of the symmetrized strain are related to the particle displacement $u(\vec{r})$, by

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right)$$

The equations of motion of an elastic body with a mean density ρ , are given by [1]:

$$\rho \ddot{u}_i = C_{iklm} \frac{\partial^2 \vec{u}_m}{\partial r_k \partial r_l} \quad (5-3)$$

which relates u_i , the local cartesian components of displacement from the equilibrium position, to the spatial derivatives of $\vec{u}$ and the elastic constants C_{iklm} .

Solution of (5-3) is simplified considerably by restrictions placed on C_{iklm} by crystal symmetry [4]. For a given $\vec{q}$, plane wave solutions to eqn. (5-3) can be found, and one obtains 3 modes, usually of mixed polarization. The scattering tensor for any crystal can be entirely computed from the above equation in terms of the elastic constants and Pockel's coefficients, as we will discuss below.

If we assume a plane wave solution of the form:

$$\vec{u}_i = \vec{u}_{oi} e^{i(\vec{q} \cdot \vec{r} - \omega t)}$$

then from (5-3), $\rho \omega^2 \vec{u}_{oi} = C_{iklm} \vec{q}_k \vec{q}_l$

where $\vec{q}_k, \vec{q}_l$ are components of the $\vec{q}$ vector.

For the long wavelength acoustic modes (for $\vec{q} \rightarrow 0$), $\omega = vq$, where v is the appropriate sound velocity. Thus

$$[C_{iklm} \hat{q}_k \hat{q}_l - \rho v^2 \delta_{im}] \vec{u}_{om} = 0 \quad (5-4)$$

where $\hat{q}_k = \vec{q}_k / |\vec{q}|$ is the cosine of the angle between $\vec{q}$ and the $\hat{k}$ -axis (or equivalently the k -component of the unit vector $\hat{q}$).

Equations (5-4) have non-trivial solutions only if the secular determinant vanishes:

$$|C_{iklm} \hat{q}_k \hat{q}_l - \rho v^2 \delta_{im}| = 0 \quad (5-5)$$

Solutions of (5-5) gives 3 roots v_i which are the velocities of the three acoustic modes.

If we use the six component elastic constants C_{mn} , after eliminating those that are identically zero for salol , the secular equation (5-5) can be expressed as:

$$\begin{bmatrix} \lambda_{11} - \rho v^2 & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \lambda_{22} - \rho v^2 & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \lambda_{33} - \rho v^2 \end{bmatrix} = 0 \quad (5-6)$$

where

$$\begin{aligned} \lambda_{11} &= c_{11} \hat{q}_x^2 + c_{66} \hat{q}_y^2 + c_{55} \hat{q}_z^2 \\ \lambda_{12} &= (c_{12} + c_{66}) \hat{q}_x \hat{q}_y \\ \lambda_{13} &= (c_{13} + c_{55}) \hat{q}_z \hat{q}_x \\ \lambda_{23} &= (c_{44} + c_{23}) \hat{q}_y \hat{q}_z \\ \lambda_{23} &= c_{66} \hat{q}_x^2 + c_{23} \hat{q}_y^2 + c_{44} \hat{q}_z^2 \\ \lambda_{33} &= c_{55} \hat{q}_x^2 + c_{44} \hat{q}_y^2 + c_{33} \hat{q}_z^2 \end{aligned} \quad (5-6a)$$

If the elastic constants are known, eqn. (5-6) can be solved for any direction of $\vec{q}$, and will give 3 eigenvalues of velocity v_i ($i=1,2,3$) namely $\rho v_i^2 = C_i$ where C_i is proportional to a combination of elastic constants. Each v_i can then be put back into the original eqn. (5-4) which can be written in our present notation as:

$$\begin{aligned}
 (\lambda_{11} - \rho v^2) u_x + \lambda_{12} u_y + \lambda_{13} u_z &= 0 \\
 \lambda_{12} u_x + (\lambda_{22} - \rho v^2) u_y + \lambda_{23} u_z &= 0 \\
 \lambda_{13} u_x + \lambda_{23} u_y + (\lambda_{33} - \rho v^2) u_z &= 0
 \end{aligned} \tag{5-7}$$

Eqs. (5-7) then give the displacement eigenvector associated with each of these three velocities v_i . Conversely, if the velocities are measured, one can calculate the elastic constants of the crystal by solving eqns. (5-6) and (5-7). For salol, the elastic constants have not yet been measured either by ultrasonic techniques or by Brillouin scattering. Determination of the salol elastic coefficients was therefore a part of this thesis.

If $\vec{q}$ is chosen in a high symmetry direction, the displacement eigenvectors will be parallel to or perpendicular to $\vec{q}$, corresponding to one longitudinal (L) and two transverse (T) or shear modes. For general $\vec{q}$ -directions, $\vec{u}$ may be neither parallel to nor perpendicular to $\vec{q}$. Such mixed polarization modes will be indicated by QT (quasi-transverse) or QL (Quasi-longitudinal) to show that $\vec{u}$ is more nearly perpendicular or parallel to $\vec{q}$. For a general $\vec{q}$, equations (5-6) and (5-7) become very complicated to solve for the case of orthorhombic salol. In order to obtain the simplest possible expressions for solution,

I chose six simple $\hat{q}$ -directions to determine the elastic constants of salol. The expressions $v^2 = f(c_{ij})$ will be derived for each of those $\hat{q}$'s.

(2) Effect of sound waves on optical properties

In order to determine the Pockel's coefficients and polarization selection rules, we discuss in brief the effect of the sound waves on the optical properties of the crystal. In Brillouin scattering the thermally excited acoustic modes couple to the light through the modulation of the dielectric constant by the strain.

In the long wavelength limit, the distortion of the local dielectric constant is determined by the local strain through the elasto optic effect and is mathematically described [4] by:

$$\delta \epsilon_{ij} = -\epsilon_i \epsilon_j P_{ijkl} x_{kl}$$

where ϵ_i is one of the three principal values of the dielectric tensor and the P_{ijkl} ($= P_{jikl} = P_{ijlk}$) are the Pockel's (elasto optic or photoelastic) coefficients. In reduced notation $\delta \epsilon_{ij}$ can be expressed as:

$$\delta \epsilon_{ij} = -\epsilon_i \epsilon_j P_{mn} x_n \quad (5-7a)$$

The form of the 6x6 Pockel's tensor P_{mn} for salol is given in appendix A. For each mode, the 6-component strain x_n is related to the wave vector $\hat{q}$ and local displacement $\hat{u}$ by:

$$\begin{aligned}
 x_1 &= qu (\hat{q}_x \hat{u}_x) \\
 x_2 &= qu (\hat{q}_y \hat{u}_y) \\
 x_3 &= qu (\hat{q}_z \hat{u}_z) \\
 x_4 &= qu (\hat{q}_y \hat{u}_z + \hat{q}_z \hat{u}_y) \\
 x_5 &= qu (\hat{q}_x \hat{u}_z + \hat{q}_z \hat{u}_x) \\
 x_6 &= qu (\hat{q}_x \hat{u}_y + \hat{q}_y \hat{u}_x)
 \end{aligned} \tag{5-8}$$

where the products $\hat{q}_i \hat{u}_j$ are determined by the solution of eqns. (5-7).

(3) Calculation of Brillouin Scattering tensors

Since the intensity of scattered light is proportional to the mean square of the fluctuations in the dielectric constant $\delta\epsilon$ [5], from eqn. (5-7a) the intensity of the scattered light will be proportional to the square of the Pockel's coefficients. In general the matrices of Pockel's coefficients are not symmetric, ie, $P_{mn} \neq P_{nm}$ [4].

The intensity of the scattered light is given by:

$$I \sim \langle (\delta \epsilon_{ij})^2 \rangle = \langle (qu)^2 \rangle \epsilon_i^2 \epsilon_j^2 \left[P_{ijkl} (\hat{u}_k \hat{q}_l + \hat{u}_l \hat{q}_k) \right]^2$$

where the mean square Fourier strain component $\langle (qu)^2 \rangle$ given by thermodynamic fluctuation theory [6] In thermal equilibrium at temperature T:

$$\langle (qu)^2 \rangle = \frac{k_B T}{2 V s v^2} \quad (5-9)$$

If we now write the intensity of light scattered by mode α ($\alpha=1,2,3$) in terms of a Rayleigh ratio [7], defined as the scattered intensity per unit volume per unit solid angle per unit incident intensity polarized along the $\hat{e}_i$ direction, it can be shown starting from the excess polarization

$$\delta \vec{P}_i = \delta \epsilon_{ij} \vec{E}_j / 4 \quad \text{that:}$$

$$R_i^\alpha = \frac{k_B \pi^2 T \epsilon_i^2 \epsilon_j^2 n_s}{2 \lambda_s^4 s v_\alpha^2 n_o} \left[\hat{e}_j \cdot T \cdot \hat{e}_i \right]^2 \quad (5-10)$$

where $T^\alpha = T_{ij}^\alpha$

and $T_{ij}^\alpha = P_{ijkl} (\hat{u}_k \hat{q}_l + \hat{u}_l \hat{q}_k)$ (5-10a)

Here λ is the wavelength of scattered light, ρ is the average crystal density, v is the sound velocity of the acoustic mode, n_s and n_o being the refractive index of light inside the crystal for scattered and incident light respectively.

The tensor T_{ij} appearing in the Rayleigh ratio shown in eqn. (5-10a) is called the Brillouin scattering tensor. It can be given in 6-component form for salol by:

$$\begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} = \begin{bmatrix} P_{11} & P_{12} & P_{13} & 0 & 0 & 0 \\ P_{21} & P_{22} & P_{23} & 0 & 0 & 0 \\ P_{31} & P_{32} & P_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & P_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & P_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & P_{66} \end{bmatrix} \times \begin{bmatrix} q_x u_x \\ q_y u_y \\ q_z u_x \\ (q_y u_z + q_z u_y) \\ (q_z u_x + q_x u_z) \\ (q_x u_y + q_y u_x) \end{bmatrix}$$

and subsequently reduced to a 3x3 matrix according to:

$$\begin{bmatrix} T_1 & T_6 & T_5 \\ T_6 & T_2 & T_4 \\ T_5 & T_4 & T_3 \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{12} & T_{22} & T_{23} \\ T_{13} & T_{23} & T_{33} \end{bmatrix}$$

The calculation of the T-matrix thus involves carrying out the matrix multiplication in eqn. 5-11 .

Equations (5-10) gives the scattering cross section for each acoustic mode in terms of these T_{ij} tensors. These T_{ij} tensors determine the selection rules, and once they are calculated we can determine which modes will be observed for a given $\vec{q}$ and a given choice of polarization of the incident and scattered radiation. For example, if T is calculated as:

$$T^{\alpha} = \begin{bmatrix} T_{11} & 0 & 0 \\ 0 & T_{22} & 0 \\ 0 & 0 & T_{33} \end{bmatrix}$$

for a certain $\vec{q}$ and for mode α , and the incident and scattered wavevectors are chosen as $\vec{k}_0 = k_0 \hat{y}$ and $\vec{k}_s = k_s \hat{x}$, then this particular mode may be observed only in the scattering configuration $y(z,z)x$, with both $\vec{E}_0$ and $\vec{E}_s$ polarized along the z -direction (perpendicular to the yx scattering plane) and in no other polarization.

4) Corrections to the Rayleigh ratio

The Rayleigh ratio R expressed in eqn. (5-10) needs to be corrected for two factors. One is for the solid angle which is bigger outside than inside the crystal. The solid angle correction to R can be represented by:

$$R_{\text{XTAL}} = \frac{d\Omega_{\text{XTAL}}}{d\Omega_{\text{AIR}}} R_{\text{AIR}}$$

and

$$\frac{d\Omega_{\text{XTAL}}}{d\Omega_{\text{AIR}}} \sim \left(2 \left(\frac{n_{\text{AIR}}}{n_{\text{XTAL}}} \right) \right)^2$$

where: $d\Omega_{XTAL}$ = solid angle subtend at the scattering
column inside the crystal
 $d\Omega_{AIR}$ = solid angle subtended outside the crystal
 n_{XTAL} = average refractive index of the crystal.

The second correction factor is due to incomplete transmission of light at the crystal surface :

$$R_{XTAL} = \frac{1}{T} R_{OBS}$$

where

$$T = 1 - R = 1 - \left(\frac{n_{XTAL} - n_{AIR}}{n_{XTAL} + n_{AIR}} \right)^2$$

These two factors combined give the internal Rayleigh ratio or scattering cross section per unit volume for the crystal in terms of the observed R_{OBS} :

$$R_{XTAL} = \left(\frac{n_{AIR}}{n_{XTAL}} \right)^2 R_{OBS} / T \quad (5-19)$$

C. Numerical calculation of $\oint v^2$ and T_{ij} for salol

In the first part of this section, I shall carry out a specific calculation of $\oint v^2$ and T_{ij} according to the procedure described in section (B).

In case (1) light is incident along $\frac{1}{\sqrt{2}}(0\bar{1}\bar{1})$ and scattered along $\frac{1}{\sqrt{2}}(01\bar{1})$. In case (2) light is incident along (010) and scattered along (100). This calculation was performed twice. In (a) the crystal is assumed to be optically isotropic with an average refractive index $\bar{n} = (n_x + n_y + n_z)/3$. In (b), the crystal is optically anisotropic with different n_x , n_y and n_z .

$$\text{case (1): } \hat{k}_i = \frac{1}{\sqrt{2}}(0\bar{1}\bar{1})$$

$$\hat{k}_s = \frac{1}{\sqrt{2}}(01\bar{1})$$

(1) optically isotropic crystal

The phonon wave vector is given by:

$$\vec{q}_{\text{isotr}} = k_s \hat{k}_s - k_i \hat{k}_i$$

$$= k_i (\hat{k}_s - \hat{k}_i)$$

$$\text{assuming } |\vec{k}_s| = \bar{n} \frac{\omega}{c} \approx |\vec{k}_i|$$

$$= k_i \hat{y} / \sqrt{2}$$

$$\hat{q}_{\text{isotr}} = \frac{\vec{q}_{\text{isotr}}}{q} = \hat{y}$$

From eqn. (5-6a),

$$\lambda_{11} c_{66}, \lambda_{22} = c_{22}, \lambda_{33} = c_{44}$$

$$\text{and } \lambda_{12} = \lambda_{13} = \lambda_{23} = 0$$

Using these λ 's, we can solve the secular equation (5-5)

giving 3 eigenvalues ρv^2 in terms of elastic constants:

$$\rho v_1^2 = C_{66}$$

$$\rho v_2^2 = C_{22} \quad (5-13)$$

$$\rho v_3^2 = C_{44}$$

Substituting $\rho v_1^2 = C_{66}$ in eqn. (5-7), we can determine the eigenvectors or local displacement vector which can be normalized to 1 by

$$u_x^2 + u_y^2 + u_z^2 = 1.$$

For $\rho v^2 = C_{66}$, $\hat{u} = (100)$. Since $\hat{q}$ is along $\hat{y}$, and $\hat{u}$ is along $\hat{x}$, mode 1 is a pure transverse mode. Let's call it TA1 mode. Similarly for $\rho v_2^2 = C_{22}$, we get $\hat{u} = \hat{y}$ which is an LA mode (pure longitudinal). And for $\rho v_3^2 = C_{44}$, we get $\hat{u} = \hat{z}$ which is a TA2 mode.

As clearly seen in equation (5-13), the elastic constants C_{66} , C_{22} , C_{44} can be determined from the measurements of sound velocities v_1 , v_2 , v_3 . All three sound velocities are related to the measured Brillouin shift ν_B by (since the medium is considered isotropic):

$$\nu = \frac{\nu_s \lambda_s}{2\pi \sin \frac{1}{2}\theta} \quad (5-14)$$

where θ is the scattering angle, λ_s is the wavelength of scattered light and n is the refractive index of the isotropic medium.

Now the next question is: In which polarizations do we see TA1, TA2 and LA? This information is essential in order to relate the observed Brillouin shifts to the proper sound velocities.

Let's first take the case of the TA1 mode, with $v_1^2 = c_{66}$. Since we already know $\hat{q}$, $\hat{u}$ and the P_{mn} matrix for salol we can get all six components of the T-tensor [with $\hat{q}_x = \hat{q}_z = 0$, $\hat{q}_y = 1$, and $\hat{u}_x = 1$, $\hat{u}_y = \hat{u}_z = 0$] from eqn. (5-11)

$$\begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} = \begin{bmatrix} P_{11} & P_{12} & P_{13} & 0 & 0 & 0 \\ P_{21} & P_{22} & P_{23} & 0 & 0 & 0 \\ P_{31} & P_{32} & P_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & P_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & P_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & P_{66} \end{bmatrix} \cdot \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ P_{66} \end{bmatrix}$$

Converting the six-component T-tensor into 3x3 T_{ij} according to eqn. (5-12), we have:

$$\left[T_{ij} \right]_{TA1} = \begin{bmatrix} 0 & P_{66} & 0 \\ P_{66} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

From this tensor, it can be seen that the TA1 mode may be observed for polarizations $\hat{e}_s = \hat{x}$ and $\hat{e}_i = \hat{y}$, or $\hat{e}_s = \hat{y}$ and $\hat{e}_i = \hat{x}$. Since the scattering plane is the yz-plane, the mode TA1 may be observed in VH or HV polarization (or equivalently, in the configurations

$$\begin{aligned} & -y-z(x, y-z) \quad y-z \\ \text{or} \quad & -y-z(y+z, x) \quad y-z \end{aligned}$$

The Rayleigh ratio for this mode is:

$$R_{TA1} = \frac{k_B T \pi^2 \epsilon_x^2 \epsilon_y^2 n_s^2}{2 \lambda_s^4 \eta v_{TA1}^2 n_o^2} P_{66}^2$$

Using equation 8-6, one can now determine the Pockel's coefficient P_{66} , by measuring the integrated intensity of this TA1 mode, and comparing with the benzene spectrum obtained under similar experimental conditions.

Proceeding in the same way, one finds the matrices $[T_{ij}]_{TA2}$ and $[T_{ij}]_{LA}$ to be:

$$T_{ij} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & P_{44} \\ 0 & P_{44} & 0 \end{bmatrix} \quad \text{and} \quad T_{ij} = \begin{bmatrix} P_{12} & 0 & 0 \\ 0 & P_{22} & 0 \\ 0 & 0 & P_{32} \end{bmatrix}$$

The selection rules predict that TA_2 may be observed in (HH) [or $-y-z(y+z, y-z)y+z$], and LA may be observed in (VV) and (HH) configurations.

(2) Optically anisotropic crystal

In the anisotropic case, the phonon wave vector q is affected by the difference in the refractive indices n_x , n_y and n_z and we get a different $\vec{q}$ for different polarizations. A detailed calculation of the change in the inverse dielectric tensor due to strains and rotations associated with the acoustic waves in an optically anisotropic medium is given in [8].

Since the phonon wave vector may vary with respect to the polarization of incident and scattered light, one has to consider four different choices of polarizations VV, VH, HV and HH, where V is perpendicular to and H is in the scattering plane.

First we solve the general wave equation [9]

$$\nabla \times (\nabla \times \vec{E}) + \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = - \frac{\chi}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \quad (5-15)$$

to determine the velocities and polarizations of

electromagnetic waves through an anisotropic medium with $n_x = \sqrt{1+\chi_{11}}$, $n_y = \sqrt{1+\chi_{22}}$ and $n_z = \sqrt{1+\chi_{33}}$. It can be easily shown that, for any general wave incident along $\vec{k}_{\text{ext}} = (k_x, k_y, k_z)$, we have two different solutions for k inside a birefringent crystal, each with its own eigenvector or polarization $\vec{E} = \vec{E}(r) \exp[i(\vec{k} \cdot \vec{r} - \omega t)]$. Eqn. (5-15) can be reduced to:

$$\begin{aligned} \left[\left(n_x \frac{\omega}{c} \right)^2 - k_y^2 - k_z^2 \right] E_x + k_x k_y E_y + k_x k_z E_z &= 0 \\ k_y k_x E_x + \left[\left(n_y \frac{\omega}{c} \right)^2 - k_x^2 - k_z^2 \right] E_y + k_y k_z E_z &= 0 \\ k_z k_x E_x + k_z k_y E_y + \left[\left(\frac{\omega}{c} n_z \right)^2 - k_x^2 - k_y^2 \right] E_z &= 0 \end{aligned} \quad (5-16)$$

Eqn. (5-16) may have nonzero solution for E only if the secular determinant vanishes:

$$\begin{bmatrix} \left(\frac{n_x \omega}{c} \right)^2 - k_y^2 - k_z^2 & k_x k_y & k_x k_z \\ k_y k_x & \left(\frac{n_y \omega}{c} \right)^2 - k_x^2 - k_z^2 & k_y k_z \\ k_z k_x & k_z k_y & \left(\frac{\omega}{c} n_z \right)^2 - k_x^2 - k_y^2 \end{bmatrix} = 0 \quad (5-17)$$

In our specific case, for an incident beam with wavevector $\vec{k}_0 = (k/\sqrt{2}) (0, \bar{1}, \bar{1})$, the two solutions obtained from (5-17) are:

$$\begin{aligned} k_{01} &= n_x \frac{\omega}{c} \\ \text{and } k_{02} &= \frac{\sqrt{2} n_y n_z}{\sqrt{n_y^2 + n_z^2}} \frac{\omega}{c} \end{aligned} \quad (5-18)$$

Substituting the eigenvalues (5-18) into eqn. (5-16) one can derive the electric field vector $\vec{E}$. We find that, for

$$k_{01} = n_x \omega/c, \quad \hat{E}_{01} = \hat{x} \text{ (vertical)}$$

$$\text{and } k_{o2} = \frac{\sqrt{2} n_y n_z}{\sqrt{n_y^2 + n_z^2}} \frac{\omega}{c} \quad \vec{E}_{o2} = .64\hat{y} - .78\hat{z} \text{ (horizontal)}$$

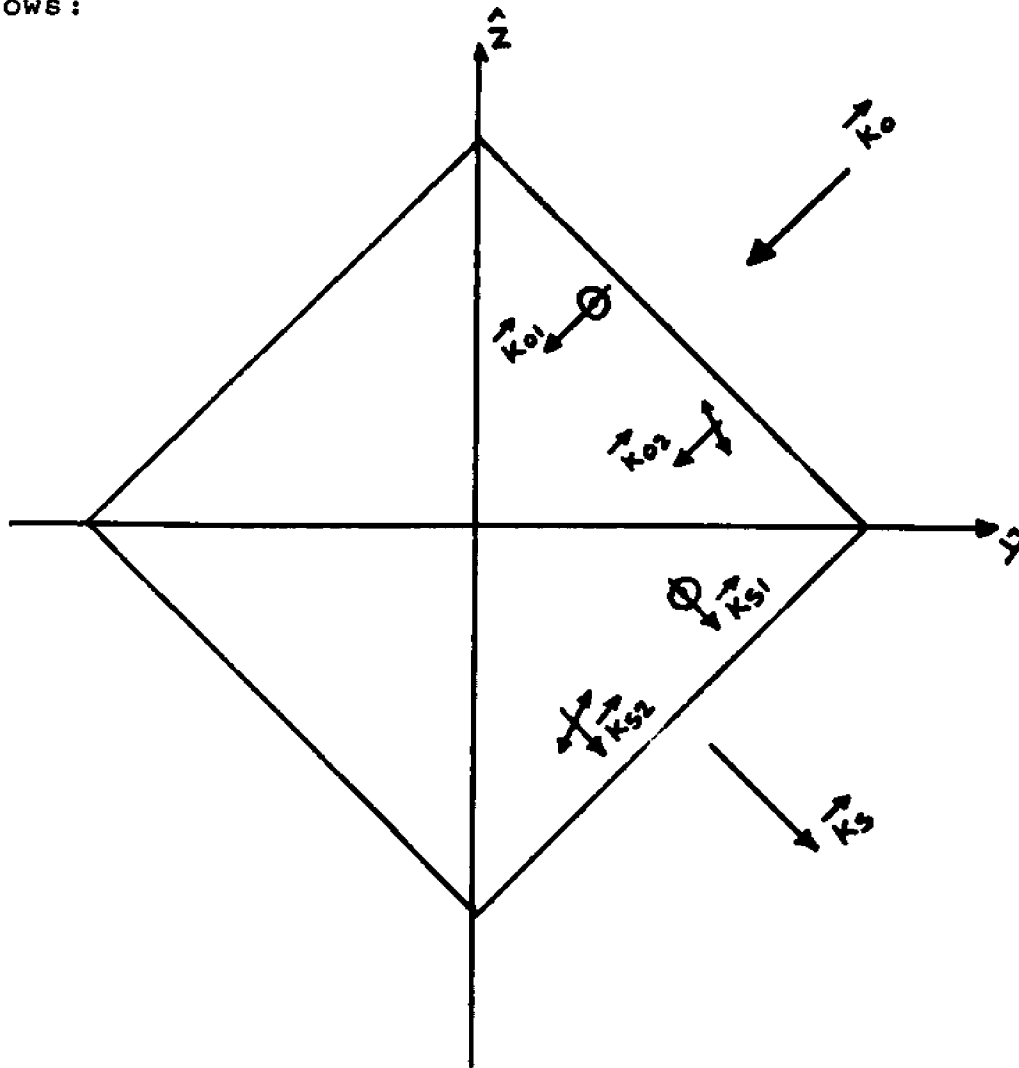
Similarly, one obtains two solutions for the scattered beams

$\vec{k}_s = (k_s/\sqrt{2})(0, 1, \bar{1})$ with their associated polarizations which are:

$$k_{s1} = n_x \omega/c \text{ with } \hat{E}_{s1} = \hat{x} \text{ (vertical)}$$

$$k_{s2} = \frac{\sqrt{2} n_y n_z \omega}{\sqrt{n_y^2 + n_z^2} c} \text{ with } \hat{E}_{s2} = .64\hat{y} + .78\hat{z} \text{ (horizontal)}$$

The solutions inside the crystal may be represented as follows:



Now, the phonon wave vector $\hat{q}$ for any of those four polarizations can easily be determined from the solutions obtained in (5-18).

(a) Calculation of the phonon wave vectors $\vec{q}$

For scattering configuration -y-z(x,x)y-z, we have

$$\vec{q}_{VV} = \vec{k}_{s1} - \vec{k}_{o1} = \frac{n_x \omega}{c} (\hat{k}_o - \hat{k}_s)$$

and $\hat{q}_{VV} = \hat{y}$

For the VH scattering configuration we have for q_{VH} :

$$\vec{q}_{VH} = \vec{k}_{s2} - \vec{k}_{o1} = \frac{\omega}{c} \left(\frac{n_y n_z}{\sqrt{n_x^2 + n_z^2}} \hat{k}_o - n_x \hat{k}_s \right)$$

Using the experimentally determined refractive index values (see chapter VII)

$$\hat{q}_{VH} = .998\hat{y} - .06\hat{z}$$

Similarly for HH configurations, $\vec{q}_{HH} = \vec{k}_{s2} - \vec{k}_{o2}$

$$\text{and } \hat{q}_{HH} = \hat{y}$$

Table (5-4) summarizes the values of $\hat{q}$ for all scattering configurations which I have used in this experiment

(b) Calculation of Brillouin scattering tensor for $\hat{q}_{VH}$

Consideration of the optically anisotropic crystal properties produces changes in the direction of $\hat{q}$ in the VH and HV cases here, while in the VV and HH cases, $\hat{q}$ remains

the same as in case (1). In calculating the scattering tensor for $\hat{q}_{VH} = .998\hat{y} + .06\hat{z}$, we can show how the eigenvalues $\mathfrak{S} v^2$ and eigenvectors $\hat{u}$ are affected by it.

For $\hat{q}_{VH} = 0.998\hat{y} - .06\hat{z}$ using eqn. (5-6a), and solving the secular eqn. (5-5), one obtains the three eigenvalues:

$$\mathfrak{S} v_1^2 = 0.0031 C_{55} + 0.997 C_{66}$$

$$\mathfrak{S} v_2^2 = 0.5 C_{44} + .499 C_{22} + 0.0016 C_{33} + .25 \left[(3.99 C_{22} - 3.97 C_{44} - 0.0128 C_{33})^2 + 0.0576 (C_{23} + C_{44})^2 \right]^{1/2}$$

$$\mathfrak{S} v_3^2 = 0.5 C_{44} + .499 C_{22} + 0.0016 C_{33} - .25 \left[(3.99 C_{22} - 3.97 C_{44} - 0.0128 C_{33})^2 + 0.0576 (C_{23} + C_{44})^2 \right]^{1/2}$$

and associated eigenvectors u 's are determined from (5-7), which are:

$$\begin{aligned} \hat{u}_1 &= \hat{x} \\ \hat{u}_2 &= \frac{1}{\sqrt{a_2}} (\hat{y} - b_2 \hat{z}) \\ \hat{u}_3 &= \frac{1}{\sqrt{a_3}} (\hat{y} - b_3 \hat{z}) \end{aligned}$$

where:

$$a_2 = 1 + b_2^2$$

$$b_2 = [8.98 C_{22} - 8.95 C_{44} - 0.029 C_{33} - 4.17 \{ (3.9 C_{23} - 3.97 C_{44} - 0.013 C_{33})^2 + 0.0576 (C_{23} + C_{44})^2 \}^{1/2}] / (C_{23} + C_{44})$$

$$a_3 = 1 + b_3^2$$

$$b_3 = [8.98 C_{22} - 8.95 C_{44} - 0.029 C_{33} + 4.17 \{ (3.9 C_{23} - 3.97 C_{44} - 0.013 C_{33})^2 + 0.0576 (C_{23} + C_{44})^2 \}^{1/2}] / (C_{23} + C_{44})$$

At this point, we can assign the modes. Mode 1 is clearly pure transverse (TA1), Mode 2 will be called Quasi-longitudinal (QL) because of its higher frequency, and mode 3 Quasi-transverse (QT).

Since the scattering configuration is given by $-y-z$ ($x, z-y$) $y-z$, one needs to calculate only the T_{12} and T_{13} components of the scattering tensor for each of the QL, QT and TA1 modes. Once these components are determined, the Rayleigh ratio for that particular mode will be proportional to $[\hat{e}_s \cdot T_{eff} \cdot \hat{e}_i]^2$, where T_{eff} will be given by:

$$T_{eff} = (T_{13} + T_{12})$$

therefore,

$$[\hat{e}_s \cdot T_{eff} \cdot \hat{e}_i]^2 = (1/2)[T_{13} + T_{12}]^2$$

Calculation of the eigenvalue, eigenvector and effective tensor T_{eff} can also be carried out for $\hat{q}_{HH}$, $\hat{q}_{HV}$ and $\hat{q}_{VY}$ in exactly the way shown above, and the results are summarized in table 5-5 y(1). Similar tables for other $\hat{q}$'s are shown in table 5-5.

(3) Calculation for misorientation

It was observed that one of my samples, salol 16 (see fig. 8-48), showed 5 Brillouin components in its spectrum although the presumed scattering configuration Y(VT)X should only yield 3 components. It was later found that the x and z axes of the crystal were misoriented by $\Psi = 11^\circ$. This misorientation is believed to be the reason for observing more than 3 modes in this sample in Y(ZT)X configuration.

Since the y (or b) face which is the naturally occurring planar face for solution grown crystals was correct, the incident wave vector is $\vec{k}_0 = k \hat{y}$. The scattered wave vector, instead of being along the x-direction, is $\Psi = 11^\circ$ upwards or downwards due to the misorientation. Let

$$\vec{k}_s = k (\cos \Psi \hat{x} + \sin \Psi \hat{z}).$$

As mentioned earlier, there are two different solutions for $\vec{k}$ inside the crystal; Eqn. (5-17) can be solved for $\vec{k}_0$ and $\vec{k}_s$, and the solutions are shown in table (5-1):

Table 5-1

Incident:	$\hat{k}_0 = \hat{y}$	
	$k_{01} = 1.651 \frac{\omega}{c}$	with $\hat{E} = \hat{z}$ (vertical)
	$k_{02} = 1.547 \frac{\omega}{c}$	with $\hat{E} = \hat{x}$ (horizontal)

Scattered:	$\hat{k}_s = 0.982\hat{x} + 0.2\hat{z}$	
	$k_{s1} = 1.805 \frac{\omega}{c}$	with $\hat{E} = \hat{z}$ (vertical)
	$k_{s2} = 1.045 \frac{\omega}{c}$	with $\hat{E} = .982\hat{x} - .2\hat{z}$ (horizontal)

One can now determine all the participating phonon vectors $\hat{q}$ for the various scattering configurations.

For comparison, the following table shows the variations in $\hat{q}$ for a perfect ($\Psi = 0$) and misoriented ($\Psi = 11^\circ$) crystal.

If we calculate the scattering tensor for mode 1 of the $\hat{q}_{VV} = .526\hat{x} - .844\hat{y} + .107\hat{z}$ phonon vector, we get the scattering tensor $[T_{ij}]_{\text{mode 1}}$ for that mode which shows that this mode 1 may be observed in any of the scattering configurations.

From eqn. (5-6a), we see that for $\hat{q} = a'\hat{x} + b'\hat{y} + c'\hat{z}$ all λ 's are nonzero with a' , b' and $c' \neq 0$, which gives an eigenvector of the form

$\hat{u} = a\hat{x} + b\hat{y} + c\hat{z}$, where a , b , c are complicated combinations of the c_{ij} 's.

Using (5-17), the scattering tensor now can be given in table (5-3).

Table 5-2

Calculation of phonon wave vector $\vec{q}$ for perfectly oriented and misoriented crystals

Scattering configuration	Phonon vector $\hat{q}$	
	for perfect orientation	for $\Psi = 11^\circ$
y(VV)x	$.71\hat{x} - .71\hat{y}$	$.526\hat{x} - .844\hat{y} + .107\hat{z}$
y(VH)x	$.738\hat{x} - .675\hat{y}$	$.72\hat{x} - .675\hat{y} + .147\hat{z}$
y(HH)x	$.76\hat{x} - .65\hat{y}$	$.744\hat{x} - .65\hat{y} + .151\hat{z}$
y(HV)x	$.73\hat{x} - .64\hat{y}$	$.55\hat{x} - .83\hat{y} + .112\hat{z}$

Table 5-3

Brilluoin scattering tensor for the α -th mode ($\alpha=1,2,\dots,12$) where
the crystal is misoriented by $\Psi = 11^\circ$, with $\hat{q} = a'\hat{x} + b'\hat{y} + c'\hat{z}$
and the eigenvector $\hat{u} = a\hat{x} + b\hat{y} + c\hat{z}$

$$[T_{ij}] = \begin{bmatrix} aa'P_{11} + bb'P_{12} + cc'P_{13} & (ab' + ba')P_{66} & (c'a + a'c)P_{55} \\ (ab' + ba')P_{66} & aa'P_{21} + bb'P_{22} + cc'P_{23} & (cb' + c'b)P_{44} \\ (c'a + a'c)P_{55} & (cb' + c'b)P_{44} & aa'P_{31} + bb'P_{32} + cc'P_{33} \end{bmatrix}$$

where a' , b' , c' are given in table 5-3 for all possible combinations. The Brillouin scattering tensors have the same structure for all 12 ($\alpha = 1, 2, 3$ for $\hat{q}_{VV}$, 4, 5, 6 for $\hat{q}_{VH}$ and 7, 8, 9 for $\hat{q}_{HH}$ and 10, 11, 12 for $\hat{q}_{HV}$) modes. Inspection (see table 5-5yx(10) shows that in the scattering configuration $Y(VT=VV+VH)X$ a maximum of six of those 12 modes may be visible. The Brillouin spectrum of salol 16 in fig. 8-48 shows five such Brillouin modes.

(D) Table of Brillouin Scattering Tensors

Table 5-5 shows the summary of the Brillouin scattering tensor calculation for all possible phonon vectors listed in table 5-4. Table 5-5 gives the T-matrices, the velocities and direction cosines of the phonons propagating in all those possible directions. Also shown are the components of the T-Tensor studied for various choices of polarization for the incident light and scattered light (V=light polarized perpendicular to the scattering plane, H=light polarized in the scattering plane). In order to obtain the Pockel's coefficients, one has to go back to eqn. 5-19 by measuring the intensity of that mode. The values of the determined elastic coefficients and Pockel's coefficients will be presented in ch. IX.

Table 5-4

 $\hat{q}$ for isotropic and anisotropic crystal calculations

Sample	Scatt. config	$\hat{q}_{\text{isotr}}$	$\hat{q}_{\text{VV}}$	$\hat{q}_{\text{VH}}$	$\hat{q}_{\text{HH}}$	$\hat{q}_{\text{HV}}$
salol 2	$y(e_i, e_j)x$	(.71, -.71, 0)	(.71, -.71, 0)	(.74, -.67, 0)	(.76, -.65, 0)	(.73, -.68, 0)
salol 2	$y(e_i e_j)z$	(0, .71, .71)	(0, .71, .71)	(0, -.65, .76)	(0, -.68, .74)	(0, .73, -.68)
salol 2	$x(e_i e_j)z$	(-.71, 0, .71)	(-.71, 0, .71)	(-.76, 0, .65)	(-.73, 0, .68)	(-.76, 0, .65)
	$z(e_i e_j)x$	(.71, 0, .71)	(.71, 0, .71)	(.67, 0, .74)	(.73, 0, .68)	(.74, 0, .67)
salol 8	$\frac{1}{\sqrt{2}}(110)(e_i e_j)110/\sqrt{2}$	(010)	(010)	(010)	(010)	(010)

table 5-4 continued...

salol 8	$\bar{1}10(e_i e_j)110$	(100)	(100)	(100)	(100)	(100)
salol 7	$0\bar{1}\bar{1}(e_i e_j)01\bar{1}$	(010)	(010)	(0, .999, -.06)	(010)	(0.999, -.06)
salol 7	$0\bar{1}1(e_i e_j)0\bar{1}\bar{1}$	(001)	(001)	(0.055, .999)	(001)	(0, .055, .999)
salol 3	$\bar{1}0\bar{1}(e_i e_j)\bar{1}01$	(001)	(001)	(.998, -.06, 0)	(001)	(.06, 0, -.998)
salol 3	$\bar{1}01(e_i e_j)101$	(100)	(100)	(.998, -.06, 0)	(100)	(.998, -.06, 0)

Table 5-5 x (1)

Brillouin scattering tensors of salol calculated both by isotropic and anisotropic considerations of the crystal

$$(I) \quad \hat{k}_1 = \frac{1}{\sqrt{2}} (110) \text{ and } k_s = \frac{1}{\sqrt{2}} (\bar{1}10)$$

or

$$(II) \quad k_i = \frac{1}{\sqrt{2}} (101) \text{ and } k_s = \frac{1}{\sqrt{2}} (\bar{1}01), \text{ isotropic consideration} \\ \hat{q} = (100)$$

$$(a) \quad \begin{aligned} \mathfrak{S} v_{T1}^2 &= c_{66} \\ \hat{u}_{T1} &= (010) \end{aligned} \quad [T]_{T1} = \begin{bmatrix} 0 & P_{66} & 0 \\ P_{66} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$(b) \quad \begin{aligned} \mathfrak{S} v_{T2}^2 &= c_{55} \\ \hat{u}_{T2} &= (001) \end{aligned} \quad [T]_{T2} = \begin{bmatrix} 0 & 0 & P_{55} \\ 0 & 0 & 0 \\ P_{55} & 0 & 0 \end{bmatrix}$$

$$(c) \quad \begin{aligned} \mathfrak{S} v_L^2 &= c_{11} \\ \hat{u}_{LA} &= (100) \end{aligned} \quad [T]_{LA} = \begin{bmatrix} P_{11} & 0 & 0 \\ 0 & P_{21} & 0 \\ 0 & 0 & P_{31} \end{bmatrix}$$

table 5-5x(1) contd...

Polarization Choice	Observed Components		
	TA1	TA2	LA
(1) -x+y (z,z) x+y	0	0	$[T_{31}]^2$
-x+y (z,-x+y) x+y	0	$1/2[T_{31}]^2$	0
-x+y (x+y,z) x+y	0	$1/2[T_{13}]^2$	0
-x+y (x+y,-x+y) x+y	$1/4[T_{12}]^2$	0	$1/4[T_{11}+T_{22}]^2$
(2) -x+z (y,y) x+z	0	0	$[T_{22}]^2$
-x+z (y,-x+z) x+z	$1/2[T_{12}]^2$	0	0
-x+z (x+z,y) x+z	$1/2[T_{12}]^2$	0	0
-x+z (x+z,-x+z) x+z	0	$1/4[T_{13}]^2$	$1/4[T_{11}+T_{33}]^2$

Table 5-5 x(2)

 $\hat{k}_1 = \frac{1}{\sqrt{2}} (\bar{1}, 1, 0)$ and $\hat{k}_s = \frac{1}{\sqrt{2}} (110)$, anisotropic consideration

Scatt. config.	$\hat{q}$	$\mathfrak{S}^V$	$\hat{u}$	$[\hat{e}_s \cdot T_{eff} \cdot \hat{e}_i]^2$
VV	(100)	$\mathfrak{S}^V_{T12} = C_{66}$	(010)	0
		$\mathfrak{S}^V_{T22} = C_{55}$	(001)	0
		$\mathfrak{S}^V_{L2} = C_{11}$	(100)	P_{31}^2
VH	(100)	$\mathfrak{S}^V_{T12} = C_{66}$	(010)	0
		$\mathfrak{S}^V_{T22} = C_{55}$	(001)	$1/2P_{35}^2$
		$\mathfrak{S}^V_{L2} = C_{11}$	(100)	0
HV	(100)	$\mathfrak{S}^V_{T12} = C_{66}$	(010)	0
		$\mathfrak{S}^V_{T22} = C_{55}$	(001)	$1/2P_{35}^2$
		$\mathfrak{S}^V_{L2} = C_{11}$	(100)	0
HH	(100)	$\mathfrak{S}^V_{T12} = C_{66}$	(010)	$1/4P_{36}^2$
		$\mathfrak{S}^V_{T22} = C_{55}$	(001)	0
		$\mathfrak{S}^V_{L2} = C_{11}$	(100)	$1/4(P_{11} + P_{21})$

TABLE 5-5 γ (3)

- I) $\hat{k}_i = \frac{1}{\sqrt{2}} (110)$ and $k_s = (1\bar{1}0)$
 II) or $k_i = \frac{1}{\sqrt{2}} (0\bar{1}\bar{1})$, $k_s = \frac{1}{\sqrt{2}} (01\bar{1})$, isotropic considerations
 $\hat{q} = (010)$

(a) $\mathcal{S}^v_{T_1^2} = c_{66}$
 $\hat{u}_{T_1} = (100)$

$$T = \begin{bmatrix} 0 & P_{66} & 0 \\ P_{66} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

(b) $\mathcal{S}^v_{T_2^2} = c_{44}$
 $\hat{u}_{T_2} = (001)$

$$T = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & P_{44} \\ 0 & P_{44} & 0 \end{bmatrix}$$

(c) $\mathcal{S}^v_{L^2} = c_{22}$
 $\hat{u}_L = (010)$

$$T = \begin{bmatrix} P_{12} & 0 & 0 \\ 0 & P_{22} & 0 \\ 0 & 0 & P_{32} \end{bmatrix}$$

Polarization choice

Observed Components

		LA	TA 1	TA 2
II) VV	$-y-z (x, x) y-z$	$[T_{11}]^2$	0	0
VH	$-y-z (x, y-y-z) y-z$	0	$1/2[T_{12}]^2_{T_1}$	0
HV	$-y-z (y-z, x) y-z$	0	$1/2[T_{12}]^2_{T_1}$	0
HH	$-y-z (y-z, -y-z) y-z$	$1/4[T_{22}+T_{33}]^2$	0	$1/4[T_{23}]^2_{T_2}$

table 5-5 y(3) contd....

I) VV	x+y (z,z) x-y	$[T_{33}]^2 LA$	0	0
VH	x+y (z,x+y) x-y	0	0	$1/2[T_{23}]^2 T_2$
HV	x+y (x-y,z) x-y	0	0	$1/2[T_{23}]^2 T_2$
HH	x+y (x-y,x+y) x-y	$1/4[T_{11}+T_{22}]^2$	$1/4[T_{12}]^2$	T_1 0

Table 5-5 Y (4)

For: $\hat{k}_1 = \frac{1}{\sqrt{2}}(-\hat{y}-\hat{z})$, $\hat{k}_2 = \frac{1}{\sqrt{2}}(\hat{y}-\hat{z})$, anisotropic consideration.

scatt.

config.	$\hat{q}$	$\mathfrak{g} v^2$	$\hat{u}$	$[e_s \cdot T_{eff} e_i]^2$
VV	(010)	$\mathfrak{g} v_{L^2}^2 = C_{22}$	(010)	p_{12}^2
		$\mathfrak{g} v_{T_1^2}^2 = C_{66}$	(100)	0
		$\mathfrak{g} v_{T_2^2}^2 = C_{44}$	(001)	0

VH (0, .998, -.06)

$$\begin{aligned}
 \mathfrak{g} v_{T_1^2}^2 &= .0031 C_{44} + .997 C_{22} & (100) & .498 p_{66}^2 \\
 \mathfrak{g} v_{OL^2}^2 &= r_1 + .25 q_1 & \frac{1}{\sqrt{1+k_1^2}} (0, 1, -b_1) & (.998 p_{32} + 0.6 b_1 p_{33})^2 \\
 \mathfrak{g} v_{OT^2}^2 &= r_2 - .25 q_1 & \frac{1}{\sqrt{1+k_2^2}} (0, 1, -b_2) & (.998 p_{32} + 0.6 b_2 p_{33})^2
 \end{aligned}$$

table 5-5 y(4) contd....

with

$$r_1 = .5C_{44} + .4985C_{22} + .0016C_{33}$$

$$q_1 = (3.988C_{22} - 3.97C_{44} - .0128C_{33}) + .0576(C_{23} + C_{44})^2$$

$$b1 = (p - .25q_1) / (C_{23} + C_{44})$$

$$b2 = (p + .25q_2) / (C_{23} + C_{44})$$

$$p = 8.982C_{22} - 8.953C_{44} - .0289C_{33}$$

HH	(010)	$9v_L^2 = C_{22}$	(010) $(P_{12} + P_{32})/4$
		$9v_{T1}^2 = C_{66}$	(100) 0
		$9v_{T2}^2 = C_{44}$	(001) $P_{44}^2/4$

HV	(0, .998, -.06)		
	$9v_{T1}^2 = .0031C_{44} + .997C_{22}$	(100)	$.498 P_{66}^2$
	$9v_{QL}^2 = r_1 + .25q_1$	$\frac{1}{\sqrt{1+b_1^2}}$	$(0, 1, -b_1) (.998P_{32} + .06P_{33})^2$
	$9v_{QT}^2 = r_1 - .25q_1$	$\frac{1}{\sqrt{1+b_2^2}}$	$(0, 1, -b_2) (.998P_{32} + .06P_{33})^2$

$r_1, q_1, b1, b2$ are as of (VH) scattering configuration.

Table 5-5 y (5)

$\hat{k}_1 = 1/\sqrt{2}(110)$ and $\hat{k}_2 = 1/\sqrt{2}(1, -1, 0)$ anisotropic consideration

Scatt.	Config.	$\hat{q}$	g_{V2}	$\hat{n}$	$[\hat{e}_1, \hat{e}_2, \hat{e}_3]$
VV	(010)	$g_{V1}^2 = c_{66}$ $g_{V2}^2 = c_{44}$ $g_{V3}^2 = c_{22}$	(100) (001) (010)	0 0 0	p_{32}^2
VH	(010)	$g_{V1}^2 = c_{66}$ $g_{V2}^2 = c_{44}$ $g_{V3}^2 = c_{22}$	(100) (001) (010)	0 $p_{44}^2/2$ 0	0
HV	(010)	$g_{V1}^2 = c_{66}$ $g_{V2}^2 = c_{44}$ $g_{V3}^2 = c_{22}$	(100) (001) (010)	0 $p_{44}^2/2$ 0	0
HH	(010)	$g_{V1}^2 = c_{66}$ $g_{V2}^2 = c_{44}$ $g_{V3}^2 = c_{22}$	(100) (001) (010)	$1/4(p_{66}^2)$ 0 $1/4(p_{12}^2 + p_{22}^2)$	0

Table 5-5 z (6)

$$(I) \quad \hat{k}_1 = \frac{1}{\sqrt{2}} (-1, 0, -1) \text{ and } \hat{k}_s = \frac{1}{\sqrt{2}} (-1, 0, 1)$$

or

$$(II) \quad \hat{k}_s = \frac{1}{\sqrt{2}} (0, -1, 1) \text{ and } \hat{k}_1 = \frac{1}{\sqrt{2}} (0, -1, -1),$$

isotropic consideration

$$\hat{q} = (001)$$

$$(a) \quad \mathfrak{S}^{\nu T_1^2} = c_{55} \quad T = \begin{bmatrix} 0 & 0 & p_{55} \\ 0 & 0 & 0 \\ p_{55} & 0 & 0 \end{bmatrix}$$

$$\hat{u}_{T1} = (100)$$

$$(b) \quad \mathfrak{S}^{\nu T_2^2} = c_{44} \quad T = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & p_{44} \\ 0 & p_{44} & 0 \end{bmatrix}$$

$$\hat{u}_{T2} = (010)$$

$$(c) \quad \mathfrak{S}^{\nu L^2} = c_{33} \quad T = \begin{bmatrix} p_{13} & 0 & 0 \\ 0 & p_{23} & 0 \\ 0 & 0 & p_{33} \end{bmatrix}$$

$$\hat{u}_L = (001)$$

table 5-5 Z(6) contd....

Polarization Choice	Observed Components		LA
	TA1	TA2	
1) $-z(y,y)-x+z$	0	0	$[T_{22}]_L^2$
$-x-z(y,-x-z)-x+z$	0	$1/2[T_{23}]^2_{T_2}$	0
$-x-z(-x+z,u)-x+z$	0	$1/2[T_{23}]^2_{T_2}$	0
$-x-z(-x+z,-x-z)-x+z$	$1/4[T_{13}]^2_{T_1}$	0	0
11) $-y+z(x,x)-y-z$	0	0	$[T_{11}+T_{33}]_L^2$
$-y+z(x,-y+z)-y-z$	$1/2[T_{13}]^2_{T_1}$	0	0
$-y+z(-y-z,x)-y-z$	0	$1/4[T_{23}]^2_{T_2}$	$[1/4(T_{22}+T_{33})]^2$

Table 5-5 z (7)

$\hat{k}_i = \frac{1}{\sqrt{2}}(-1, 0, -1)$ and $\hat{k}_s = \frac{1}{\sqrt{2}}(-1, 0, 1)$, anisotropic considerations

Scatt. config.	$\hat{q}$	g^v	$\hat{u}$	$[\hat{e}_s \cdot T_{eff} \hat{e}_i]^2$
VV	(001)	$g^v_{T1^2} = c_{55}$ $g^v_{T2^2} = c_{44}$ $g^v_{L^2} = c_{33}$	(100) (010) (001)	0 0 p_{23}^2
VH	(-.06, 0, .996)	$g^v_{T1^2} = .993c_{44} + .008c_{66}$ $g^v_{QL^2} = r + .25q$ $g^v_{QT^2} = r - .25q$ where $r = .004c_{11} + .5c_{55} + .496c_{33}$ $q = [(.128c_{11} + 15.76c_{55} - 15.888c_{44})^2 + .128(c_{13} + c_{55})]^{1/2}$ $p = .04c_{11} + 5.47c_{55} - 5.51c_{33}$ $b_1 = (p - 2.78q)/(c_{13} + c_{55})$ $b_2 = (p + 2.78q)/(c_{13} + c_{55})$	(010) $(-.06p_{66} + .996p_{44})^2$ $\frac{1}{\sqrt{1+b_1^2}}(1, 0, -b_1)$ $\frac{1}{\sqrt{1+b_2^2}}(1, 0, -b_2)$	0 0
HH	(001)	$g^v_{T1^2} = c_{55}$ $g^v_{T2^2} = c_{44}$ $g^v_{L^2} = c_{33}$	(100) (010) (001)	0 0 $1/4(p_{13} + p_{33})^2$
HV	(.06, 0, .996)	$g^v_{T1^2} = .008c_{66} + .993c_{44}$ $g^v_{QL^2} = r + .25q$ $g^v_{QT^2} = r - .25q$	(010) $\frac{1}{\sqrt{1+b_1^2}}(1, 0, -b_1)$ $\frac{1}{\sqrt{1+b_2^2}}(1, 0, -b_2)$	$(.06p_{66} + .996p_{44})^2$ 0 0

Table 5-5 xy (8)

x±y phonon, isotropic consideration

$$\hat{q} = \frac{1}{\sqrt{2}} (1, -1, 0)$$

(a-b) . QL, QT modes :

		QL	QT
eigenvalue	$3v^2$	$r + .25 q$	$r - .25 q$
eigenvector	$\hat{u}$	$\frac{1}{\sqrt{1+b^2}} (1, -b, 0)$	$\frac{1}{\sqrt{1+b^2}} (1, -b, 0)$
parameters	a	$1 + b^2$	$1 + b^2$
	b	$p - .5 q$	$p + .5 q$

where:

$$p = (.5C_{11} - .5C_{22})$$

$$q = [(C_{11} - C_{22})^2 + 4(C_{12} + C_{66})^2]^{1/2}$$

$$r = .25C_{11} + .25C_{22} + .5C_{66}$$

$$[T]_{QL,QT} = \frac{1}{\sqrt{2a}} \begin{bmatrix} P_{11} + bP_{12} & -(1+b)P_{66} & 0 \\ -(1+b)P_{66} & P_{21} + bP_{22} & 0 \\ 0 & 0 & P_{31} + bP_{32} \end{bmatrix}$$

$$(c) \hat{q} = \frac{1}{\sqrt{2}} (1, -1, 0), \hat{u}_{T1} = (0, 0, 1), 3v_{T1}^2 = .5C_{44} + .5C_{55}$$

$$[T]_{TA1} = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & P_{55} \\ 0 & 0 & -P_{44} \\ P_{55} & -P_{44} & 0 \end{bmatrix}$$

table 5-5 xy(8) contd....

<u>Polarization Choice</u>	<u>Observed components</u>		
	QL	QT	T1
y(VV)x	$[T_{33}]_{QL}^2$	$[T_{33}]_{QT}^2$	0
y(VH)x	0	0	0
y(HV)x	0	0	$[T_{32}]_{T1}^2$
y(HH)x	$[T_{12}]_{QL}^2$	$[T_{12}]_{QT}^2$	0
Y(VT)x	$[T_{33}]_{QL}^2$	$[T_{33}]_{QL}^2 [T_{32}]_{T1}$	0

Table 5-5 xy (9)

$\hat{k}_i = (010)$, $\hat{k}_s = (100)$, anisotropic consideration.

Scatt.

config. $\hat{q}$ $g v^2$ $\hat{u}$ $[e_s \cdot T \cdot e_i]^2$

VV $(-1, 1, 0)$

$$g v_{T1}^2 = .5 C_{44} + .5 C_{55}$$

$$g v_{QL}^2 = r_1 + .5 q_1$$

$$g v_{QT}^2 = r_1 - .5 q_1$$

(001)

$$\frac{1}{\sqrt{1+b_1^2}} (1, -b_1, 0) (p_{31} + b_1 p_{32})^2$$

$$\frac{1}{\sqrt{1+b_2^2}} (1, b_2, 0) (p_{31} + b_2 p_{32})^2$$

table 5-5 xy(9) contd...

where:

$$r_1 = .25 C_{11} + .25 C_{22} + .5 C_{66}$$

$$q_1 = [(C_{11} - C_{22})^2 + 4 (C_{12} + C_{66})^2]^{1/2}$$

$$b_1 = (p - .5 q_1) / (C_{12} + C_{66})$$

$$b_2 = (p + .5 q_1) / (C_{12} + C_{66})$$

$$p = 0.5 C_{11} - 0.5 C_{22}$$

VH (1.04, -.96, 0) / $\sqrt{2}$

$$8v_{T1}^2 = .55 C_{55} + .46 C_{44}$$

(001)

$$(.74 p_{55})^2$$

$$8v_{QL}^2 = r_1 + .25 q_1$$

$$\frac{1}{\sqrt{1+b_1^2}} (1, b_1, 0)$$

0

$$8v_{QT}^2 = r_1 - .25 q_1$$

$$\frac{1}{\sqrt{1+b_2^2}} (1, -b_2, 0)$$

0

with

$$r_1 = .273 C_{11} + .228 C_{22} + .501 C_{66}$$

$$q_1 = [(1.09 C_{11} - .178 C_{66} - .912 C_{22})^2 + 3.96 (C_{12} + C_{66})^2]^{1/2}$$

$$p = 0.55 C_{11} - 0.009 C_{66} - 0.46 C_{22}$$

$$b_1 = (p - 0.5 q) / (C_{12} + C_{66})$$

$$b_2 = (p + 0.5 q) / (C_{12} + C_{66})$$

Table 5-5 xy (9) continued

Scatt.	$\hat{q}$	$g v^2$	$\hat{u}$	$[e_s \cdot T_{eff} e_i]^2$
HH	$\frac{1}{\sqrt{2}}(1.08, -.92, 0)$			
		$g v_{T1}^2 = .58C_{55} + .42C_{44}$	(001)	0
		$g v_{QL}^2 = r_1 + .25q_1$	$\frac{1}{\sqrt{1+b_1^2}}(1, -b_1, 0)$	$(1.08b_1 + .92) p_{66}^2$
		$g v_{QT}^2 = r_1 - .25q_1$	$\frac{1}{\sqrt{1+b_2^2}}(1, -b_2, 0)$	$(1.08b_2 + .92) p_{66}^2$
where:		$r_1 = .29C_{11} + .5C_{66} + .21C_{22}$		
		$q_1 = [(1.16C_{11} - .32C_{66} - .84C_{22})^2 + 3.19(C_{12} + C_{66})^2]^{1/2}$		
		$p = .59C_{11} - .16C_{66} - .43C_{22}$		
		$b_1 = (p - .51q_1)/(C_{12} + C_{66})$		
		$b_2 = (p + .51q_1)/(C_{12} + C_{66})$		
HV	$\frac{1}{\sqrt{2}}(1.04, -.97, 0)$			
		$g v_{T1}^2 = .53C_{55} + .46C_{44}$	(001)	$.54p_{55}^2$
		$g v_{QL}^2 = r_1 + .25q_1$	$\frac{1}{\sqrt{1+b_1^2}}(1, -b_1, 0)$	0
		$g v_{QT}^2 = r_1 - .25q_1$	$\frac{1}{\sqrt{1+b_2^2}}(1, -b_2, 0)$	0

Table 5-5 yx (10)

$\hat{k}_i = (010)$, $\hat{k}_g = (.982, 0, 0.2)$;
 x and z axis misoriented by $\Psi = 11^\circ$

Scatt. config.	$\hat{q}$	mode	$\hat{u}$	$[e_g \cdot \text{Teff} \cdot e_i]^2$
y(VV)x	(.53, -.844, .11)	QL	(a,b,c)	$[T_{33}]_{QL}^2$
		QT1	(a',b',c')	$[T_{33}]_{QT1}^2$
		QT2	(a',b',c')	$[T_{33}]_{QT2}^2$
y(VH)x	(.72, -.68, .15)	QL	"	$[T_{23}]_{QL}^2$
		QT1	"	$[T_{23}]_{QT1}^2$
		QT2	"	$[T_{23}]_{QT2}^2$
y(HV)x	(.55, -.83, .11)	QL	"	$[T_{13}]_{QL}^2$
		QT1	"	$[T_{13}]_{QT1}^2$
		QT2	"	$[T_{13}]_{QT2}^2$
y(HH)x	(.74, -.65, .15)	QL	"	$[T_{12}]_{QL}^2$
		QT1	"	$[T_{12}]_{QT1}^2$
		QT2	"	$[T_{12}]_{QT2}^2$

Y(VT)X, will thus allow the observation of six diff. modes.

Table 5-5 zx (11)

$\hat{k}_i = (001)$ and $\hat{k}_g = (100)$, isotropic consideration.

$$q = \frac{1}{\sqrt{2}}(101)$$

(a-b). QL, QT modes:

		QL	QT
eigenvalue	$g v^2$	$r + .25q$	$r - .25q$
eigenvector	$\hat{u}$	$\frac{1}{\sqrt{1+b^2}}(1, 0, -b)$	$\frac{1}{\sqrt{1+b^2}}(1, 0, -b)$
	b	$(p - .5q)/(c_{13} + c_{55})$	$(p + .5q)/(c_{13} + c_{55})^2$

$$\text{where: } r = .25c_{11} + .5c_{55} + .25c_{33}$$

$$p = .5c_{11} - .5c_{33}$$

$$q = [(c_{11} - c_{33})^2 - 4(c_{13} + c_{55})^2]^{1/2}$$

$$[T]_{QL,QT} = \frac{1}{\sqrt{2a}} \begin{bmatrix} p_{11} - bp_{13} & 0 & (1-b)p_{55} \\ 0 & p_{21} - bp_{23} & 0 \\ (1-b)p_{55} & 0 & p_{31} - bp_{33} \end{bmatrix}$$

(c). TAL mode: $\hat{u}_{T1} = (010)$; $g v^2 T1 = .5c_{66} + .5c_{44}$

$$[T]_{TAL} = \begin{bmatrix} 0 & p_{66} & 0 \\ p_{66} & 0 & p_{44} \\ 0 & p_{44} & 0 \end{bmatrix}$$

Polarization choice

Observed components

		TAL	QL	QT
$z(y,y)x$	VV	0	$[T_{2QL}]$	$[T_2]_{QT}^2$
$z(y,z)x$	VH	$[T_{23}]_{TAL}^2$	0	0
$z(x,y)x$	HV	$[T_2]^2$	0	0
$z(x,z)x$	HH	0	$[T_{13}]_{QL}^2$	$[T_{13}]_{QT}^2$

Table 5-5 zx (12)

$\hat{k}_i = (001)$ and $\hat{k}_s = (100)$, anisotropic consideration

Scatt. config.	$\hat{q}$	$\hat{u}$	$[e_s \cdot \text{Teff} \cdot e_i]^2$
VV	$\frac{1}{\sqrt{2}}(101)$		
	$\mathcal{S}V_{T1}^2 = .5C_{66} = .5C_{44}$	(010)	0
	$\mathcal{S}V_{QL}^2 = r - .25q$	$\frac{1}{\sqrt{1+b_1^2}}(1,0,-b_1)$	$(P_{21} - P_{23}b_1)^2$
	$\mathcal{S}V_{QT}^2 = r - .25q$	$\frac{1}{\sqrt{1+b_2^2}}(1,0,-b_2)$	$(P_{21} - P_{23}b_2)^2$
	where: $r = .25C_{11} + .5C_{55} + .25C_{33}$		
	$q = [(C_{11} - C_{33})^2 - 4(C_{13} + C_{55})^2]^{1/2}$		
	$p = .5C_{11} - .5C_{33}$		
	$b_1 = (p - .5q)/(C_{13} + C_{55})$		
	$b_2 = (p + .5q)/(C_{13} + C_{55})$		
VH	(.67, 0, .74)	$\mathcal{S}V_{T1}^2 = .449C_{66} + .548C_{44}$	(010) $.274P_{44}^2$
		$\mathcal{S}V_{QL}^2 = r + .25q$	$\frac{1}{\sqrt{1+b_1^2}}(1,0,-b_1)$ 0
		$\mathcal{S}V_{QT}^2 = r - .25q$	$\frac{1}{\sqrt{1+b_2^2}}(1,0,-b_2)$ 0
HV	(.74, 0, .67)	$\mathcal{S}V_{T1}^2 = .548C_{66} = .449C_{44}$	(010) $.274P_{44}^2$
		$\mathcal{S}V_{QL}^2 = r + .25q$	$\frac{1}{\sqrt{1+b_1^2}}(1,0,-b_1)$ 0
		$\mathcal{S}V_{QT}^2 = r - .25q$	$\frac{1}{\sqrt{1+b_2^2}}(1,0,-b_2)$ 0
HH	(.73, 0, .68)	$\mathcal{S}V_{T1}^2 = .533C_{66} + .46C_{44}$	(010) 0
		$\mathcal{S}V_{QL}^2 = r + .25q$	$\frac{1}{\sqrt{1+b_1^2}}(1,0,-b_1) (.68 - .73b_1)p_{55}$
		$\mathcal{S}V_{QT}^2 = r - .25q$	$\frac{1}{\sqrt{1+b_2^2}}(1,0,-b_2) (.68 - .73b_2)p_{55}$
where:	$r = .267C_{11} + .497C_{55} - .23C_{33}$		
	$p = .538C_{11} - .076C_{55} - .464C_{33}$		
	$q = [(1.07C_{11} - .15C_{55} - .92C_{33})^2 - 3.94(C_{13} + C_{55})^2]^{1/2}$		
	$b_1 = (p - .504q)/(C_{13} + C_{55})$		
	$b_2 = (p + .504q)/(C_{13} + C_{55})$		

Table 5-5 yz (13)

$\hat{k}_1 = (010)$ and $\hat{k}_2 = (001)$, isotropic consideration

$$q = \frac{1}{\sqrt{2}}(0, -1, 1)$$

(a-b). QL, QT modes

	QL	QT
eigenvalue	$g v^2$	$r + .25q$
eigenvector	$\hat{u}$	$\frac{1}{\sqrt{1+b^2}}(0, 1, -b)$
parameters	$b = (p - .5q)/(C_{44} + C_{23})$	$(p + .5q)/(C_{44} + C_{23})$
where:	$p = .5C_{22} - .5C_{33}$ $q = [(C_{22} - C_{33})^2 + 4(C_{44} + C_{23})^2]^{1/2}$ $r = .5C_{44} + .25C_{22} + .25C_{33}$	

$$[T]_{QL,QT} = \frac{1}{\sqrt{2a}} \begin{bmatrix} -p_{12} - b p_{13} & 0 & 0 \\ 0 & p_{22} - b p_{23} & (1+b)p_{44} \\ 0 & (1+b)p_{44} & p_{32} - b p_{33} \end{bmatrix}$$

(c) TAl mode: $3 v_{T1}^2 = .5C_{66} + 5C_{55}$

$$\hat{u}_{T1} = (100)$$

$$[T]_{T1} = \begin{bmatrix} 0 & -P_{66} & P_{55} \\ -P_{66} & 0 & 0 \\ P_{55} & 0 & 0 \end{bmatrix}$$

Polarization Choice		Observed Component		
		QL	QT	TAl
y(x,y)z	VV	$[T_{11}]_{QL}^2$	$[T_{11}]_{QT}^2$	0
y(x,y)z	VH	0	0	$[T_{12}]_{T1}^2$
y(z,x)z	HV	0	0	$[T_{13}]^2$
y(z,y)z	HH	$[T_{23}]_{QL}^2$	$[T_{23}]_{QT}^2$	0

Table 5-5 yz (14)

$\hat{k}_1 = (010)$, $\hat{k}_2 = (001)$, anisotropic consideration

Scatt.

config. $\hat{q}$ $\mathcal{S}v^2$ $\hat{u}$ $[e_s \cdot T_{eff} e_i]^2$

VV $\frac{1}{\sqrt{2}}(0, -1, 1)$

$$\mathcal{S}v_{T1}^2 = .5C_{66} + .5C_{55} \quad (100) \quad 0$$

$$\mathcal{S}v_{QT}^2 = r + .25q \quad \frac{1}{\sqrt{1+b_1^2}}(0, 1, -b_1) \quad (P_{12} + b_1 P_{13})^2$$

$$\mathcal{S}v_{QL}^2 = r + .25q \quad \frac{1}{\sqrt{1+b_2^2}}(0, 1, -b_2) \quad (P_{12} + b_2 P_{13})^2$$

r, p, q, b_1, b_2 given in table 5-5 yz (11)

VH $\frac{1}{\sqrt{2}}(0, -.92, 1.08)$

$$\mathcal{S}v_{T1}^2 = .42C_{66} + .58C_{55} \quad (100) \quad .212 p_{66}^2$$

$$\mathcal{S}v_{QT}^2 = r + .25q \quad \frac{1}{\sqrt{1+b_1^2}}(0, 1, -b_1) \quad 0$$

$$\mathcal{S}v_{QL}^2 = r + .25q \quad \frac{1}{\sqrt{1+b_2^2}}(0, 1, -b_2) \quad 0$$

HV $\frac{1}{\sqrt{2}}(0, -.984, 0.92)$

$$\mathcal{S}v_{T1}^2 = .484C_{66} + .42C_{55} \quad (100) \quad .234 p_{55}^2$$

$$\mathcal{S}v_{QT}^2 = r + .25q \quad \frac{1}{\sqrt{1+b_1^2}}(0, 1, -b_1) \quad 0$$

$$\mathcal{S}v_{QL}^2 = r + .25q \quad \frac{1}{\sqrt{1+b_2^2}}(0, 1, -b_2) \quad 0$$

HH $\frac{1}{\sqrt{2}}(0, -.954, 1.04)$

$$\mathcal{S}v_{T1}^2 = .46C_{66} + .54C_{55} \quad (100) \quad 0$$

$$\mathcal{S}v_{QT}^2 = r + .25q \quad \frac{1}{\sqrt{1+b_1^2}}(0, 1, -b_1) \quad P_{44}(.954b_1 + 1.04)^2$$

$$\mathcal{S}v_{QL}^2 = r + .25q \quad \frac{1}{\sqrt{1+b_2^2}}(0, 1, -b_2) \quad P_{44}(.954b_2 + 1.07)^2$$

where: $r = [(.92C_{22} - 1.09C_{33} + .17C_{44})^2 + 3.068(C_{44} + C_{23})^2]^{1/2}$

$$p = .462 C_{22} - .04C_{44} - .548C_{33}$$

$$b_1 = (p + .502q) / (C_{44} + C_{23})$$

$$b_2 = (p - .502q) / (C_{44} + C_{23})$$

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CHAPTER VI

EXPERIMENTAL APPARATUS AND PROCEDURES

A. Introduction

The experiments described in this thesis involved both Brillouin and Raman scattering spectroscopy using an Argon ion laser.

In Brillouin scattering spectroscopy, a beam of laser light (single mode) is focused onto a small volume of the sample to be studied. The light scattered from the sample containing a number of Brillouin components as well as an elastic (Rayleigh) component is collected and frequency analysed by a high-resolution Fabry-Perot Interferometer (either single pass or triple pass). Elastic scattering at the frequency of the incident laser light usually produces the most intense component. Inelastic components appear at frequencies shifted (Brillouin shift) with respect to the laser frequency on both the Stokes(lower frequency) and anti-Stokes(higher frequency) sides. The main purpose of the Brillouin scattering melting experiment was to measure the frequency shift, the intensity and the deconvoluted

linewidth (corrected for finite instrumental linewidth) of the Brillouin components very accurately as the sample was heated to the melting temperature T_M . As stated earlier, the purpose of the experiment was to look for any anomalies in the velocity and attenuation of acoustic phonons which may appear close to the solid-liquid transition.

Raman Scattering experiments were also performed in order to look for any changes in the linewidth, intensity and Raman shift of the optic phonons near T_M and to observe new Raman modes activated by symmetry-breaking defects. The scattered laser light containing numerous Raman modes ($\nu > 10\text{cm}^{-1}$) was frequency analysed by a Tandem grating spectrometer. Unlike the Brillouin experiment, here only the anti-Stokes components were studied. The detailed experimental procedure and a short description of the apparatus used is given below.

B. Brillouin Scattering Experiment: Procedures

The experimental arrangement used in the Brillouin Scattering experiment is schematically presented in Fig. 6-1. The argon-ion laser (either at $4880\text{\AA}$ or $5145\text{\AA}$) was run in single mode operation by the use of an intracavity etalon. A

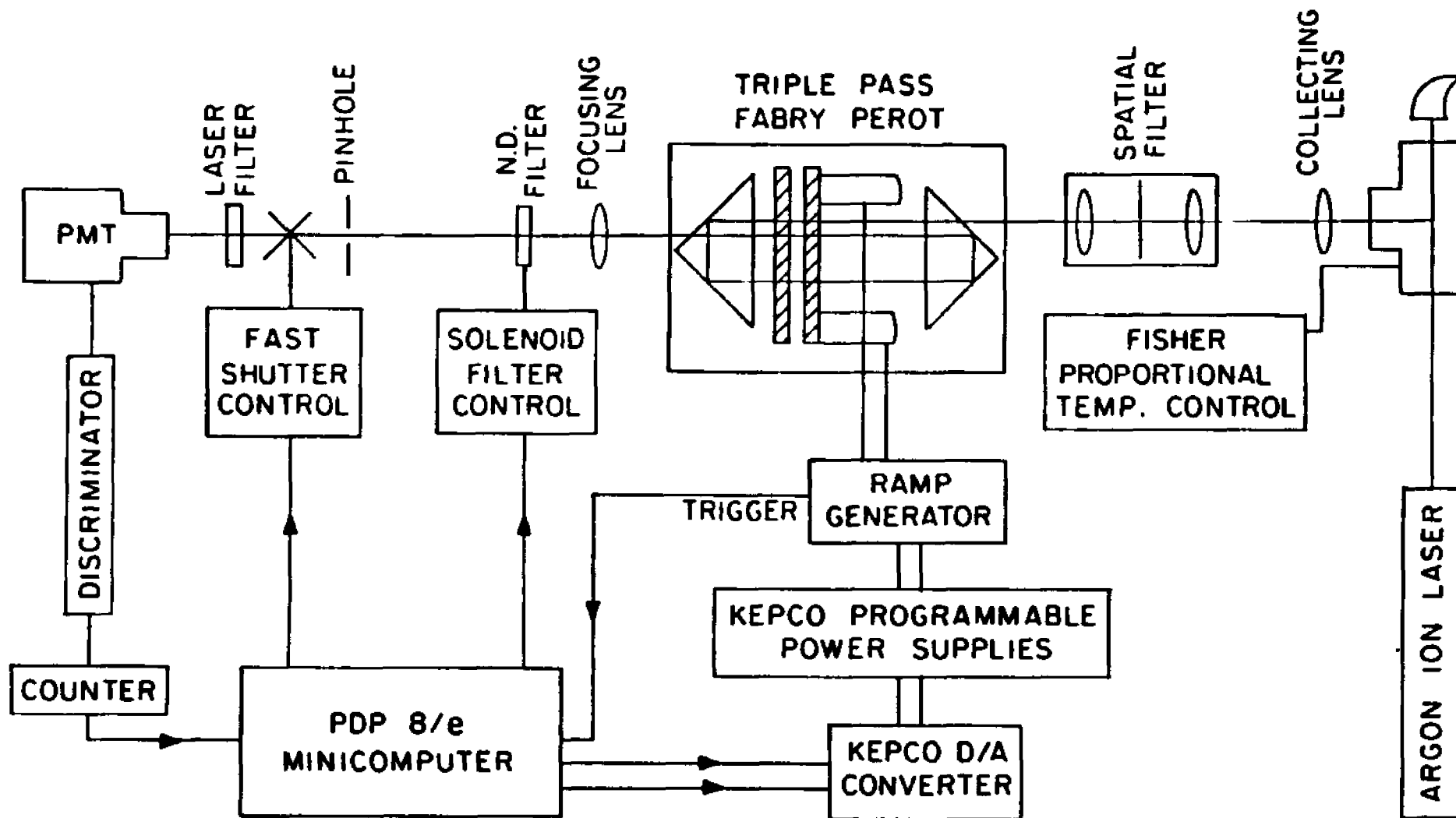


Fig. 6-1: Schematic diagram of the Brillouin scattering experiment set up showing a triple pass Fabry Perot Interferometer with computer controlled alignment system.

check on the stability and quality of the single mod laser output was performed from time to time with a small spherical Fabry-Perot (FPS)[8] with a free spectral range (the free spectral range FSR is determined by the spacing $d(\text{cm})$ between the Fabry- Perot mirrors and is given by the expression $\nu_{\text{FSR}} = 1/2d$ in units of wavenumbers) ν_{FSR} of 8 GHz, whose output was monitored on an oscilloscope. The oscilloscope's sawtooth ramp output was used to scan the small FPS. By simultaneous use of a photodiode power meter, one can also maximize the single mode output by careful manipulation of the intracavity air etalon.

The laser beam was focused into the sample contained in a sample cell inside the thermostat by a lens so that the beam focuses at the center of the crystal. With the help of a polarization rotator, the incident beam could be made either vertically or horizontally polarized (with respect to the plane containing the wave vectors of the incident and scattered light). Light scattered at 90° was collected by a lense . The polarization of the scattered light was selected by a polaroid analyser, and its aperture was determined by an adjustable iris diaphragm. The scattered light was collimated and passed through a spatial filter which served to define the scattering volume and to improve the effective instrumental finesse. The size of the pinhole in the spatial filter was chosen to match the image of the scattering column in the focal plane.

The scattered light from the region of the crystal defined by the spatial filter was then analysed by a piezoelectrically scanned (single pass or triple pass) plane Fabry Perot Interferometer (Tropel Model 360). A preliminary experiment was also performed with a pressure scanned FPP. The Fabry Perot plates were matched and rotated to achieve maximum parallelism in those regions of the plates which were utilized in the single or triple pass operation. The output of the Fabry Perot was focused on another pinhole of appropriate diameter that compromised between instrumental width and signal output, before being imaged onto a phototube. The intensity of the scattered light was measured by an ITT FW-130 photomultiplier tube operated at a cathode voltage of 1830 volts d.c. A narrowband laser filter was placed in front of the phototube to eliminate the Raman scattering intensity.

Photon counting was used in the detection system. The electrical pulses emitted by the photomultiplier were processed by a discriminator. The rate at which photo-electrons are emitted (proportional to the intensity of scattered light) from the PMT was measured either by a rate meter, whose output was then recorded on a strip chart recorder, or by a PDP-8 minicomputer, which had been programmed to function as a multiscaler. Most of the Brillouin data was collected by the PDP-8 minicomputer which

was synchronized with the interferometer ramp generator, whereas Raman data were recorded with the ratemeter and strip chart recorder. A total of 512 24-bit memory channels were used in the Brillouin experiment. The counting time per channel was set so that the 512 channels covered slightly more than two free spectral ranges. The spectrum stored in the PDP-8 memory could be transferred to the PDP-10 mainframe computer for storage and subsequent analysis. Fig. 8-1(a) shows a typical Brillouin spectrum thus obtained. Sequential scans were taken to build up the Brillouin components until a satisfactory signal to noise ratio was obtained. To keep a record of all necessary experimental conditions during the collection of a particular spectrum, a raw x-y plot of the data in the PDP-8 was recorded by a HP 7040A x-y plotter interfaced to the PDP-8 computer.

C. Raman Scattering Experiment: Procedure

The experimental arrangement of the Raman scattering apparatus is shown in Fig 6-2. Here I used the same laser as in the Brillouin experiment, except that the air-spaced etalon was removed (the laser output power increased four times). The experimental procedure is similar to that described above. In this case the scattered light, containing numerous Raman modes, was analysed using a Spex 1401 double grating spectrometer and photon counting

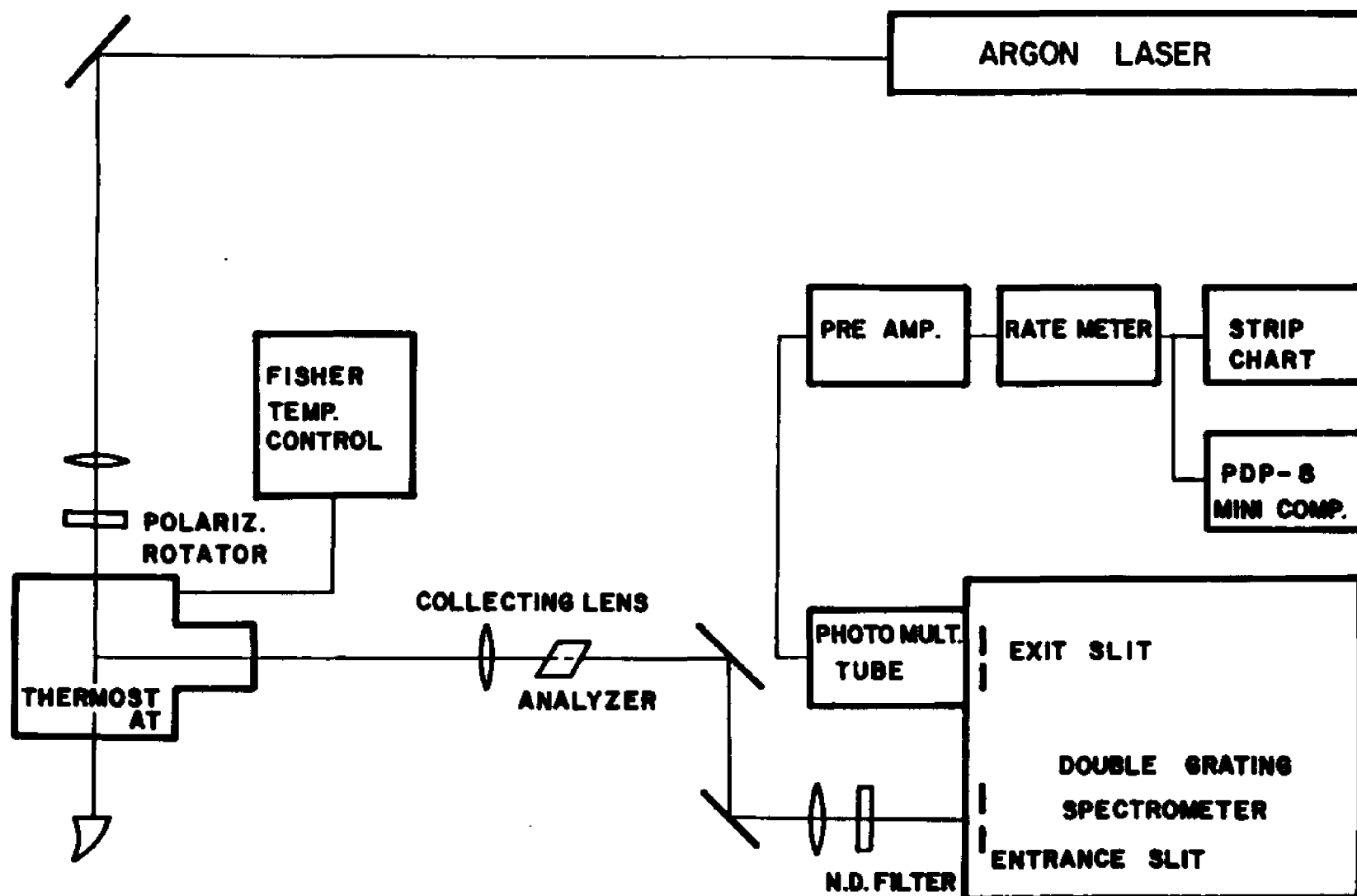


DIAGRAM
FIG. 6-2 SCHEMATIC OF RAMAN EXPERIMENT SET UP

electronics and was recorded on a strip chart recorder (or occasionally stored in the PDP-8 core). The scattering angle was also 90° . Both the green 5145Å and blue 4880Å lines of the argon-ion laser were used. The collimated scattered light was reflected from a system of two mirrors, so that the scattering column could be focused vertically onto the vertical spectrometer slits which, along with a brass horizontal slit, determined the effective scattering volume.

Light leaving the spectrometer was focused onto the cathode of the FW-130 PMT whose output was processed as described above. I collected both short slow scans (up to 200 cm^{-1} from the laser line) and fast long scans (upto 2000 cm^{-1}) for different scattering configurations. Typical short and long scan Raman spectra of salol at room temperature are shown in Fig 8-49 and 8-50 respectively. This in short is how the Brillouin and Raman experiments were performed. Following is a detailed description of each part of the experimental procedure with a description of the associated equipment and how it functions.

D. Detailed description of experimental system and equipment

(1) Lasers:

The laser mainly used in these experiments was a Spectra

Physics Model 165 argon-laser, giving stable multi-mode single line outputs at 5145Å and 4880Å of 5 Watts and 4 Watts respectively. The normal experimental conditions

utilized an output of approximately 100mw at 20A plasma tube current. The output attenuates greatly in the course of time which required a periodic check on the output by a photodiode power meter. [Periodic pressure checks of the plasma tube, weekly water filter changes and cleaning of the Brewster windows by SP prescribed procedures were key points in maintaining a satisfactory output].

In making Brillouin scattering linewidth measurements of the spectrum it was extremely important to have the laser output in a single mode. Single mode operation was obtained by adjusting the tilt of an intracavity air spaced etalon placed in front of the Brewster window of the laser tube. Problems which may affect the smooth operation of the laser were temperature fluctuation and mechanical vibration of the experiment room. The tilt adjustment in the air spaced etalon was stable for as long as an hour after the laser had warmed up. Temperature stability of 0.01°C is required to prevent mode hopping [1]. Frequency jitter is the modulation of the laser frequency (on the order of 10MHz) due to fluctuations in the laser cavity length. These fluctuations were induced by acoustic vibrations originating from mechanical perturbations. A chief source of this perturbation was believed to be the turbulent flow of water around the plasma tube. Frequency stability of 1MHz has been

obtained [2] by mounting the mirrors separately, isolated from tube and water. A small SP Model 80 He-Ne laser (output ~ 5 mW) was also used for refractive index measurements of the crystal.

(2) Fabry Perot Interferometers

(a) General description

Two types of interferometers were used. During initial experiments on succinonitrile a pressure scanned plane parallel Fabry Perot [9] with quartz spacers of different length was used to scan the Brillouin spectrum. The instrument operated with a finesse typically between 30 and 40 and a free spectral range ν_{FSR} of 7.5 GHz. The principle of scanning is to change the optical path between the plates by changing the pressure of the gas contained between the plates [9]. The pressure dependence of the refractive index was easily determined from the experiment. From $n = (1 + 4\pi N\alpha)^{1/2} \approx 1 + 2\pi N\alpha$, one can see that $n-1 \sim N$ or for low density, $n-1 \sim P$. From obtained values for nitrogen, $n=1+9.83 \cdot 10^{-6} P$, where P is the pressure inside the cavity in psi. Both nitrogen gas and freon were successfully used in the experiment to pressure scan. Plate separations from 3 mm upto 2 cm were used. Plate parallelism was obtained by adjusting the mechanical screws and simultaneously looking at the interferometer fringes through a telescope.

The second type of interferometer used in the main experiments with salol was a Tropel 360 piezoelectric Fabry-Perot Interferometer driven by a Tropel 361 Ramp Generator. This was operated both in single pass and triple pass[10,11]. The tropel Fabry Perot used $\lambda/200$ plane mirrors which were coated respectively for 93% reflectivity (triple pass) and 98% reflectivity (single pass) in the spectral region 4500-5500Å. Three piezoelectric ceramic transducers (PZT) scan and align one of the plane mirrors with respect to the other mirror which remains fixed. The ramp sawtooth voltage (0 to 700 Volts) supplied by the Tropel 361 Ramp Generator was applied in the scanning mode to all three PZT elements. Two corner cube retro reflectors were utilized to obtain triple pass operation. The finesse (ratio of free spectral range to Rayleigh linewidth) of the interferometer was 40-60 for singlepass and 60-70 for triple pass operation with a contrast of 10^4 to 10^6 .

(b) Alignment:

The most important factor in getting a good quality spectrum is the maintenance of the mirror parallelism, which is the main stabilization problem. Rough alignment is done by adjusting the spring screws of the front mirror

and simultaneously looking for a uniform output as light scattered from a paper card passes through the interferometer. Finer alignment is obtained by adjusting the bias control knobs on the front of the ramp generator, each of which is connected to one of the PZT stacks. The best condition of alignment can be detected with an experienced eye by looking at the interference fringe pattern of light scattered by polystyrene[7]. By choosing a peak-to-peak ramp voltage of 400V, a scan time of 100 msec and an appropriate neutral density filter in front of the PMT, one can obtain 2.5 free spectral ranges where at least three Rayleigh lines are observable with the PMT output displayed directly on an oscilloscope. By proper manipulation of the control knobs one finds the narrowest and strongest Rayleigh line on the oscilloscope, at which point data collection from the sample can be started [3].

It is necessary to set the ramp voltage to scan over more orders than are actually used in the data acquisition to allow for drifts in the laser frequency or the interferometer during the accumulation of data. A high performance multipass system is described in [4]. However, during data acquisition, mirror parallelism may be perturbed. Maintenance of this mirror parallelism can be achieved either by using a servosystem that

continuously adjusts the alignment of the mirrors to maintain a maximum peak signal or by a software routine which can align the mirrors through computer control of the bias voltages in the PZT stacks to maintain a maximum peak signal. In my experiment, the latter technique was employed. A detailed description of the computer controlled alignment will be found in section (E).

(c) FP Throughput

The throughput of the Fabry-Perot was measured by focusing the laser beam on to a paper card, collimating the scattered light and directing it to the center of the Interferometer. The voltage across the PZT stacks was adjusted for maximum transmission ($\lambda = 5145\text{\AA}$), and the power of the transmitted light, P_{max} was determined by a coherent Radiation light meter Model 212. Keeping everything else unchanged, the Fabry-Perot was then removed, and the power of the direct beam P was measured. The throughput $T = \frac{P_{\text{max}}}{P}$ was found to be:

$$T(\text{singlepass}) = 0.634$$

$$T(\text{triplepass}) = 0.05$$

(3) Double Grating Spectrometer

The double grating spectrometer is widely used for Raman spectroscopy. The diffraction gratings are generally blazed for a given order of interference, and this may result in upto 70% of the incident light going into a given order for a given wavelength region. The Spex 1401 used in our experiments consists of two Czerny Turner 3/4 m grating spectrometers mounted in series in a single housing with an aperture of $f/6.8$. The two gratings in the double instrument are driven by a common screw. The entrance and exit slit widths were chosen to be $200\text{ }\mu\text{m}$ and the intermediate slit $150\text{ }\mu\text{m}$. The scan rates used were $25\text{ cm}^{-1}/\text{min}$ (slow), and $100\text{ cm}^{-1}/\text{min}$ (fast). The strip chart could be marked at 50 cm^{-1} intervals to calibrate the frequencies of the Raman components. For details of the Double Grating Spectrometer see [5].

(4) Photomultiplier Tube

The light leaving the spectrometer or FPP was focused onto the cathode of an ITT FW130 photomultiplier tube. The tube was maintained at -20°C by a model TE-104 Products for Research thermoelectric refrigeration unit . Keeping the PMT at low temperature reduces its dark count significantly to 2-50 counts/sec. The PMT voltage was supplied by a Fluke 415B power

supply. A sudden increase in dark count which occurred occasionally was due to condensation that resulted in considerable moisture accumulation on the cathode. In such a case, the cooling system was shut down for a day, then the tube was taken out and dried (preferably in darkness), and also the tube housing was dried, and then reassembled. After the cooling system was turned on again, the expected dark count rate returned within 2-3 hours.

(5) Photon Counting Electronics

Photon counting electronics comprised a single photon amplifier and discriminator from UniPhoton System Inc. Model 10145. The PMT output, which consists of electrical pulses, is processed through this preamplifier discriminator module whose output is either fed to the ratemeter and subsequently recorded on a strip chart recorder (Honeywell Model 194) or to a PDP-8 minicomputer.

(6) Spatial Filter

As stated earlier, the spatial filter positioned between FPP and collimating lens was used to define the scattering column. The size of the pinhole in it was chosen to match the image of the scattering column in the focal plane. Use

of the spatial filter substantially improved the finesse of the interferometer. In my experiment, I chose a scattering column length which is

$$r = \frac{f_1}{f_2} r' = 400 \mu m$$

where f_1 = focal length of collimating lens = 22 cm
 f_2 = focal length of SF front lens = 5.5 cm
 r' = diameter of SF pinhole = 100 μm .

(7) Programmable Power Supply

As will be discussed later, a KEPCO programmable power supply (model OPS-500) together with a KEPCO D/A converter [KEPCO Model PC-2] supplies an additional bias voltage controlled by the PDP-8 computer, to two of the PZT Stacks in series with the Ramp Generator bias voltages. This is a part of the computer controlled alignment system. Their output may be as high as 120 V D.C, and the step at which the bias voltage is changed can be controlled by the computer.

(8) Fast Shutter Control

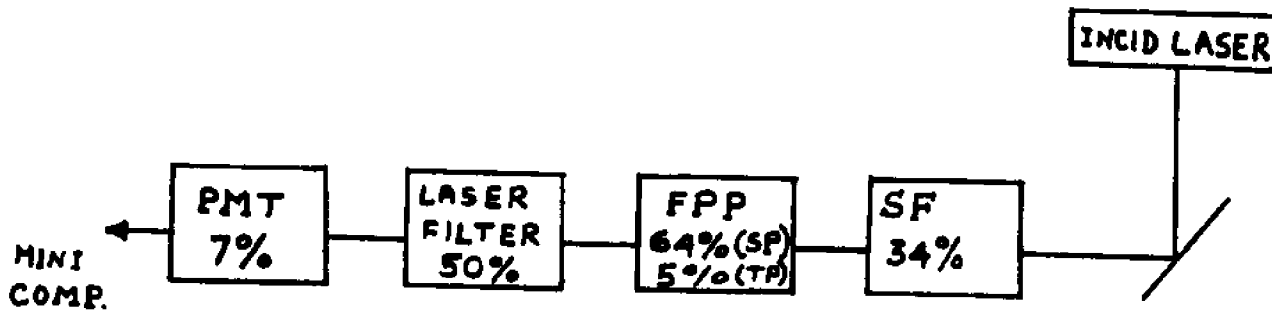
In order to protect the phototube from exposure to the intense Rayleigh line during data collection, a fast electronic shutter assembly was included in the optics (Uniblitz Model DS 122, Vincent Assoc., Rochester, NY). During a typical data sweep, the number of incoming counts in each channel is monitored by the computer. When the count rate reaches a certain limit, the shutter is kept closed for a sufficient number of channels (which can also be specified) to block out the Rayleigh Peak.

(9) Ramp Generator

The Ramp Generator (Tropel Model 361) supplies D.C. voltage to all three FPP PZT stacks. The peak-to-peak output can be 200-1500 V D.C. The reference output is 1/200 th of the actual output and can be displayed on a oscilloscope. By proper choice of ramp amplitude one can select the number of FSR's to be displayed on the oscilloscope. When the scan is stopped, a manual scan is made possible by the common knob. Mirror parallelism depends on Ramp voltage stability. Ramp durations of 50 msec to 1000 sec may be chosen.

(10) Calibration of the optical efficiency

Starting from the scattering column, I went through all the optical components through which the scattered light passed, and determined each of their efficiencies. Special care was given to the determination of quantum efficiency of the PMT which came out to be 7%. Following is a summary of those measurements showing the efficiency of each of the components in the optical system.



E. Computer Control and Interfacing of the Experiment

One of the most important problems is to keep the mirror parallelism stable which is vital to the signal finesse and output strength. Through appropriate software, a PDP-8E minicomputer has been made to control various aspects of the experiment.

(1) Computer controlled alignment: program description

During data acquisition for a prolonged time, various effects may perturb the mirror parallelism, as a result of which the signal decreases and the finesse worsens. A principle reason for interfacing the experiment (shown in fig. 6-1) with the PDP-8 computer was to align the system during data collection and to compensate for drifts in the laser or FPP. The most useful computer program for my experiment was ZP2 which was written by R. Fenstermacher, C. Ecolivet and W. Yao and has been modified during past years in our laboratory. An important function of this program is to periodically realign the mirrors which would otherwise lose their parallelism in the course of time.

The ZP2 program may be brought into the PDP-8 core from the PDP-10 computer through another operating program, called STORQ. As soon as ZP2 is run and all necessary parameters are initialized, the computer jumps to the alignment routine. The most important initialization parameters are:

- X1: Bintime (selected as $1/154$ of the ramp duration.
- X2: Initial bias voltages
- X3: Step size at which bias voltages will be changed to search for maximum signal.
- X4: Value of count rate at which the shutter should close

X5: Number of channels during which the shutter should remain closed.

X6: Number of data scans between alignments

X7: Number of complete cycles (data collection and alignment) in the experiment.

Typically, a ramp duration of 2 sec was set on the ramp generator, the number of data scans between alignments was 50, and 5 cycles of data collection were employed. The complete experiment takes about 8 minutes.

How the program works:

In order to activate the alignment routine, the computer interrupts the data acquisition in order to realign the Fabry Perot. During the alignment routine the computer first actuates a relay which inserts a solenoid-operated neutral density filter in the optical path. This filter reduces the peak intensity of the Rayleigh line to below the threshold set for the shutter to close. The computer then monitors the countrate at the central Rayleigh peak and adjusts the bias voltages with the step size chosen by parameter X3 for maximum signal. The adjustment can be done in both increasing and decreasing directions. The adjustment of the bias is done through the two Kepco OPS-500 programmable power supplies which are connected in series

with the bias controls of two of the three PZT stacks. These are located at 90° with respect to the third stack which serves as the pivot of the motion which ensures that the two adjustments are independent. The computer controls the output of the programmable power supplies through two Kepco SN-8 D to A converters.

At the start of the alignment routine, the computer first locates and stores the size and location of the Rayleigh line near the center of the sweep. At each subsequent sweep, the computer changes the bias voltage by a fixed increment. If the size of the Rayleigh peak has increased from the previous cycle, the new bias voltage is retained and the same process is repeated on the next cycle. If the size of the Rayleigh peak in this cycle is reduced, the new bias voltage is rejected the sign of the voltage step is reversed and the program continues to the next alignment phase.

During the alignment routine, the above process is repeated for both stacks and for voltage increments of both polarities. At the end of the cycle, the position of the Rayleigh peak with respect to the center of the sweep is recorded and used to update a variable delay which ensures that the central Rayleigh line always appears in channel 256 so that the collected spectrum is centered in the 512 channel memory. During data collection, the filter remains

out of the optical path. The fast shutter automatically closes if a strong Rayleigh line occurs to protect the PM tube. A single sweep is recorded with the filter raised to put the Rayleigh lines, at reduced intensity, in the spectrum.

(2) Other aspects of computer control

With the above alignment procedure data runs as long as 2 hour were used, and no degradation in the instrumental finesse was observed. Usually 30 minute runs were adequate to build up a good signal to noise ratio. Before permanent storage of data in the PDP-10 which is also done by a ZP2 subroutine, the quality of the spectrum could be observed on an oscilloscope (Tektronix Model D11) and an X-Y plot generated by the HP 7040 X-Y plotter through the ZP2 program, all of which are controlled by the PDP-8 with ZP2 Data files can also be recalled to the PDP-8 from the PDP-10. As soon as data collection stops, the computer automatically closes the fast shutter in front of the PMT in order to protect it from any strong light.

F. Thermal Considerations

The melting temperature of salol is $\sim 41.22^{\circ}\text{C}$ and

that of succinonitrile is $\sim 57.98^{\circ}\text{C}$. Since the main purpose of the experiment was to look for any acoustic anomalies very close to the melting transition, it was extremely important to maintain excellent temperature control and stability. It was also essential to know the temperature fluctuation ΔT in order to prevent unwanted melting of the crystal near T_m . In the following paragraphs, I will discuss the experimental considerations related to temperature control and measurement.

(1) Thermostat

Temperature control was achieved by a homemade stirred oil bath thermostat. Fig. 6-3 represents a schematic diagram of the thermostat. Water, ethylene glycol and paraffin oil were tried as the stirred fluid and millipore-filtered paraffin oil was found to be the best. The oil can be stirred by an external motor at a very slow speed. The thermostat is a brass cylinder, with four flat glass windows for entrance and exit of the laser beam and collection of light scattered through 90° . At about $3/4$ height, a rectangular block with a circular hole was mounted through which the sample holder can be inserted and immersed in the fluid. The height of the sample holder can be adjusted by unscrewing the holder and adjusting it by hand. The stirred paraffin oil can maintain a temperature uniform to 0.20°C throughout the bath.

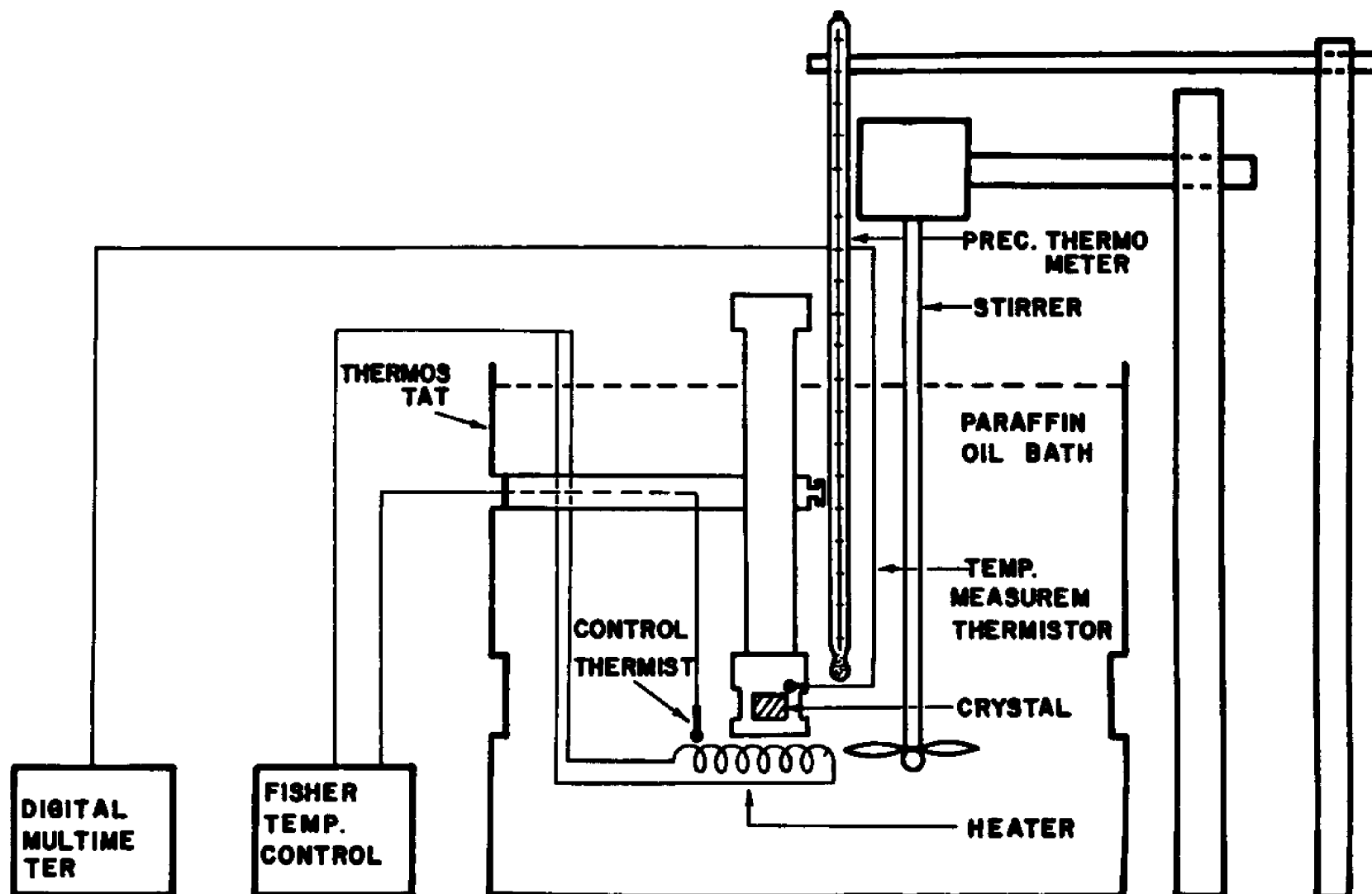


**FIG. 6-3 SCHEMATIC DIAGRAM OF THERMAL LAY OUT
OF MELTING EXPERIMENT SHOWING THERMOSTAT**

(2) Temperature Control and Measurement

The thermostat has three thermistors built into it, with external connection outlets. One of the thermistors was placed close to the 20Ω heating coil to sense and control temperature. The sample temperature was controlled by a Fisher proportional temperature control (Model 22) connected to the first thermistor sensor. The heating coil is connected to the output of the Fisher controller. It was observed that the resistance of the $4\text{ k}\Omega$ thermistor at room temperature decreased to 800Ω close to melting. The range of resistances to balance the bridge had been determined for all six ranges of the controller, and the $4\text{ k}\Omega$ thermistor was chosen to cover the temperature range at which experiments would be performed.

A separate experiment was performed to determine the best gain factor of the controller to achieve the least amount of temperature fluctuation during a temperature rise.

Through this experiment, I determined the most appropriate gain factor of the controller as well as the best method to measure temperature. The thermistor which is used to read the sample temperature had a temperature coefficient of 0.3 (i.e. the resistance decrease from 25°C to 50°C is by a factor of 0.3). Its resistance could be

read either directly by a digital multimeter (5 1/2 digit, Fluke Model 8800 A) or indirectly by a resistance bridge.

The experimental arrangement for temperature control and measurement is shown in Fig. 6-4 . A chart recorder was connected to the null output of the resistance bridge. The imbalance voltage ΔV was then calibrated against temperature change of the bath and resistance change of the thermistor. $\Delta V = 0.65 \text{ mV}$ was equivalent to a resistance change of 10Ω in thermistor and a temperature change of 0.2°C in the oil bath.

With the Fisher controller, the temperature was set to 40°C and the temperature stabilized within 8h. At this point the resistance bridge was zeroed by varying the resistance of the resistance decade box. The chart recorder was also accordingly zeroed to the middle line of the chart, and the scale and sensitivity were set in such a way that a fluctuation of $\Delta V = \pm 0.5\text{mV}$ could be detected (equivalent to temperature fluctuation $\Delta T = \pm 0.0015^\circ\text{C}$) on the strip chart. The Fisher controller had both a fine and a coarse control knob to change temperature of the bath. The set temperature was increased by 0.01°C and the subsequent increase and fluctuation of the bath temperature was recorded on the strip chart for various gain factors of the Fisher Controller. Ten such gain factors were tried. The best gain factor determined through this procedure was

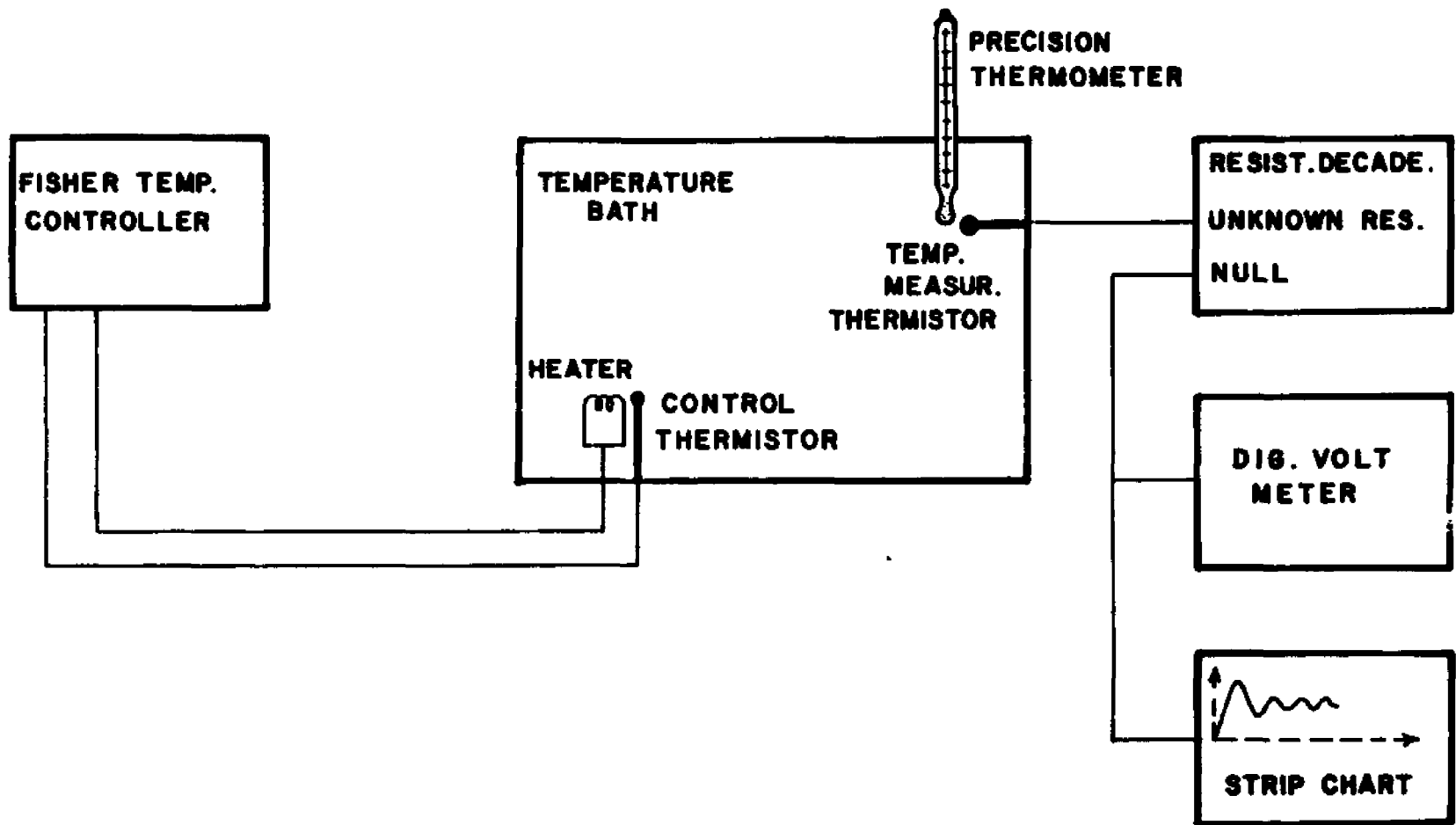


FIG.6-4.SCHEMATIC DIAGRAM SHOWING PRECISION CONTROL AND MEASUREMENT OF TEMPERATURE

5.4, which restricted short term temperature fluctuations to $\delta T = \pm 0.001^{\circ}\text{C}$. Furthermore the chart recorder was kept on up for 48 hours and recorded a temperature fluctuation of $\Delta T = \pm 0.005^{\circ}\text{C}$. The main reason for the higher ΔT in the latter case was the fluctuation of the room temperature itself which was $\pm 0.8^{\circ}\text{C}$. Once the experiment was started, the crystal was kept at a temperature very close to T_m for 6-7 days and the temperature fluctuation was observed. It was essential to determine the temperature fluctuation in the worst situation, i.e. very close to T_m .

The next part of the experiment was to determine the most accurate method of measuring temperature. Three different temperatures (30.7°C , 34.62°C , 38.63°C) were set on the Fisher controller, and in each case the bath temperature was measured by a precision thermometer (to 1/100th of a degree), and the thermistor resistance was measured both by the digital multimeter and the resistance bridge. The current driven through the thermistor by the digital multimeter was also determined each time. The same measurements were repeated on four consecutive days. The reproducibility of the resistance measurement by the digital multimeter was found to be slightly better than that by the resistance bridge. The results can be summarized as follows:

Precision Thermometer $T = (38.29 \pm 0.01)^{\circ}\text{C}$

Digital Multimeter $R = (1133.75 \pm 0.25)\Omega \approx 38.301 \pm .005^{\circ}\text{C}$

Resistance Bridge $R = (1141.3 \pm 0.7)\Omega \approx 38.445 \pm .014^{\circ}\text{C}$

So resistance measurement by the digital multimeter was adopted in all subsequent experiments, and a simultaneous temperature reading on the precision thermometer was always taken. The resistance of the thermistor was calibrated against temperature by fitting R-T data in the temperature range of 40°C to 42°C to a suitable curve.

The temperature measuring thermistor was moved to the interior of the sample cell and seated about 1/8 of an inch above the crystal in order to give a more accurate representation of the crystal temperature. After a certain temperature was set, the temperature reading was taken two to four hours later, allowing enough time for equilibration. Spectrum were taken at a particular temperature on several different days to check the reproducibility. The thermostat had no isolation on the top, and a temperature gradient of $0.02^{\circ}\text{C}/\text{cm}$ was measured by the thermometer inside the bath. In order to insure more stability, the thermostat was usually filled to the brim with paraffin oil and the crystal depth from the surface was 12 cm.

(3) Sample cell

During the first set of experiments with succinonitrile, its growth tube was used as the sample cell. In that set up, Brillouin spectra could be taken even after melting of the sample. Both round cylindrical and rectangular tubes were used. During melting experiments with salol, a round cylindrical glass tube was used as a sample cell initially. The crystal was placed on the bottom of the tube and it was filled with glycerol, a highly transparent index matching fluid. The temperature measuring thermistor was placed inside the tube a little above ($\sim .05''$) the crystal. Later on it was observed that very close to melting, the crystal floated upward in the fluid making it impossible to take data very close to T_m . Then a soft foam block was used to press the crystal gently, and this allowed taking spectra very close to T_m . Several sets of data were taken with this sample cell. But in a later experiment it was found that the melting point T_m of the same sample pieces varied substantially depending on whether the crystal was in fluid or air. Therefore it was necessary to design a sample cell containing no fluid (see fig. 6-5) so that the crystal could be melted in air.

The new sample cell, consisting of two parts was made of

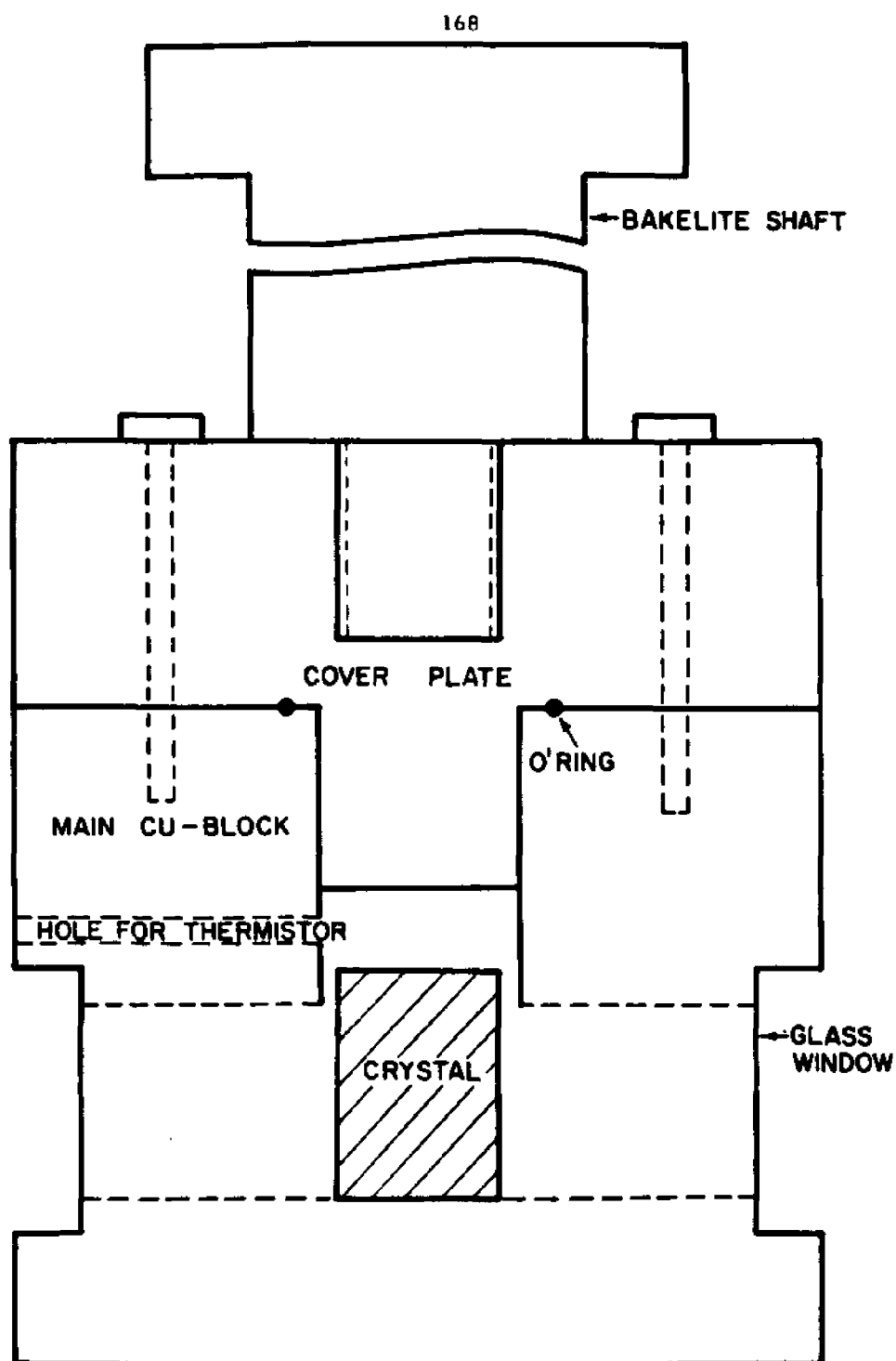


FIG. 6-5 Cross sectional view of the CU-sample holder.

copper. The top part was made as a cover which could be screwed to a bakelite rod (5"long) to allow it to be submerged deep inside the fluid. The lower part of the cover was made to fit snugly inside the cell to minimize the air space inside the cell. The lower section of the cell holder had four flat glass windows epoxied to the copper. The crystal rested on the bottom, 1/8" below the window level. A $8 \times 9 \times 12 \text{ mm}^3$ hollow space was provided for the crystal. By making a thin hole in the wall of the cell holder, a thermistor was inserted in such a way that the thermistor top almost touched the crystal's top face. The thermistor was also epoxied permanently to the cell, and connected to the digital multimeter. In order to prevent penetration of fluid into the sample space, an O-ring was placed in a groove on the top of lower section. Both sections were then screwed together lightly from the four corners. The laser beam which was incident normal to the windows, passed through the crystal and out through the opposite window. The scattering column could be adjusted up to 3/8" vertically and 2" horizontally in order to select the best possible part of the sample.

(4) Laser Heating of the Focal Volume

One of the most important thermal consideration in the melting experiment was the heating of the scattering column

of the crystal by the laser. It was observed that a 150 mW argon ion laser can increase the crystal temperature up to 1°C and may cause unwanted crystal melting even though the set temperature is 1°C below T_m . Due to such laser heating, several experiments had to be abandoned in the middle. This problem was reduced by choosing a laser power output between 30 and 50 mW. Before leaving for the day, the laser power was lowered to 20 mW, then the laser was shut off. The bath temperature was kept below 40°C overnight. The next day the laser was turned on at 20 mW and slowly increased to the previous day's value. Then the temperature was raised more slowly. And when close to melting, the laser was kept on for three consecutive days and data were collected overnight. Since most of the interesting features of the melting experiment showed up very close to melting for a very short duration ($\sim 1/2$ hour) before the crystal completely melted, it was necessary to take careful data for a prolonged period ($\sim 72\text{h}$). A detailed calculation has been made [6] to obtain a relation between the actual temperature of the focal volume and the temperature determined by the thermistor. It was found that

$$: T_{\text{THERM}} = T_{\text{ACT}} - M_L P$$

with $M_L = 0.5^{\circ}\text{K/mW}$ where P is the laser power in milliwatts.

My experimental result $\Delta T \sim 1.0^{\circ}\text{C}$ which is very close to the calculated $\Delta T = m_L P = 0.75^{\circ}\text{C}$ with $P = 150$ mW.

G. Summary of Equipment

Following is a summary of all the equipments used in the Brillouin and Raman scattering experiments.

Apparatus	Manufacturer	Model
Argon ion laser	Spectra Physics	165
Fabry Perot Interferometer	Tropel	360
Ramp Generator	Tropel	361
Dual beam Oscilloscope	Tektronix	556
Double Grating Spectrometer	Spex	1401
Photomultiplier tube	ITT	FW-130
Refrigeration for PMT	Prods. for Research	TE100
PMT Power Supply	J. Fluke Co.	415B
Rate meter	Ortec	441
Strip chart recorder	Honeywell	194
Minicomputer	DEC	PDP-8E
Small Fabry Perot	Coherent Optics	760
XY Plotter	Hewlett Packard	7040A
Preamplifier, Discriminator	Uniphoton Systems Inc.	
Programmable power supplies	KEPCO	OPS-500
Digital Multimeter	Racal Dana	5001

Apparatus	Manufacturer	Model
Proportional Temperature Controller	Fisher	22
Proportional Temperature Controller	YSI	15
Fast Shutter	Uniblitz	SD 122
Floppy Disc system	Data System Design	440
Laser power meter	Coherent Radiation	212
Mainframe Computer	DEC	PDP-10
Diamond Saw	Micromech MFG	3723018
He-Ne Laser	Spectra Physics	80

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CHAPTER VII

EXPERIMENTS

A. Introduction

Although the main part of this thesis was an experimental study of the melting transition in salol, experiments were also performed at room temperature on various samples of salol in order to determine the complete set of elastic and elasto-optic coefficients of salol through Brillouin scattering. During the initial part of the program, melting experiments on succinonitrile were also performed using a pressure-scanned Fabry Perot Interferometer. Several sets of Raman scattering experiments were also done in order to look for anomalies in optic phonons similar to those found in acoustic phonons in the Brillouin experiments. Section D is a short description of all samples which I grew and a brief summary of the experiment. Since one loses the crystal as it is brought to melt during each experimental run, I had to prepare a large number of samples for every such run.

Orientation of the samples was performed according to the morphology indicated in figure 4-4 which had been determined by Professor H. Cummins during his preliminary investigations on salol in 1977-78 at the Ecole Normale Supérieure in Paris (in conjunction with Dr. P. Lallemand). The orientation was further confirmed by a polariscope. Careful grinding and polishing were necessary in order to get the crystal accurately oriented. An accuracy of $\pm 2^\circ$ could thus be obtained.

B. Brillouin Scattering Experiments

1. Melting experiments

As can be seen from section D, a large number of melting experiments were performed. The first set of experiments was made on succinonitrile crystals which were in plastic growth tubes, each sample tube being passed through various numbers of zone refining passes. Since the temperature control in the initial stage was poor and the spectrum quality was inferior, only one set of succinonitrile data from sample D3 (10 zone refining passes) was chosen for Brillouin shift and linewidth analysis. Before starting my main experiments with salol, I grew single crystal ammonium bisulphate together with M.

Copic of the University of Ljubljana, Yugoslavia. After several unsuccessful attempts to obtain Brillouin spectra of this crystal at room temperature, I gave up and turned to salol. Poor optical quality was one of the main reasons for this failure.

As soon as I could grow good high quality single crystal salol from solution, the melting experiments were switched to salol, and spectra were collected with a triple-pass piezo-electrically scanned FPP, according to the experimental procedure described in section B of chapter VI. The main motivation for switching to salol was based on my mentor's involvement with it during his sabbatical leave in Paris which provided much valuable information on salol e.g. orientation, growth procedure, morphology and structure. The optical quality of my salol crystals was very good and with elastic scattering also weak, all the three acoustic modes (LA, TA₁, TA₂) could be observed with almost all the samples. In the later part of my project, I started to grow very good quality salol by the zone refining technique used by O. Mesquita and D.Neal who were working on a related project on the dynamics of the crystal-melt interface of salol. As can be seen from the table in section (D) which summarizes all the experiments, very few of the experiments could be

completed successfully. Most samples melted long before the anomalies were expected to appear. In some cases, very strong elastic scattering near T_m overshadowed the inelastic components making it impossible to extract any useful information. In some of the samples the orientation changed very close to T_m . Initially, salol was placed in a glass cell containing glycerol. It was observed that salol density decreases slightly at T_m and the sample tends to float upward. A second attempt was made by restraining the sample by very light sponges to prevent it from floating and thus not to lose orientation. Since the most useful data was obtained within one hour before it melts, it was necessary to take as many spectra as possible. Since the scattering column inside the sample could not be moved, manual realignment became extremely difficult at such times. Thus many data had to be discarded because of poor finesse of the spectra near T_m . For accurate resolution of Brillouin shifts and linewidths which are expected to change by a very small fraction, high finesse was essential.

A separate experiment was performed to determine the exact melting point of the sample, as well as to see whether T_m depends on where the sample is placed. The temperature of a water bath in which the samples were

melted was controlled by a Fisher temperature controller. Five pieces of salol cut from the same crystal were placed in glass tubes containing air, water, paraffin oil, ethylene glycol and glycerol respectively. Each tube was submerged to equal depth of water. The bath was gradually heated. From 40.90°C on, the temperature was raised by steps of .01°C, and kept for a day. It was observed that salol in air melts at 40.97°C (it remained crystalline at 40.96°C for 24 hr, and as soon as the temperature was increased by 0.01°C the next day, the piece melted within an hour). Another later experiment showed that very good quality zone refined crystals melted at 41.2°C. It was further observed that salol dissolves more or less in all the fluids during melting. This led us to design the new sample holder shown in fig.6-5 to continue the experiments. Another reason for rejecting most of the initial data was poor temperature control ($\Delta T \approx \pm .05^\circ\text{C}$) which was subsequently improved to $\pm .002^\circ\text{C}$. The last problem of the experiment was laser heating of the scattering column, which forced me to keep the laser output power very low. (details are given in ch. VI). Through this sacrifice of signal output, I could slow down the melting process in order to record the gradual changes of hypersonic velocity and attenuation as the crystal was slowly brought to melt.

For detailed analysis I chose the data from salol 18, salol B and salol A which were recorded under the best experimental conditions. The analysis procedure will be described in chapter VIII.

2. Room Temperature Experiments

One part of my project was to determine the complete set of elastic and elasto-optic coefficients of salol which were not yet known. Brillouin scattering is a very powerful technique for determining both the elastic and elasto-optic coefficients (Pockel's coefficients). For this purpose, a sufficient number of samples with different orientations had to be prepared so that from the measured Brillouin shifts and integrated intensity all C_{ij} and P_{ij} 's could be determined using the equations developed in chapter V. The Brillouin scattering tensors were also calculated for all orientations of the samples which were used in the experiment. Elastic coefficients are easily derivable from measured Brillouin shifts. In order to obtain the Pockel's coefficients and to determine the absolute scattering cross sections of salol, the integrated intensity of each salol Brillouin component was compared with a benzene spectrum taken at the same time

and under similar experimental conditions. Since no reliable data on benzene absolute cross sections were available, a second experiment was done with benzene and quartz (for quartz both the P_{ij} 's and C_{ij} 's are well known), also under similar conditions. The elasto-optic coefficients of salol were finally determined by calibrating against quartz.

Room temperature experiments were done on:

(a) salol 11, 1 and 16 from which spectra were recorded at scattering configurations

(1) $y(zz)x, y(xz)x, y(zy)x, y(xy)x$

(2) $y(xx)z, y(xy)z, y(zy)z, y(zx)z$

(3) $z(yy)x, z(yz)x, z(xy)z, z(xz)x$

(b) salol 7, with scattering configurations

(1) $-y-z(x,x)y-z$

(2) $-y-z(x,-y-z)y-z$

(3) $-y-z(y-z,-y-z)y-z$

(4) $-y+z(x,x)-y-z$

(5) $-y+z(x,-y+z)-y-z$

(6) $-y+z(-y-z,-y+z)-y-z$

(c) and from salol 8, with scattering configurations

(1) $x+y(z,z)x-y$

(2) $x+y(z,x+y)x-y$

(3) $x+y(x-y,x+y)x-y$

(4) $-x+y(z,z)x+y$

(5) $-x+y(z,-x+y)x+y$

(6) $-x+y(x+y,-x+y)x+y$

Determination of the C_{ij} 's and P_{ij} 's will be carried out in chapter VIII.

C. Raman Scattering Experiment

The available Raman scattering experimental facilities in our laboratory prompted us to take several Raman spectra of salol during the melting transition. All the experiments were done with salol inside the Cu cell. Since the signal was strong, all possible Raman spectra at configurations of VV, VH, HV and HH could be collected.

At the beginning of the experiment, the laser frequency was carefully determined. The usual fast scan rate of spectrometer was $100 \text{ cm}^{-1}/\text{min}$ and the slow scan rate was $50 \text{ cm}^{-1}/\text{min}$. The strip chart recorder speed was adjusted to the scan rate. In order to protect the PMT, an appropriate strength neutral density filter was placed in front of the entrance slit. A telescope mounted in the grating spectrometer allows the viewer to focus the image of the scattering column on the entrance slit. The usual dark count of the PMT was $\sim 2 \text{ cts/sec}$. The summary of experiments described in section (D) indicates the various Raman experiments performed on different salol samples. The entrance, intermediate and exit slit widths were

selected to minimize the instrumental width. In contrast to Brillouin experiments, high quality crystals were not required in order to get strong Raman signals. Because of the high contrast of the tandem grating spectrometer very strong elastic scattering which sets in near T_m does not affect the rest of the Raman modes of the crystal. Also very clean Raman spectra could be recorded both during and after melting. In fact I could collect Raman spectra continuously from solid to liquid in sample 16A.

(D) Summary of Brillouin and Raman scattering experiments:

- 1) Succinonitrile, SUCC D4,
grown through 4 zone
refining passes
passes from undistilled
powder Good optical quality.
Visible inclusions, clean
scattering column.
October 27-30,80.
Brillouin melting experiment
Pressure scanned FPP. d=14mm.
temp. control $\pm 0.05^\circ\text{C}$. Data collection by
chart recorder and PDP-8. All spectra in (VV)
configuration. Melted at T_m 58.1 $^\circ\text{C}$.
Simult. solid and liquid components observ-
able. Temperature range: 23.2 $^\circ\text{C}$ to
69.5 $^\circ\text{C}$. Several liquid spectrum taken.
Sudden melting. Finesse was very unstable
reddish scattering column during melting.
Melt was yellowish only LA mode visible.
- 2) SUCC ED1
Grown from distilled powder.
2 zone refining passes.
Clean looking, bright
scattering column Nov. 5-6,80
Brillouin melting experiment
experimental condition as above. T_m
58.12 $^\circ\text{C}$. Temp. range: 24.1 $^\circ\text{C}$ -67.4 $^\circ\text{C}$.
Finesse remains unchanged upto 5h. elastic
softening observed in LA mode only.
- 3) SUCC D3
From distilled powder. 10
zone refining passes.
excellent, very clean
scattering column. Nov. 7-8,80
Brillouin scattering melting experiment.
experimental condition as of SUCC. D4.
 T_m 58.20 $^\circ\text{C}$. Temp range: 22.7 $^\circ\text{C}$ -
68.0 $^\circ\text{C}$. Less elastic scattering.
Finesse worsened near T_m clear melt.
elastic softening LA mode only
- 4) SUCC D5
From undistilled powder
5 zone refining passes. Very
clean looking. Nov. 8-9,80
Brillouin melting experiment.
Experimental condition as of SUCC. D4
 T_m 58.05 $^\circ\text{C}$. Temperature range: 24.5 $^\circ\text{C}$ -
69.4 $^\circ\text{C}$. Least elastic scattering.
Simultaneous existence of solid liquid for
long time. Temp. control better. Finesse
remained very good, even up to T_m . LA
mode only. Elastic softening.
- 5) $\text{NH}_4(\text{HSO}_4)$ Amonium
bisulphate. NH4-1
Grew from solution. Cut
with 100 , 010 and 001
faces. Visible inclusions.
Jan, 81
Brillouin scattering room temperature
experiment tried in y(zz)x, x(yy)z, and
y(xx)z. Very strong elastic scattering.
d=9.5 mm PZT scanned FPP. Tried both single
pass and triplepass. Signal to noise ratio
was very poor. scattering column not
visible. Experiment aborted. only LA was
visible.

- 6) salol 10
Room temperature Brillouin scattering
Grown from solution, very clean, cut with 100, 001 and (010) faces. June, 81
All 3 modes TA₁, TA₂ and LA were visible. Spectra were taken with FPP, PZT scanned at plate separation of d=5 mm, 10 mm and 15 mm, in order to determine which of the Brillouin components belong to a particular Rayleigh line.
- 7) salol L (LIQUID)
Room temperature Raman experiment
Twice distilled. Strong scattering column. Made from solution grown seed. June 25, 81
Used 150 mW 5145 Å argon laser determined all liquid components.
- 8) salol 6
Raman scattering melting experiment.
Solution grown. Very good optically. Cut with (100, (001), (010) faces. July 6-11, 81
Spectra taken in y(xx)z, 23.6°C-41.4°C T_m 41.4°C. Laser output 150 mW. Slit width: 200-300-200 (entrance, intermediate and exit slit). Chart speed: 40 sec/inch Scan rate: 37 cm⁻¹/min. Careful temperature very close to T_m. A bump was observed at 18810 cm⁻¹ which could not be reproduced. Slight shift in frequency was observed, presumably due to thermal expansion.
- 9) salol 9
Brillouin scattering melting experiment
Cut along principal axis. Grown from solution. Very good quality. Sept. 30-Oct. 4, 81
Triple pass FPP, using computer alignment routine. d=15.35 mm. T_m=41.50°C. Temperature control ±.04°C. Time for temperature to stabilize: 30 min. Each spectra collected for 6 minutes, in Y(VV)Z. Laser output 135 mW. Single mode 5145 Å argon laser used. LA, TA₁, TA₂ were all clearly visible. Finesse 40-50. Parameters in ZP2 chosen such a way that fast shutter should close when CR 600 cts/sec, remain closed for 6 channels. Voltage change for alignment +4V per step. Clear elastic softening observed and at very close to T_m. crystal melted suddenly. complete data was not possible to obtain.

- 10) salol B
Solution grown. Cut along principal axis. Very clean. Small elastic scattering
July 3-8, 82
Brillouin melting experiment. First determined best $d=15.63$ mm, so that all modes were well separated. Each spectrum collected at Y(VT)Z for 9.5 minutes. Best temperature control achieved $\pm .002^\circ\text{C}$. Also temperature measured both by thermometer and thermistor. Cu-cell holder used. Sample in air. Each temperature was repeated several times. Continuous presence during experiments for 3 days. All other experimental condition as of salol 9. Sample very carefully and slowly melted. Showed clear linewidth broadening and slight elastic softening. Spectra within $.005^\circ\text{C}$ of T_m obtained.
- 11) salol A
Solution grown. Very small elastic scattering. Cut along principal axis.
July 9-16, 82
Brillouin scattering melting experiment. Same experimental condition as of salol B. Laser power 65 mW, $d=16.08$ mm. Several spectra at same temp.. Crystal melted at $T_m 41.52^\circ\text{C}$. Experimeter continuously present for 48 hours. Precise temperature control and measurement. Time allowed for stabiliz of $.01^\circ\text{C} = 3$ hour. Sample made snugfit in cell not to move even after melt. Strong elastic scatt. Melting crystal surface blocked laser. Observed clear elastic softening, and linewidth broadening.
- 12) salol C
Solution grown. Cut along principal axis. Experiment on Aug. 13, 82.
Room temperature Raman experiment. Krypton laser 6741Å. Output 40 mW. Determined all A_g , B_{1g} , B_{2g} , B_{3g} modes of salol in 12 configurations.
- 13) salol 16
Grown by zone refining. Cut along principal axis. Very small elastic scattering
September 8-13, 82
Brillouin scattering melting experiment $d=14.33$ mm, at Y(VT)Z configuration. Sample was glued with double sticker tap on the bottom of cell holder. Designed to heat the crystal through air, to make melting very slow. Spectra upto $T=39^\circ\text{C}$ were taken, and due to sudden outbreak of non linearity in ramp output, the experiment had to be abandoned.

December 9, 82

The same sample was later used in Raman scattering melting experiment. Short scan rate = $50\text{cm}^{-1}/\text{min}$, long scan rate = $100\text{cm}^{-1}/\text{minute}$. Dark count (PMT) ~ 2 cts./sec. 5145A argon laser, at 225 mW output. Both short and long scan Raman spectra at all four configurations of Y(XY)Z were taken up to $T=40.8^\circ\text{C}$. At that point laser made a hole through the sample, and the experiment had to be abandoned. Relative change in intensities were observed close to T_m .

14) salol 7

Solution grown. Very good quality. Crystal cut with faces along (011), (011) and (100) experiment done December 23-28, 82

The above experiment in the setup of salol 16 was continued. Very low power laser 49mW was used, and enough precaution to stop laser creating a hole. Raman spectra collected also by PDP-8. Crystal melted at $T_m=40.81^\circ\text{C}$. Continuous presence allowed to record all changes during the very slow melting of the sample, at VV, VII, VIII and HV configurations. Relative intensities were observed to change dramatically close to T_m . Liquid Raman spectra at temperature little above T_m were also taken.

15) salol 16A

Zone refined, melt grown. Cut along principal axis. Highly transparent. Experiment done on January 16, 1983.

This Raman scattering melting experiment was designed to study possible depolarization effect. It was believed that incident light may get depolarized (polarization rotated) as it passes through crystal. In this experiment, as the crystal was slowly melting both Raman Spectra and intensity of transmitted light were measured. All spectra recorded at Z(YX)X, Z(YZ)X, Z(XZ)Z, Z(XY)X. It was observed that I_{HV} changes dramatically at T_m . Since the temperature change was very slow, continuous liquid spectra of the same sample was also taken.

16) salol 18

Melt grown from distilled powder. Cut with faces along (101), (101) and 010). Experiment between March 18 -April, 1983. Exceptionally high quality.

Brillouin scattering melting experiment. Single pass FPP used. Similar experiment condition as of salol 8. $d=15.13\text{mm}$. Temperature range: 23.5°C - 41.22°C , $T_m=41.22^\circ\text{C}$. All spectra collected at 101(VT)101 for 4 minutes. Sample was glued to the bottom of cell to prevent from moving. Very good temperature control ($\pm 0.002^\circ\text{C}$). Slow melting, and spectrum within 0.01°C of T_m were believed to be obtained. Finesse remained good for long time. Periodic realignment done without moving laser beam from crystal. Clear softening and line broadening of all three modes were observed.

17) salol 8

Solution grown. High quality. Cut with faces along (001), (010) and (100).

Room temp. Brillouin experiment. Spectra taken on single pass FPP, at high finesse 55. Data collection for 3 minutes 20 seconds each time. Also benzene spectra taken under similar experimental condition. $d=5.00, 14.03\text{ mm}$. Phonon wave vector $\hat{q}=\hat{x}$ and $\hat{q}=\hat{y}$.

18) salol 7
described before

Room temperature Brillouin scattering. Experimental condition as of salol 8. Phonon wave vector $\hat{q}=\hat{y}$ and $\hat{z}$.

19) salol 3
Solution grown. Strong elastic scattering. Cut with faces along (101), (101) and (010)

Spectra taken at VV, VH, HH and VH config. Phonon wave vector $\hat{q}=\hat{x}$ and $\hat{z}$.

20) salol 1,2

Both are solution grown. Cut along principal axis, fair quality. Misoriented by $\approx 11^\circ$.

Spectra taken VV, VH, VT and HH config. for $q=\frac{1}{2}(10\bar{1})$ at Z(VY)X, Z(YZ)X, Z(XZ)X for $q=\frac{1}{2}(1,10)$ at Y(ZZ)X, Y(ZY)X, Y(XZ)X, Y(XY)X for $q=\frac{1}{2}(01\bar{1})$ at Y(XX)Z, Y(XY)Z, Y(ZY)Z. Observed four Brillouin modes at Y(VT)X configuration due to misorientation.

21) salol 15, 16

Salol 15 also melt grown. Zone refined. Very good quality. Cut along principal axis. Misoriented by $\Psi = 10^\circ$.

All spectra taken at scattering configurations and for the same wave vector $\vec{q}$'s as of salol 1 and salol 2. Observed five different brill. modes due to misorientation at Y(VT)X.

22) salol A1, B1, C1, D1

First three cut along principal axis, with prism on one face. Solution grown. D1 cylindrical, melt grown, also cut prism.

All three samples were used for refractive index measurement. All were of high optical quality, and were very carefully oriented by polariscope. The prism cut was made such a way that the plane of the prism contained one of the principal axis of the crystal.

23) salol 11

Solution grown. Accurately oriented by $\Psi = +1^\circ$. Cut along principal axes (100) (010) and (001). March, 1983

Room temperature Brillouin experiment to determine C_{ij} 's and P_{ij} 's of salol. Spectra obtained at :

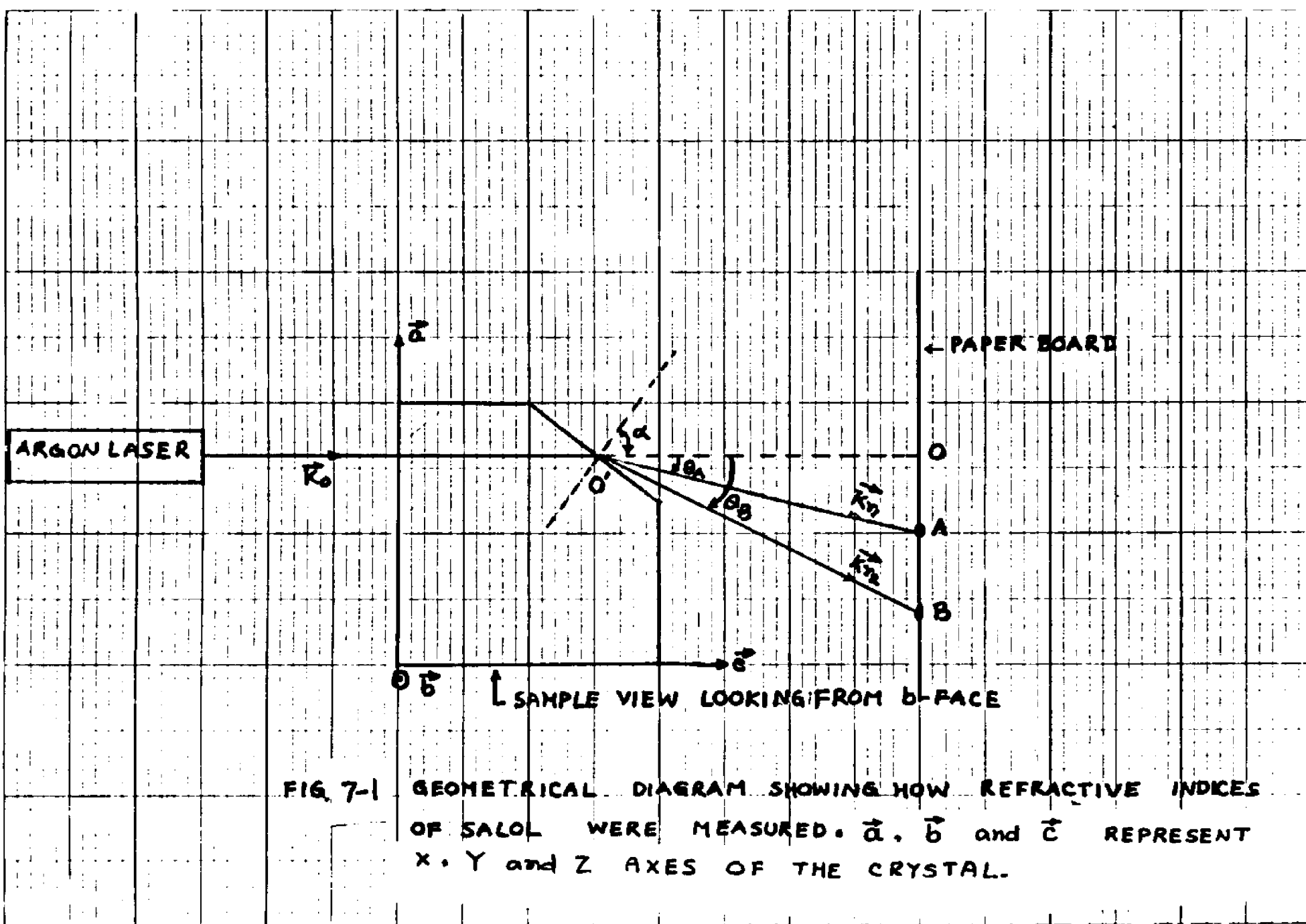
(1) Y(ZZ)X, Y(Z,Y)X, Y(X,Y)X and Y(VT)X (2) Y(X,X)Z, Y(X,Y)Z, Y(Z,Y)Z and Y(VT)Z (3) Z(Y,Y)X, Z(Y,Z)X, Z(X,Z)X and Z(VT)X. $d=15.4$ mm. All three modes LA, TA1 and TA2 were observed.

E. Miscellaneous Measurements

(1) Determination of refractive indices of salol

Salol is a birefringent crystal whose values of n_x , n_y and n_z differ substantially from each other. I measured those indices carefully by the prism method. For this purpose, several samples were prepared with a smooth prism cut on one face of the sample. The experimental arrangement is shown in fig. 7-1.

First I made a prism cut as shown in the figure from an X Y Z cut sample, and mounted it on a goniometer. The 5145 Å argon laser beam was incident along the z direction of the crystal. With the help of the goniometer the prism angle α is easily determined. The samples were oriented by a polariscope within an accuracy of $\psi = \pm 1^\circ$. Normal incidence of the laser beam on the a face was achieved by adjusting the reflected beam back to the laser tube. A paper board was placed on the opposite side of the sample where the refracted beam could be observed. Without the crystal in position, the location of the direct beam on the paper board was first marked as point 0.



With the crystal in place, two refracted beams coming out of the crystal were easily observed. It can be shown from Maxwell's equations that a beam of light with wave vector $\vec{k}_0 = k_0 \hat{z}$ has two solutions inside the crystal which are:

$$k_{r1} = n_x \frac{\omega}{c} \quad \text{with polarization } \hat{e} = \hat{x} \text{ (vertical)} \quad (1)$$

and

$$k_{r2} = n_y \frac{\omega}{c} \quad \text{with polarization } \hat{e} = \hat{y} \text{ (horizontal)} \quad (2)$$

Due to the difference between n_x and n_y , two distinct beams of transmitted light were visible on the board. By using a polarizer, it was verified that one of the beams (A) $\hat{e}$ polarized and the other (B) was $\hat{y}$ polarized. Since both beams obey Snell's law we have:

$$n_x \sin \alpha = n_0 \sin (\alpha + \theta_A) \quad (3)$$

$$n_y \sin \alpha = n_0 \sin (\alpha + \theta_B) \quad (4)$$

n_x and n_y can be calculated from eqn. (3) and (4).

θ_A and θ_B were determined from the measured distances $O'O, O'A$ and $O'B$. At least three measurements were taken with

every sample. Proceeding in the same way using two other samples with prism cuts through the ab-face and bc-face, I determined n_x, n_z and n_y, n_x respectively. In this way each of the indices n_x, n_y and n_z was determined twice, and the averages of the values are shown in table 7-1(a) and (b). Another experiment was also done on a cylindrical sample grown from the melt and n_x and n_z were determined. Since the cylinder faces are usually b faces, only n_x and n_z could be determined from cylindrical samples.

Refractive indices were also determined by using both 6328 Å He-Ne and 4880 Å argon laser light to determine the wavelength dependence of n . All results are given in table 7-1(a) and (b). In determining the error of n , I considered the error in measuring $\angle OA, \angle OB, \angle OO$ and the prism angle as well as the standard deviation from average values. The exact expression for n_x and n_y can be derived from fig. 7-1 are given by:

$$n_x = \frac{\sin(\alpha + \tan^{-1} \frac{OA}{OO})}{\sin \alpha} \quad (5)$$

$$n_y = \frac{\sin(\alpha + \tan^{-1} \frac{OB}{OO})}{\sin \alpha} \quad (6)$$

Table 7-1(a)

Summary of results of refractive index experiments

sample	direction of K_0	Prism angle	n(5145Å)		
			n_x	n_y	n_z
salol A1	(001)	21.25°	1.535	1.805	—
salol B1	(100)	24.16°	—	1.819	1.653
salol C1	(010)	21.08°	1.545	—	1.643
salol D1	(010)	16.67°	1.562	—	1.658
			n(4880Å)		
			n_x	n_y	n_z
salol A1			1.540	1.816	—
salol B1			1.838	1.668	—
salol C1			1.550	—	1.650
salol D1			1.565	—	1.670
			n(6328Å)		
			n_x	n_y	n_z
salol A1			—	—	—
salol B1			—	—	—
salol C1			1.547	—	1.639
salol D1			1.532	—	1.655

Table 7-1(b)

Average values of salol refractive indices

Wavelength	n_x	n_y	n_z
4880Å	$1.552 \pm .023$	$1.827 \pm .032$	$1.663 \pm .022$
5145Å	$1.547 \pm .027$	$1.812 \pm .023$	$1.651 \pm .016$
6328Å	$1.540 \pm .023$	—	$1.647 \pm .021$
4880Å	$n(\text{liquid}) = 1.598 \pm .008$		

(2) Determination of salol density

An experiment to determine the density salol was done with a solution grown salol crystal by Archimedes principle with a very accurate balance (accuracy= ± 0.001 gm.). The resulting specific gravity of salol was 1.2822.

The density of salol is given by:

$$\begin{aligned}\rho_{\text{SALOL}} &= \rho_{\text{H}_2\text{O}}(25^\circ\text{C}) \times \text{specific gravity} \\ &= 1.2784 \text{ g/cm}^3\end{aligned}$$

(3) X-ray Diffraction

I tried to obtain x-ray diffraction pictures of salol using a Cu-tube at anode voltage of 30 kV. The crystal was mounted on the goniometer by adjusting one of the principal axes to be exactly parallel to the collimated beam. X-ray film was exposed for half an hour. The picture did not show good contrast of the Bragg spots. Several more attempts were made to get a clear x-ray picture ,but were not successful.

References

1. T.C. Damen, S.P.S. Porto and B. Tell, Phys. Rev., 142,
570(1966)

CHAPTER VIII

DATA ANALYSIS AND RESULTS

Section I: Data Analysis

A. Introduction

Since the principal goal of the Brillouin scattering experiments was to detect changes in the linewidth and frequency of the Brillouin components, it was essential to determine those quantities accurately. The free spectral range of the Fabry-Perot Interferometer was chosen to be as small as possible so that the modes were well separated from each other with overlapping orders, facilitating the observation of small changes. In order to determine the linewidth and center frequency of each of the modes, I used a non-linear least squares fitting procedure which will be described below.

B. Analysis of the Brillouin scattering data

(1) Melting experiment data

The summary of experiments in chapter VII indicates that many melting experiments were performed. However,

only four of those experiments were analyzed carefully. In order to determine the linewidth and center frequency of the Brillouin components, I used two fitting programs. Each Brillouin spectrum was stored in the PDP 10 mainframe computer. A decimal output of each file was printed with systematically ordered channel numbers. From them, I could estimate the linewidth, peak height and center frequency of each Brillouin mode. Both of the fitting programs required initial guesses for those parameters. Here is a short description of each of the fitting programs.

(a) TAUROS-FITZAP Program

In this fitting procedure developed by W. Yao, the nonlinear least squares fitting program (TAUROS) used was developed at CERN in the 1960's. The Rayleigh line and all Brillouin components are assumed to be Lorentzians whose intensity spectrum is given by:

$$I(\omega) = \frac{(\Gamma^2/2) H}{(\omega - \omega_0)^2 + (\Gamma/2)^2} \quad (8-1)$$

where Γ is the full width at half maximum, ω_0 is the center frequency and H is the peak height of each mode. The parameters H , Γ and ω_0 are varied (initial values are guessed) in order to get a best fit satisfying a convergence criterion. Fitting is restricted to $\pm N$

channels from the center of the mode (usually ± 10 channels). All the fitted values of Γ , and the center frequencies ω_0 are given in terms of channel numbers. Although the Γ and ω_0 values determined through this procedure are much better than hand calculation, still the accuracy is not very great. The greatest error arises from the background value which has to be either specified by the user or the computer will calculate it as an average between two specified channels. As can be seen from the TAUROS - fitted diagram offig 8-1(b), the data outside the fitting region can play no role in determining Γ and ω_0 . In order to determine the peak height, the constant background value is simply subtracted from H (Fit) which is also not correct. As output of this program, one gets center frequencies and linewidths of all the Brillouin and Rayleigh lines. Since all lines are assumed to be Lorentzian, the real Brillouin linewidths are obtained simply by subtracting the determined Rayleigh linewidth from the observed Brillouin linewidth, since the convolution of two Lorentzian is another Lorentzian of width equal to the sum of the two initial widths. This procedure sometimes gives negative numbers for Brillouin linewidths. Most of these problems have been almost eliminated by a new fitting program named NLLSQ-DECON3 which is described below.

(b) NLLSQ-DECON3 program

This program, developed by D. Neal of our group, is based on the nonlinear least squares fitting program NLLSQ developed at Bell Labs. DECON3 provides a more realistic approach than FITZAP to eliminating the instrumental linewidth effects from the Brillouin spectrum. To compute the true center frequency and linewidth of the Rayleigh and Brillouin components, it is necessary to know separately the form of the observed spectrum, the intensity spectrum of the source and the bandpass function of the interferometer. I will assume that the source spectrum and the bandpass function of the spectrum analyzer together determine a single instrument function $I(\omega)$, and that $I(\omega)$ is identical to the observed spectrum of the Rayleigh component. Following a model given by Leidecker and La Macchia [19] I will consider all the lineshapes as Voigt functions, which are convolutions of Gaussian and Lorentzian functions. By fitting each of the modes to a parametrized Voigt function (the NLLSQ program can vary up to 18 parameters), the lineshape can be approximated either to be a Lorentzian (if the Voigt parameter $a > 30$) or a Gaussian ($a < 30$). If both the Rayleigh and Brillouin lines are Lorentzian, then the deconvolution is very simple. Since the convolution of two Lorentzian functions is another Lorentzian whose width is the sum of the constituent widths.

$$\Gamma_B = \Gamma_{obs} - \Gamma_R$$

where Γ_B is the deconvoluted linewidth, Γ_R is the Rayleigh (and instrumental) linewidth and Γ_{OBS} is the observed linewidth. On the other hand, in the case of an instrument function with a Gaussian lineshape, and a Brillouin component with a Lorentzian lineshape, this Voigt function fitting procedure is very useful. In general if $O(\omega)$ is the observed lineshape, $I(\omega)$ is the instrumental linewidth and $B(\omega)$ is the deconvoluted Brillouin lineshape, they are related by:

$$O(\omega) = \int I(\omega) \otimes B(\omega)$$

DECON3 is capable of extracting the center frequency, linewidth and peak height of each Brillouin mode $B(\omega)$. As input one needs to estimate the Rayleigh linewidth, the number of Brillouin components and the center frequency for each of the modes. By fitting 256 data points out of the total 512 channels (one half) at a time, the fitting procedure determines the background, which eliminates the error in FITZAP due to the assumption of constant background. After finishing the left half of the spectrum, it then fits the right half. In this way a maximum number of parameters up to 18 could be varied. For the fitting of each 512 channel data, it took about 2 1/2 hours of computer time.

As output of this program, the computer gives a Voigt parameter for both Brillouin and Rayleigh lines, the center frequency of the Rayleigh lines and center frequency, halfwidth and peak height of each of the Brillouin components. For a comparison, a TAUROS-FITZAP fitting and NLLSQ-DECON3 fitting of the raw Brillouin spectrum of salol 8 (in fig. 8-1(a)) are shown in fig.8-1(b) and (c). For a numerical estimation of the fitted values, the following comparison is given here for that particular salol spectrum shown in fig 8-1(b) and (c).

		TAUROS-FITZAP	NLLSQ-DECON3	By Hand
Brillouin	ν_{TA1}	6.009GHz	6.015GHz	6.003GHz
Shift	ν_{TA2}	9.528GHz	9.49GHz	9.582GHz
	ν_{LA}	12.054GHz	12.065GHz	12.11GHz
Linewidth	Γ_{TA1}	354MHz	341MHz	456MHz
(observed)	Γ_{TA2}	534MHz	518MHz	603MHz
	Γ_{LA}	430MHz	445MHz	533MHz
Rayleigh linewidth		372MHz	340MHz	453MHz
Peak height	H_{TA1}	590	660	3.53 (arb.)
(Counts/second)	H_{TA2}	185	201	1.0 (arb.)
	H_{LA}	527	54	3.10 (arb.)

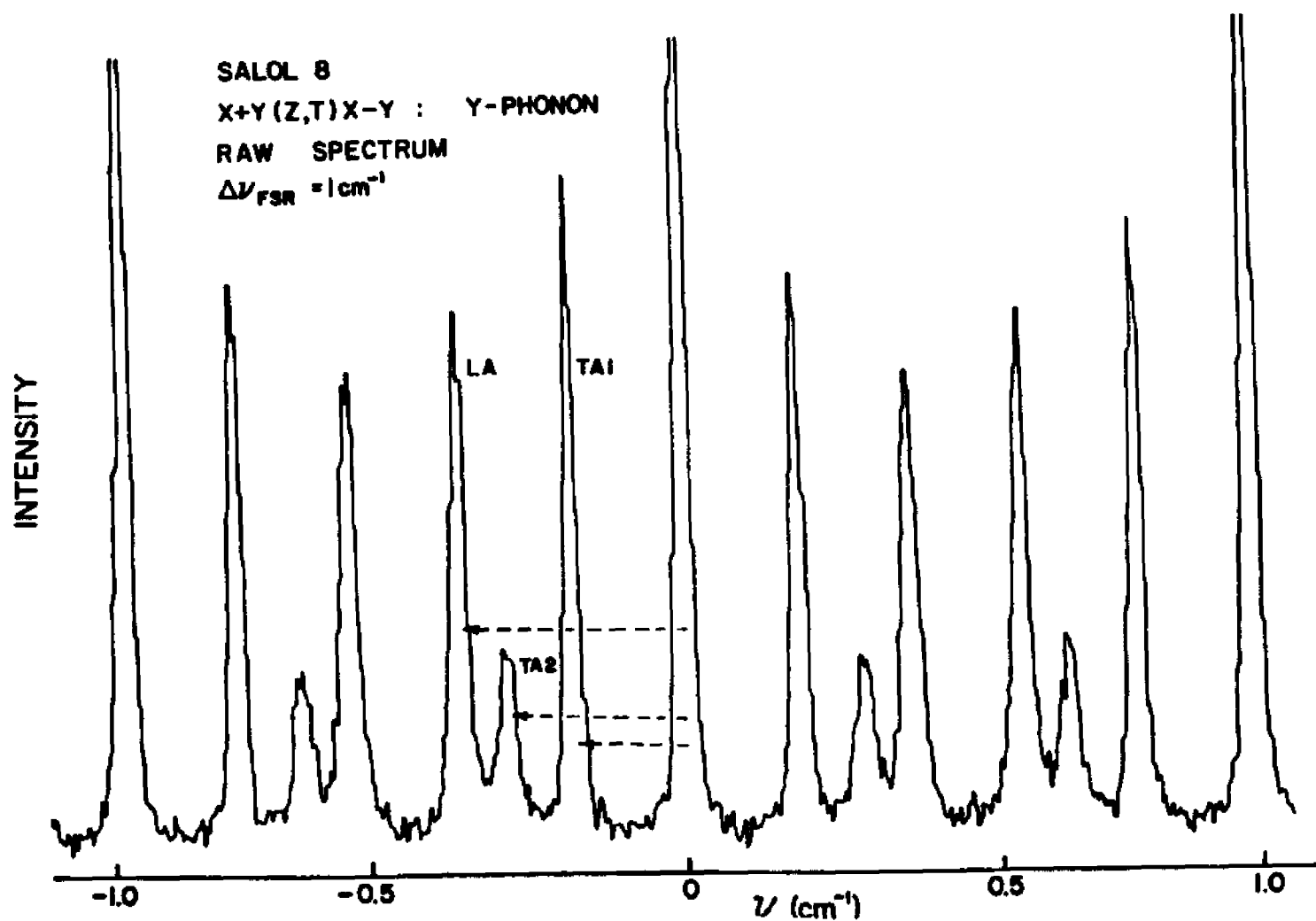


Fig. 8-1 (a) Brillouin spectrum of salol 8 in scattering configuration $X+Y(Z,T)X-Y$ as obtained from x-y plotter, showing an LA and two transverse modes TA1 and TA2. The spectrum is collected for 3 min. 20 sec. The free spectral range is 1cm^{-1} (30 GHz). The phonon wave vector q is along (010).

Fig. 8-1 (b) The raw spectrum in (a) fitted to a Lorentzian by the TAUROS-FITZAP program to determine the center and linewidth of each of the Brillouin components. The deconvoluted linewidths are extracted simply by subtracting the Rayleigh linewidth (center line) from the observed linewidths of the Brillouin components.

Fig. 8-1 (c) The raw spectrum in (a) fitted to parametrized Voigt functions by the nonlinear least squares fitting program NLLSQ-DECON3. The deconvoluted linewidth is extracted by fitting the observed spectrum $O(\omega)$ given by: $O(\omega) = \int d\omega' d\omega'' B(\omega'') I(\omega')$ where $B(\omega'')$ is the deconvoluted spectrum and $I(\omega')$ is the instrumental function.

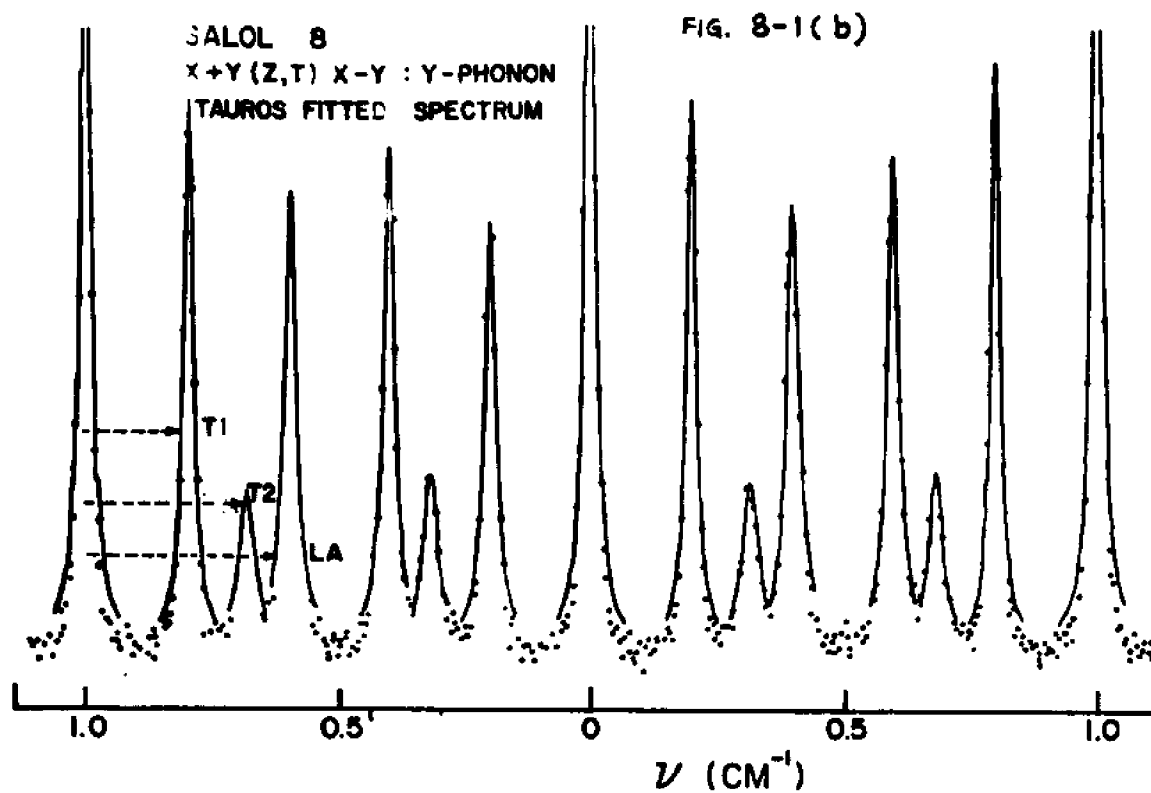
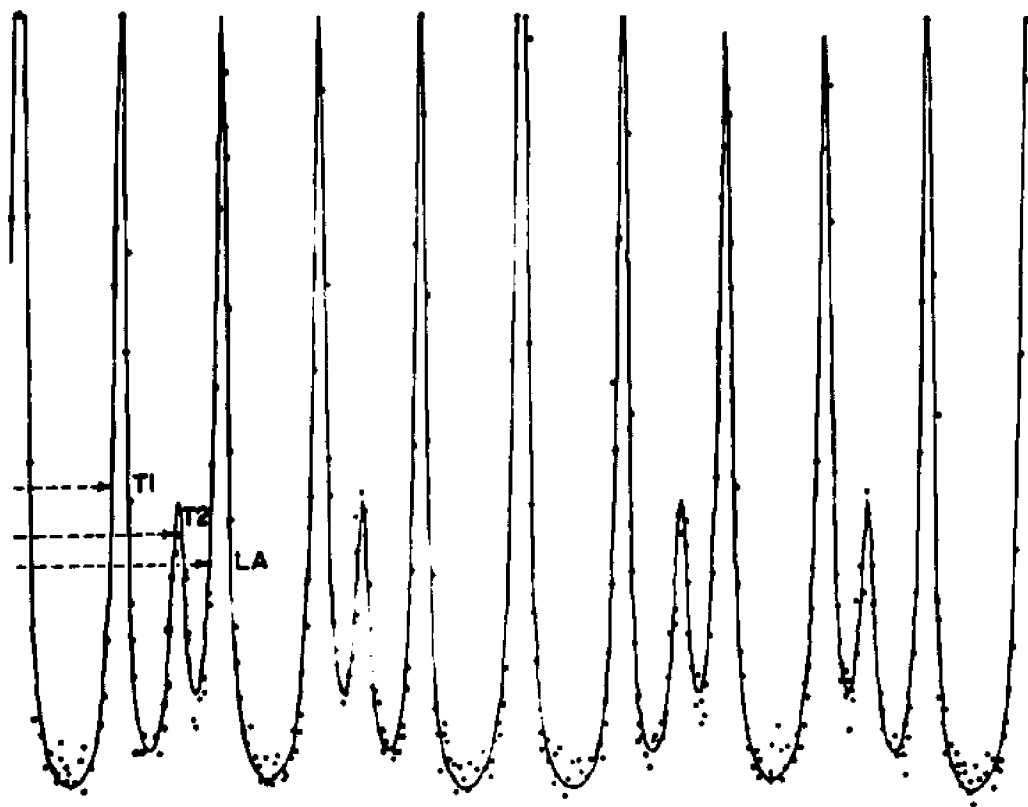


FIG. 8-1(c)

SALOL 8 X+Y(Z,T) X-Y : Y-PHONON
NLLSQ-DECON 3 FITTED SPECTRUM

INTENSITY



The major part of the analysis of Brillouin spectra was done with the NLLSQ-DECON3 fitting program. salol B, salol A and Salol 18 were chosen for such analysis. For each of the samples, observed linewidth, deconvoluted linewidth and Brillouin shift for all three (TA1, TA2 and LA) modes were tabulated with their corresponding temperatures in $^{\circ}\text{K}$. SUCC. D5 was analyzed by the TAUROS-FIZAP procedure. These Γ -T, and ν_g -T tabulated files were manipulated by various programs to get the results described in Section II of this chapter.

(2) Room Temperature Data

Since the elastic coefficients and Pockels coefficients of salol had to be determined from the room temperature data, both the frequency shift and the integrated intensity were extracted from NLLSQ-DECON3 fits of all the room temperature data. From Brillouin shifts, the sound velocities of each of the modes, LA, TA1 and TA2 were determined. Then the eigenvalue equations $\rho v^2 = f(c_{ij})$ and associated Brillouin scattering tensors developed in chapter V were used for specified scattering configurations to determine the complete elastic coefficient tensor.

To determine the integrated intensity of each of Brillouin modes of salol and its corresponding benzene spectrum, the observed linewidth and peak height from NLLSQ-DECON3 fits of spectra for each configuration were recorded. Equation 3-6 was then used to determine the Pockel's coefficients of salol, which will be presented in tabular form, in Section II of this chapter.

(C) Determination of the Pockel's coefficients of salol

From NLLSQ-DECON3 analysis of the salol and benzene spectra, the Voigt parameter a was found to be around 10^4 which suggests that each component is a Lorentzian. To determine the Pockel's coefficient according to equation (5-19) and (5-10) in chapter V, we need to determine experimentally the integrated intensity to which the Rayleigh ratio is proportional. If the Lorentzian is expressed in terms of its full width at half maximum Γ , center frequency ω_0 and peak height H , by:

$$I(\omega) = \frac{(\Gamma^2/2) H}{(\omega - \omega_0)^2 + (\Gamma/2)^2}$$

then the integrated intensity of the scattered light I_s

is:

$$I_s = \int \frac{\Gamma H (\Gamma/2) d\omega}{(\omega - \omega_0)^2 + (\Gamma/2)^2} = \pi \Gamma H \quad (8-2)$$

Since the Rayleigh ratio is proportional to the scattered intensity ($R \sim I_s$) measurement of Γ and H will determine the Rayleigh ratio within a constant of proportionality:

$$R \sim \Gamma_{\text{obs}} H$$

Γ_{obs} and H are found from nonlinear least squares fitting of each spectrum. The proportionality constant relating R to $\Gamma_{\text{obs}} H$ was determined by comparison with a benzene spectrum recorded before or after a set of salol spectra. The Rayleigh linewidth remained unaltered when a benzene spectrum and a salol spectrum were recorded sequentially under identical experimental conditions. Since benzene cross section data for 5145 Å were not available [20], I calibrated the benzene Rayleigh ratio by comparing its spectrum with that of a quartz sample (taken under identical experimental conditions) whose absolute cross sections and Pockel's coefficients are well known [21].

(a) Comparison of Quartz and Benzene.

The Rayleigh ratio for any crystal is given by

equations (5-10) of chapter V:

$$R^{\alpha} = \left(\frac{n_s}{n_o} \right)^2 \frac{\pi^2 k_B T \epsilon_i^2 \epsilon_j^2}{2 \lambda_s^4 g v_{\alpha}^2} \left[\hat{e}_j \cdot T \cdot \hat{e}_i \right]^2 \quad (5-10)$$

where T is the Brillouin scattering tensor for mode- α and v is the sound velocity.

For comparison, I took a benzene spectrum and a quartz spectrum under the following experimental circumstances (see the spectra in fig. 8-2(a) and (b) respectively):

Experimental parameter	Benzene	Quartz
scattering configuration	(VV)	X(Z,Z)Y
FPP plate separation d	15.68 mm	15.68 mm
Date of collection	July 1, 1983, 11AM	July 1, 1983, 11:30AM
Duration of run	21 min. 20 sec 640 cycles	21 min. 20 sec 640 cycles
Analysis procedure	NLLSQ-DECON3	NLLSQ-DECON3
Laser wavelength	5145.36A	5145.36A
Laser output	135mW	135mW
Room Temperature	23.5°C	23.6°C
Rayleigh line width	142 MHz	148 MHz
Brillouin Linewidth (observed)	Γ_{obs} 283 MHz	203 MHz
Peak height	H 4830 cts/s	134.7 cts/s

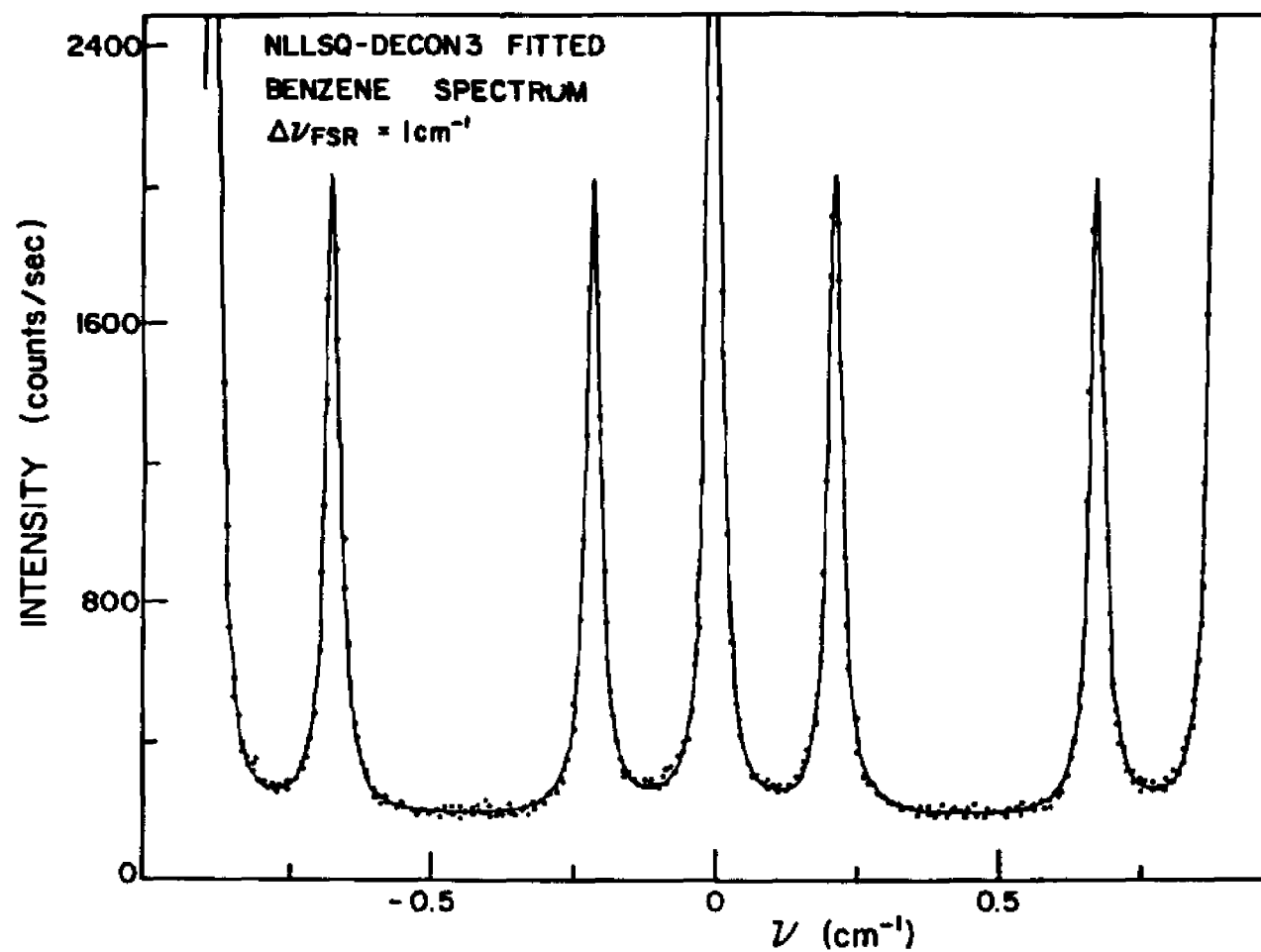
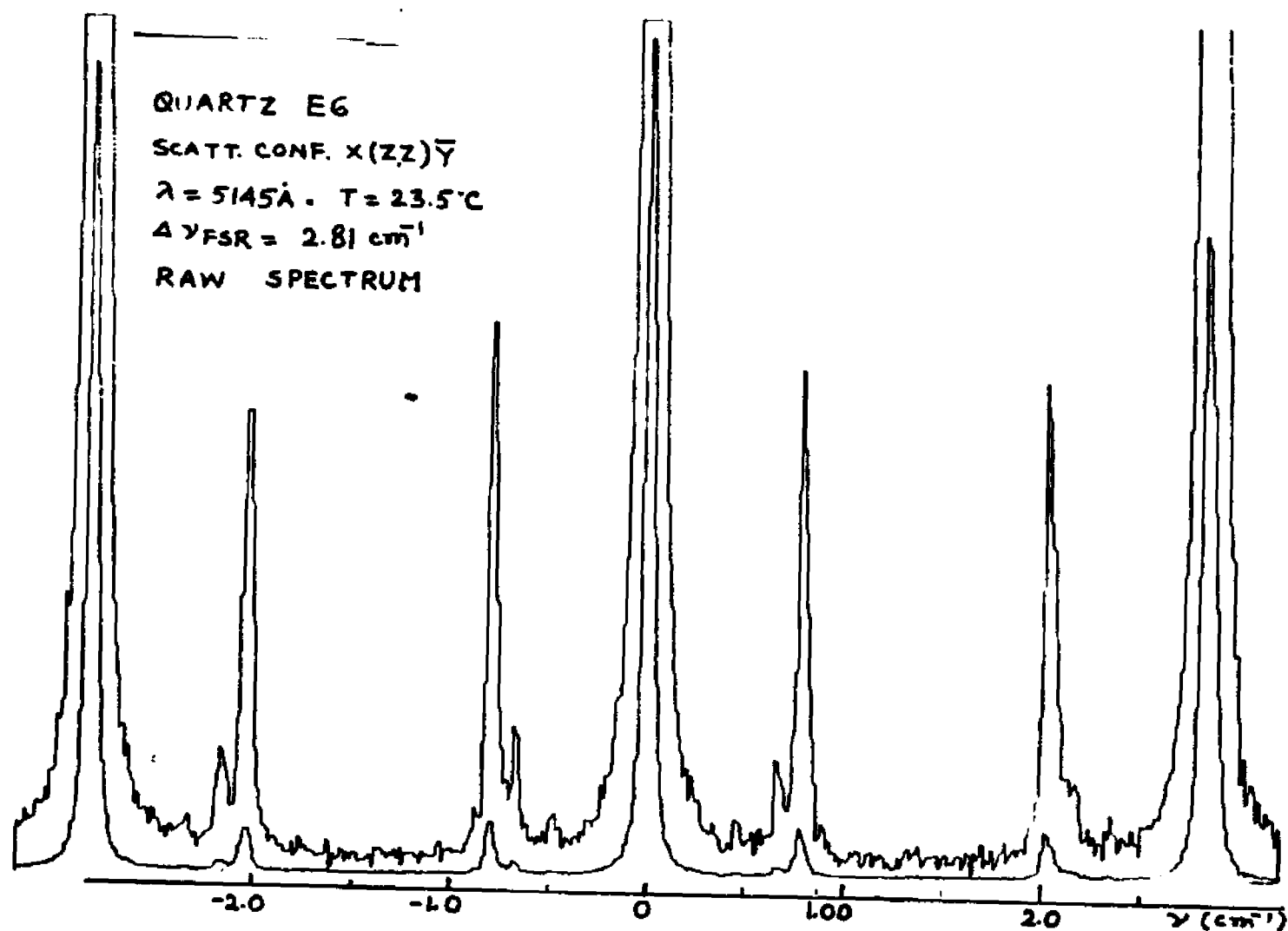


Fig. 8-2 (a) Brillouin spectrum of benzene collected for 21 minutes (same duration as of quartz spectrum shown in (b)) shown fitted to Voigt functions by NLLSQ-DECON 3 program, scattering configuration.

Fig. B-2(b) Quartz spectrum obtained under similar conditions as benzene in (a), also shown fitted to a Voigt function to determine the Brillouin shift and peak height. Scattering configuration: $X(ZZ)\bar{Y}$.



Since the measured intensities or Rayleigh ratio
 $R \sim \Gamma_{\text{obs}} \cdot H$. From equation (5-19), it can be easily
 derived that :

$$\frac{R_{\text{BEN}}}{R_{\text{QTZ}}} = \left(\frac{T_{\text{QTZ}}}{T_{\text{BEN}}} \right) \left(\frac{\eta_{\text{QTZ}}}{\eta_{\text{BEN}}} \right)^2 \frac{(\Gamma H)_{\text{BEN}}}{(\Gamma H)_{\text{QTZ}}} \quad (8-3a)$$

where R_{BEN} and R_{QTZ} are respectively the Rayleigh
 ratio of benzene and quartz. Using the experimental value
 of the Rayleigh ratio of quartz for the QL-mode (see
 appendix A-III for a detailed calculation), the Rayleigh
 ratio of benzene can now be given by:

$$R_{\text{BEN}} = 3.9 \cdot 10^{-11} b_1 \quad (8-3b)$$

where $b_1 = \frac{\pi^2 k_B T}{2 \lambda_s^4}$, and is same for benzene, quartz and
 salol. For $T=20^\circ\text{C}$ and $\lambda_s = 5145\text{\AA}$, $R_{\text{BEN}} = 5.648 \times 10^{-6}$.

Similarly, the ratio of the Rayleigh ratio of salol
 for a particular mode to that of benzene can be determined
 from the observed spectra taken under similar experimental

conditions (like benzene and quartz), and is given for the α -mode by:

$$\frac{R_{SAL}^{\alpha}}{R_{BEN}} = \left(\frac{T_{BEN}}{T_{SAL}} \right) \left(\frac{\eta_{BEN}}{\eta_{SAL}} \right)^2 \frac{1}{k_t K_P} \left(\frac{\Gamma_{SAL}^{\alpha} H_{SAL}^{\alpha}}{\Gamma_{BEN} H_{BEN}} \right) \quad (8-4)$$

where: Γ_{SAL} is the observed linewidth of the mode of salol

Γ_{BEN} : observed linewidth of Benzene mode

H_{SAL}, H_{BEN} : Peak height of height of salol and Benzenemodes

$k_t = \frac{\text{duration of salol spectrum}}{\text{duration for corresponding benzene spectrum}}$

duration for corresponding benzene spectrum

K_P : correction factor for polarization configuration

$= \frac{\text{throughput at current polarization}}{\text{thoroughput at (VV)}}$

Since benzene spectra were taken only in (VV) polarization, $K_P=1$ for the acoustic modes of salol if also collected at (VV) configuration. For other salol spectra which were collected at other polarization configurations viz. VH, HV, HT, HH, or VT, the factor K_P had to be introduced to normalize the benzene intensity corresponding to those polarization configurations. By

measuring the throughputs of the scattered intensity from a paper card at VV, VH, HV, HT, HH AND VT by the power meter, the K_p factors were determined as: $K_p(VH) = 0.463$, $K_p(HV) = 0.476$, $K_p(HH) = 0.607$, $K_p(VT) = 3.71$ and $K_p(HT) = 2.78$. For example, $K_p(VH) = 0.463$ means that in order to compare the intensity of a salol mode obtained in VH configuration with that of a benzene mode obtained in VV configuration, the intensity of the benzene modes must be reduced by a factor of 0.463. From equation (5-10), the Rayleigh ratio of the α -th mode in salol is given by:

$$R_{SAL}^{\alpha} = b_1 \frac{\epsilon_i^2 \epsilon_j^2}{g_{SAL} v_{\alpha}^2} \left[\hat{e}_j \cdot T^{\alpha} \hat{e}_i \right]^2 \quad (8-5)$$

where the $_{ij}$ -component of T^{α} contains the Pockel's coefficient or some linear combination of Pockel's coefficients. The final expression of $[\hat{e}_j \cdot T^{\alpha} \hat{e}_i]$ for the α -th mode of salol can thus be given (by combining equation 8-4 and 8-5) by:

$$\left[\hat{e}_j \cdot T^{\alpha} \hat{e}_i \right]_{SALOL}^{\alpha} = 6.432 \times 10^{-6} \left(\frac{v_{\alpha}}{\epsilon_i \epsilon_j} \right) \left[\frac{\Gamma_{SAL}^{\alpha} \chi_{SAL}^{\alpha}}{\Gamma_{BEN}^{\alpha} \chi_{BEN}^{\alpha}} \right]^{1/2} \quad (8-6)$$

where v_α is the sound velocity of the α -th mode of salol and $\hat{e}_j, \hat{e}_i$ are the scattered and incident light polarization directions.

In other words, if the α -th mode of salol is observed in polarization configuration $(\hat{e}_j, \hat{e}_i)$, then by measuring its velocity v_α , the observed linewidths Γ_{SAL} and Γ_{BEN} , and peakheights H_{SAL} and H_{BEN} one can calculate the Pockel's coefficients of salol contained in the T_{ij} component of the scattering tensor T by using equation(8-6).

(D) Raman Spectra Analysis

Although several sets of Raman spectra were collected at temperatures ranging from room temperature through the melting transition of salol, no quantitative analysis of these spectra was performed. By plotting the strip chart records of spectra at different temperatures on the same graph, a qualitative visualization could be made of the gradual change in Raman shift and relative intensity of lower frequency Raman modes. The Raman results will be discussed in section II of this chapter and in chapter 9.

Section II: RESULTS

A. Introduction

This section contains the results of the experiments conducted throughout this thesis project. As discussed earlier, the experiments were of two types (1) melting experiments and (2) room temperature experiments. These experiments resulted in measurements of the Brillouin shift and integrated peak height of the observed Brillouin modes. The present experimental project was designed to study possible anomalies of the elastic properties of solids at or near their melting points with the Brillouin scattering technique. Very few melting studies by light scattering techniques have been reported so far [1-5]. The linewidth results were analysed by a simple dislocation model in the context of the dislocation theory of melting which predicts a drastic increase of defect concentration close to T_M . A qualitative analysis of the Brillouin shift data in the context of Born's melting theory was also attempted. As we approach the detailed experimental results in the next section, we shall see how the dislocation model analysis of the results relates to existing defect theories of melting.

B. Results of Brillouin experiments on melting.

Figure 8-3 and 8-4 show raw spectra of salol B and salol A from room temperature up to very close to T_m . The center frequency and the linewidth of the Brillouin modes at each temperature were determined by the NLLSQ-DECON3 fitting program (described earlier). The results of the analysis are given below.

(1) Temperature dependence of Brillouin shift and Born theory

According to Born's theory of melting, a crystal melts at the temperature at which it loses its stability against shear. Calculation for a cubic crystal has shown that violation of the condition $C_{44} > 0$ leads to shear instability and melting [6]. From the calculation in chapter V, one can see the relationship between the elastic coefficients and the phonon velocity. Let us take the case of each sample one at a time.

(a) Salol A and Salol B.

The scattering configuration employed was $Y(VT)Z$, which means incident light propagating normal to the b-face and polarized along $\hat{x}$, and scattered light

Fig. 8-3: Raw spectra of salol B obtained at various temperatures up to $T = 40.92^{\circ}\text{C}$ ($T_m = 40.925^{\circ}\text{C}$), in scattering configuration: $Y(X,T)Z$. Brillouin components associated with the Rayleigh line at the left edge of the figure are indicated by arrows. The rapid increase in observed linewidth is clearly visible very close to T_m . The change in relative intensity of the QT mode near T_m is also seen. Salol B was grown from solution.

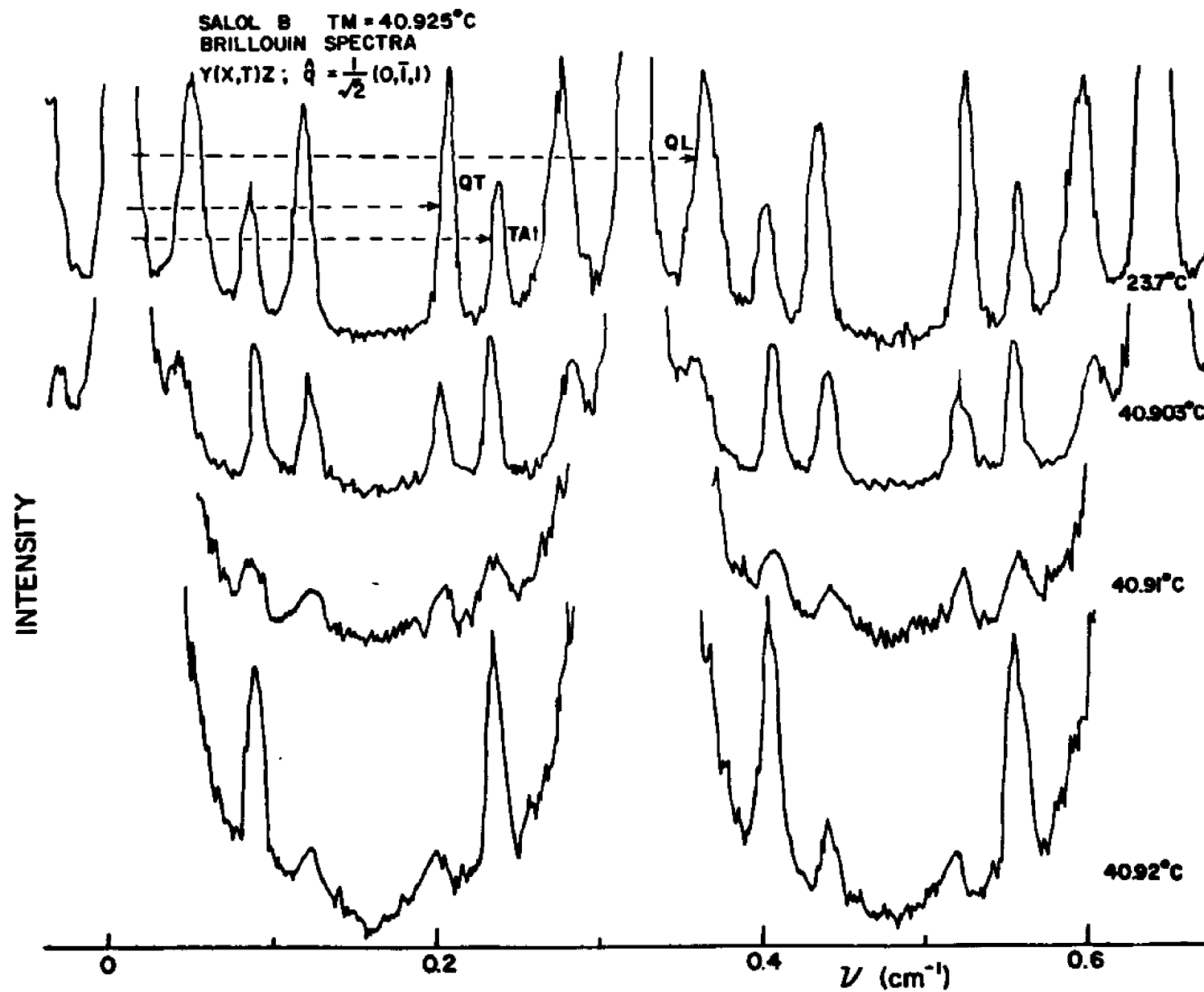
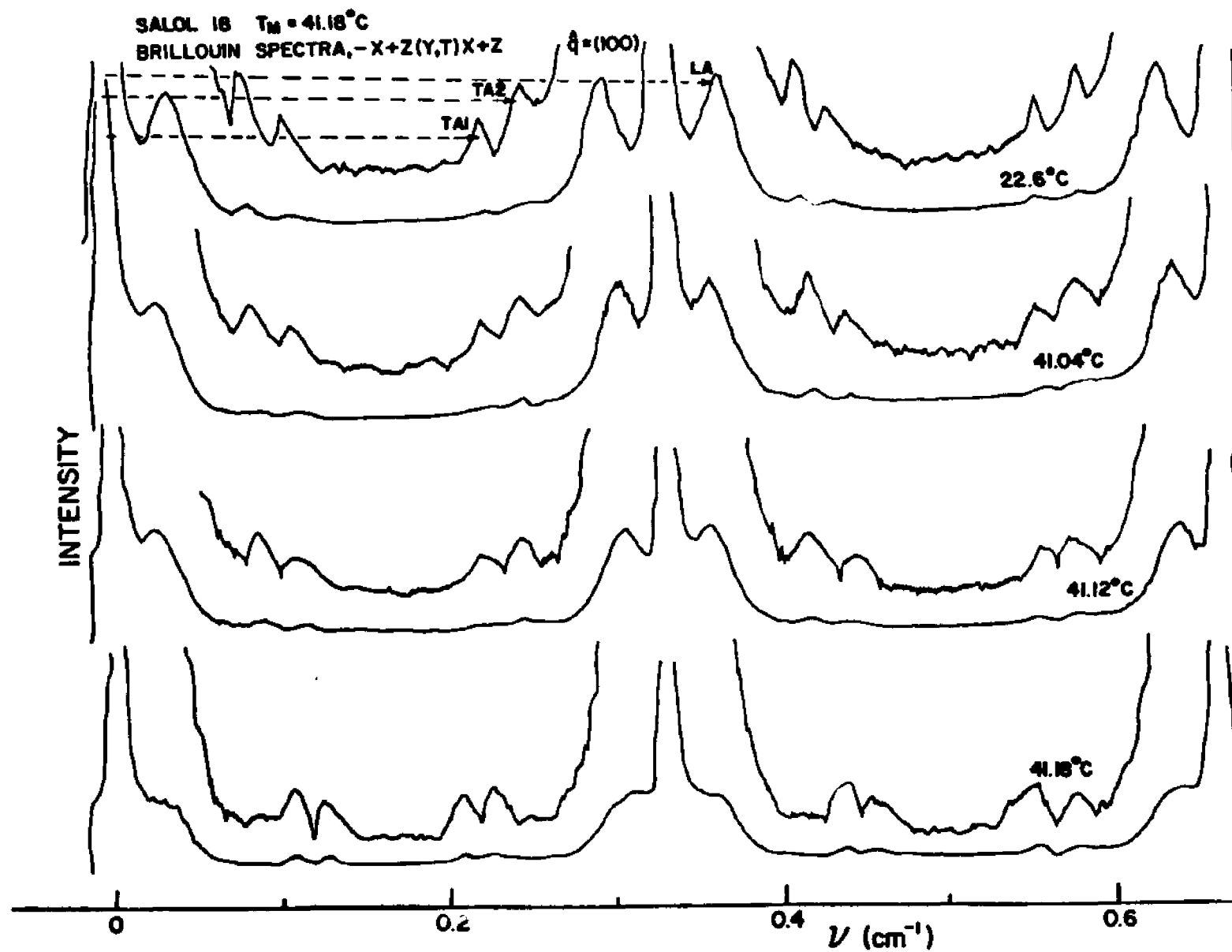


Fig. 8-4: Raw spectra of salol 18 (melt grown) shown up to $T = 41.18^\circ$ ($T_m = 41.22^\circ\text{C}$), in scattering configuration: $-X+Z(Y,T)X+Z$. A simultaneous softening and broadening of the Brillouin modes near T_m is observable. The relatively weaker elastic component and higher melting temperature of salol 18 may be related to its high purity relative to the solution grown salol B.



propagating normal to the c-face collected without any analyser (in both V and H polarization) All three modes TA1, QL and QT were visible. Neglecting the optical anisotropy, the phonon wave vector for this scattering configuration is given by:

$$\hat{q} = (1/\sqrt{2}) (\hat{x} + \hat{z})$$

And the eigenvalues are:

$$\mathfrak{S}_{v_{TA1}}^2 = .5C_{66} + .5C_{55}$$

$$\mathfrak{S}_{v_{QL}}^2 = .5C_{44} + .25C_{22} + .25C_{33} + .25[(C_{22} - C_{33})^2 + 4(C_{44} + C_{23})^2]^{1/2} \quad (8-7)$$

$$\mathfrak{S}_{v_{QT}}^2 = .5C_{44} + .25C_{22} + .25C_{33} + .25[(C_{22} - C_{33})^2 + 4(C_{44} + C_{23})^2]^{1/2}$$

where TA1 is a pure transverse mode, and QL and QT are quasi longitudinal and quasitransverse modes respectively.

(b) Salol 18

Scattering configuration -101(VT) 101

wave vector $\hat{q} = (100)$

eigenvalues

$$\mathfrak{S}_{v_{TA1}}^2 = C_{55}$$

$$\mathfrak{S}_{v_{TA2}}^2 = C_{66}$$

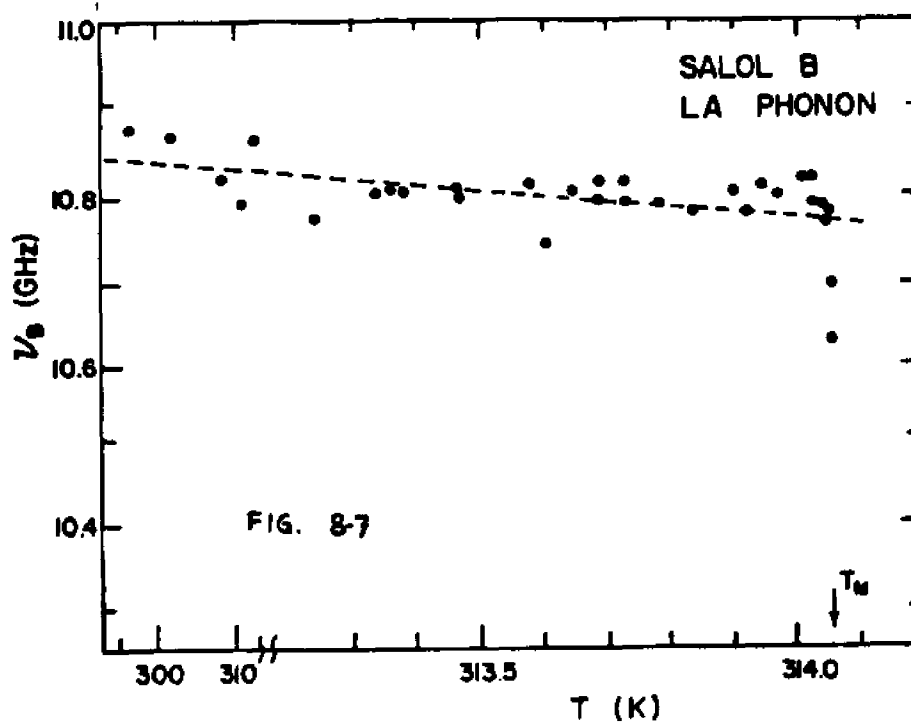
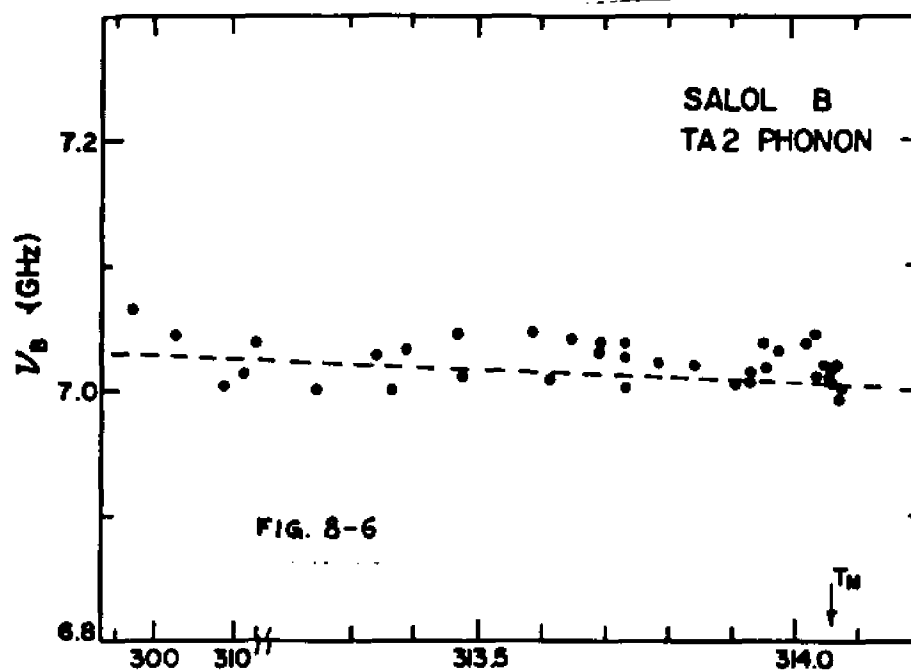
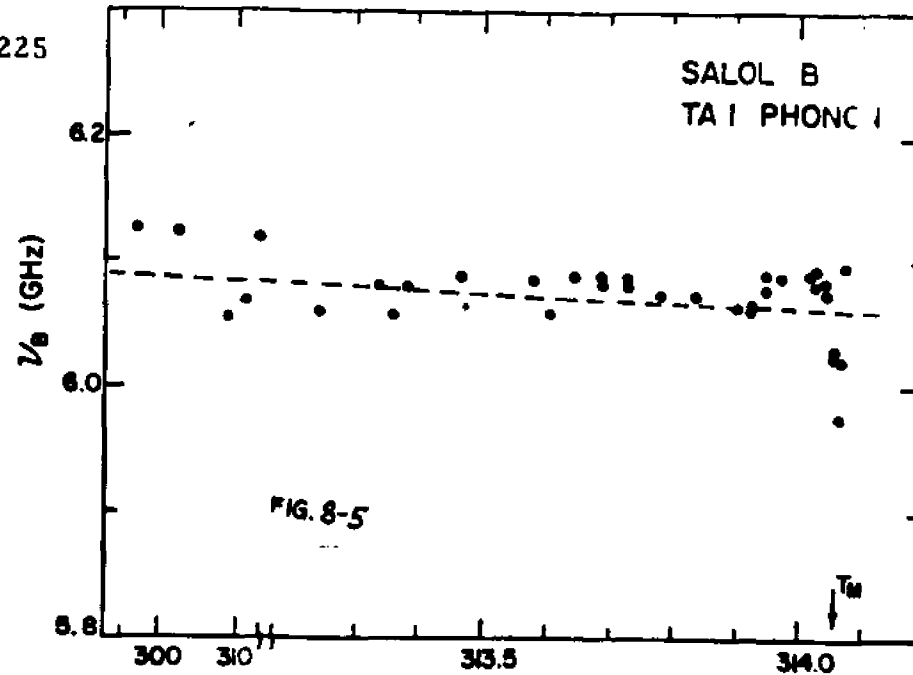
$$\mathfrak{S}_{v_{LA}}^2 = C_{11}$$

(8-8)

where TA1 and TA2 are pure transverse modes, and LA is a pure longitudinal mode.

The temperature dependences of the Brillouin shifts in GHz are presented in figure 8-5, 8-6, 8-7 respectively for the TA1, QT and QL modes of salol B. Figures 8-8, 8-9, and 8-10 are for the TA1, TA2 and QL modes of salol 18. The temperature dependence of the Brillouin shifts of the acoustic modes of salol A are shown in figures 8-11, and 8-12 respectively. All these frequency shifts were determined by using the NLLSQ-DECON3 fitting program described in the previous section. Finally fig 8-13 represents the temperature dependence of the Brillouin shift of the only visible LA mode of succinonitrile, SUCC D5, which was analysed by the TAUROS-fitting procedure. Three raw spectra of SUCC D3 at various temperatures including spectra just before and after melting are shown in fig. 8-14. As can be seen from the plots, the Brillouin shift or the effective elastic coefficient C_{eff} gradually decreases, and in agreement with the Born conjecture decreases substantially as the melting point is approached. But whether or not C_{eff} completely vanishes at T_m was not possible to determine from this experiment because of the very strong elastic scattering during melting. However, nobody has yet seen such clear gradual

- Fig. 8-5: Temperature dependence of the Brillouin shift ν_B of the TA1 mode of salol B ($T_m = 40.925^\circ\text{C}$ shown by arrow). The dotted line is the Brillouin shift including the temperature dependence due to thermal expansion, called ν_{BGD} obtained by the best linear fitting of ν_B vs T up to $T_m - 0.5^\circ\text{C}$ this is shown to visualize the "extra" softening of the Brillouin modes near T_m which presumably resulted from defects generated near T_m . The temperature scale is broken in order to illustrate the temperature dependent behavior of ν_B around T_m more clearly.
- Fig. 8-6: Temperature dependence of ν_B of the TA2 mode of salol B. The center frequency of each of the component was determined by a NLLSQ-DECON3 fitting of each Brillouin spectrum to a Voigt function (see fig. 8-1(c))
- Fig. 8-7: Temperature dependence of ν_B of the LA mode of salol B, showing strong downward bending near T_m .



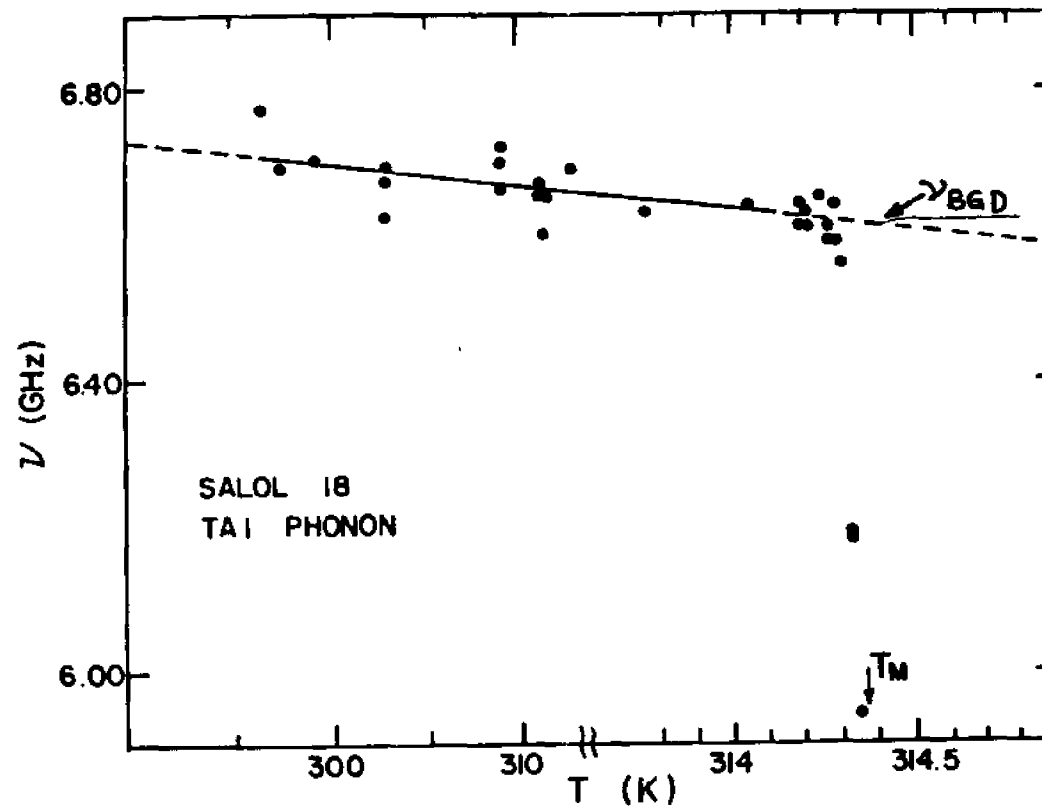


Fig. 8-8: Brillouin shift ν_B of TAl mode of salol 18 vs. temperature up to $T = 41.22^\circ\text{C}$ (314.37°K). The continuous decrease of the Brillouin shift ν_B from 6.8 GHz at room temperature to 5.95 GHz near T_m (13% decrease) is easily visible.

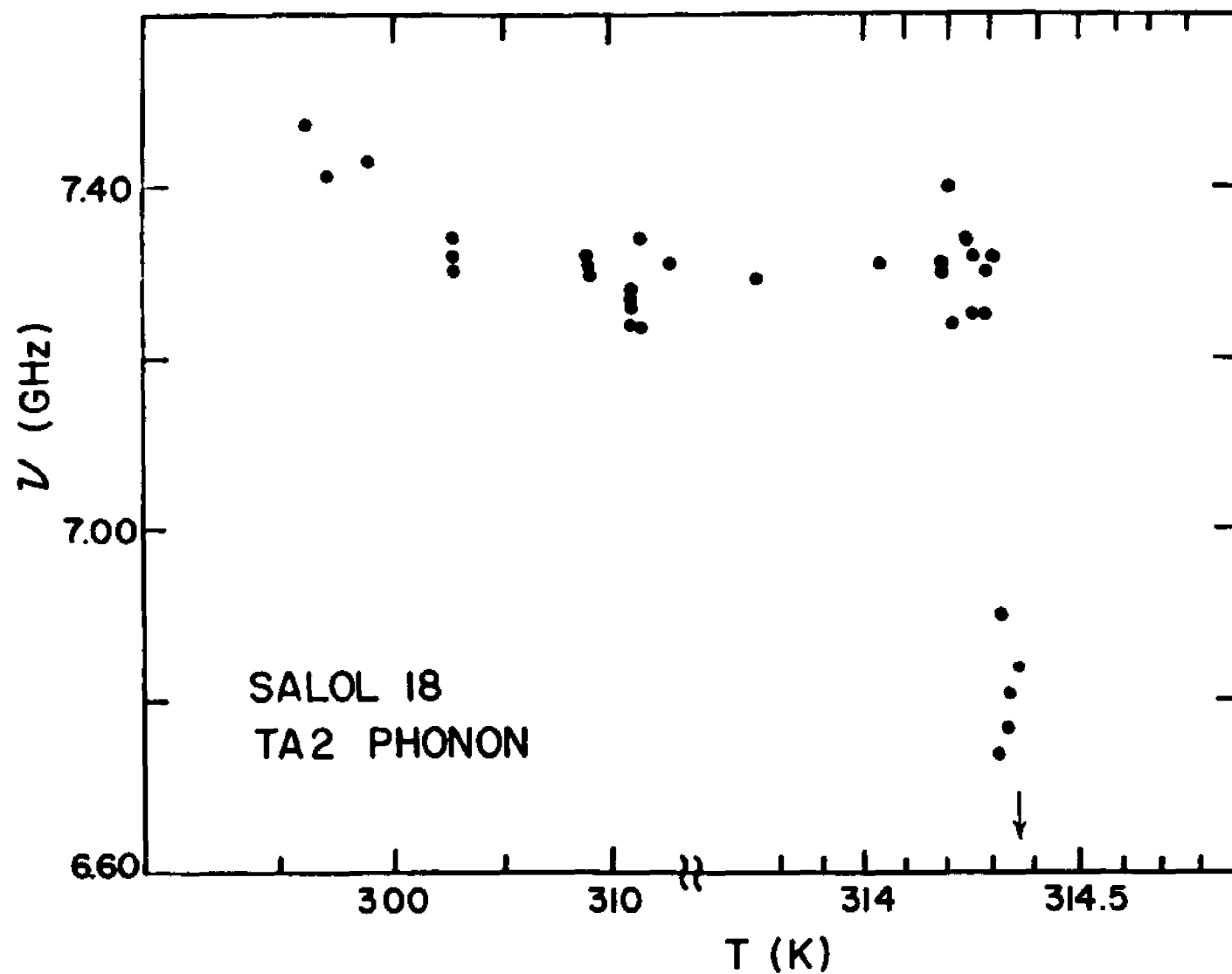


Fig. 8-9: Temperature dependence of ν of the TA2 mode of salol 18. Data collected at the same temperature on different days is shown.

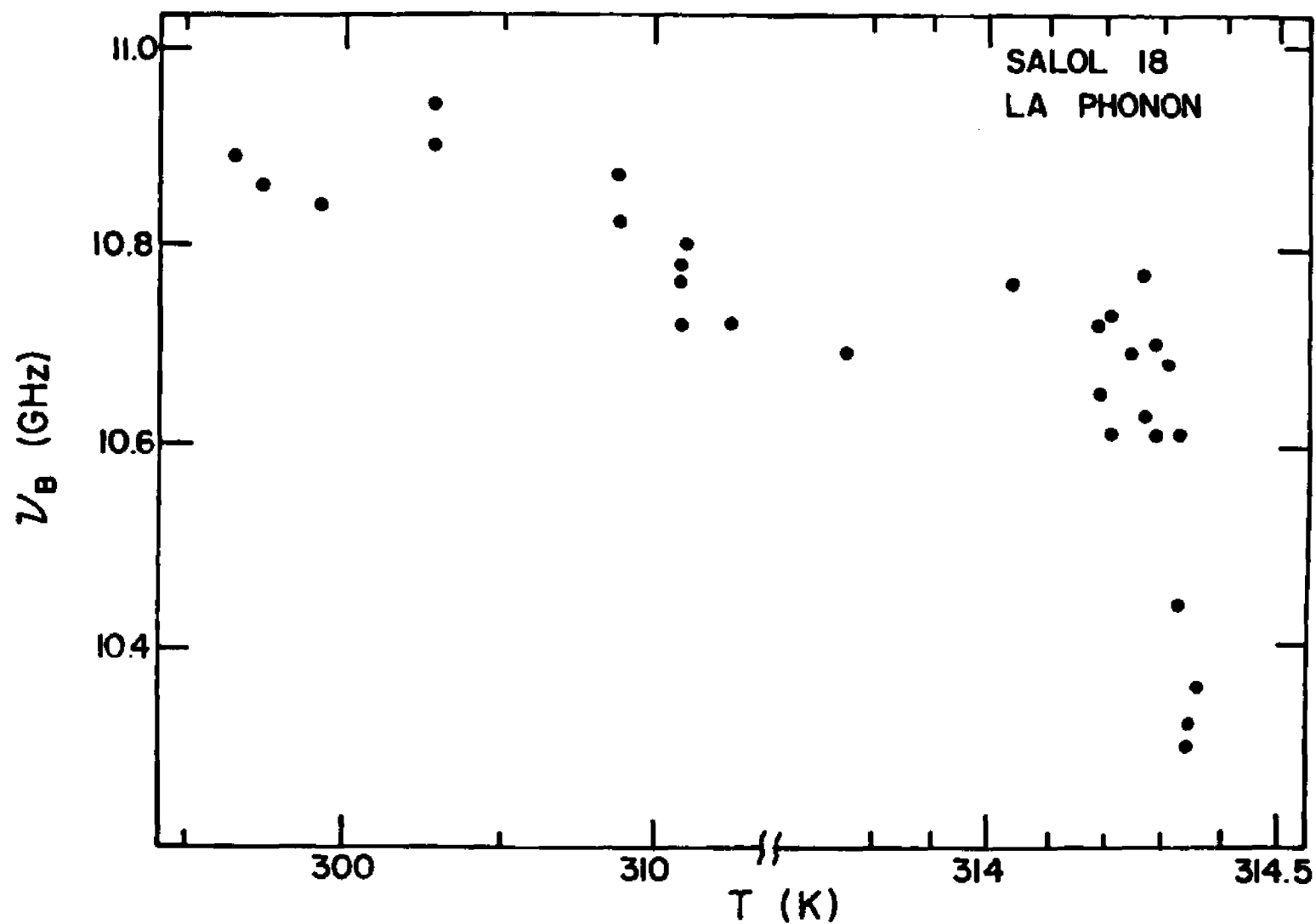


Fig. 8-10: LA mode of salol 18 against temperature. Data shown up to $T = 41.18^\circ\text{C}$. Since the onset of strong elastic scattering around $T_m (= 41.22^\circ\text{C})$ overshadows the LA modes, they aren't visible at $T \geq 41.18^\circ\text{C}$.

Fig. 8-11: ν_B vs. T of the TA1 mode in salol A, scattering configuration: $Y(X,T)Z$. The transverse Brillouin mode is seen to soften by $\sim 20\%$ during the last 0.1°C before melting. A similar decrease in C_{11} observed in fluorite crystals by Catlow et al in fig. 2-3 was attributed to the contribution of the defects generated around T_m . The dotted line shows the linear thermal decrease ($\sim 3\%$) of the Brillouin shift.

Fig. 8-12: Temperature dependence of ν_2 behavior of the second transverse mode in Salol A which also showed a softening of $\sim 15\%$ near T_m from its room temperature value.

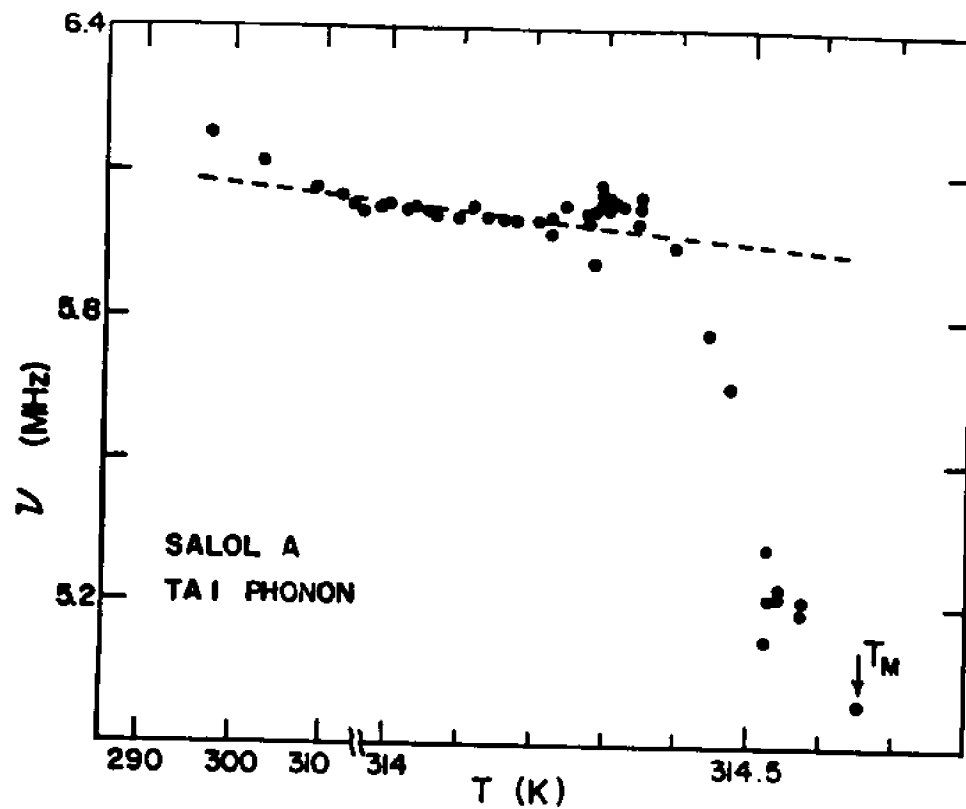


FIG. 8-11

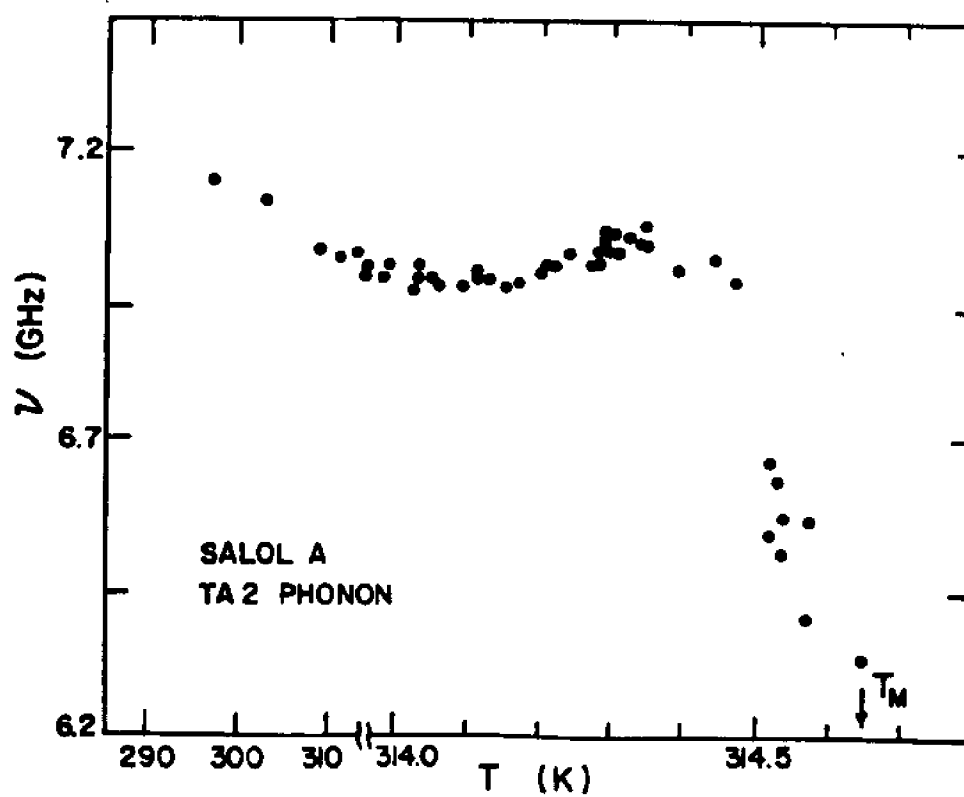
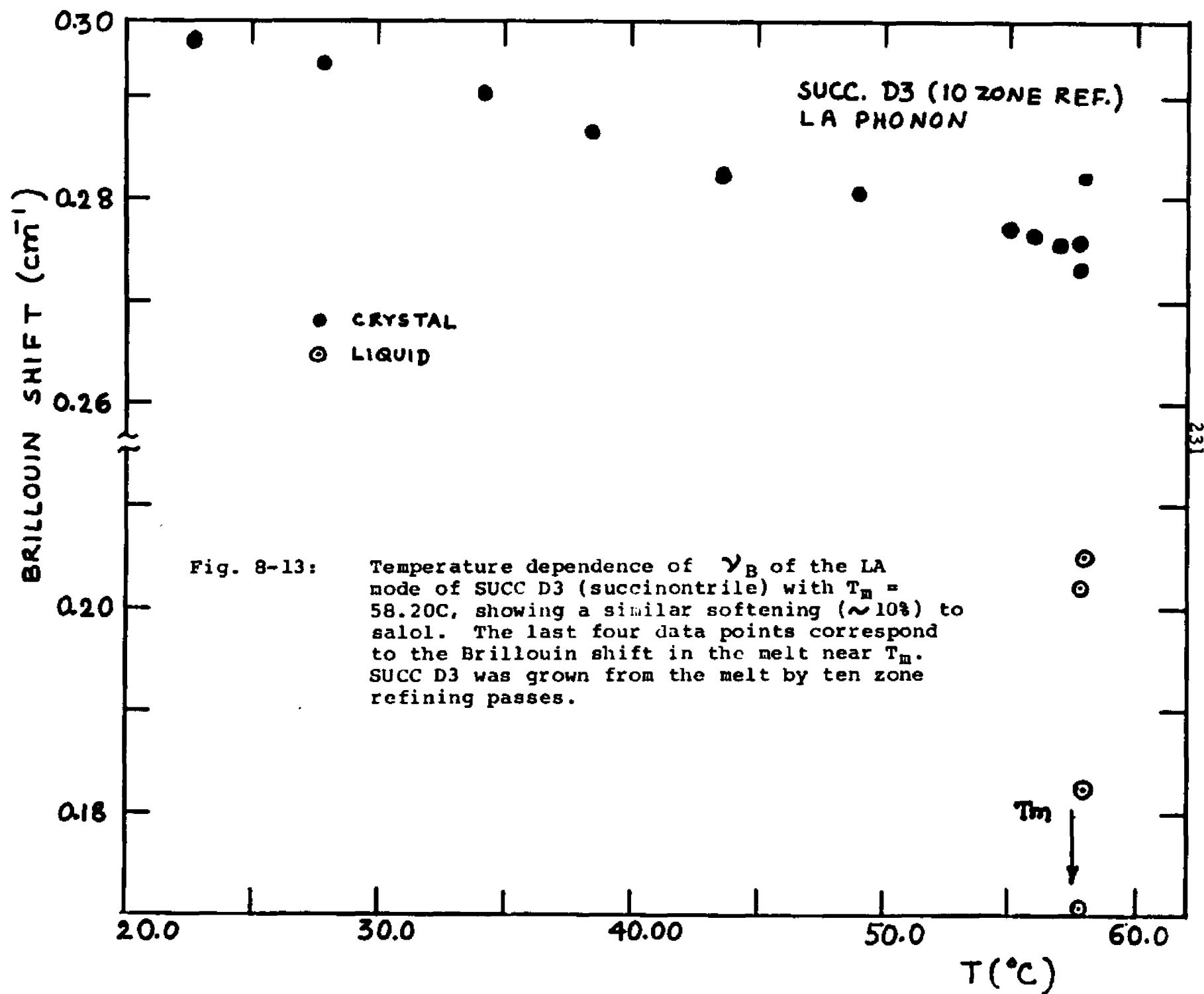


FIG. 8-12



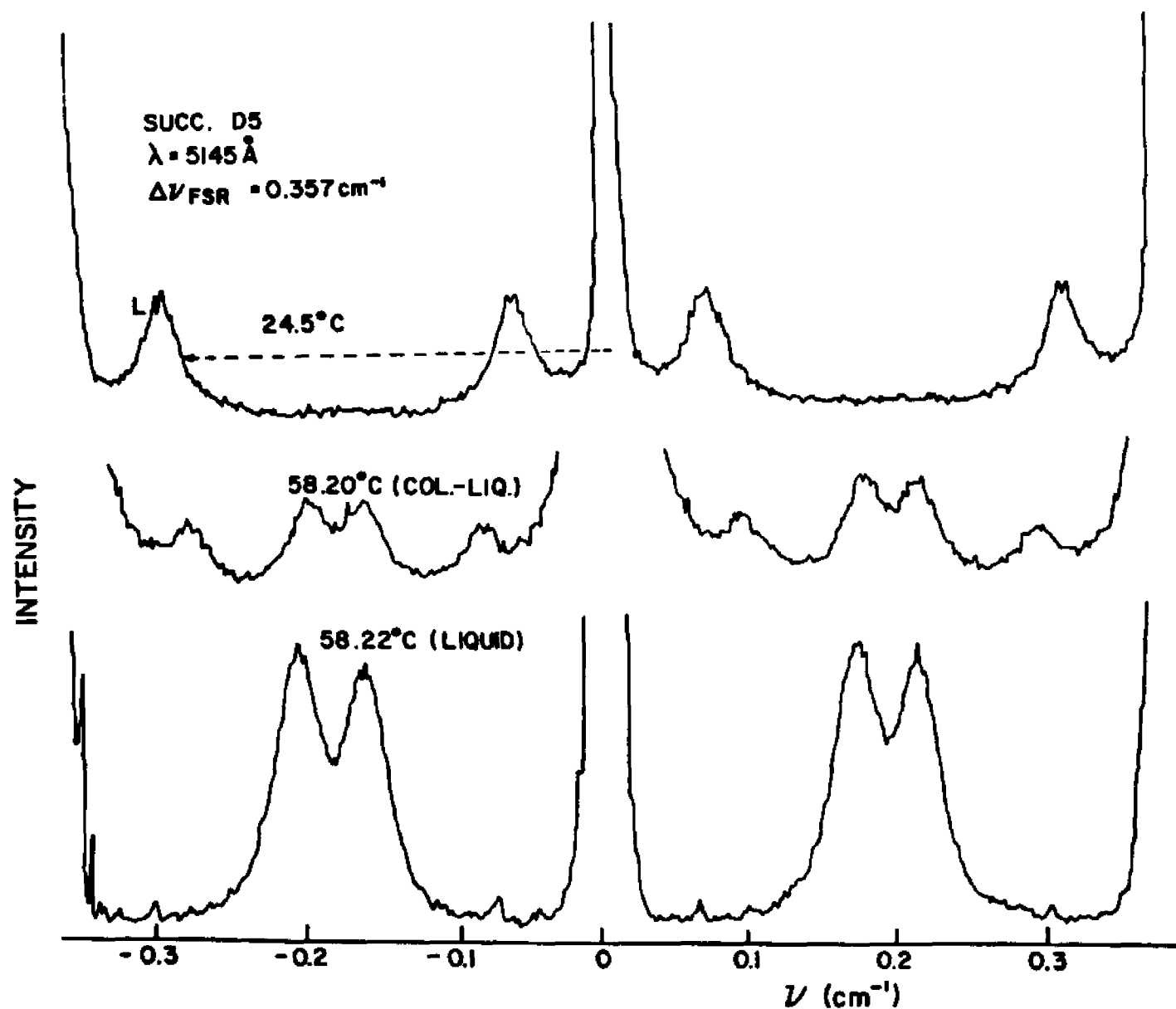


Fig. 8-14: Brillouin spectra of SUCC D3 at four different temperatures, including spectra in the liquid state. The spectrum at $T = 58.2^\circ\text{C}$ shows both the liquid and solid Brillouin components, indicating the co-existence of solid and liquid states simultaneously in equilibrium.

decrease of elastic coefficients in salol or in other materials [7-10].

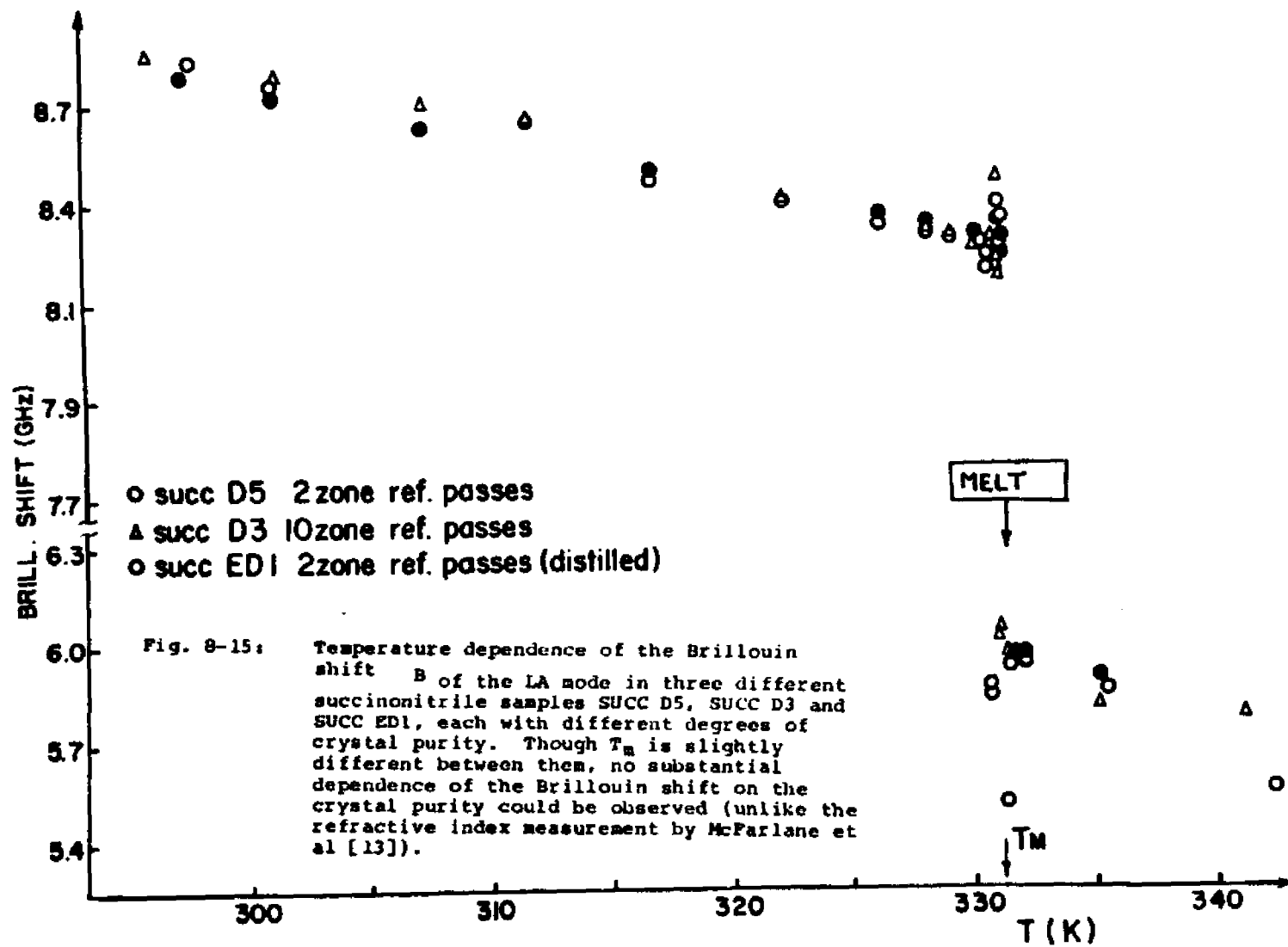
Figure 8-15 shows a Brillouin shift vs. temperature plot for three different succinonitrile samples. SUCC. D5 was grown from undistilled powder with 2 zone refining passes, SUCC. ED1 from distilled powder with 2 passes, SUCC. D3 underwent 10 zone refining passes. This experiment was designed to look for sample purity dependence of the Brillouin shifts. It can be observed that all three succinonitrile samples gave essentially the same results. The experiment was conducted from 20°C to 70°C , to take spectra up to complete melting. Similar melting experiments on succinonitrile were reported in [8].

(2) Temperature dependence of γ_{BGD} γ_{B}

This analysis was done in order to eliminate the effect of thermal expansion on the Brillouin shift. The Brillouin shifts of salol up to temperature $T=T_m-0.5^{\circ}\text{C}$ were fitted to the following function:

$$\gamma_{\text{BGD}} = \gamma_0 - \alpha_0 T \quad (8-9)$$

by a linear fitting program which adjusts the parameters γ_0 and α , [γ_0 is the $T=0$ intercept and α_0 is the slope] and



also gives the linear regression coefficient R which determines the quality of the fit. Then I computed a new data file $\nu_{\text{exp}} - \nu_{\text{B}}$ versus temperature T . The $\nu_{\text{exp}} - \nu_{\text{B}}$ versus T plots show the frequency change in excess of the linear thermal expansion term. Figures 8-16, 8-17 and 8-18 show the temperature dependence of $\nu_{\text{exp}} - \nu_{\text{B}}$ of TA1, TA2 and LA modes of Salol 18. Similar diagrams for Salol B are shown in figures 8-19 and 8-20 respectively. Discussion of these results will be presented in the next chapter.

(3) Temperature dependence of the linewidth

The most important current theory of melting is the dislocation induced melting theory [11]. According to this theory, close to the melting point a catastrophic growth of dislocations occurs which breaks the ordered crystalline structure and brings about the disordered liquid structure. Several computer simulation experiments[12] indicate that the defect (or dislocation) density should start to increase at the onset of melting, and when the substance is saturated with dislocations it melts. There is no direct way to measure the dislocation density in a crystal before and during melting. An indirect way to monitor a continuous increase

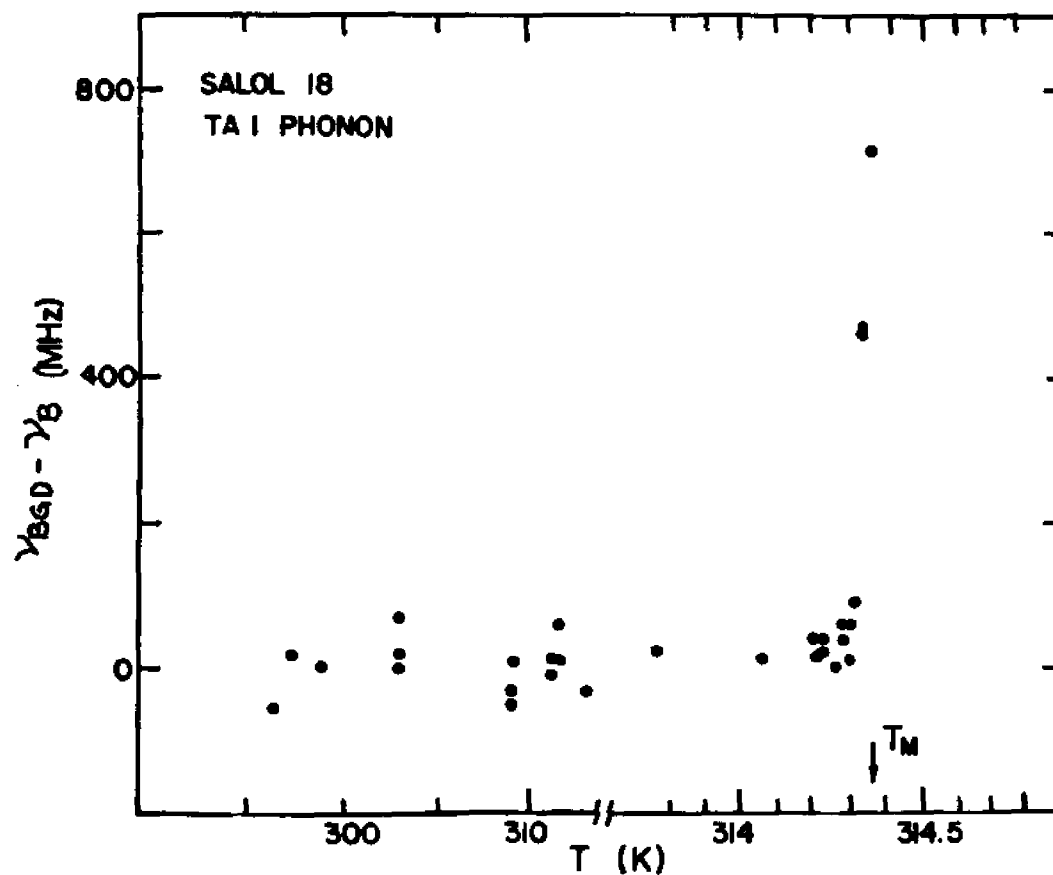


Fig. 8-16: Temperature dependent behavior of $\gamma_{BGD} - \gamma_B$ of the TA1 mode in salol 18. $\gamma_{BGD} - \gamma_B$ represents the decrease in Brillouin shift over and above γ_{BGD} which is the linear decrease of γ_B due to thermal expansion ($\sim 3\%$). $\gamma_{BGD} - \gamma_B$ is obtained by subtracting the measured γ_B from linearly fitted γ_{BGD} . The purpose of plotting the $\gamma_{BGD} - \gamma_B$ vs. T behavior is to show its qualitative similarity with the temperature dependent behavior of the linewidth which also increases rapidly near T_M .

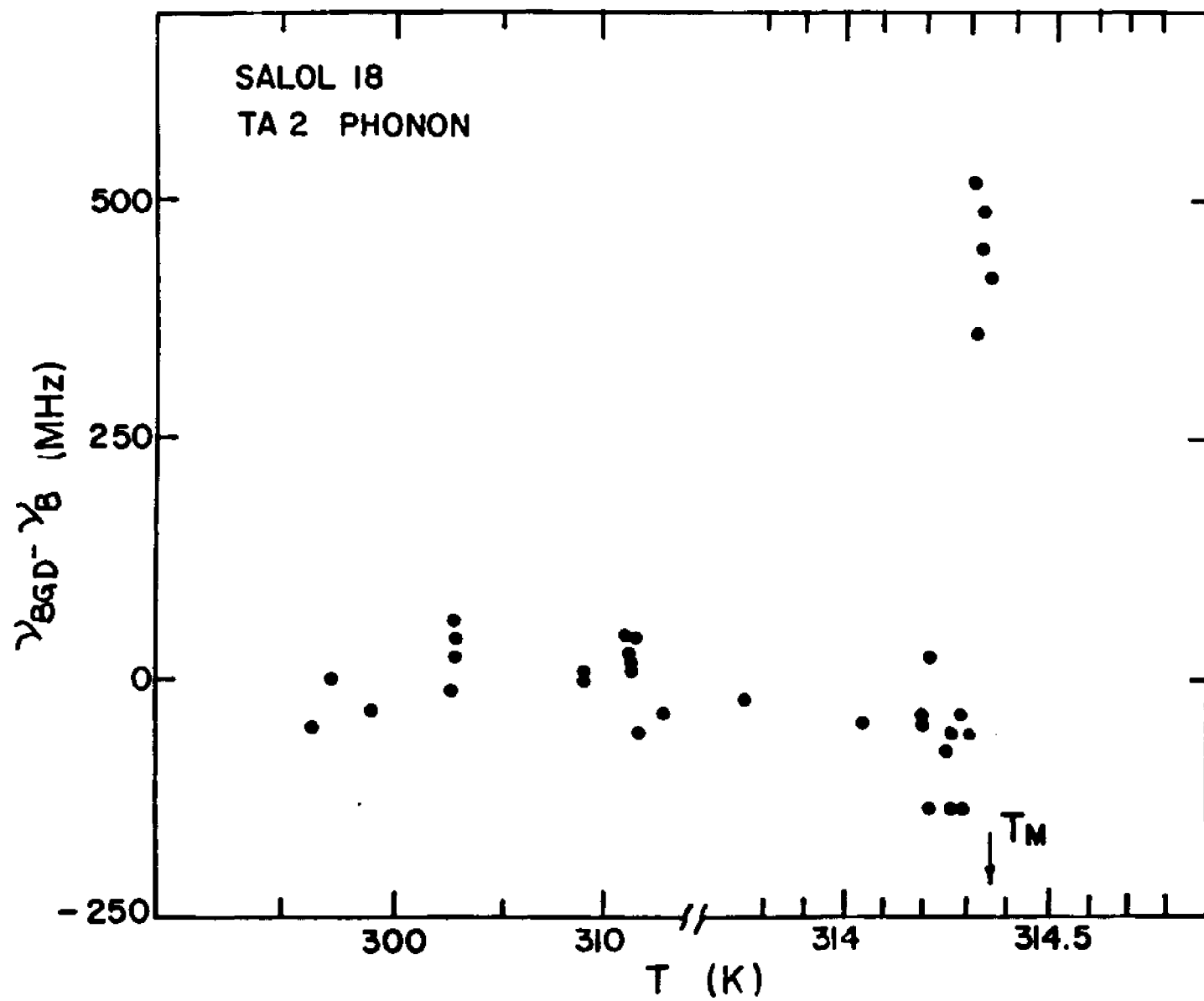
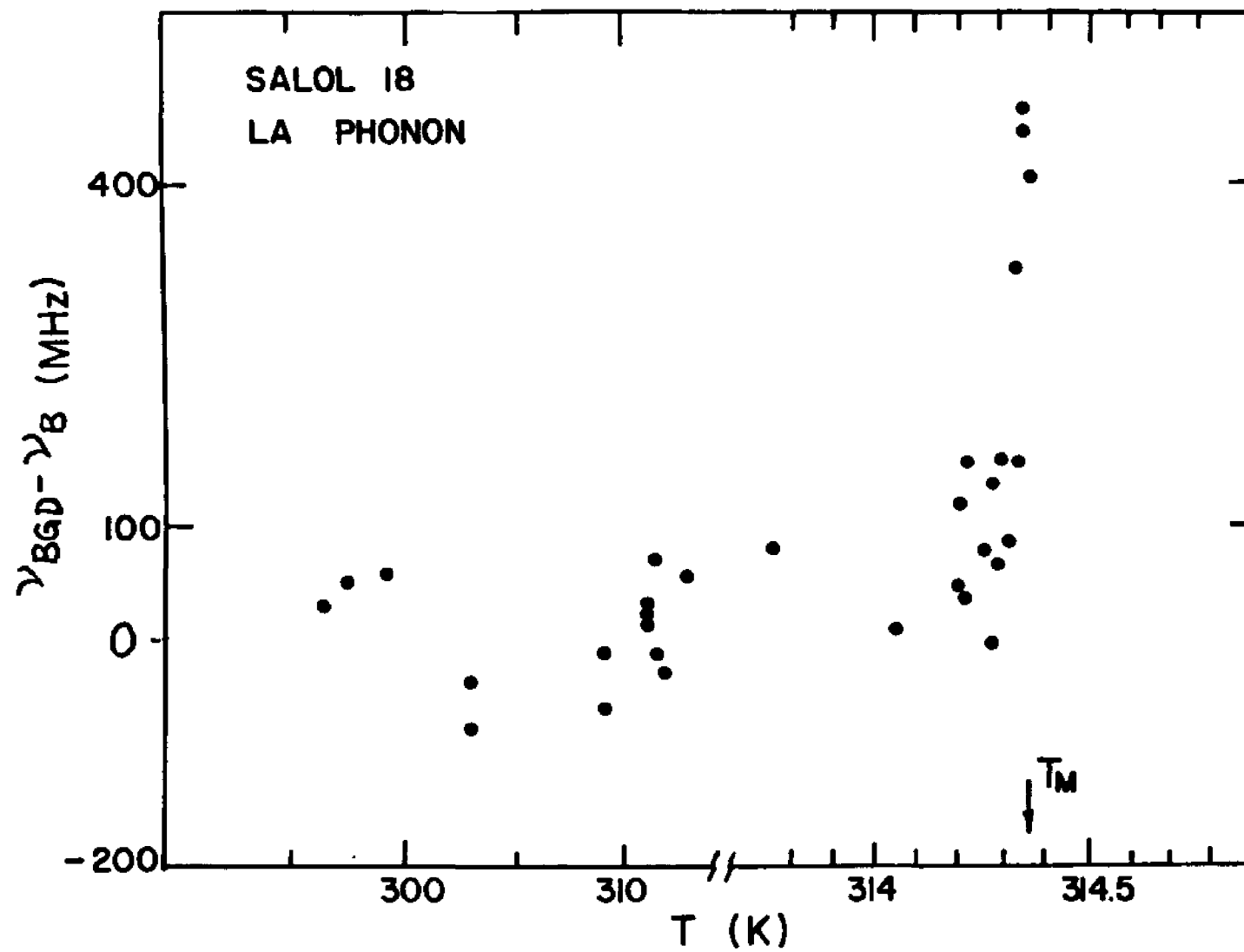


Fig. 8-17: $\gamma_{BGD} - \gamma_B$ vs. T for the TA2 mode of salol 18.



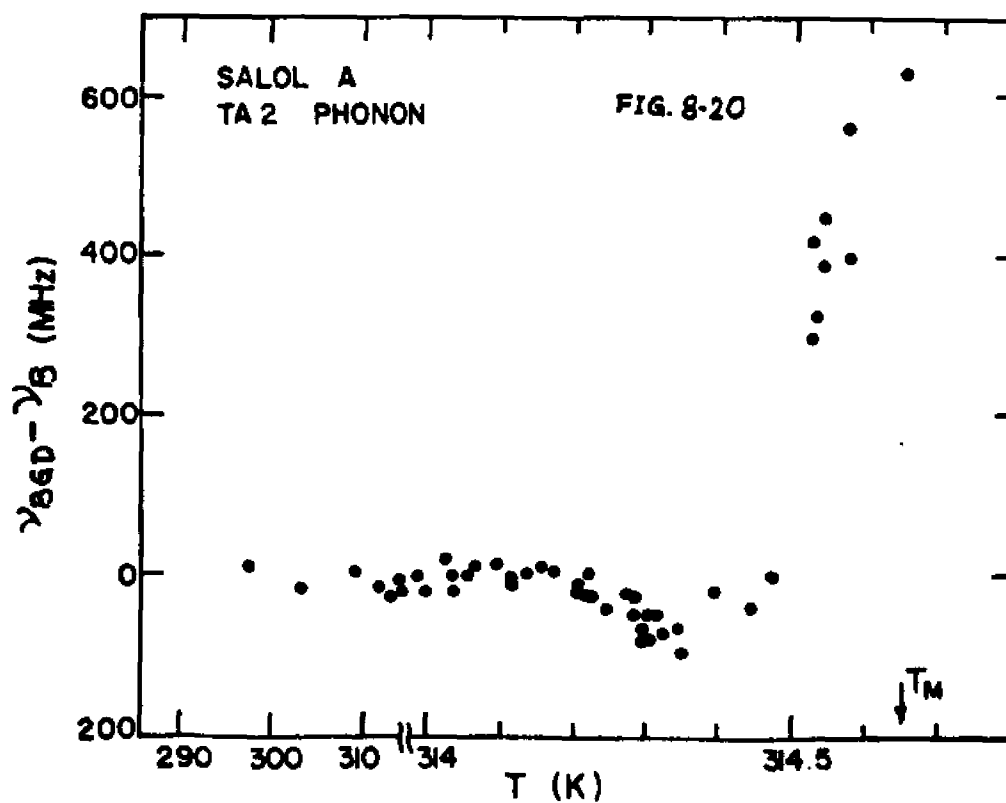
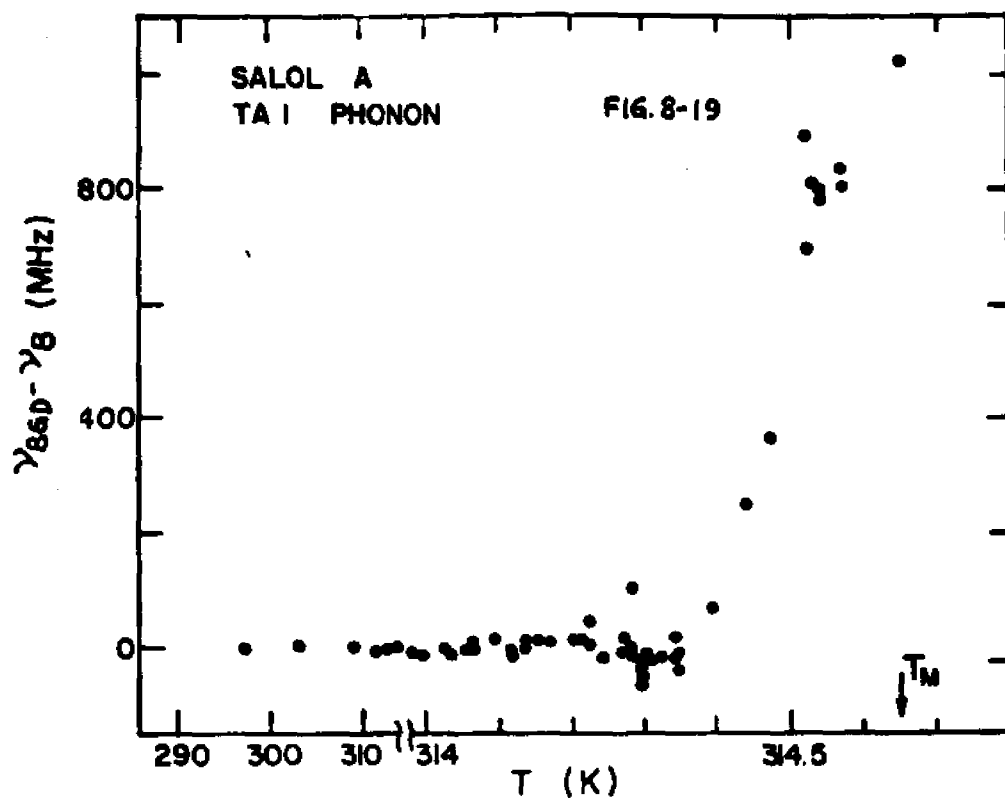


Fig. 8-19: $\nu_{\text{BGD}} - \nu_{\text{B}}$ vs temperature for the TA1 node of salol A

Fig. 8-20: Temperature dependence of $\nu_{\text{BGD}} - \nu_{\text{B}}$ of the TA2 phonon in salol A.

of dislocation density has been assumed in the present analysis which is based on dislocation-phonon interactions [13-15]. As the number of dislocations increases, more and more acoustic phonon-dislocation collisions occur, and the growing number of dislocations attenuates the propagating sound waves. Since the attenuation coefficient α_j is related to the spectral linewidth Γ_j of the j -mode by:

$$\alpha_j = \pi \Gamma_j / v_j \quad (8-10)$$

the continuous growth of dislocations (as the crystal approaches T_m) should be observable in the increasing spectral linewidth of the Brillouin modes. The dislocation density could thus be related to the sound attenuation coefficient α_j through the scattering cross section σ_j by:

$$\alpha_j = \sigma_j \rho_D(T) \quad (8-11)$$

$$\text{The } \alpha_j = \sigma_j \rho_D(T) \quad (8-11)$$

The dislocation-phonon scattering cross section σ_j which was constant. The temperature dependence of the dislocation density $\rho_D(T)$ is given by:

$$\rho_D(T) = \rho_0 e^{-\frac{E_D(T)}{k_B T}} \quad (8-12)$$

where $E_D(T)$ is the temperature-dependent dislocation

formation energy. So the linewidth of the j -th mode due to dislocations can be related to the dislocation formation energy $E_D(T)$ in this model as:

$$\Gamma_j = \frac{1}{\pi} \sigma_j \nu_j \xi_0 e^{-\frac{E_D(T)}{k_B T}} \quad (8-13a)$$

By including the background linewidth Γ_{Bj} present due to other anharmonic interaction, the total linewidth Γ_{TOT} can be expressed as:

$$\Gamma_{TOT} = \Gamma_{Bj} + \Gamma_j^0 e^{-\frac{E_D(T)}{k_B T}} \quad (8-13b)$$

where $\Gamma_j^0 = \frac{1}{\pi} \sigma_j \nu_j \xi_0$ and Γ_{Bj} is the background linewidth due to anharmonic interactions. An increase in dislocation density will thus increase the attenuation and broaden the Brillouin line. That is why a careful linewidth analysis was suggested in the beginning, and why the temperature dependence of Brillouin linewidths can test the validity of the dislocation theory of melting. The linewidth data was also analyzed to deduce the temperature dependence of dislocation formation energy which I shall discuss below. First I will present my results on the temperature dependence of the linewidth.

In presenting the temperature dependence of the

linewidth Γ , both the observed values and the deconvoluted values [extracted by NLLSQ-DECON3 program] values have been shown. Figure 8-21(a) and (b) show the temperature dependence of Γ_{obs} and Γ_{DEC} (deconvoluted) values of the TAl mode of Salol B. Similar diagrams for QT and QL modes are shown in figures 8-22(a) and (b) and 8-23(a) and (b) respectively.

The observed and deconvoluted linewidth of the salol 18 modes are shown in figures 8-24(a) and (b) 8-25(a) and (b), 8-26(a) and (b). Those of salol A are plotted in figures 8-27(a) and (b) , 8-28(a) and (b) and 8-29(a) and (b). The temperature dependence of the observed linewidth of SUCC. D5 is shown in fig. 8-30. In each of the plots, the temperature axis scale was broken to spread out the melting data which were taken in larger number in a very small temperature range near T_m ($\Delta T \approx 0.5^\circ\text{C}$) relative to fewer room temperature data taken in a much larger temperature range ($\Delta T \approx 15^\circ\text{C}$) far from T_m .

In order to get an error estimate, most of the spectra at a particular temperature were repeated over 3-4 days. To get the maximum number of data points the temperature was brought up and down many times in very small steps (0.01°C) until the sample finally melted.

Almost all the Γ versus T data show a clear linewidth broadening near T_m which is consistent with the

Fig. 8-21 (a) Temperature dependence of the observed Brillouin linewidth Γ_{OBS} of the TAL phonon in salol B. The Γ_{OBS} 's were determined from the observed fitted spectrum. A rapid increase of Γ_{OBS} near T_m is easily visible.

Fig. 8-21 (b) Temperature dependence of the deconvoluted Brillouin linewidth Γ_{DEC} of the TAL phonon in salol B. The Γ_{DEC} 's were obtained by deconvoluting the instrumental linewidth from each spectrum by the NLLSQ-DECON3 nonlinear least squares fitting program described in section I of chapter 8. (For a typical fitting of a spectrum see fig. 8-1(c) or 8-2(a)). The rapid increase of Γ_{DEC} near T_m was interpreted as being caused by a catastrophic growth of dislocations near T_m , and analysed by a simple model of the dislocation theory of melting described in chapter 8.

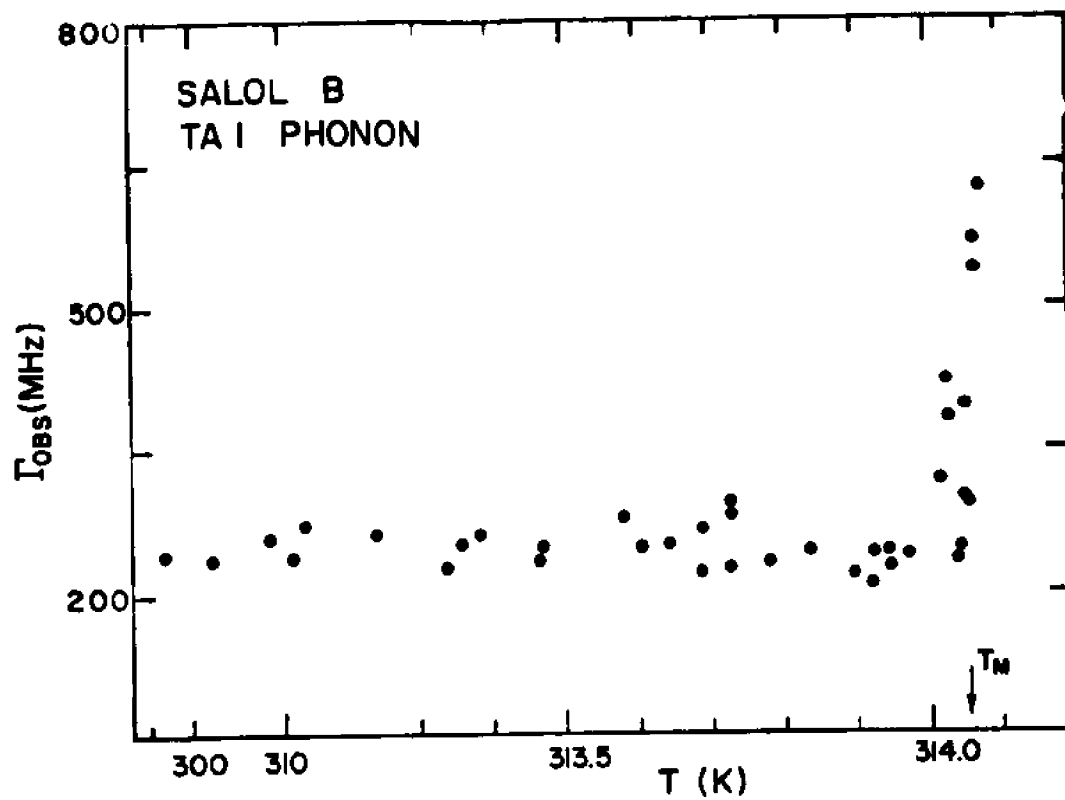


FIG. 8-21(a)

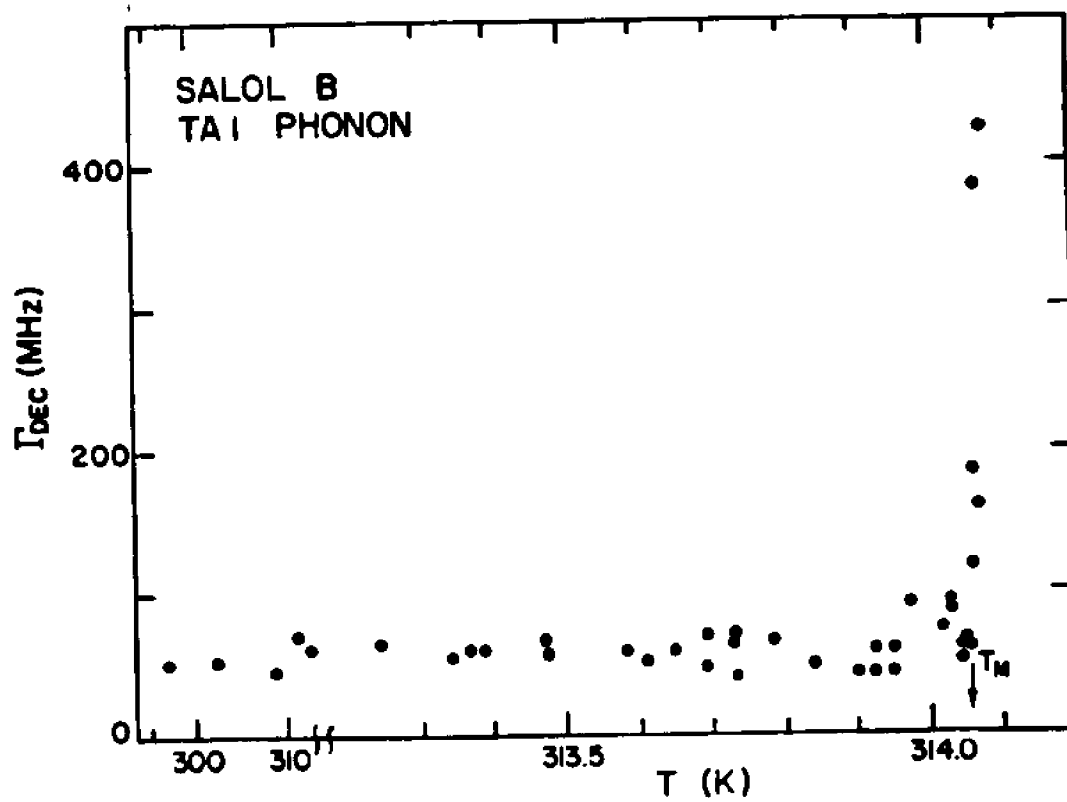


FIG. 8-21(b)

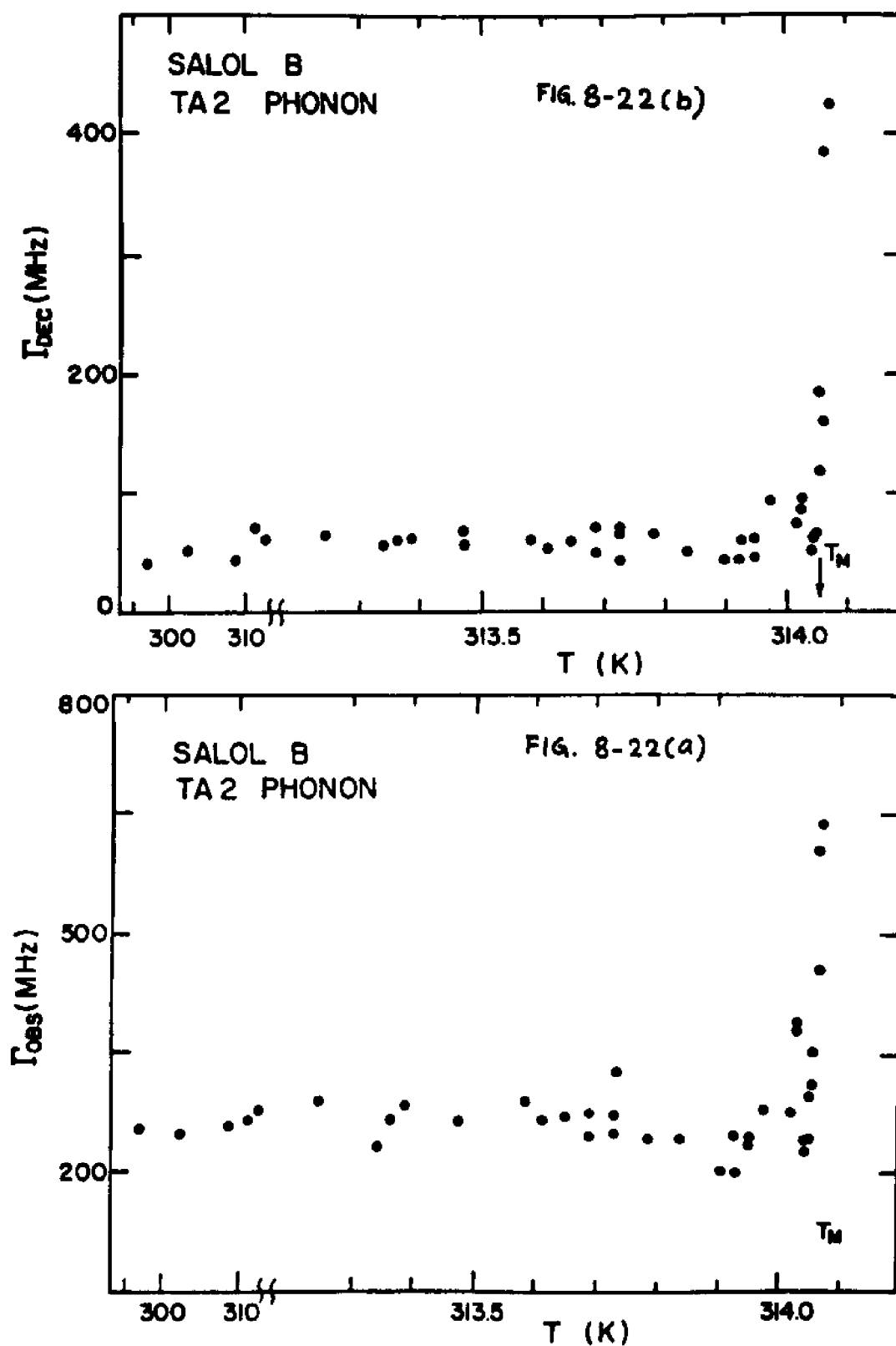


Fig. 8-22(a), (b) The Temperature dependence of Γ_{OBS} (a) and Γ_{DEC} (b) of the TA2 mode of salol B.

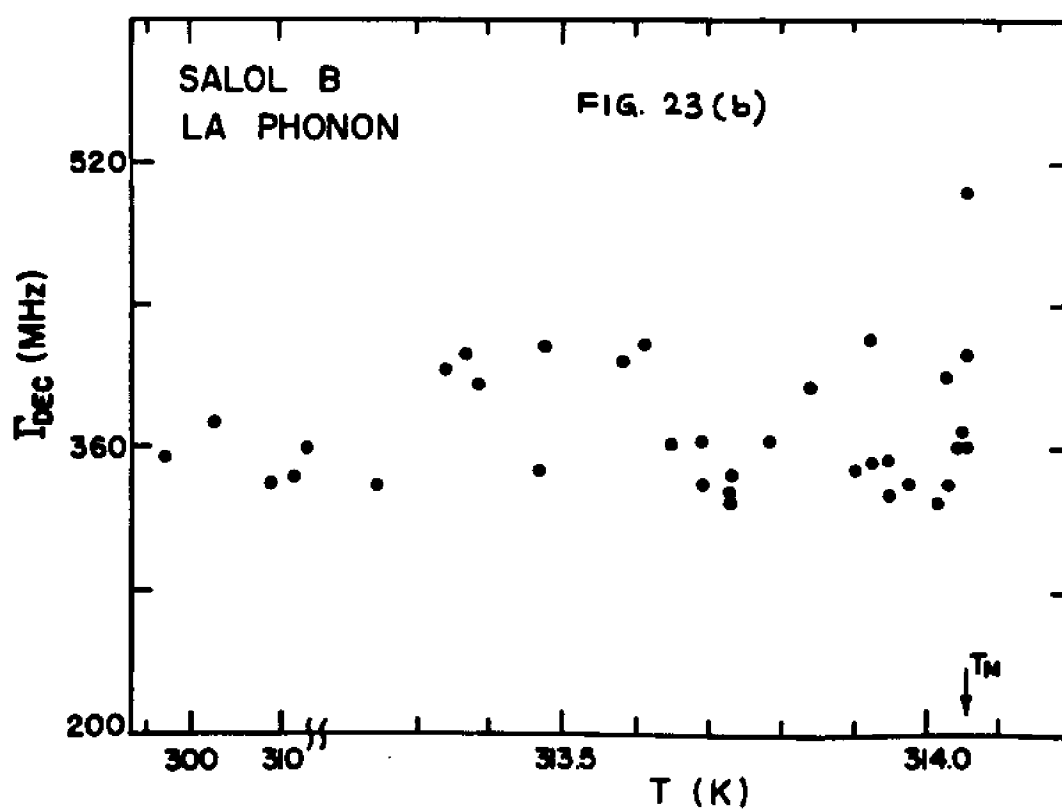
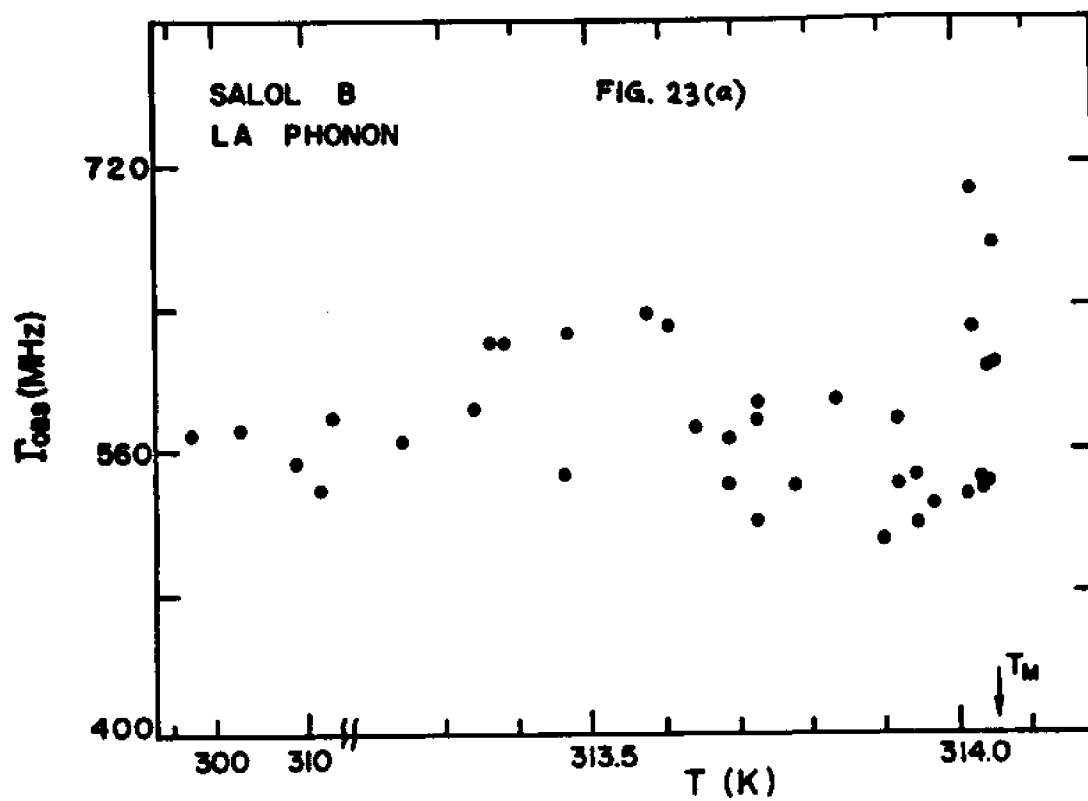


Fig. 8-23(a), (b) The temperature dependence of Γ_{obs} (a) and Γ_{dec} (b) of the 1A mode in salol B.

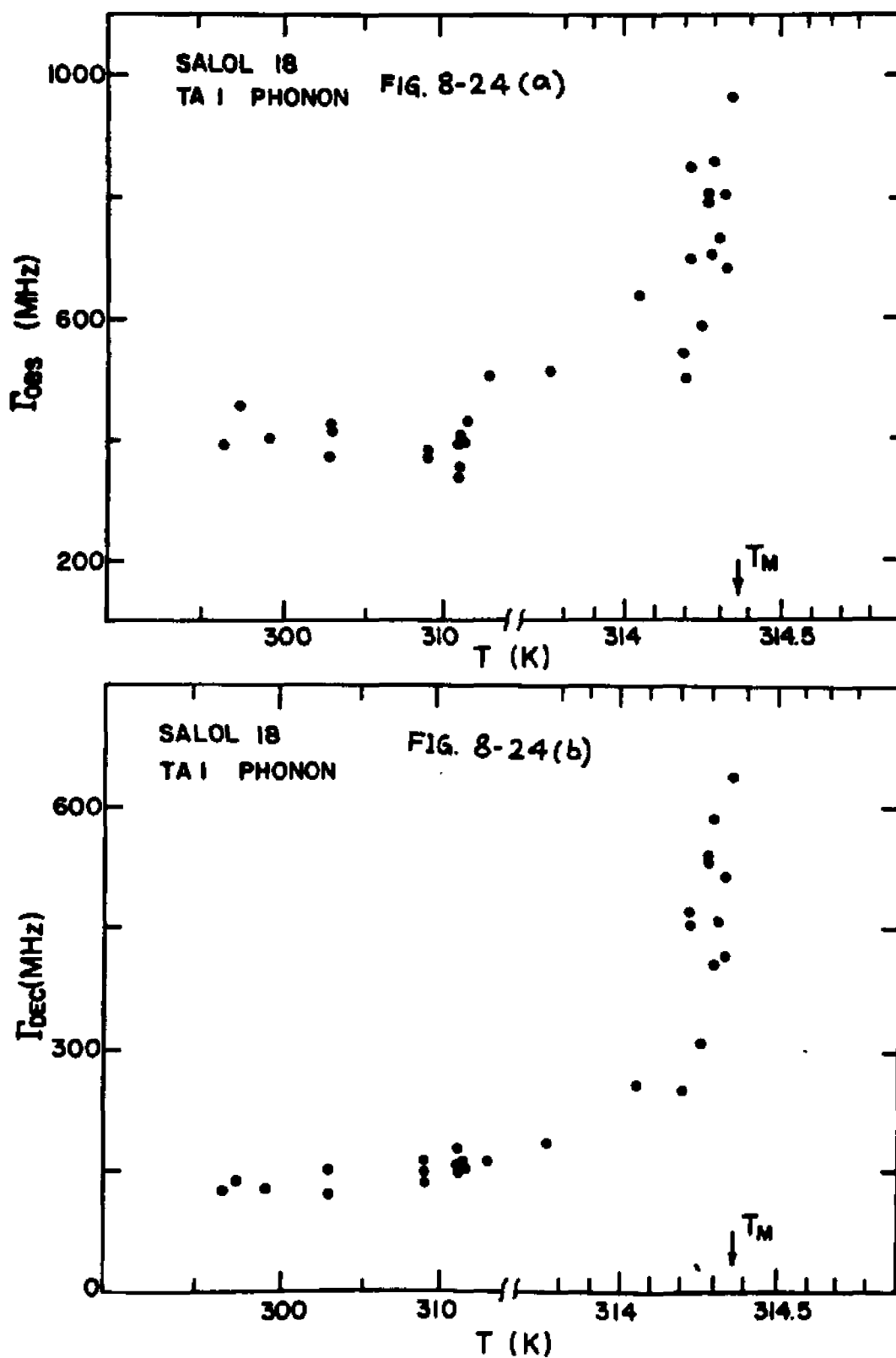


Fig. 24: Temperature dependence of the (a) observed linewidth (b) deconvoluted linewidth of the TA1 mode of salol 18. $T_m = 41.22^\circ\text{C}$ (314.37°K) Salol 18 was grown from the melt of distilled salol, and twice zone refined. The phonon wave vector is along (010).

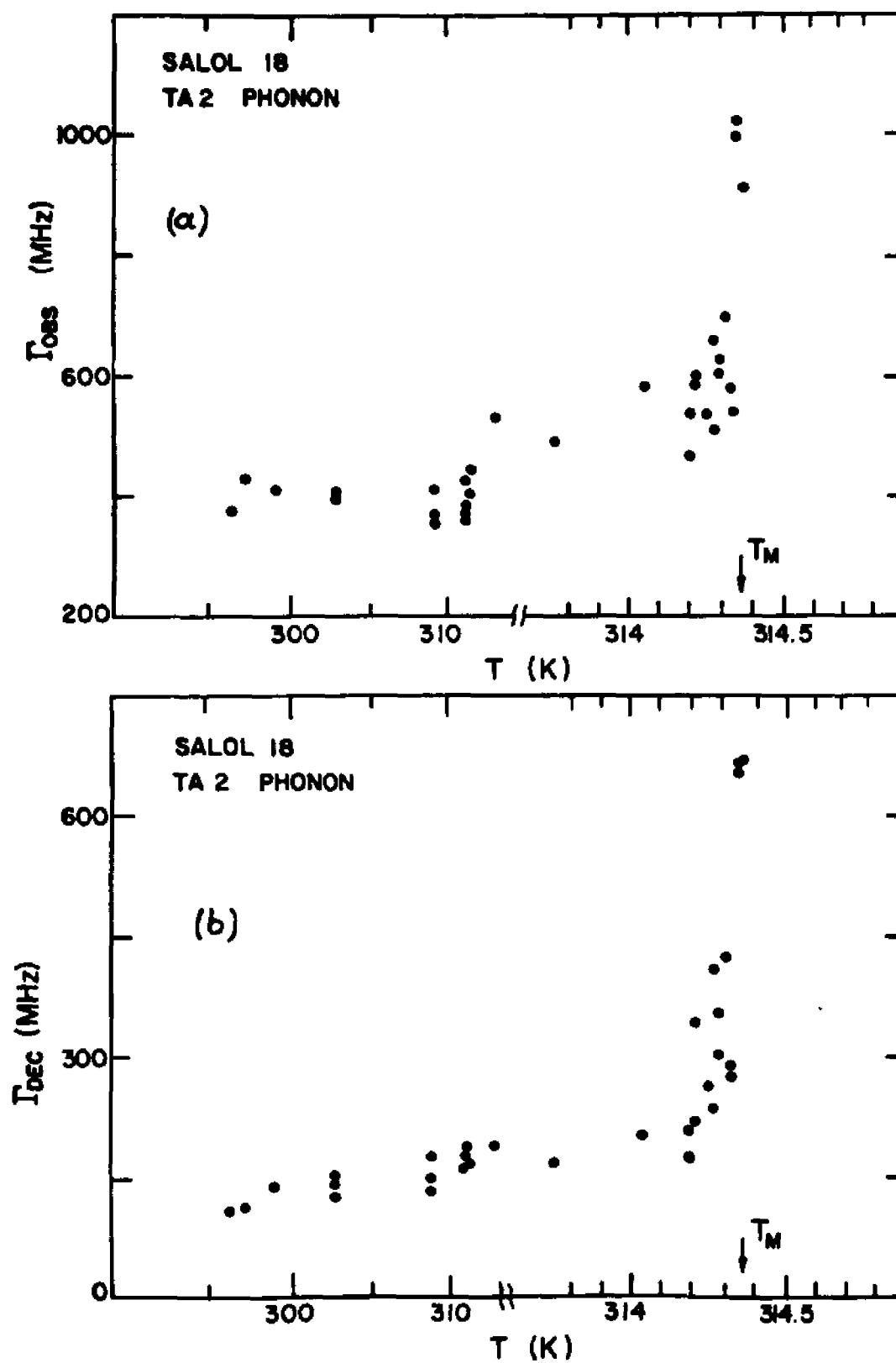


Fig. 25: Temperature dependence of the (a) observed (b) deconvoluted linewidth of the TA2 mode of salol 18, showing a rapid increase near T_M .

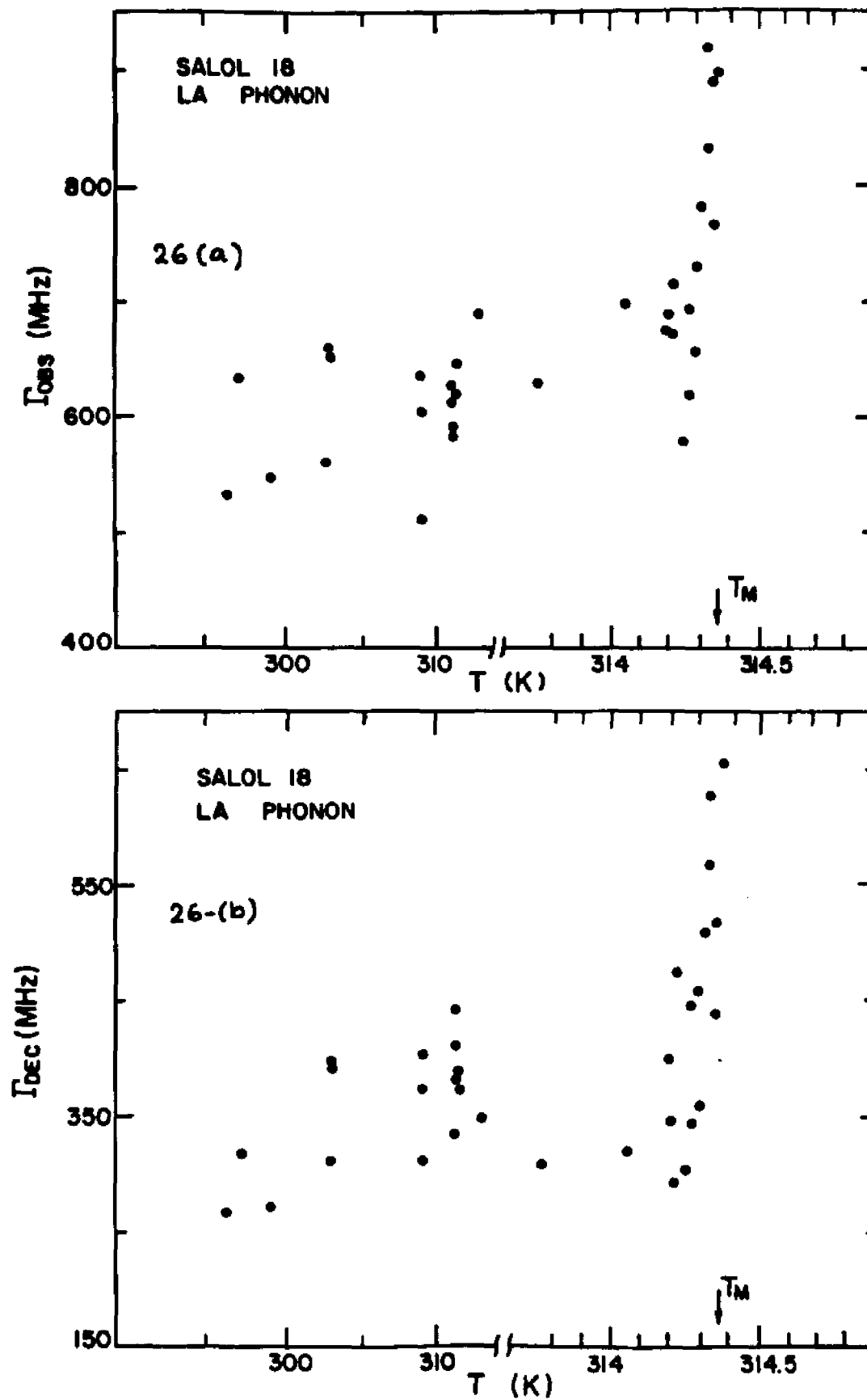


Fig.8-26: Temperature dependence of the (a) observed (b) deconvoluted linewidth of the LA mode of salol 18. The LA-mode data show more scatter than those of the TA1 and TA2 nodes.

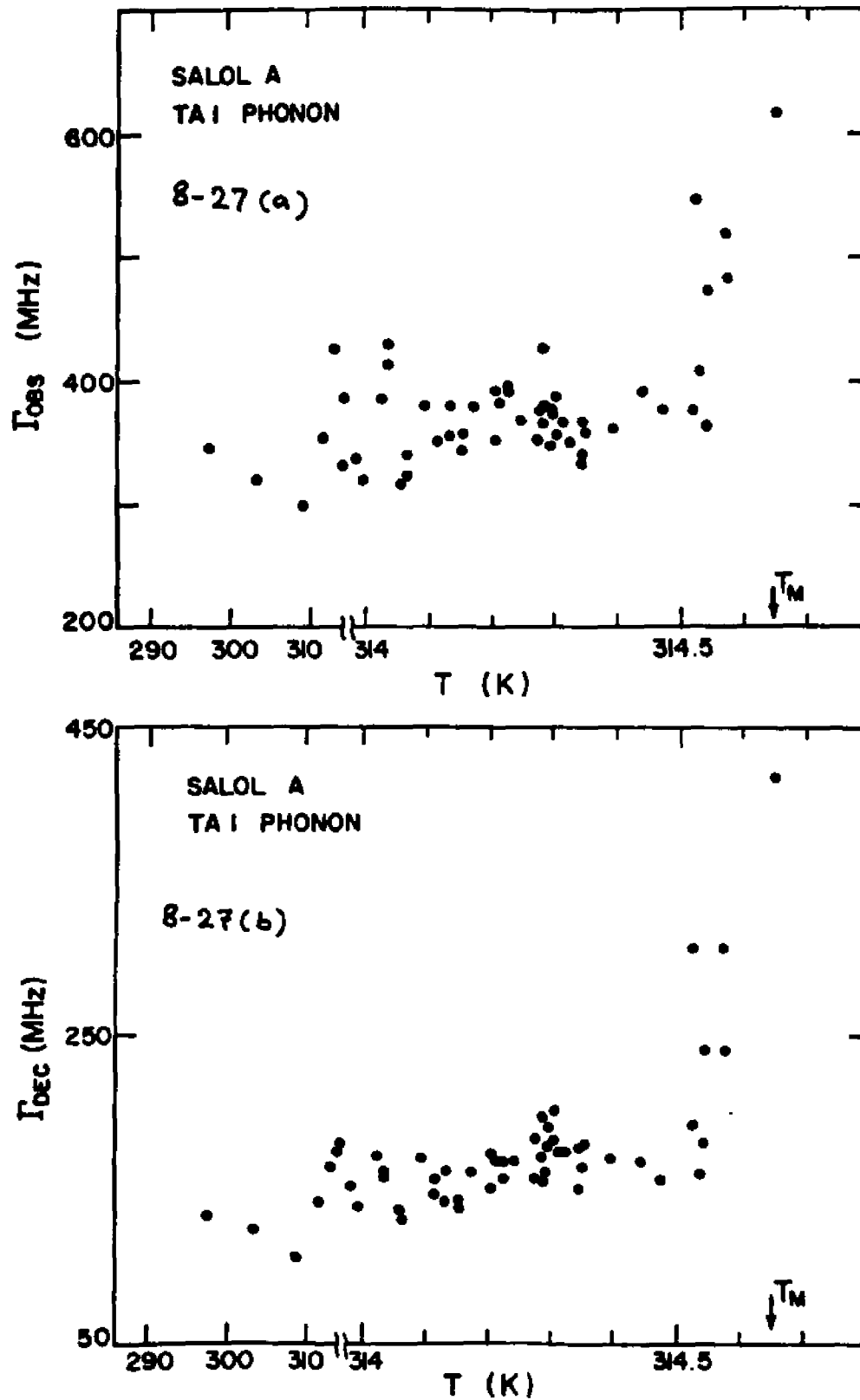


Fig. 8-27: Temperature dependence of the (a) observed (b) deconvoluted linewidth of the TAI mode of salol A. Scattering configuration: $Y(VT)Z$. The phonon wave vector is along $(0,-1,1)/\sqrt{2}$. Note that the observed linewidths show more fluctuation than the deconvoluted ones. $T_M = 41.50^\circ\text{C}$.

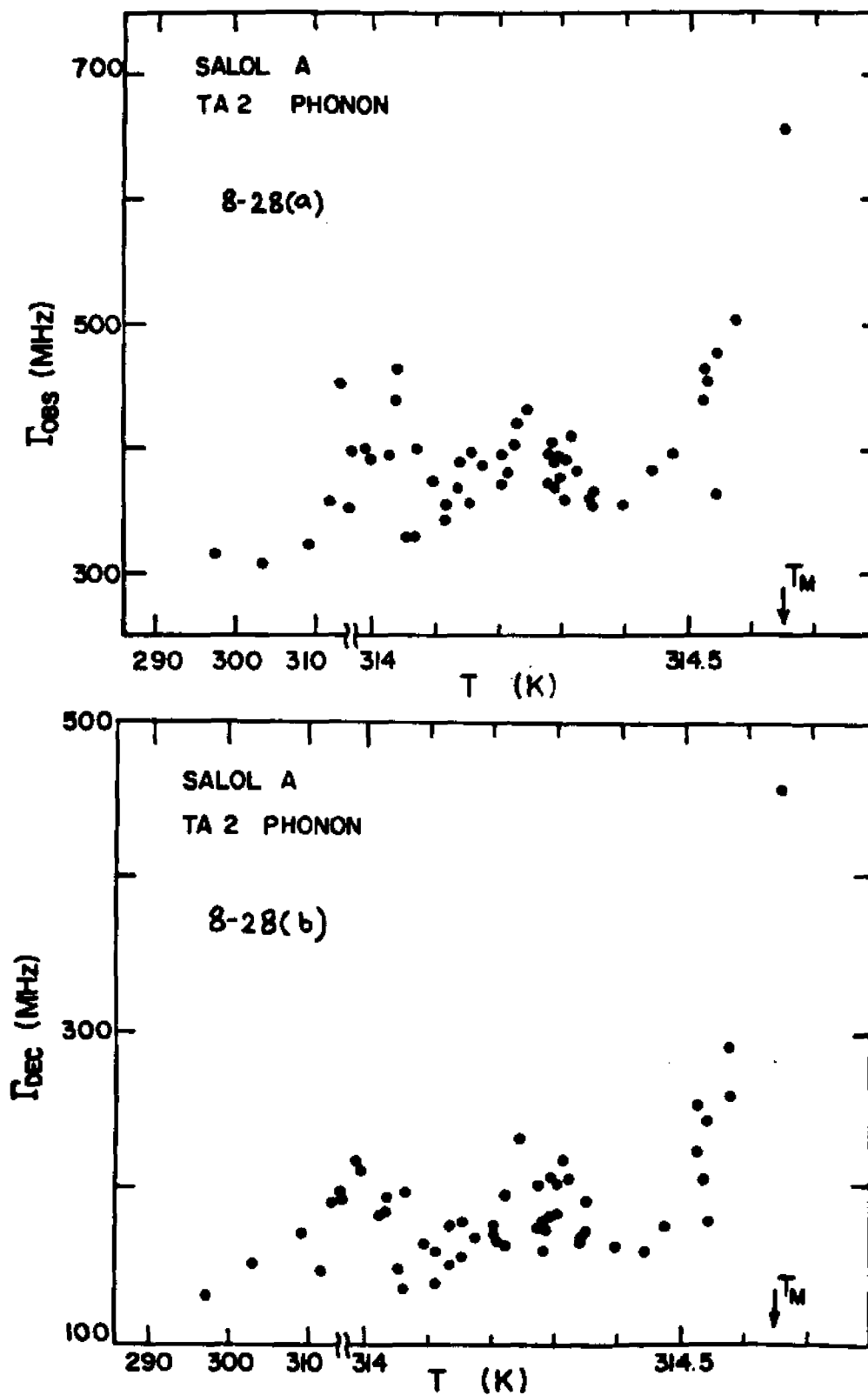


Fig. 8-28: Temperature dependence of the (a) observed (b) deconvoluted linewidths of the TA2 (quasitransverse) mode of salol A.

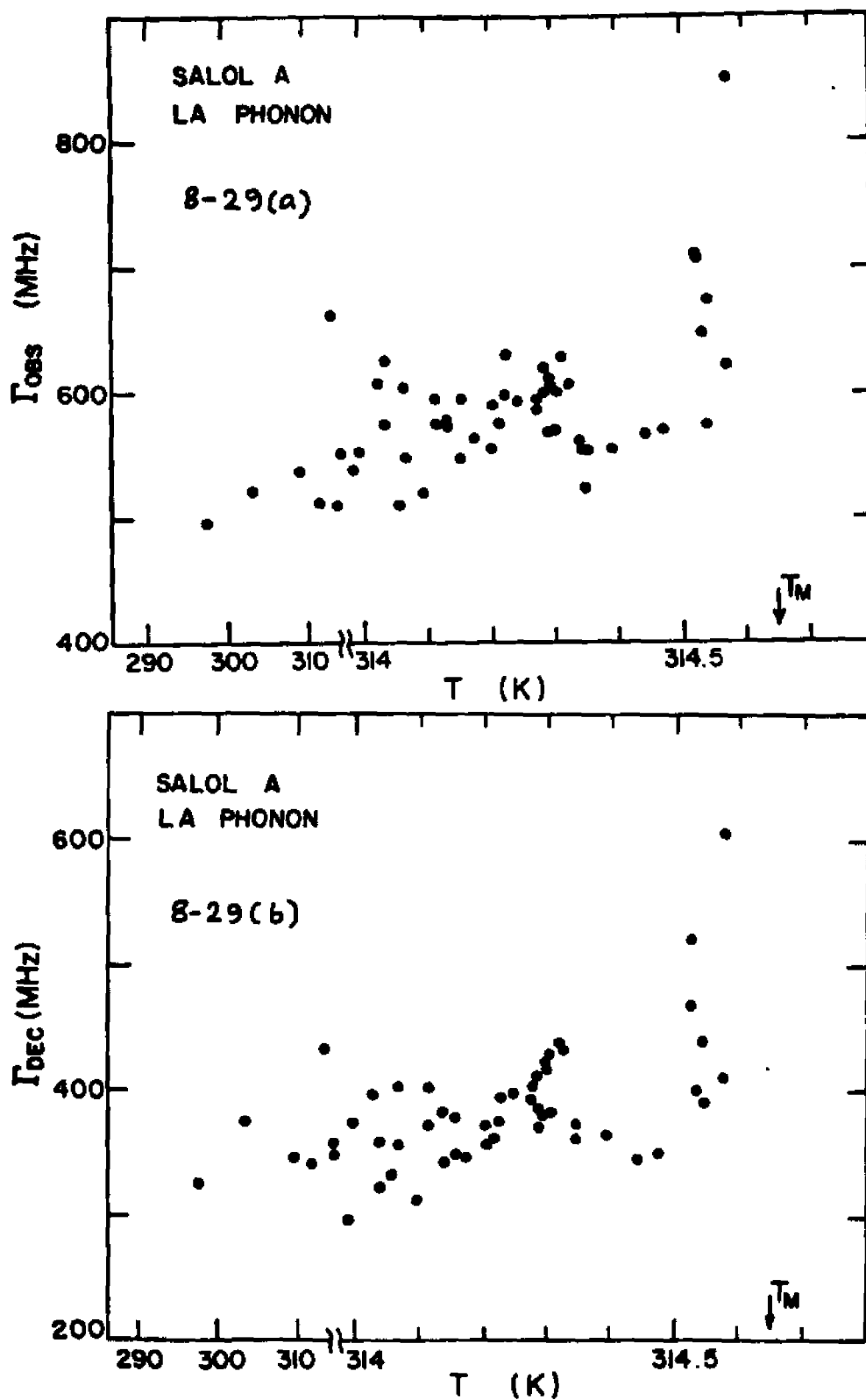
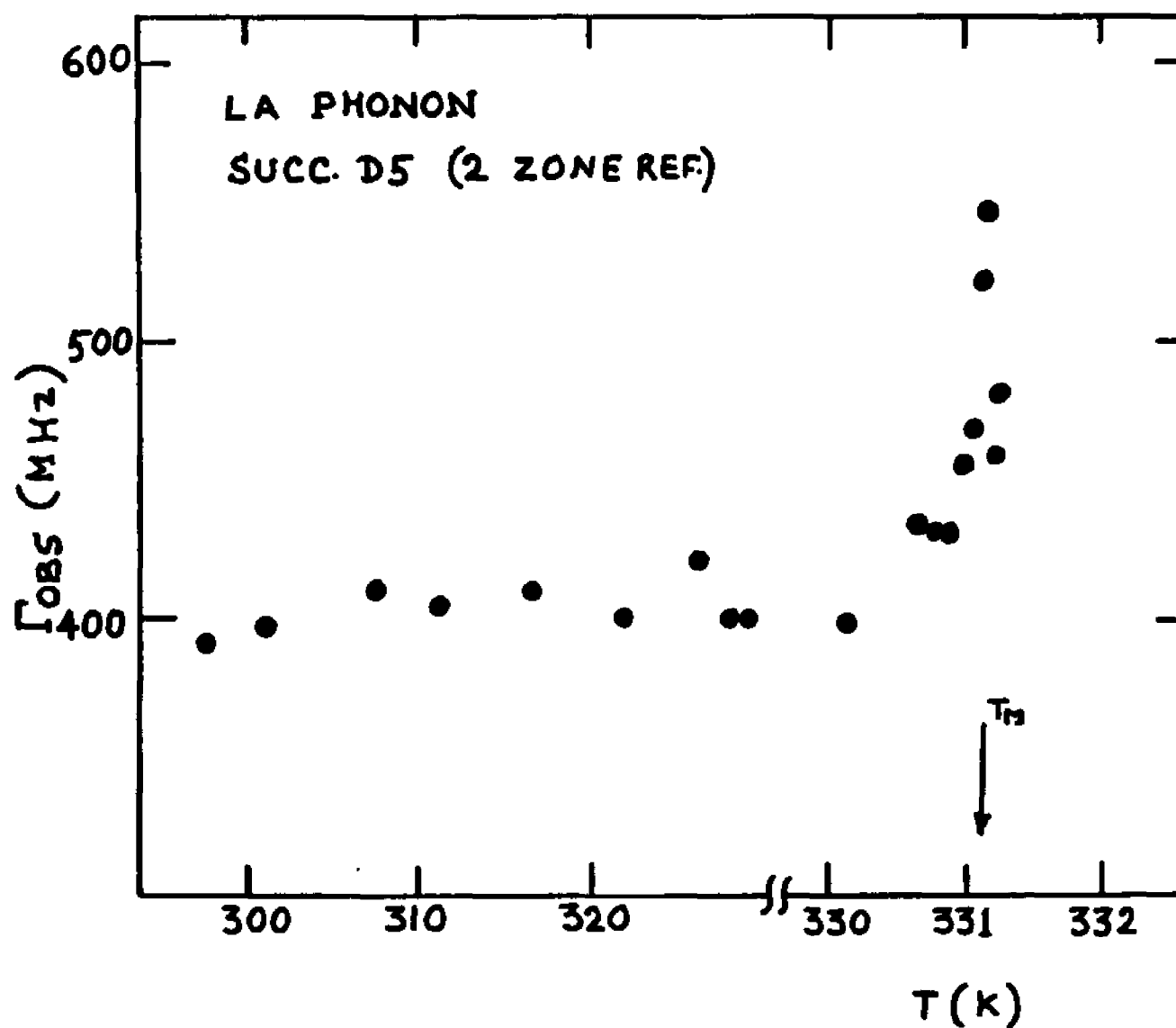


Fig. 8-29: Temperature dependence of the (a) observed (b) deconvoluted linewidth of the LA phonon (quasi-longitudinal), of salol A showing a high fluctuation of Γ at lower temperature.



predicted increase of defect density (And the resulting number of collisions between dislocations and phonons) near T_m . The intrinsic reason for the rapid increase of defect density is presumably the gradual decrease of defect formation energy $E_D(T)$ with increasing temperature. In the following I shall seek to find quantitatively how $E_D(T)$ changes with temperature.

(4) Temperature dependence of the defect formation energy

The final and most important analysis of the Brillouin linewidth measurements is the determination of the temperature dependence of the defect formation energy $E_D(T)$ from the above simplified dislocation mediated melting model. It can be seen from equation (8-13b) that

$$E_D(T) = k_B T \ln \left[\Gamma_j^0 / (\Gamma_j - \Gamma_{Bj}) \right] \quad (8-14)$$

and

$$\ln (\Gamma_j - \Gamma_{Bj}) = \ln \Gamma_j^0 - \left(\frac{1}{k_B T} \right) E_D(T) \quad (8-15)$$

In order to compute the formation energy $E_D(T)$ and the parameters Γ_{Bj} and Γ_j^0 are needed. In my analysis, I used trial values of 0%, 50% and 70% of the value of Γ_{RT}

(linewidth at room temperature) for Γ_{Bj} . The second parameter Γ_j^0 was determined from equation (8-15). Assuming $E_D(T)$ constant at low temperatures, the $\ln(\Gamma_j - \Gamma_{Bj})$ vs $(1/k_B T)$ data up to 40° C were fitted to a straight line for each of the trial background values Γ_{Bj} and Γ_j^0 was determined from the y-intercept of these fitted straight lines.

$$\Gamma_j \left(\frac{1}{k_B T} \rightarrow 0 \right) = \Gamma_j^0 \quad (\text{for } T \rightarrow \infty)$$

Fig. 8-31 shows the $\ln(\Gamma_j - \Gamma_{Bj})$ vs $(1/k_B T)$ plots for background values $\Gamma_{Bj} = 0\%$, 50% and 70% of $\Gamma_{RT} [\Gamma_{RT} \approx 30 \text{ MHz}]$ of the TA1 mode in salol B in a single plot. The lower temperature points fitted to a straight line whose y-intercept gives Γ_j^0 for each chosen Γ_{Bj} are also shown. Similar diagrams for QL and QT modes of salol B are shown in single plots in figures 8-32 and 8-33 respectively.

Once Γ_j^0 and Γ_{Bj} are known, the defect formation energy $E_D(T)$ for each temperature could be determined by using $\Gamma_j - T$ data files for each mode. Figure 8-34 shows the temperature dependence of $E_D(T)$ deduced from the linewidth of the TA1 mode of salol B for the three background values of Γ_{Bj} with Γ_j^0 taken from the fits of figure 8-31. The resulting defect formation energies for QT and QL modes of salol B are shown in figures 8-35 and

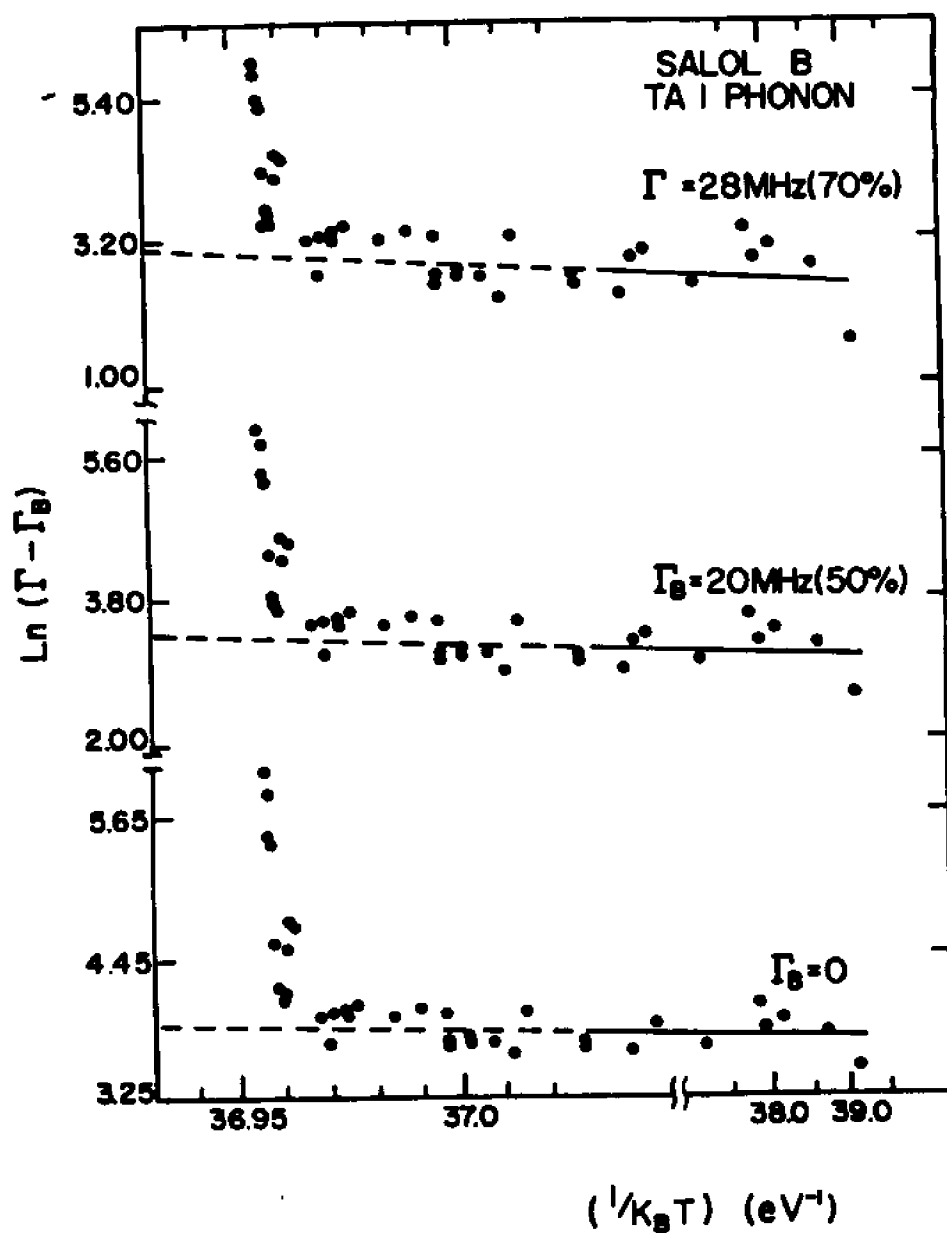


Fig. 8-31: $\ln(\Gamma - \Gamma_B)$ vs. $1/k_B T$ plots for three different trial values of the background linewidth $\Gamma_B = 0, 50\%$ and 70% of the average room temperature value of the linewidth ($\approx 35\text{MHz}$). The solid straight line is the linear fit of the low temperature Γ 's of the TA1 mode of salol B. The linewidth Γ_0 at $T \rightarrow \infty$ is extrapolated from the y-intercept of the fitted line for $1/k_B T = 0$.

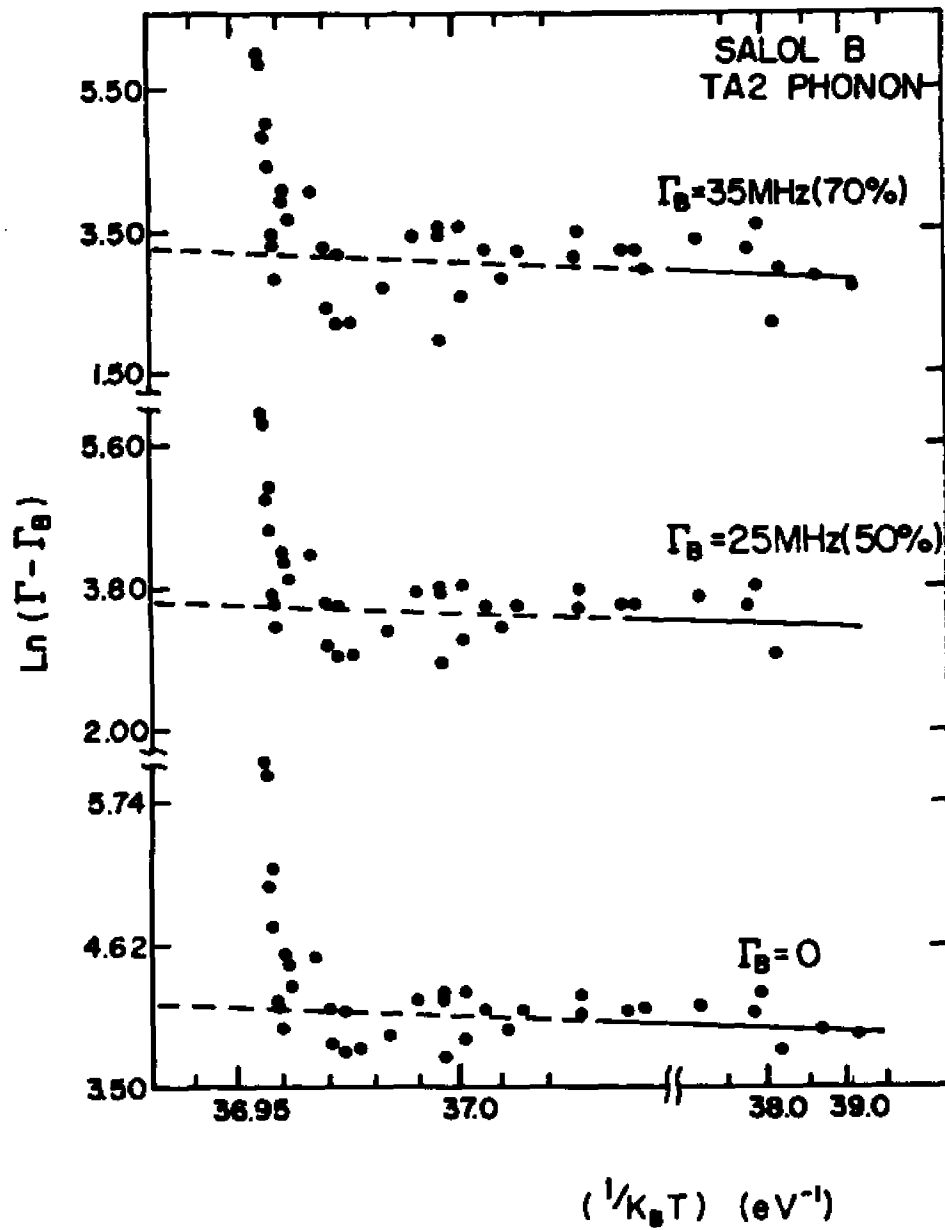


Fig. 8-32: $\ln(\Gamma - \Gamma_B)$ vs $1/k_B T$ plot of the TA2 mode (quasitransverse) of salol B, for the same trial fractional background linewidths as in fig. 8-31. Here T_{av} (room temperature) = 50MHz

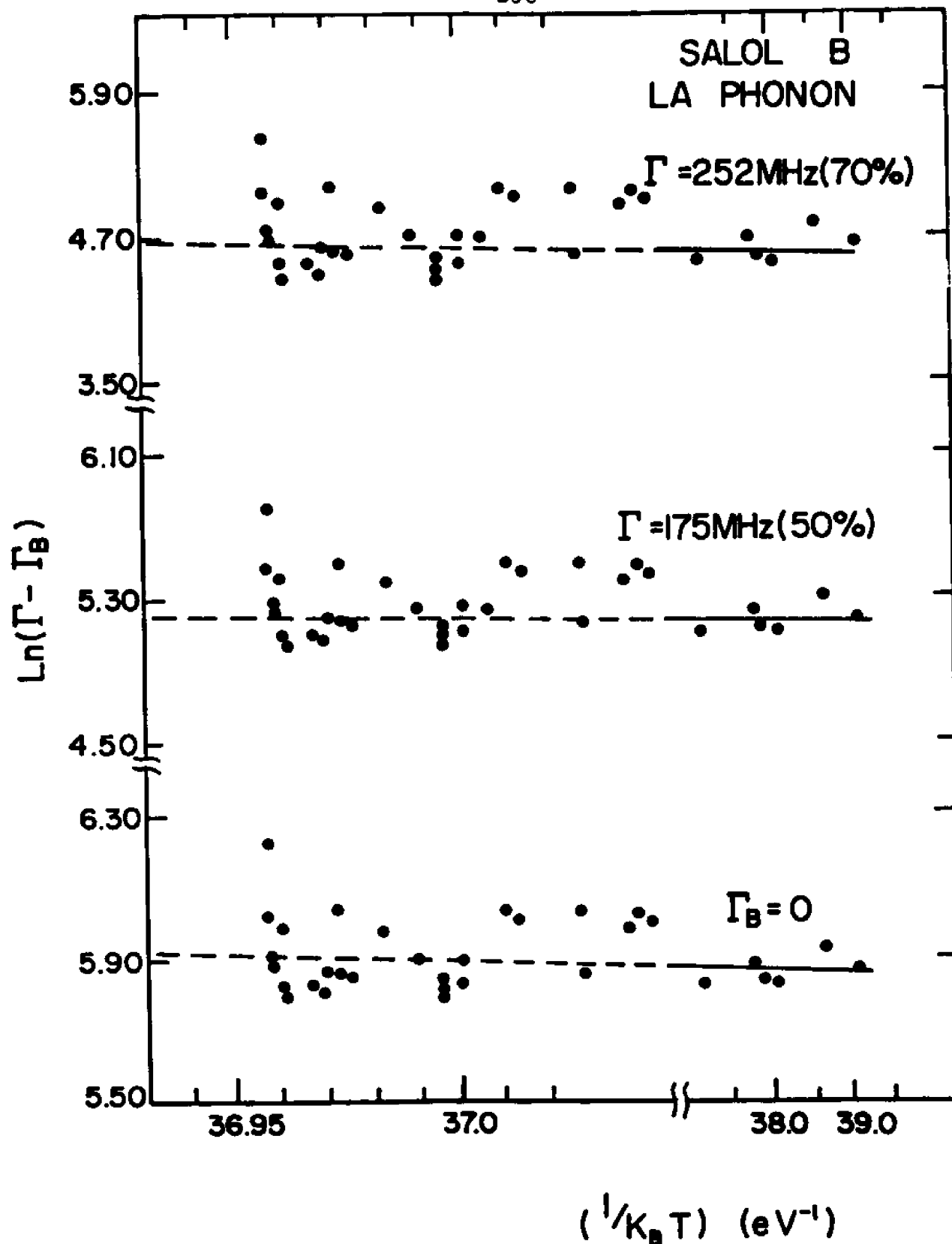


Fig. 8-33: $\ln(\Gamma - \Gamma_B)$ vs $1/k_B T$ plot for the LA node (quasi-longitudinal) of salol B, with average room temperature value $\Gamma(\text{RT}) = 350 \text{ MHz}$.

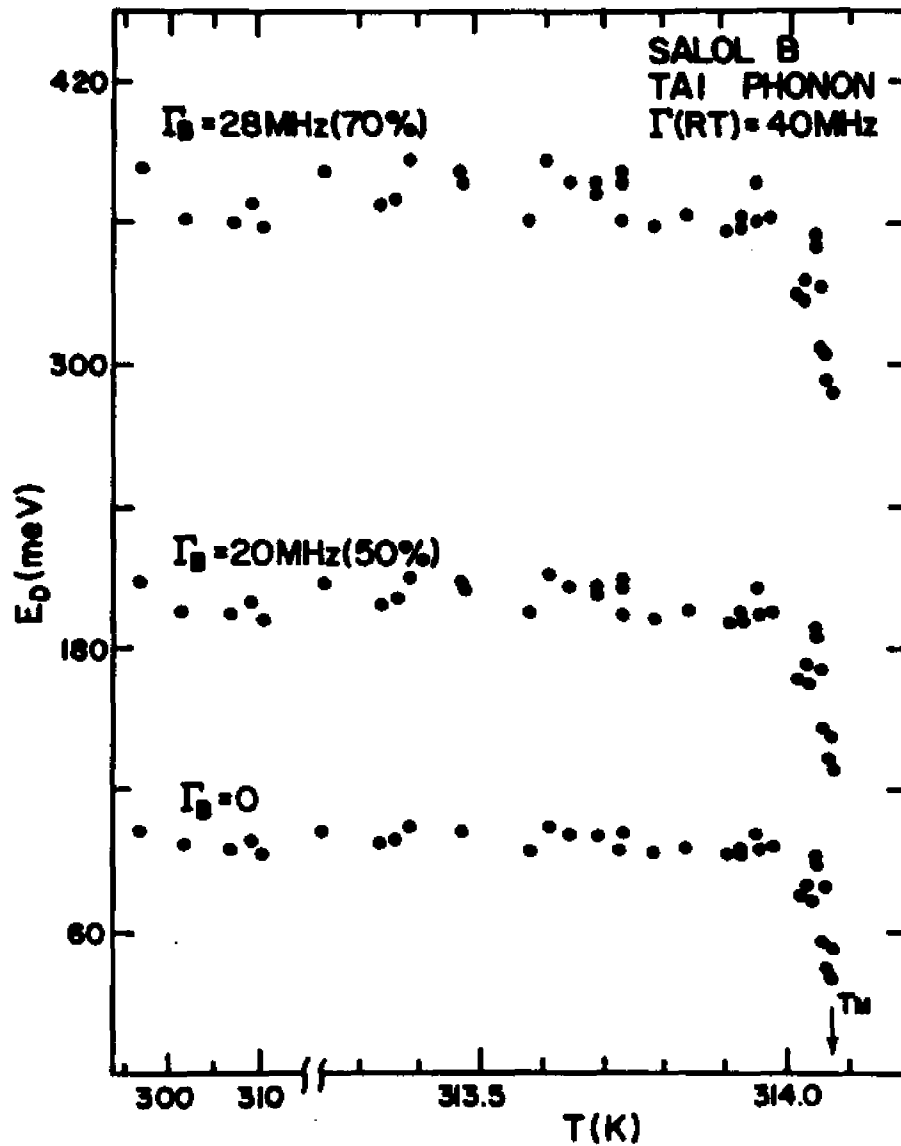


Fig. 8-34: Temperature dependence of the defect formation energy $E_D(T)$ computed from the deconvoluted linewidths Γ_B of the TAI mode of salol B for the background values shown in fig. 8-31, with a simple dislocation mediated melting model described in the text. The defect formation energy shows sudden decrease near T_m (40%) suggesting a catastrophic growth of dislocation concentration. The different background values do not change the pattern of behavior, but the absolute values do depend on the choice of the Γ_B . Γ_0 was extrapolated from fig. 8-31.

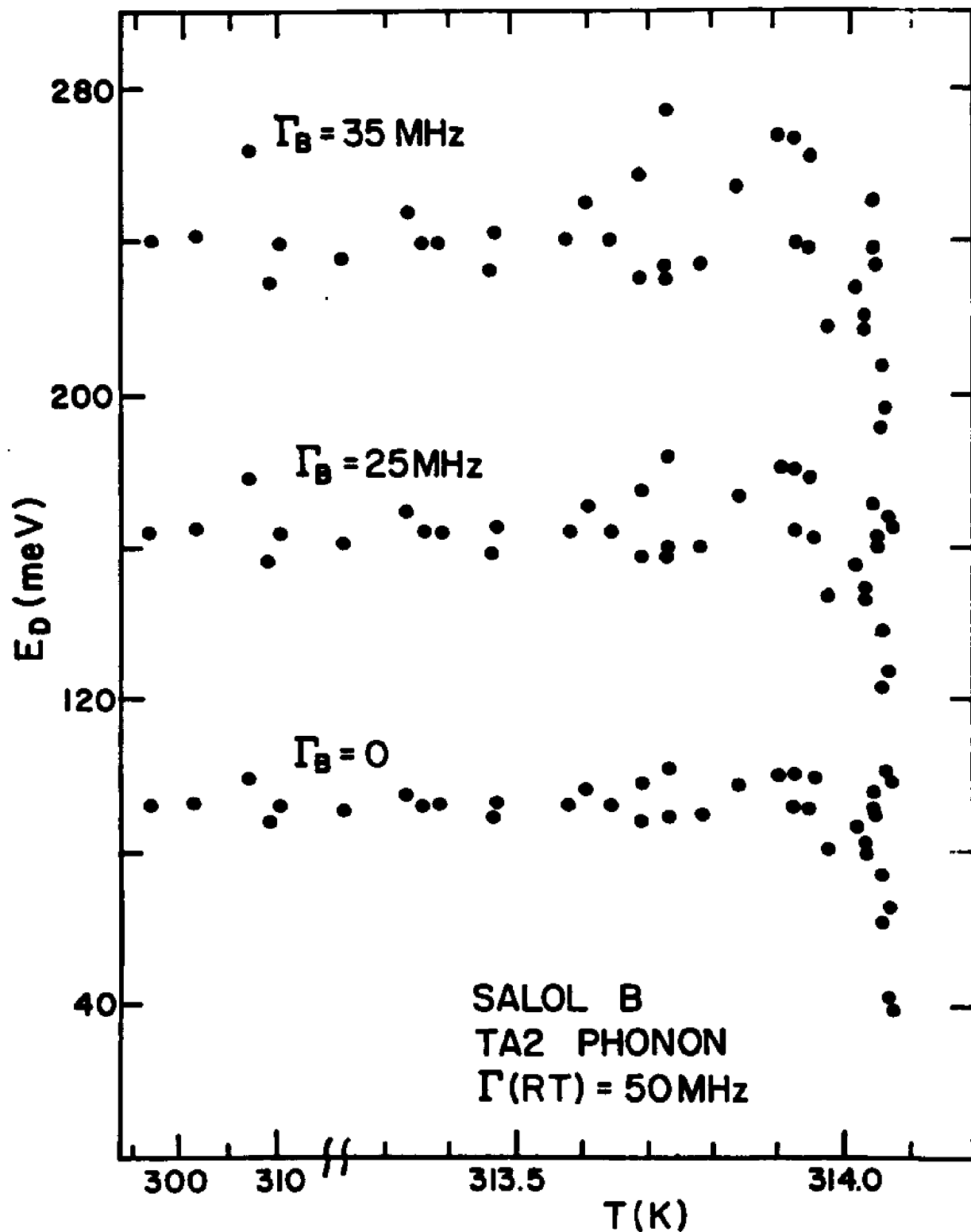
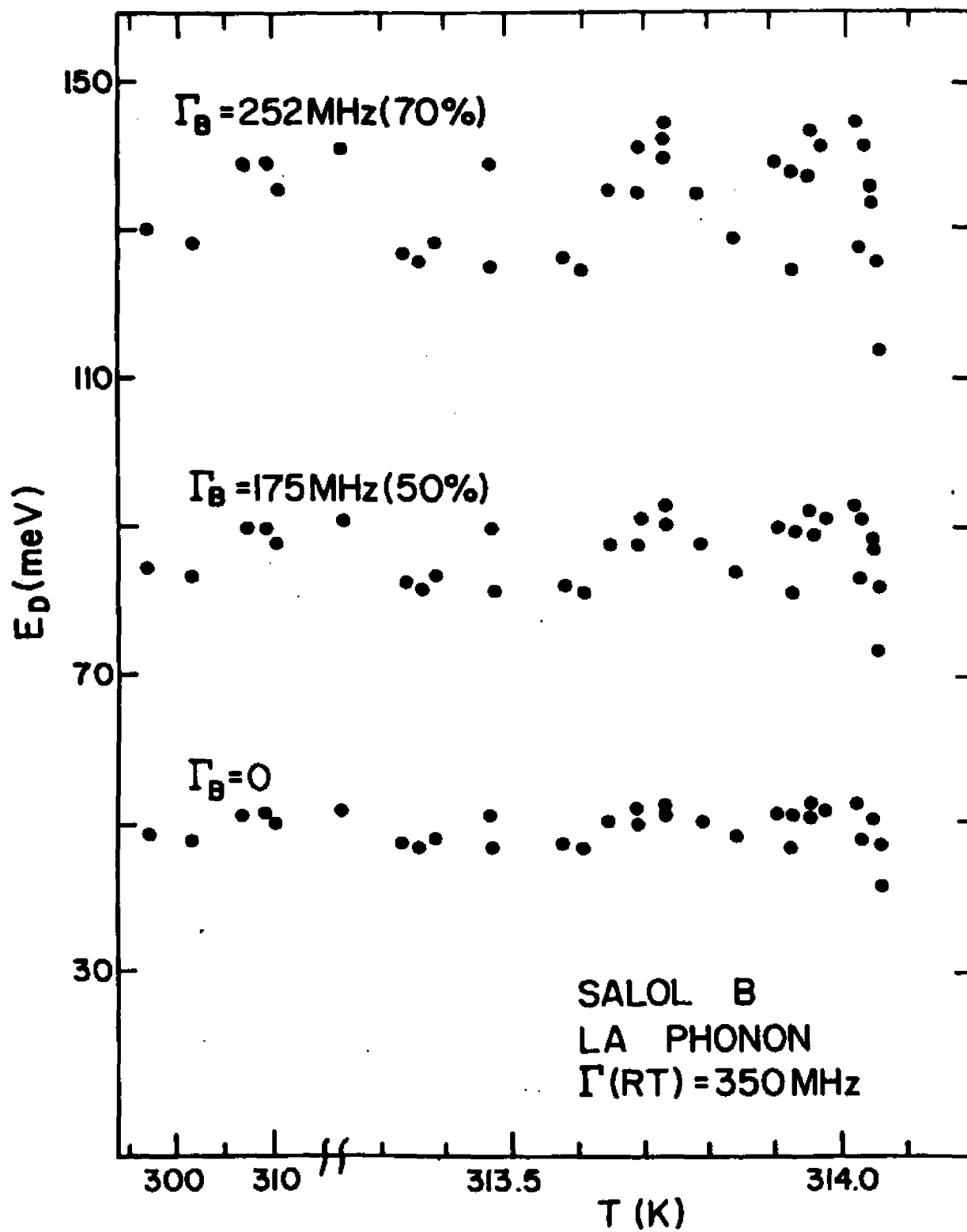


Fig. 8-35: Temperature dependence of $E_D(T)$ computed from the linewidth measurements of the TA2 (quasi-transverse) phonon of salol B, which also shows a sudden decrease near $T_m = 40.925^\circ\text{C}$ (314.08°K). $E_D(T)$ decreases more sharply than in the TA1 mode results.

Fig. 8-36: Temperature dependence of $E_D(T)$ from the LA phonon of salol B. For B more than 50% of D (average). The data show increased scattering, and smallest changes in the defect formation energies compared to those of in the transverse and quasi-transverse modes.



8-36 respectively, with Γ_{Bj} as the same fractional values of $\Gamma(RT)$. Since the defect formation energy should be independent of the choice of acoustic mode (although it may be sample dependent), I expected all the room temperature energy values for the TA1, QL and QT to be the same. Figure 8-37(a), (b) and (c) are plotted to show both the mode and background dependence of defect formation energy at room temperature for all three samples. It was observed that for $\Gamma_B / \Gamma(RT) > 0.5$, the difference $\Delta E = E_D(TA1) - E_D(TA2)$ becomes substantial. So all the other energy plots were made for two background values which are:

$$\Gamma_{Bj} = 0 \quad \text{and} \quad \Gamma_{Bj} = 0.5 \Gamma(RT)$$

Figure 8-38, 8-39 and 8-40 show the temperature dependence of the resulting defect formation energy $E_D(T)$ for TA1, TA2 and LA modes of salol 18 respectively, each plot containing plots calculated with background energies $\Gamma_{Bj} = 0, 50\%$ and 70% of $\Gamma(RT)$. Similar plots for the TA1, QL and QT modes of Salol A are given in figure 8-41, 8-42 and 8-43 respectively. Figures 8-44(a) and (b) are single plots of $\ln(\Gamma_j - \Gamma_{Bj})$ vs $1/k_B T$ and $E_D(T)$ vs T for $\Gamma_{Bj} = 0$ in TA1 mode for Salol 18. to show the temperature dependence more distinctly.

Fig. 8-37: Mode and sample dependence of the dislocation formation energy $E_D(T)$. The average absolute magnitude of $E_D(T)$ computed for various fractional value of $\gamma / (RT)$, for the three different modes of (a) salol B (b) salol A and (c) salol 18 are shown in these figures. The absolute magnitude seems to scatter significantly for .

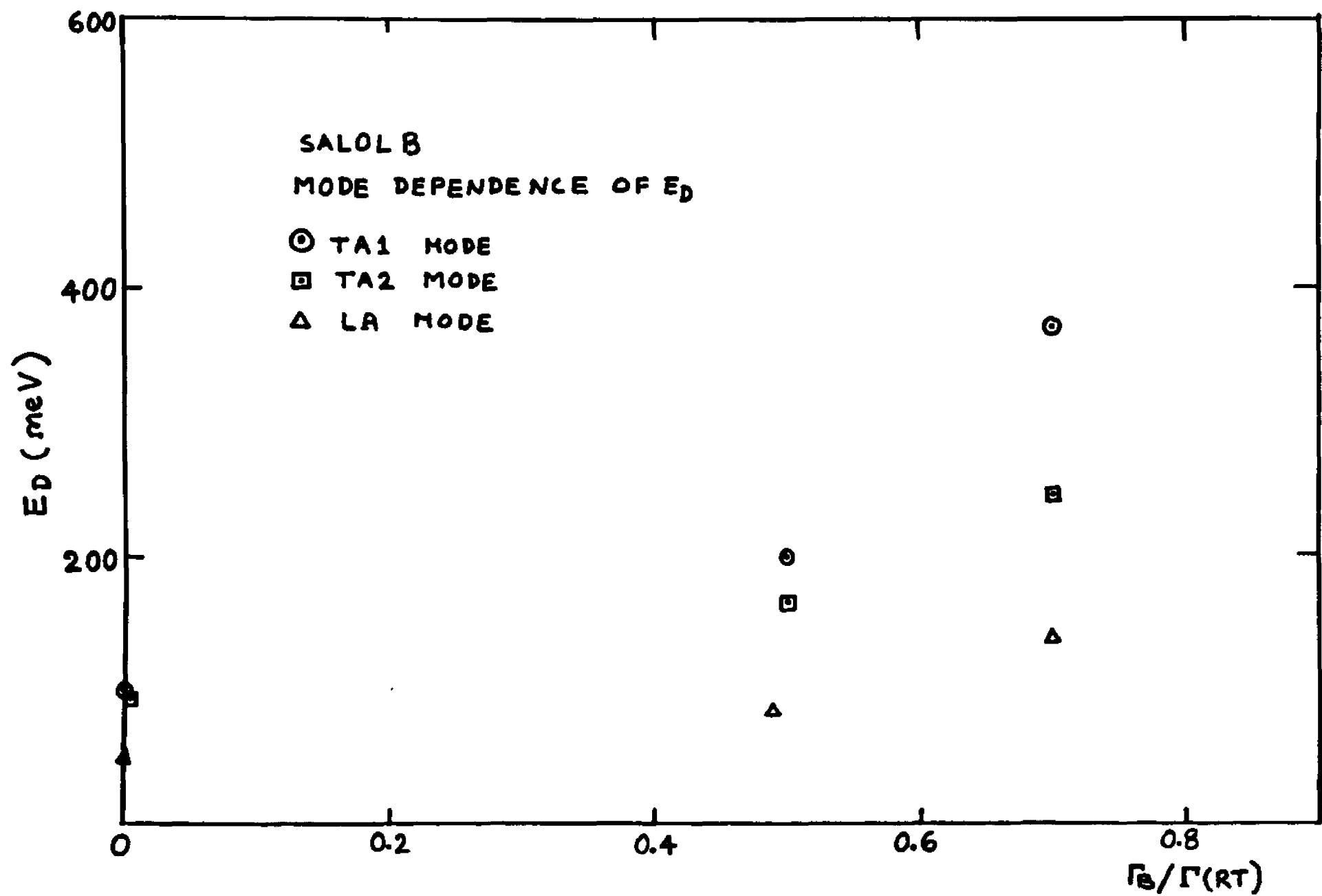


FIG. 8-37(a)

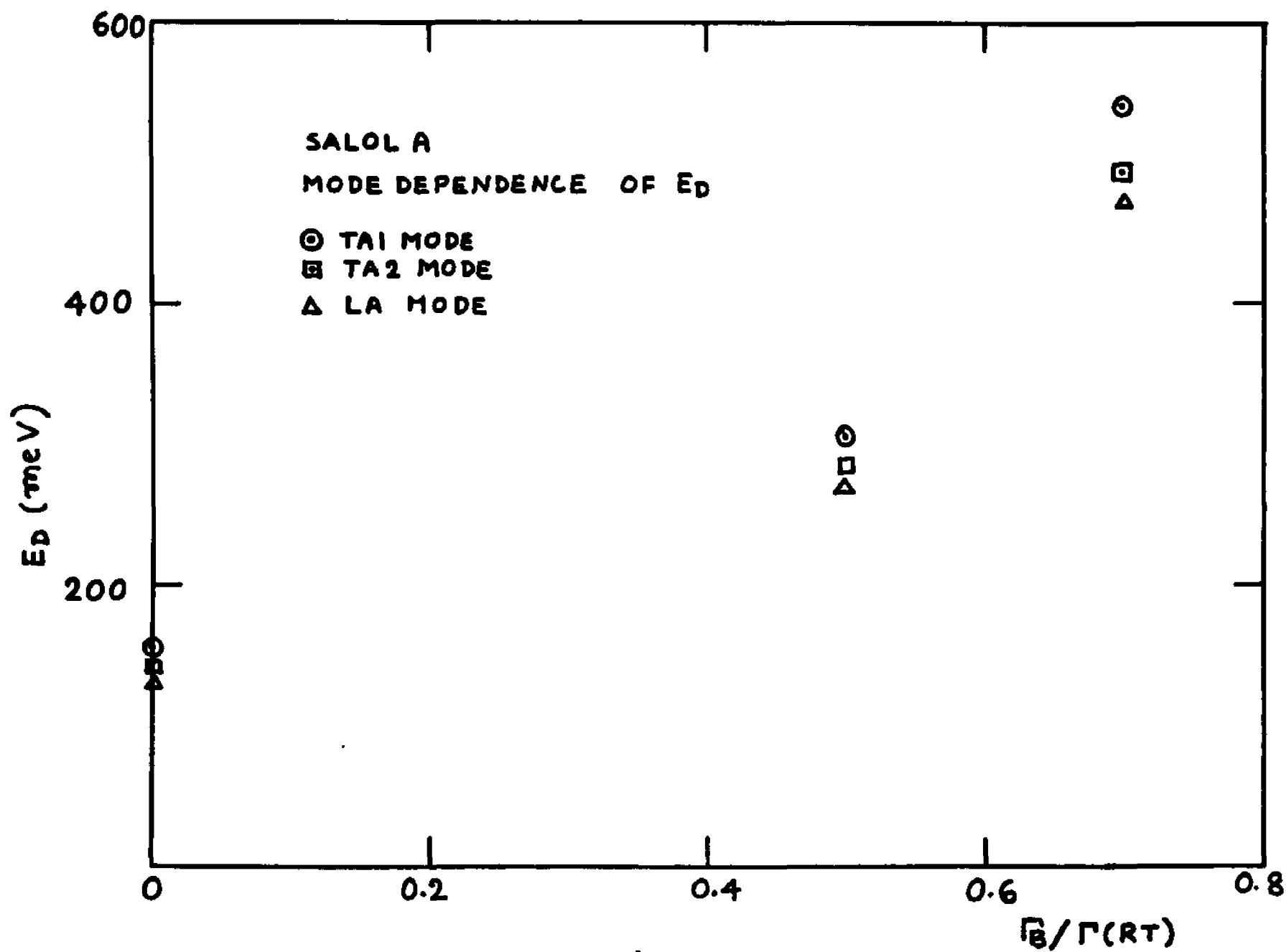


FIG. 8-37(b)

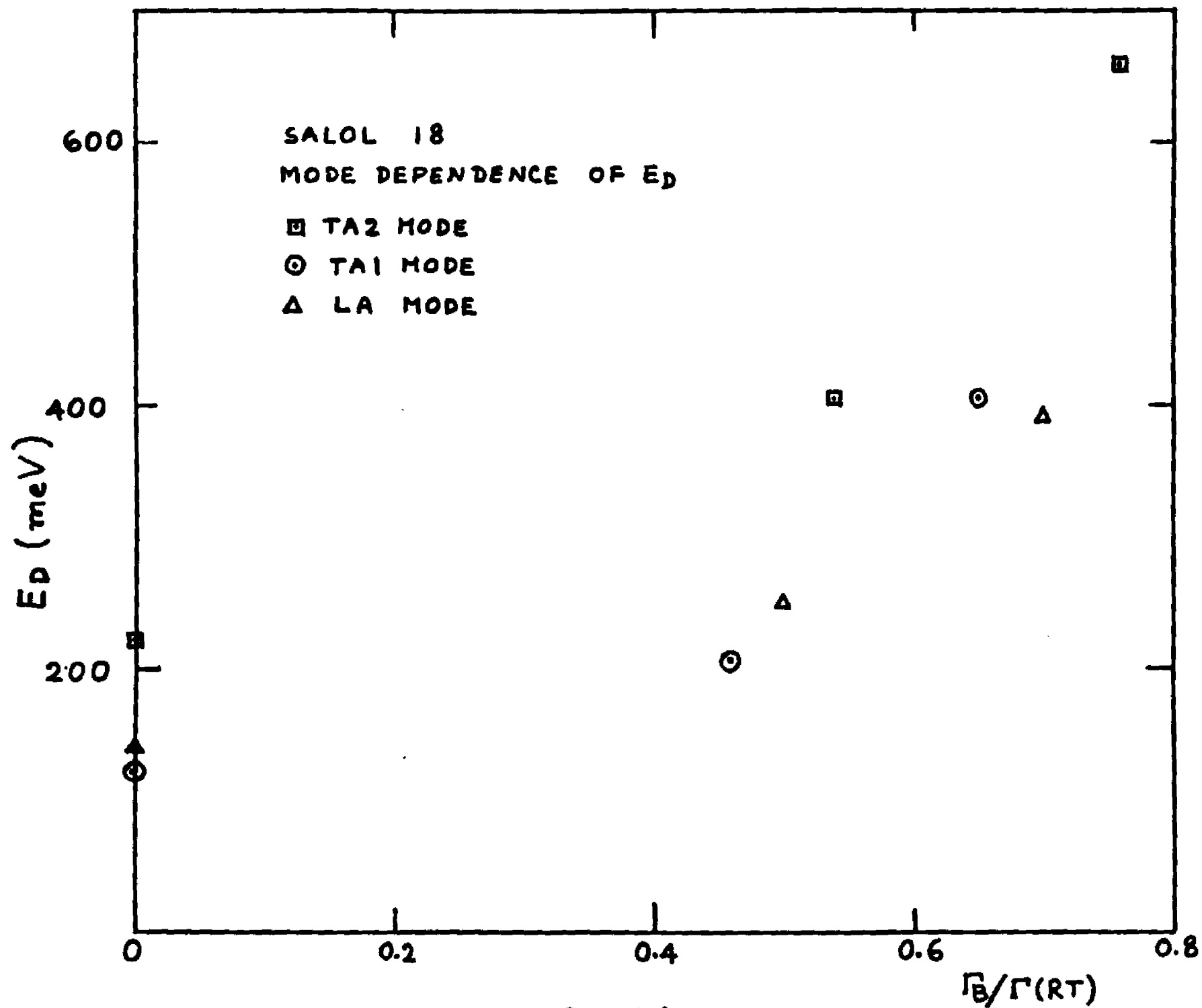


FIG. 8-37(c)

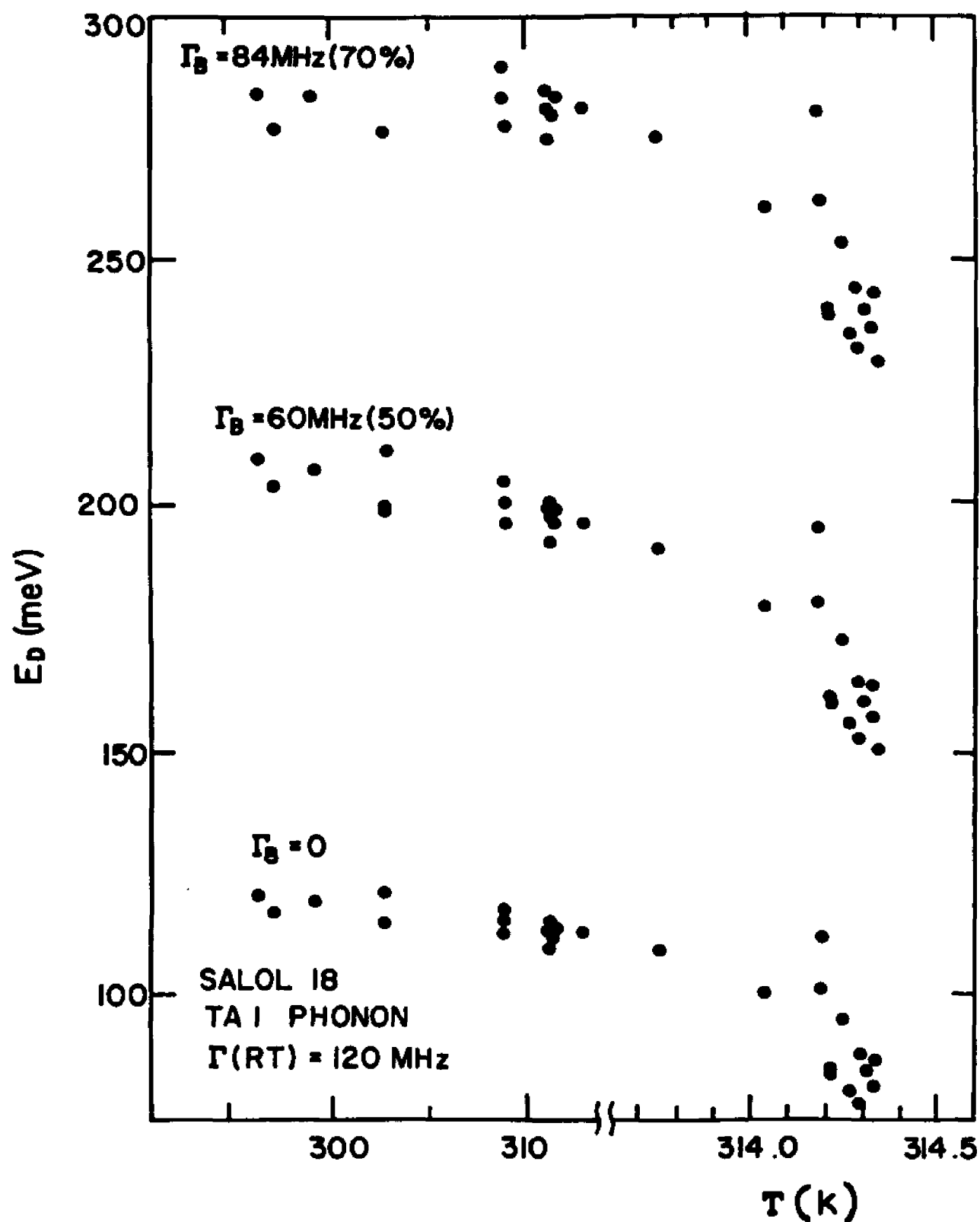


Fig. 8-38: Temperature dependence of the defect formation energy computed from the TA1 linewidth of salol 18. $\Gamma(\text{RT}) = 120\text{ MHz}$. Fractional values of background Γ_B 's are same as of fig. 8-34.

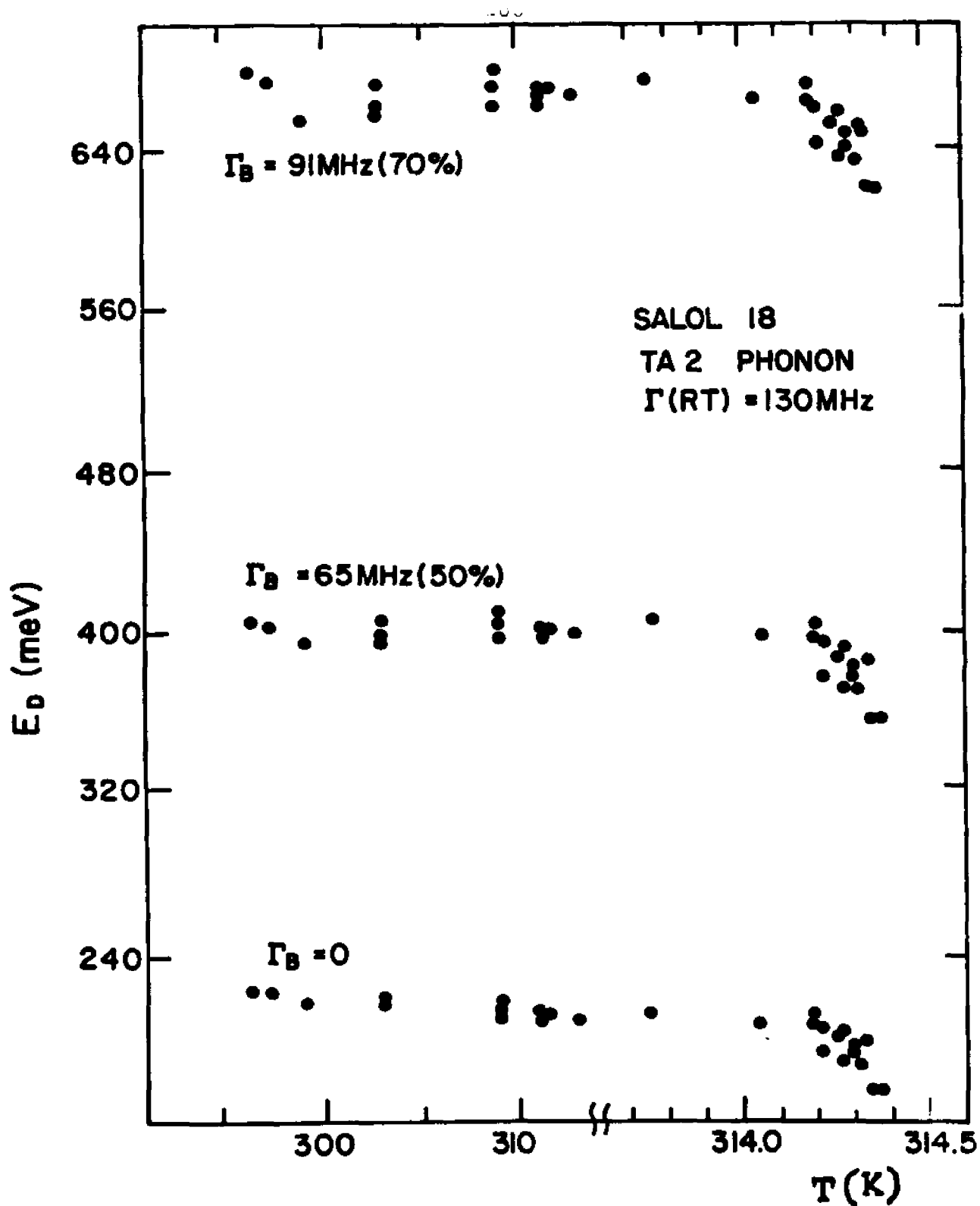


Fig. 8-39: Temperature dependence of the defect formation energy $E_D(T)$ computed from the TA2 mode linewidth of salol 18, at the same fractional values of Γ_B . The absolute values of $E_D(T)$ is here higher than for sample B.

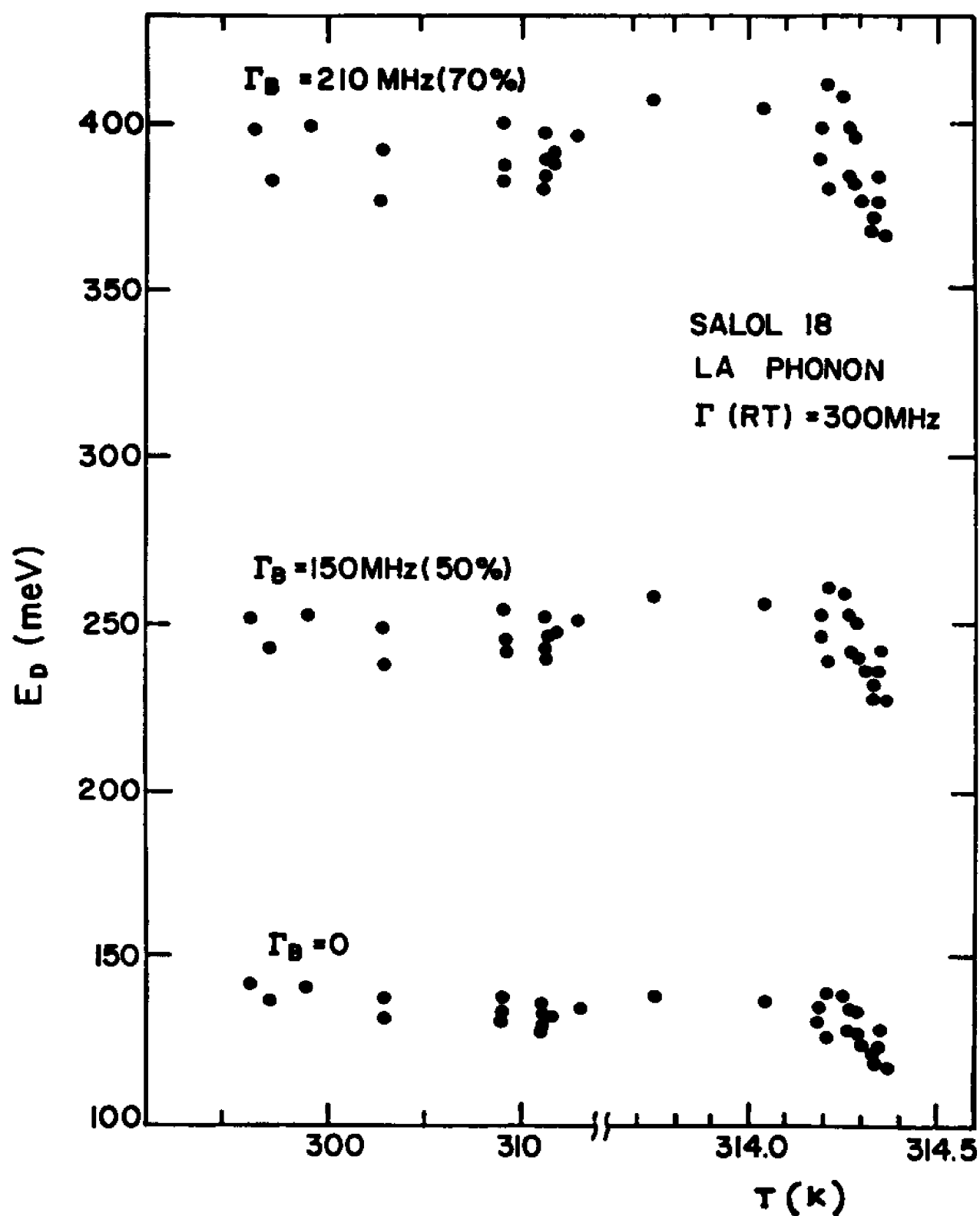


Fig. 8-40: $E_D(T)$ vs. temperature, computed from LA mode of salol 18.

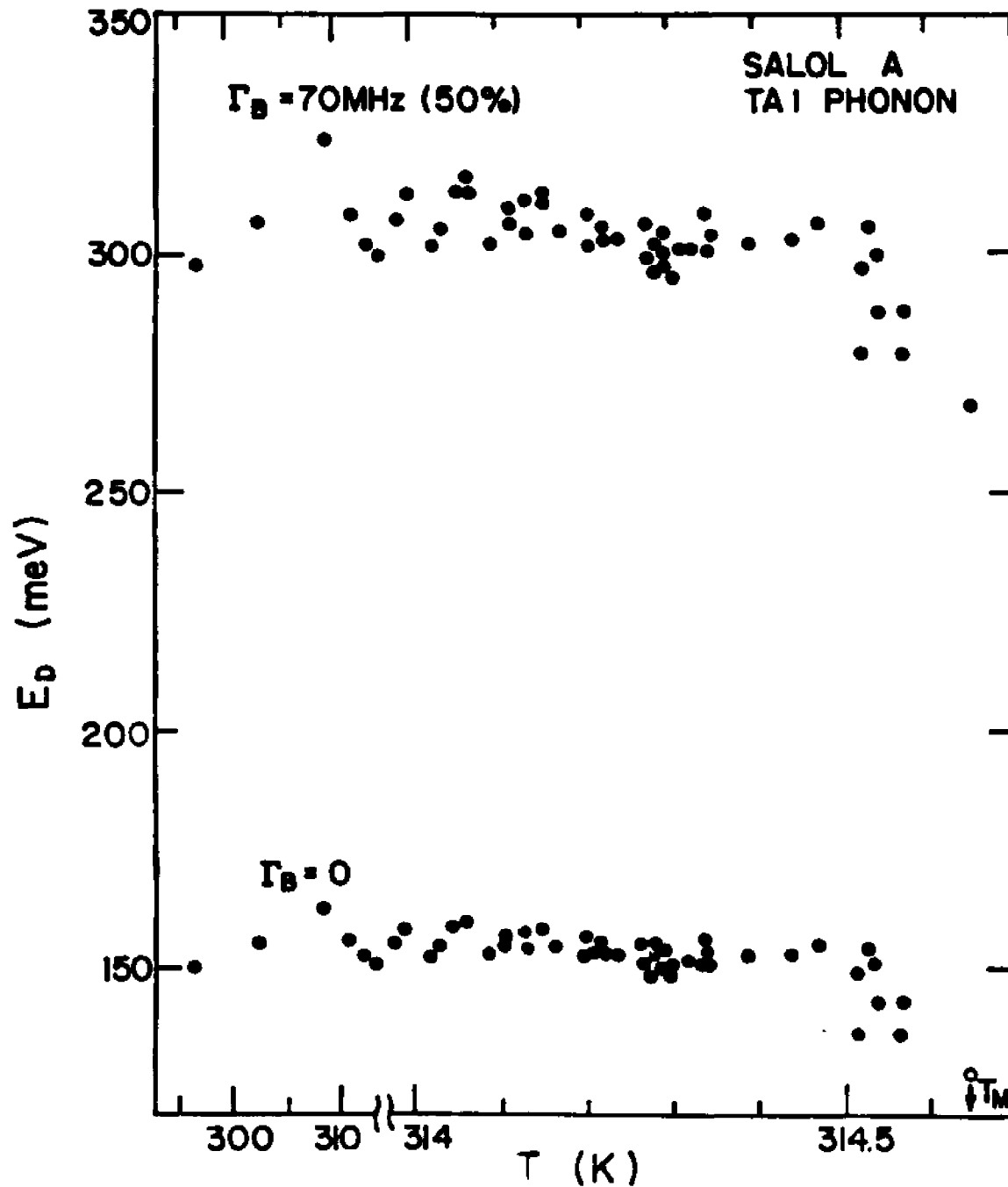


Fig: 8-41: Temperature dependence of the defect formation energy $E_D(T)$ computed from the TAI mode of salol A, for two background linewidth values which are 0% and 50% of the average room temperature value.

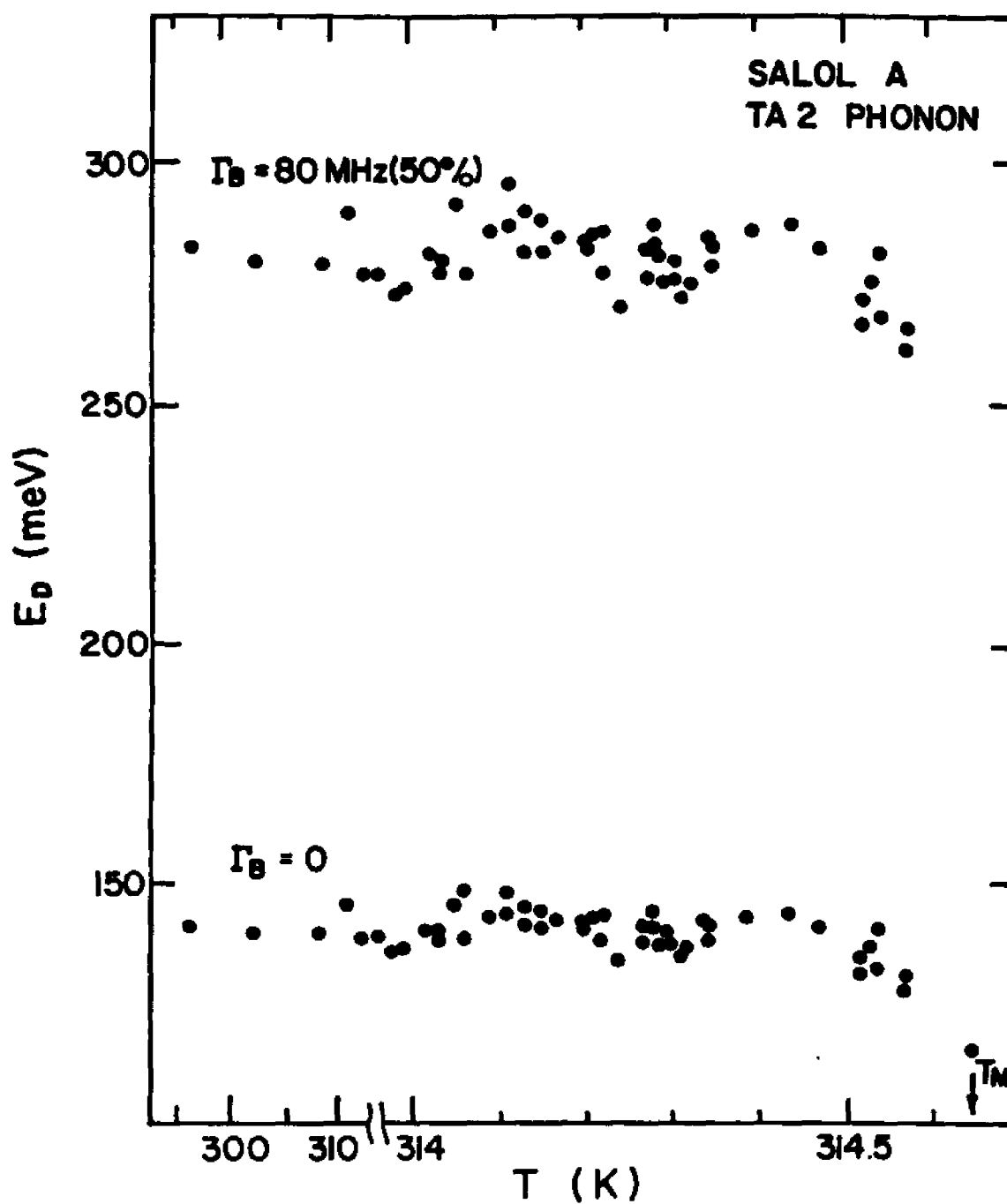


Fig. 8-42: Temperature dependence of $E_D(T)$ computed from the TA2 mode of salol A, Γ_B was the same as in fig. 8-41.

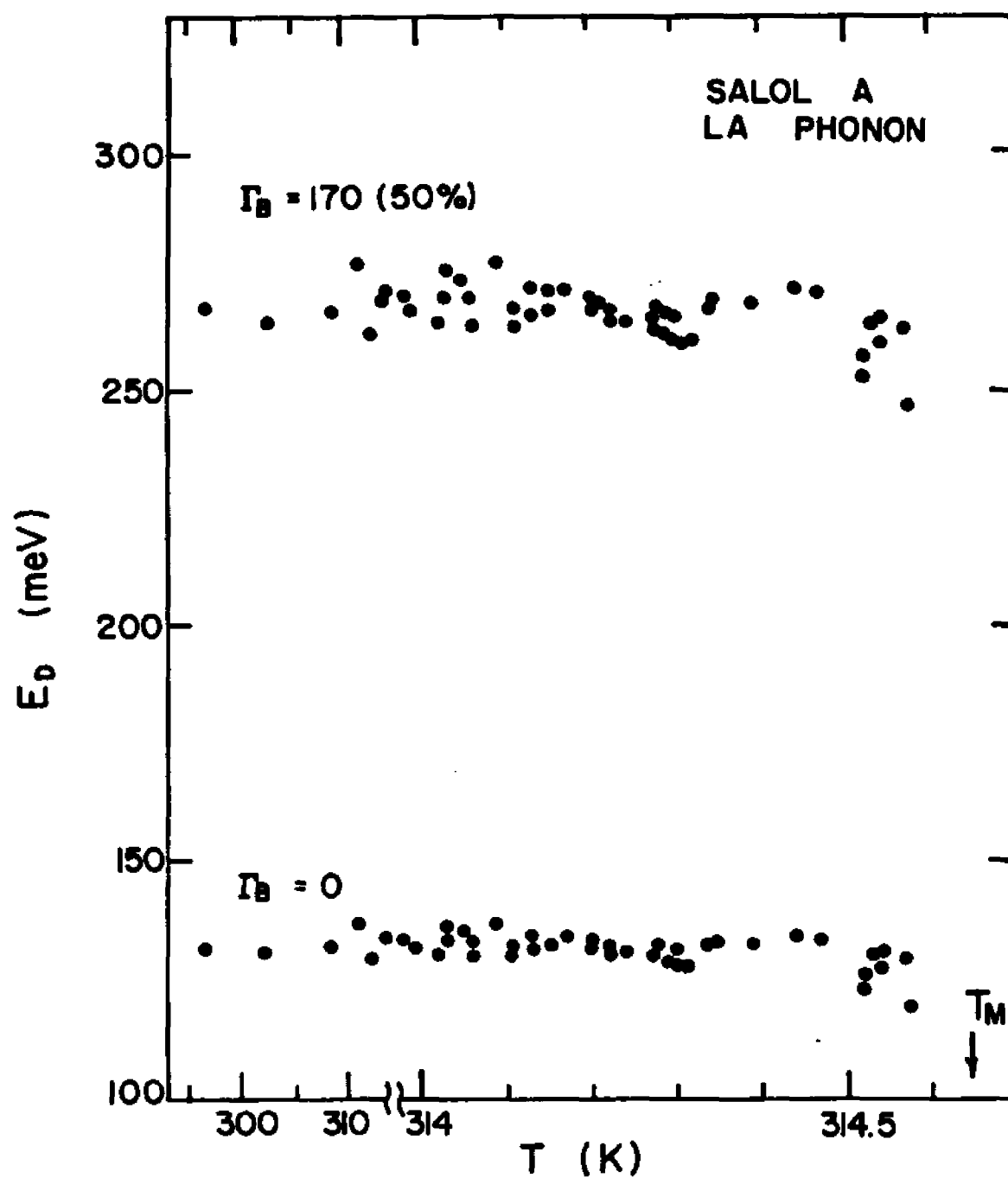


Fig. 8-43: Temperature dependence of $E_D(T)$ computed from the LA phonon of salol A.

Fig. 8-44 (a) $\ln (\Gamma - \Gamma_B)$ vs. $1/k_B T$ for the TAl phonon of salol 18 plotted for $\Gamma_B = 0$ showing the linear fitting in the low temperature region. If the linewidth showed no anomalies near T_m , the formation energy $E_D(T)$ would be constant and the plotted curve would be a straight line. The corresponding energy plot is in fig. 8-44(b).

Fig. 8-44 (b) The temperature dependence of $E_D(T)$ computed from the TAl phonon of salol 18 with parameters extracted from fig. 8-44 (a) shows a continuous decrease near T_m .

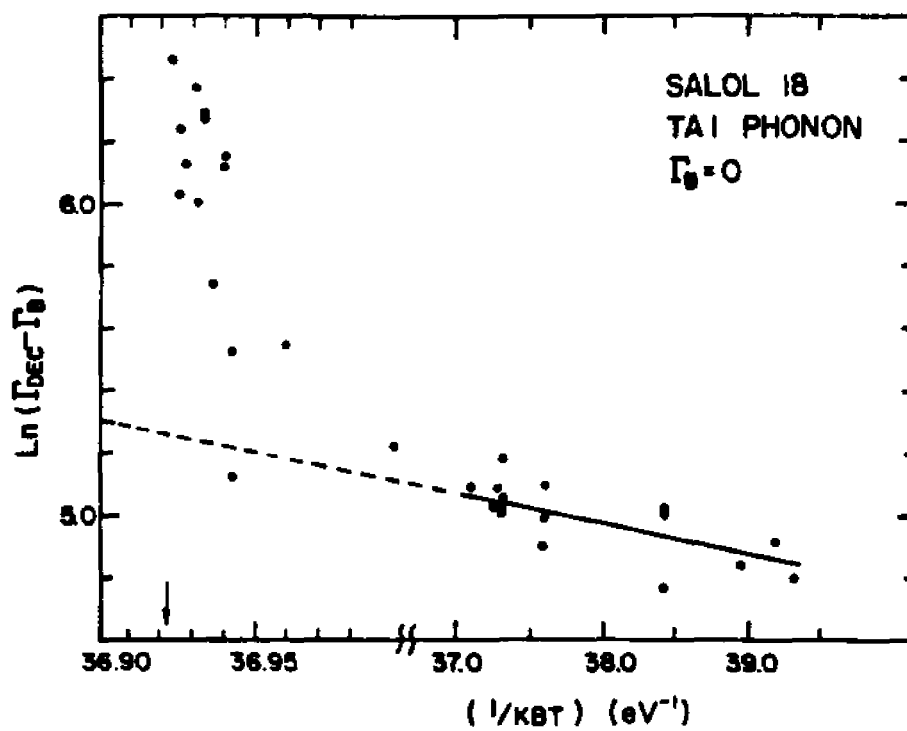


FIG. 8-44(a)

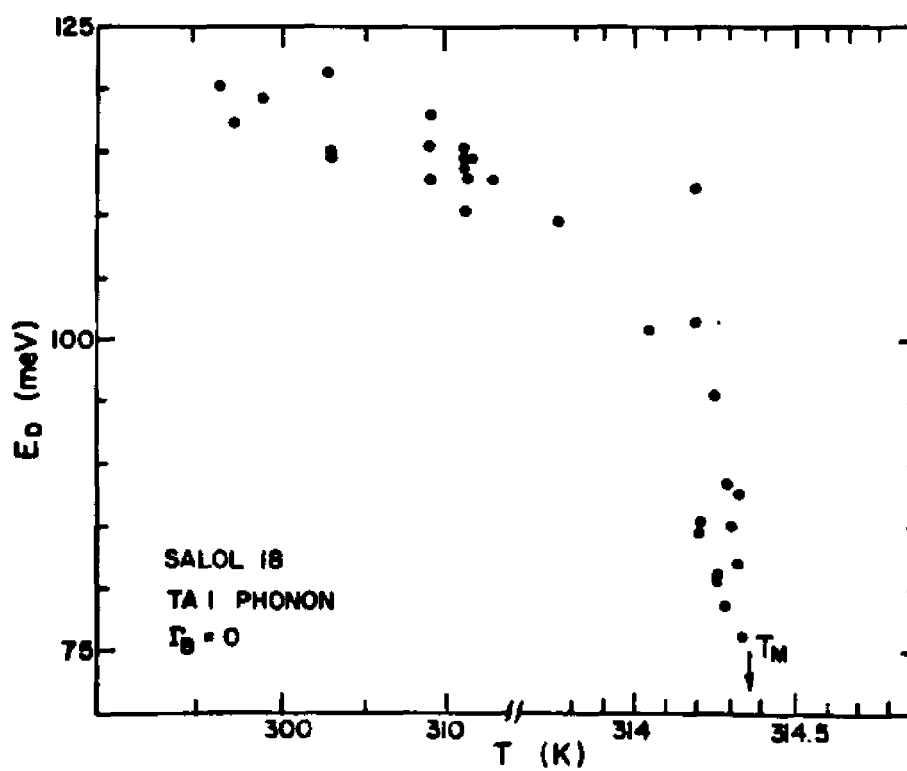


FIG. 8-44(b)

In order to allow for a catastrophic growth of dislocations at the onset of melting according dislocation theory of melting $E_D(T)$ should be very close to zero. The bending of $E_D(T)$ near T_m shows that trend in most of the energy plots. The energy decreased to a value as low as a few meV. From equation (8-12), this decrease of E_D obviously implies a simultaneous growth in defect density. Two other single energy plots for salol B and salol A for $\Gamma_B=0$ are shown in figs. 8-45 and 8-46.

(5) Temperature dependence of relative mode intensities

It was observed in several samples that the Brillouin mode intensity of one of the TA modes increased significantly with respect to the others very close to T_m . The most distinct appearance of such behavior was found in the melting experiment on salol B. Fig. 8-3 illustrates the changes in the spectrum between room temperature and the melting temperature. The TA2 mode which was weak at room temperature grew very strong near T_m . Since the finesse and laser intensity varied greatly over the duration of the experiment, the relative intensity (the ratio of the intensity of TA2 mode to TA1 mode) I_{TA2}/I_{TA1} is shown in fig 8-47 as function of temperature instead of a single mode intensity. The intensity was measured using the deconvoluted

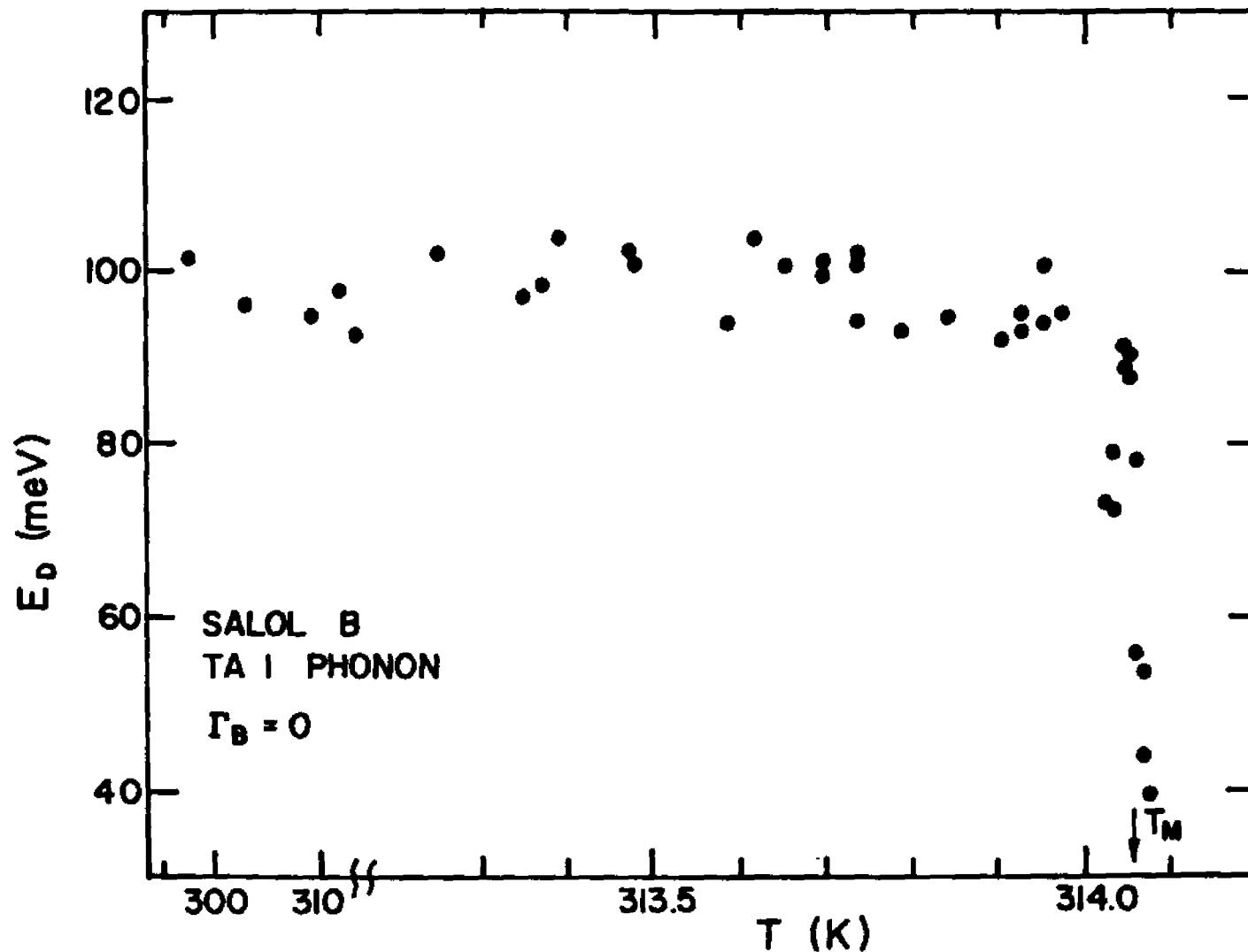


Fig. 8-45: The temperature dependent behavior of defect formation energy $E_D(T)$ computed from the TA1 mode of salol B for $\Gamma_B=0$. Near T_m , $E_D(T)$ shows a 65% decrease, indicating a catastrophic growth of defects near T_m .

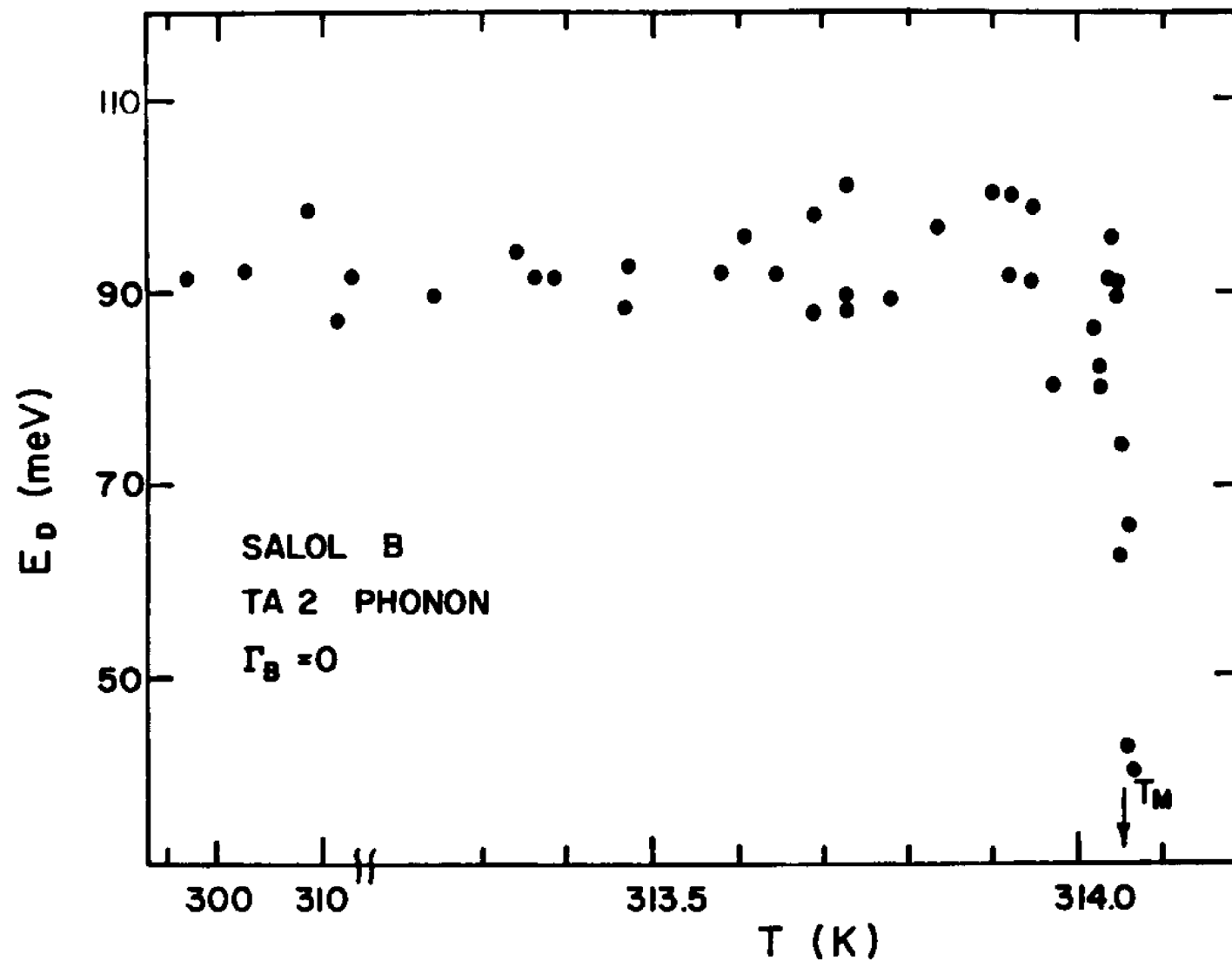


Fig. 8-46: More than 60% decrease in formation energy is shown computed from the temperature dependence of the linewidth of the TA2 phonon in salol B by the present dislocation model. Here $\Gamma_B = 0$.

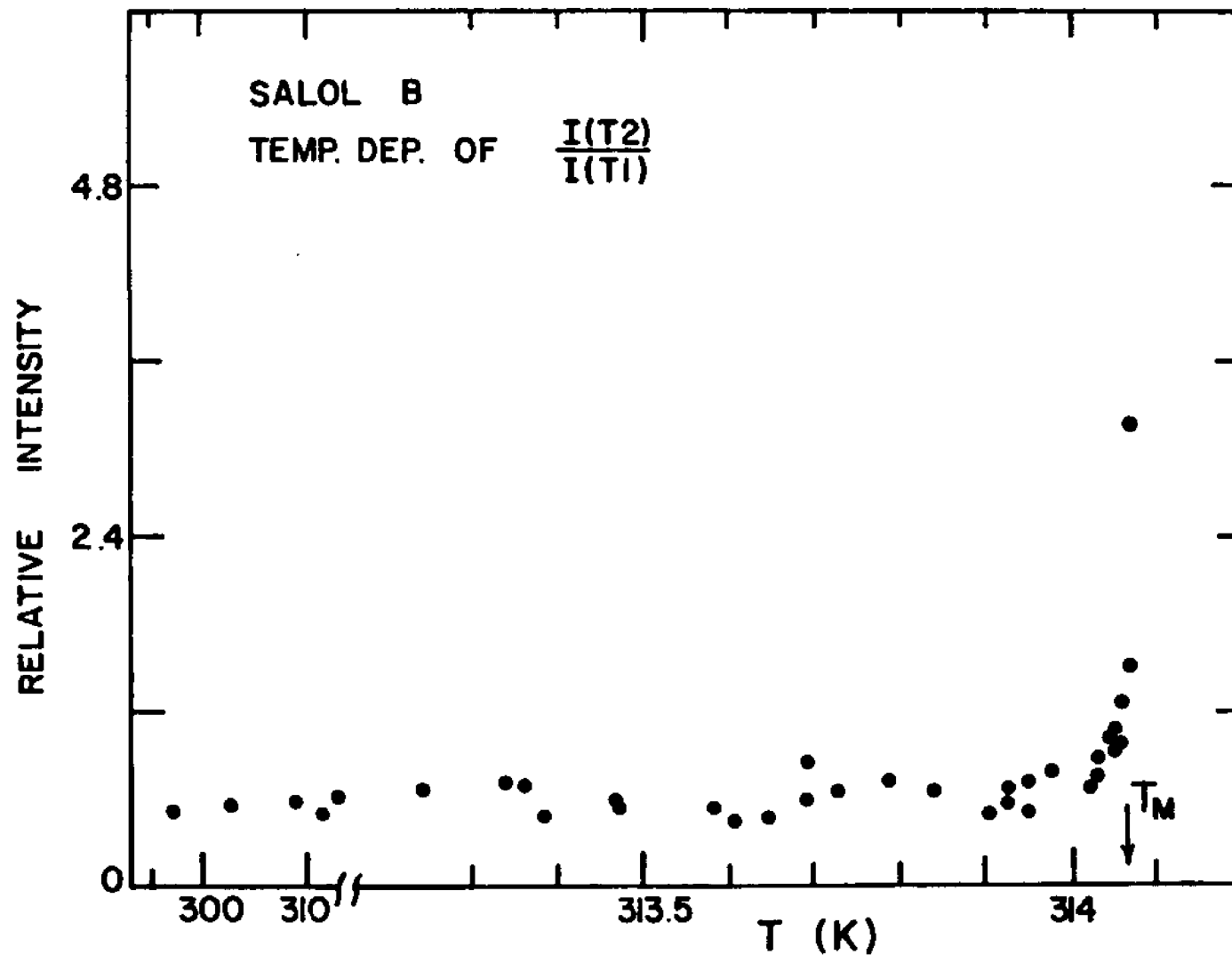


Fig. 8-47: Ratio of the intensities of the TA2 and TA1 mode of salol B which increases substantially near T_m). The continuous growth of the TA2 mode relative to the TA1 mode near T_m can also be seen in the raw spectra of fig. 8-3.

linewidth Γ_{DEC} and peak height H of the modes. This ratio can be represented as

$$\frac{I(TA2)}{I(TA1)} = \frac{\Gamma(TA2) H(TA2)}{\Gamma(TA1) H(TA1)} \quad (8-16)$$

The measurement of $I(TA2)/I(TA1)$ was also checked against a planimeter-determined ratio of integrated area of those modes, and both results agreed within 2%. By looking at the T-tensors of TA1 and TA2 modes, one can identify the associated Pockel's coefficients p_{44} and p_{55} which are proportional to $I(QT)$ and $I(TA1)$ respectively. Since Pockel's coefficients couple refractive index and strain, and refractive index is proportional to the polarizability, an increase of p_{44} against p_{55} close to T_m may suggest that the salol molecules move more freely in the yz plane than in the xz plane, as $T \rightarrow T_m$.

(6) Sample dependence

Experimental results of Brillouin shifts and linewidths for four different samples have been presented so far. The most striking difference between them is in the melting temperature T_m . It was observed that the

melting temperature for melt grown and zone refined crystals were higher than those of the solution grown crystals. The apparent melting temperature also depended on the height of the scattering column from the bottom of the crystal. The higher the column was, the higher was the measured T_m . The computed magnitude of defect formation energies also varied from sample to sample.

In the case of succinonitrile samples the crystal purity (assumed to increase with to the number of zone refining passes) played no role in the temperature dependence of the Brillouin shifts. Figure 8-15 clearly verifies that conclusion. But it was observed that the melting temperature was higher for the crystals which underwent a higher number of zone refining passes during the growth process.

(7) Effect of misorientation

One striking result of the room temperature Brillouin experiment was the effect of angular misorientation on the number of observable Brillouin modes. For a misorientation of $\gamma = 11^\circ$ of the x and z axes from the true crystal axes, I observed up to five different distinguishable Brillouin components in the Y(VT)X configuration in samples salol 1, salol 2, and salol 16. As the calculation in table (5-3) shows, these modes

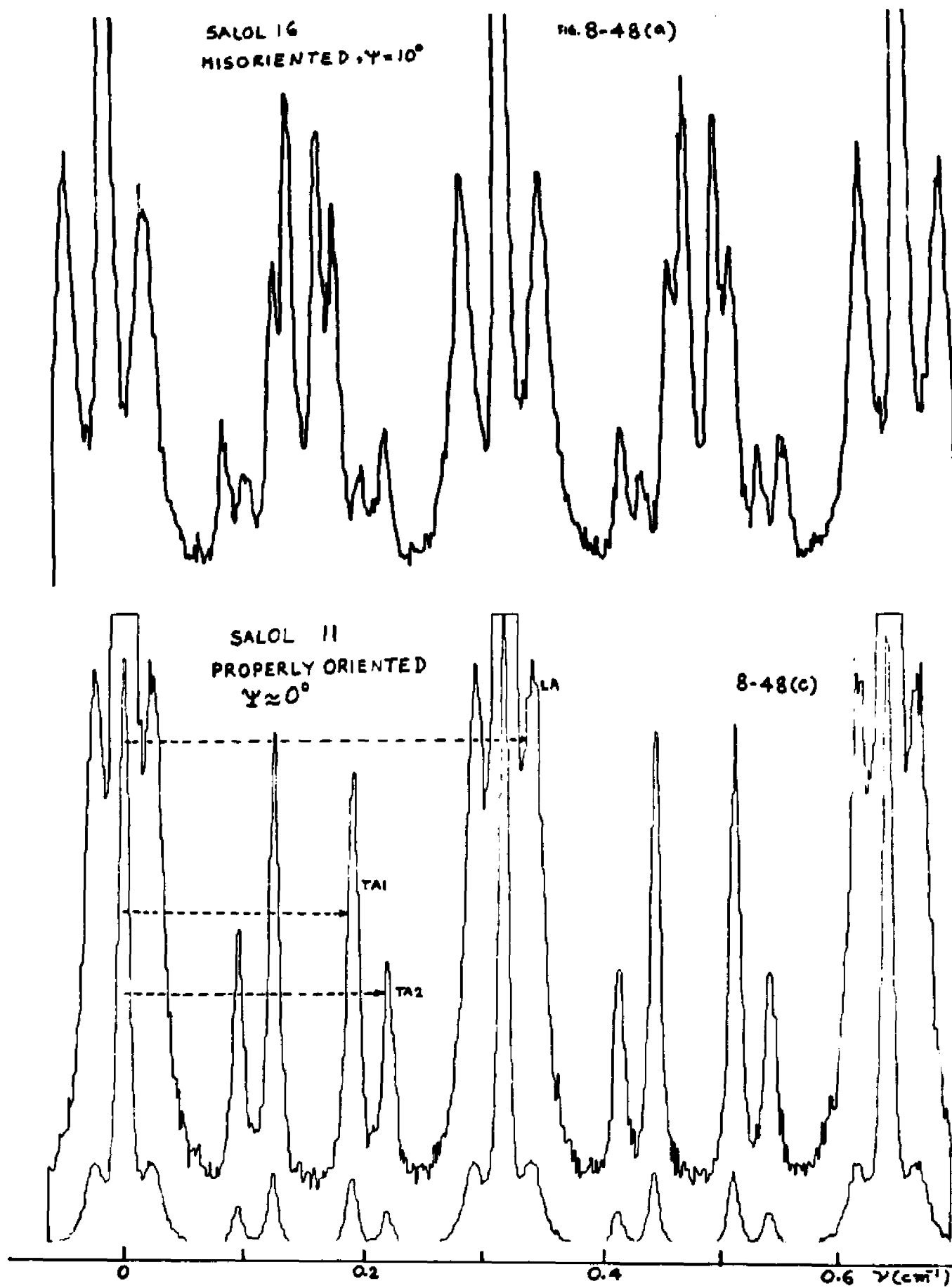
resulted from the angular misorientation of the x and z axes. The phonon propagation vectors $\hat{q}_{VY} = (.526, -.844, .107)$ and $\hat{q}_{VH} = (.72, -.68, .15)$ in the Y(VT)X configuration may make it possible to observe up to six different Brillouin components. Figs. 8-48(a) and (b) show the raw spectra of salol 16 and salol 1 in the same scattering configuration Y(VT)X, obtained under similar conditions, showing five and four different Brillouin modes respectively. This behavior was not observed in an accurately oriented (along principal crystal axes) sample, salol 11, a spectrum of which is shown in fig. 8-48(c).

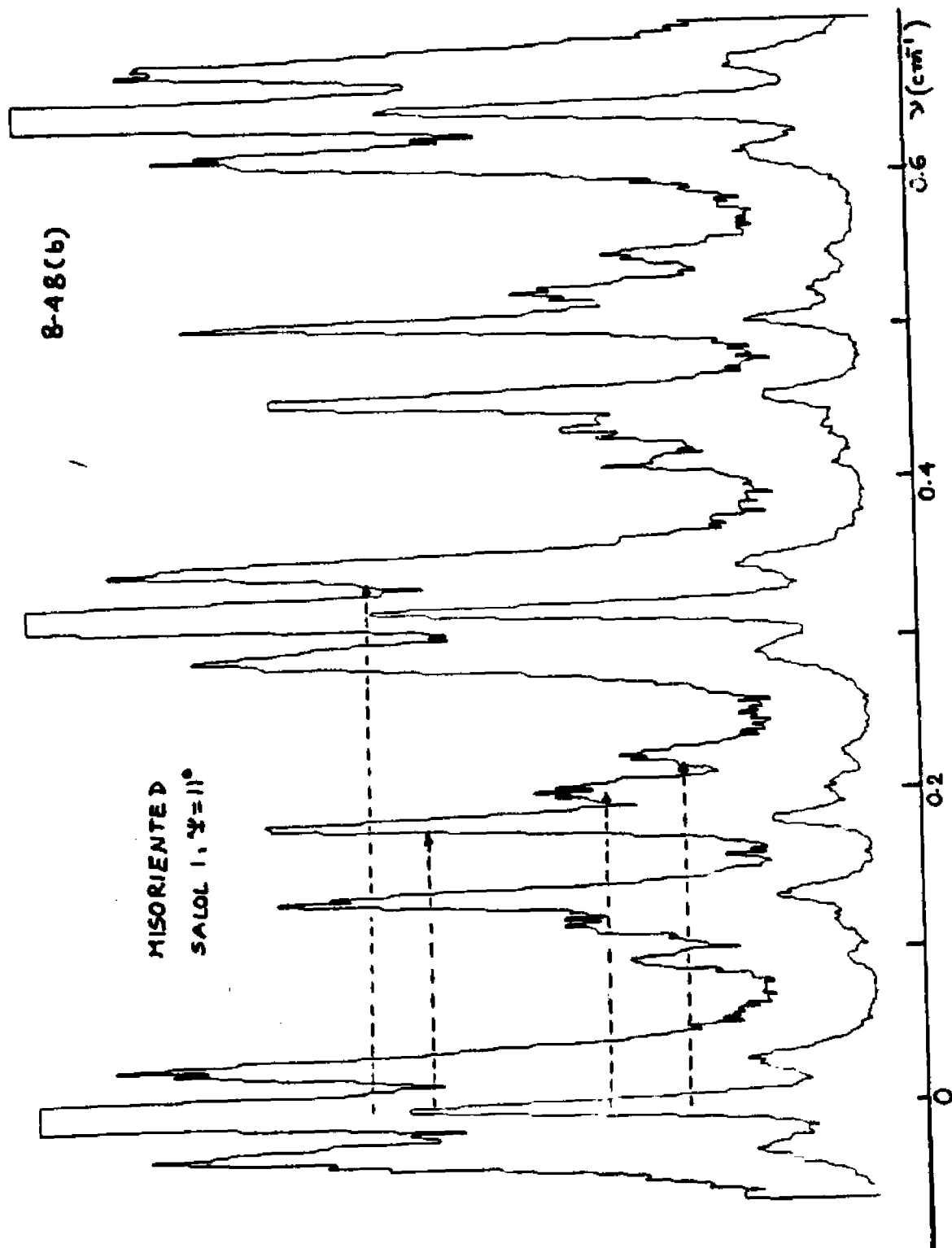
C. Room Temperature Brillouin scattering experiments:

(1) Determination of elastic and elasto-optic coefficients of salol.

It is now well established that Brillouin scattering is an effective experimental technique for determining elastic and elasto-optic constants of crystals. Using this technique, I determined all the elastic constants and deduced the complete set of elasto-optic coefficients of salol. In this chapter I shall present those results. Four different samples were used in this experiment. Salol 11 was cut with (100), (001) and (010) faces, and orientation was checked within $\pm 1^\circ$ by a polaroscope. Salol 3, 7 and 8 were cut in such a way that in the 90°

Fig. 8-48: Effect of sample misorientation. The calculation in chapter 5, for a sample misoriented by $\Psi = 11^\circ$, shows that up to six Brillouin modes may be visible in the (VT) scattering configuration. (a) raw spectrum from salol 16 ($\Psi = 10^\circ$) in the Y(Z,T)X configuration shows five different modes. (b) salol 1 ($\Psi = 11^\circ$) has four components in its Brillouin spectrum for the same scattering configuration as salol 16 (c) salol 11 (properly oriented, $\Psi \approx 0$) in Y(Z,T)X has only 3 components as predicted by the calculation for a perfectly oriented crystal. The observation of such spectra demonstrate the highly isotropic optical properties of salol.





scattering configuration, the q -vector was parallel to one of the principal axes of the crystal. The complete set of Brillouin scattering tensors were tabulated in chapter 5 for all possible scattering configurations of these samples. Spectra were recorded with (VV), (VH), (HH) and (VT) scattering configurations. Since salol is highly anisotropic, a second set of elastic constants was calculated by constructing the necessary Brillouin scattering tensors and associated eigenvalue relations with the anisotropic optical properties of the crystal included.

(a) With isotropic consideration.

By assuming the length of the phonon wave vector

$|\vec{q}| = |\vec{k}_s - \vec{k}_o|$ to be independent of the scattering configuration and differences in n_x , n_y and n_z , a straightforward calculation was carried out to determine the sound velocity from the observed Brillouin shifts of the individual components as:

$$v = \frac{2\pi\nu_B}{|\vec{k}_s - \vec{k}_o|} \quad (8-17)$$

where ν_B = Brillouin shift

$\vec{k}_s$ = wave vector of scattered light

$\vec{k}_o$ = wave vector of incident light

Table 8-1
Brillouin shift, sound velocity and ρv^2 from salol 11 by
isotropic consideration

Sample 11

Scattering configuration	q	u	Mode	Frequency [GHz]	Sound velocity [cm/sec]	ρv^2 [dynes/cm]
Y(V,T)X (110)	(0,0,1)	TA	6.794	1.426×10^5	2.601×10^{10}	$5C_{55} + 5C_{44}$
	$(1, -b_1^{**}, 0)$	QL	10.672	2.352×10^5	7.07×10^{10}	$R_1 + L_1$
	$(1, -b_2, 0)$	QT	5.871	1.284×10^5	2.107×10^{10}	$R_1 - L_1$
Y(V,T)Z (011)	(1,0,0)	TA	6.24	1.348×10^5	2.321×10^{10}	$5C_{55} + 5C_{66}$
	$(0, 1, -b_3)$	QL	12.09	2.844×10^5	10.337×10^{10}	$R_2 + L_2$
	$(0, 1, -b_4)$	QT	5.37	1.127×10^5	1.625×10^{10}	$R_2 - L_2$
X(V,T)Z (101)	(010)	TA	6.1984	1.298×10^5	2.154×10^{10}	$5C_{66} + 5C_{44}$
	$(1, 0, -b_5)$	QL	13.07	2.624×10^5	8.805×10^{10}	$R_3 + L_3$
	$(1, 0, -b_6)$	QT	6.835	1.554×10^5	3.087×10^{10}	$R_3 - L_3$

$$R_1 = .25C_{11} + 5C_{66} + .25C_{22}$$

$$L_1 = .25[(C_{11} - C_{22})^2 + 4(C_{12} + C_{66})^2]^{1/2}$$

$$R_2 = .5C_{44} + .25C_{22} + .25C_{33}$$

$$L_2 = .25[(C_{22} - C_{33})^2 + 4(C_{44} + C_{23})^2]^{1/2}$$

$$R_3 = .5C_{55} + .25C_{11} + .25C_{33}$$

$$L_3 = .25[(C_{11} - C_{33})^2 + 4(C_{13} + C_{55})^2]^{1/2}$$

** b1 and b2, b3 and b4, and b5 and b6 can be obtained from table

5-5xy(8) 5-5yz(13) and 5-5zx(11) of chapter 5 respectiv

As an example, for the scattering configuration of Y(ZZ)X, v is given by:

$$v = \frac{v_B \lambda_0}{\sqrt{2} \eta_z} \quad 8-17(a)$$

Using the measured density of salol $\rho = 1.2784 \text{ gm/cm}^3$, the eigenvalue ρv^2 was computed for each of the observed modes. The computed $\hat{q}$ and $\hat{u}$ vector, and the observed frequency shift, sound velocity and ρv^2 for all three modes of salol 11 at all possible scattering configurations are shown in table 8-1.

By substituting ρv^2 from table (8-1), the corresponding nine eigenvalue equations can be written as:

$$.5C_{55} + .5C_{44} = 2.601 \times 10^{10} \quad (8-18a)$$

$$.25C_{11} + .5C_{66} + .25C_{22}^+ \quad (8-18b)$$

$$.25[(C_{11} - C_{22})^2 + 4(C_{12} + C_{66})^2]^{1/2} = .07 \times 10^{10}$$

$$.25C_{11} + .5C_{66} + .25C_{22}^- \quad (8-18c)$$

$$.25[(C_{11} - C_{22})^2 + 4(C_{12} + C_{66})^2]^{1/2} = 2.107 \times 10^{10}$$

$$.5C_{55} + .5C_{66} = 2.32 \times 10^{10} \quad (8-18d)$$

$$.5C_{44} + .25C_{22} + .25C_{33} + .25[(C_{22} - C_{33})^2 + 4(C_{44} + C_{23})^2]^{1/2} = 10.337 \times 10^{10} \quad (8-18e)$$

$$.5C_{44} + .25C_{22} + .25C_{33} - .25[(C_{22} - C_{33})^2 + 4(C_{44} + C_{23})^2]^{1/2} = 1.625 \times 10^{10} \quad (8-18f)$$

$$.5C_{66} + .5C_{44} = 2.154 \times 10^{10} \quad (8-18g)$$

$$.5C_{55} + .25C_{11} + .25C_{33} + .25[(C_{11} - C_{33})^2 + 4(C_{13} + C_{55})^2]^{1/2} = 8.805 \times 10^{10} \quad (8-18h)$$

$$.5C_{55} + .25C_{11} + .25C_{33} - .25[(C_{11} - C_{33})^2 + 4(C_{13} + C_{55})^2]^{1/2} = 3.087 \times 10^{10} \quad (8-18i)$$

The above nine simultaneous equations can be solved to determine the nine independent elements of the elastic constant tensor of salol, and are given in table 8-2

Table 8-2

Elastic coefficients of salol in units of 10^{10} dynes/cm² determined from salol 11 assuming isotropic optical properties

$$C_{ij} = \begin{bmatrix} 6.90 & 3.07 & 2.499 & 0 & 0 & 0 \\ 3.07 & 7.71 & 6.086 & 0 & 0 & 0 \\ 2.499 & 6.086 & 11.35 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2.434 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2.768 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1.874 \end{bmatrix}$$

(b) With anisotropic consideration.

The calculation of eigenvalues and Brillouin scattering tensor components for each of the possible polarizations (VV), (VH), (HH) and (HV) was also carried out. Unlike the isotropic calculation, the length of the phonon wave vector $\vec{q}$ is now dependent on the polarization choice for the incident and scattered light. As a consequence, the frequency shift of the individual observed modes is also dependent on the polarization choice. One can clearly see this slight difference in frequency shift of the Brillouin modes in (VV), (VH) and (HV) polarizations of the salol 11 spectra shown in table 8-3 compared to those in table 8-1. A raw set of spectra for Y(VT)Z, Y(VV)Z, Y(VH)Z and Y(HH)Z are shown in fig. 8-49 (a), (b), (c) and (d).

Fig. 8-49: Room temperature raw Brillouin spectra of salol 11 which were used to determine the complete set of elastic and elasto optic constants of salol. Spectra collected for various configurations are shown: (a) $Y(X,T)Z$ (b) $Y(X,X)Z$ (c) $Y(X,Y)Z$ [VH] (d) $Y(Z,Y)Z$ [HH]. The positions of the centers of the three modes in $Y(V,T)Z$ are a little off from those of the centers at $y(VV)z$ and $y(VH)z$, which results from the anisotropic properties of salol. The QL, QT and TA1 modes belonging to the central Rayleigh line are indicated in the figure.

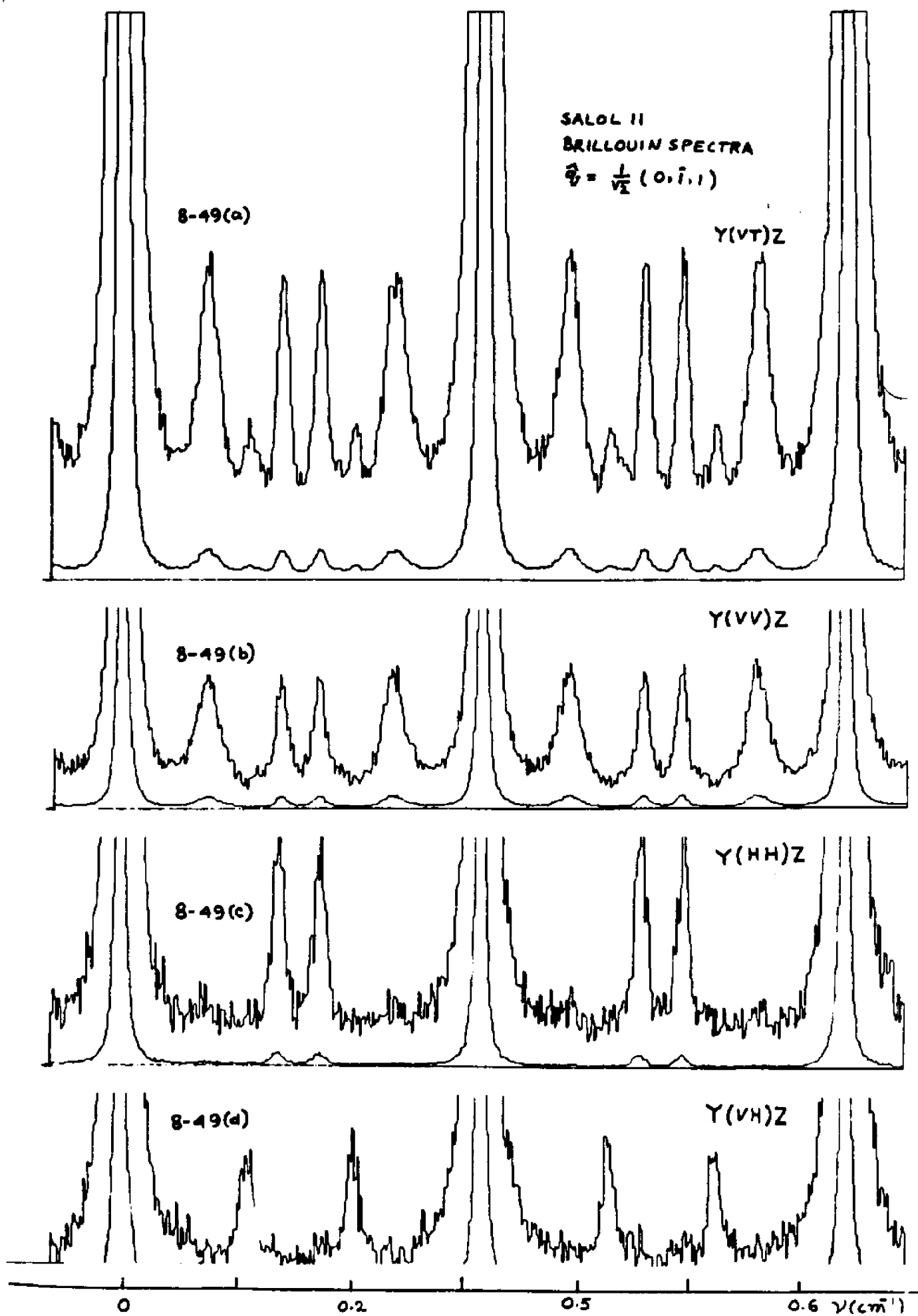


Table 8-3

Brillouinshift, sound velocity and ρv^2 from salol 11, by
anisotropic consideration

Scattering

configuration	$\hat{q}$	$\hat{u}$	Mode	Frequency [GHZ]	Sound velocity [cm/sec]	ρv^2 [dynes/cm ²]	$f(c_{ij}) = \rho v^2$
$y(z,z)x(1,-1,0)/\sqrt{2}$							
$\frac{1}{\sqrt{1+b_1^2}}(1,b_1^*,0)$	QL			10.672	2.352×10^5	7.07×10^{10}	$R1+L1^*$
$y(x,y)x(1.08,-.92,0)/\sqrt{2}$							
$\frac{1}{\sqrt{1+b_2^2}}(1,-b_2,0)$	QT			6.639	1.434×10^5	2.628×10^{10}	$R2-L2$
$y(z,y)x(1.04,-.96,0)/\sqrt{2}$							
(001)	TA			6.8273	1.433×10^5	2.625×10^{10}	$.55C_{55} + .46C_{44}$
$y(x,x)z(0,-1,1)/\sqrt{2}$							
$\frac{1}{\sqrt{1+b_3^2}}(0,1,-b_3)$	QL			12.09	2.844×10^5	10.337×10^{10}	$R3+L3$
$y(z,y)z(0,-.95,1.04)/\sqrt{2}$							
$\frac{1}{\sqrt{1+b_4^2}}(0,1,-b_4)$	QT			5.46	1.151×10^5	1.694×10^{10}	$R4-L4$
$y(x,y)z(0,-.92,1.08)/\sqrt{2}$							
(100)	TA			6.3232	1.356×10^5	2.384×10^{10}	$.42C_{66} + .58C_{55}$
$x(y,y)z(1,0,-1)/\sqrt{2}$							
$\frac{1}{\sqrt{1+b_5^2}}(1,0,-b_5)$	QL			13.07	2.624×10^5	8.805×10^{10}	$R5+L5$
$x(y,x)z(.95,0,1.05)/\sqrt{2}$							
$\frac{1}{\sqrt{1+b_6^2}}(1,0,-b_6)$	QT			6.298	1.435×10^5	2.63×10^{10}	$R6-L6$
$x(y,x)z(1.03,0,.96)/\sqrt{2}$							
(010)	TA			6.806	1.425×10^5	2.609×10^{10}	$.449C_{66} + .548C_{44}$

Table 8-3 continued....

$$R1 = .25C_{11} + .5C_{66} + .25C_{22}$$

$$L1 = .25[(C_{11}-C_{22})^2 + 4(C_{12}+C_{66})^2]^{1/2}$$

$$R2 = .29C_{11} + .5C_{66} + .21C_{22}$$

$$L2 = .25[(1.16C_{11}-.32C_{66}-.84)^2 + 3.91(C_{12}+C_{66})^2]^{1/2}$$

$$R3 = .5C_{44} + .25C_{22} + .25C_{33}$$

$$L3 = .25[(C_{22}-C_{33})^2 + 4(C_{44}+C_{23})^2]^{1/2}$$

$$R4 = .524C_{44} + .23C_{22} + .273C_{33}$$

$$L4 = .25[(.92C_{22}-1.09C_{33}+.17C_{44})^2 + 3.968(C_{44}+C_{23})^2]^{1/2}$$

and

$$R5 = .25C_{11}+.5C_{55}+ .25C_{33}$$

$$L5 = .25[(C_{11}-C_{33})^2 + 4(C_{13}+C_{55})^2]^{1/2}$$

$$R6 = .267C_{11} +.497C_{55}+.23C_{33}$$

$$L6 = .25[1.07C_{11}-.15C_{55}-.92C_{33})^2 + 3.94(C_{13}+C_{55})^2]^{1/2}$$

** b1 and b2, b3 and b4, and b5 and b6 can be obtained from table 5-5xy(9), 5-5yz(14) and 5-5 zx(12) of chapter 5 respectively. Instead of calculating the whole Brillouin scattering tensor for a particular mode, one needs to determine only the T_{ij} - component of such a tensor where i and j are respectively the polarization vector direction of incident

and scattered light (for details see section 5(C)). Again, by substituting the observed g_v^2 from the table 8-3, one can also form the equation system for the C_{ij} 's, to determine the complete set of $[C_{ij}]$ by anisotropic consideration:

$$.449C_{44} + .58C_{55} = 2.625 \times 10^{10} \quad (8-19a)$$

$$.29C_{11} + .5C_{66} + .21C_{22} - .25 [(1.16C_{11} - .32C_{66} - .84C_{22})^2 + 3.91(C_{12} + C_{66})^2]^{1/2} = 2.628 \times 10^{10} \quad (8-19b)$$

$$.25C_{11} + .5C_{66} + .25C_{12} + .25[(C_{11} - C_{22})^2 + 4(C_{12} - C_{66})^2]^{1/2} = .07 \times 10^{10} \quad (8-19c)$$

$$.42C_{66} + .58C_{55} = 2.384 \times 10^{10} \quad (8-19d)$$

$$.524C_{44} + .23C_{22} + .273C_{33} + .25[.92C_{22} - 1.09C_{33} + .17C_{44}]^2 + 3.97(C_{44} + C_{23})^2]^{1/2} = 1.694 \times 10^{10} \quad (8-19e)$$

$$.5C_{44} + .25C_{22} + .25C_{33} - .25[(C_{22} - C_{33})^2 + 4(C_{23} + C_{44})^2]^{1/2} = 10.337 \times 10^{10} \quad (8-19f)$$

$$.449C_{66} + 548C_{44} = 2.609 \times 10^{10} \quad (8-19g)$$

$$.267C_{11} + .497C_{55} + .23C_{33} + .25[(1.07C_{11} - .15C_{55} - .92C_{33})^2 + 3.94(C_{13} + C_{55})^2]^{1/2} = 263 \times 10^{10} \quad (8-19h)$$

$$.25C_{11} + .5C_{55} + .25C_{33} - .25[(C_{11} - C_{33})^2 + 4(C_{13} + C_{55})^2]^{1/2} = 8.805 \times 10^{10} \quad (8-19i)$$

Solving the system of equations 8-19, one can obtain a second set of elastic coefficients of salol by anisotropic consideration. The determined values of $[C_{ij}]$ are given in table 8-4. Elastic constants obtained with and without inclusion of the anisotropic optical properties of salol are compared in table 8-5.

Table 3-4

Elastic constants of salol in units of 10^{10} dynes/cm² determined with anisotropic optical properties of the crystal included

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{13} & c_{23} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix} = \begin{bmatrix} 5.24 & 1.936 & 5.060 & 0 & 0 & 0 \\ 1.936 & 9.062 & 5.891 & 0 & 0 & 0 \\ 5.060 & 9.1 & 3.374 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2.788 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2.36 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2.406 \end{bmatrix}$$

Table 8-5

Comparison of the elastic constants of salol, determined by isotropic and anisotropic consideration in units of 10^{10} dynes/cm².

Elastic Constant	Value determined by isotropic consideration	Value determined by anisotropic consideration
$[C_{11}]$		
C_{11}	6.90×10^{10}	5.24×10^{10}
C_{22}	7.7×10^{10}	9.962×10^{10}
C_{33}	11.35×10^{10}	8.394×10^{10}
C_{44}	2.434×10^{10}	2.788×10^{10}
C_{55}	2.768×10^{10}	2.368×10^{10}
C_{66}	1.074×10^{10}	2.406×10^{10}
C_{12}	3.07×10^{10}	0.36×10^{10}
C_{13}	2.499×10^{10}	5.906×10^{10}
C_{23}	6.086×10^{10}	5.891×10^{10}

Table 8-6

Qualitative comparison between predicted and observed modes
by isotropic and anisotropic consideration of the crystal

Sample	Scattering configuration	Observed modes	Modes predicted by isotropic and anisotropic consideration	
#3	-x+z(VV)x+z	LA, TA2 [*]	LA	LA
	-x+z(VH)x+z	TA2, LA [*]	TA2	TA2, LA
	-x+z(HH)x+z	TA1, LA [*]	TA1	TA1
	-x-z(VV)-x+z	LA, TA2 [*]	LA	LA
	-x-z(HV)-x+z	TA2, LA [*]	TA2	TA2, LA
	-x-z(HH)-x+z	TA1, TA2 [*]	TA1	TA1
#8	x+y(VV)x-y	LA, TA2 [*]	LA	LA
	x+y(VH)x-y	TA2	TA2	TA2
	x+y(HH)x-y	LA [*]	TA1	TA1
	-x+y(VV)x+y	LA, TA1 [*]	LA	LA
	-x+y(HV)x+y	TA1, TA2 [*]	TA1	TA1
	-x+y(HH)x+y	LA, TA2 [*]	TA2	TA2
#7	-y-z(VV)y-z	LA, TA2 [*]	LA	LA
	-y-z(VH)y-z	TA1	TA1	TA1, LA
	-y-z(HH)y-z	TA2	TA2	TA2
	-y+z(VV)-y-z	LA, TA1 [*]	LA	LA
	-y+z(VH)-y-z	LA, TA1 [*]	TA1	TA1, LA
	-y+z(HV)-y-z	LA, TA1 [*]	TA1	TA1, LA
	-y+z(HH)-y-z	LA, TA2 [*]	TA2	TA2

Table 8-6 continued.....

#11	y(VV)x	QL, QT	QL, QT	QL, QT
	y(VH)x	TA1"	TA1	TA1"
	y(HH)x	QT"	QT, QL	QT"
	y(VT)x	QL, QT, TA1	QL, QT, YA1	
	y(VV)z	QL, QT	QL, QT	QL, QT
	y(VH)z	TA1"	TA1	TA"
	y(HH)z	QT"	QT	QT"
	y(VT)z	QL, QT, TA1	QL, QT, TA1	
	-x(VV)-z	QL	QL, QT	QL, QT
	-x(VH)-z	TA1"	TA1	TA1"
	-x(HH)-z	QT"	QL, QT	QT"
	-x(VT)-z	QL	QL, QT, TA1	

* indicates that the observed mode is weakly visible.

(2) Determination of Pockel's coefficients

The formalism for determining the elastooptic constants or Pockel's coefficients of salol was developed in the previous section. The T_{ij} -component of the Brillouin scattering tensor for the α -mode containing one or several Pockel's coefficient is given by:

$$T_{ij} = [\hat{e}_j \cdot T \cdot \hat{e}_i] = 6.432 \times 10^{-6} \left(\frac{v_\alpha}{c_i c_j} \right) \left[\frac{(\Gamma_H)_{SAL}}{(\Gamma_H)_{BENZ} K_F} \right]^{1/2} \quad (8-6)$$

The K_F factor takes care of differences in collection time and polarization choice of a particular salol mode from the reference benzene spectrum which has been calibrated against quartz. The observed mode, frequency shift, sound velocity, and intensity relative to benzene $[(\Gamma_H)_{SAL}/(\Gamma_H)_{BENZ}]^{1/2}$ are all shown in table 8-7 for salol 11, 3, 8 and 7. The fifth column shows the T_{ij} component of the Brillouin scattering tensor for a particular mode for a specific polarization choice and scattering configuration. The sixth column shows the experimentally determined numerical value of that component for which the Pockel's coefficients can be computed.

Table 8-7

Sound velocity, intensity relative to benzene and
Brillouin scattering components of salol

Scattering configuration	Mode	Sound velocity [10 ⁵ cm/sec]	$[\hat{e}_s \cdot T \cdot \hat{e}_o]$ Tensor component	experiment- ally determined
salol 11				
y(zz)x	QL	2.352	$.4125 (b_{31} + b_{13} p_{32}) / \sqrt{2(1+b_1^2)}$	.0839
y(xy)x	QT	1.284	$.4158 (1+b_2) p_{66} / \sqrt{2(1+b_1^2)}$	.0437
y(zy)a	TA	1.426	$.2903 \quad p_{44} / \sqrt{2}$	.0297
y(xx)z	QT	2.844	$.4377 (p_{12} + b_{31} p_{13}) / \sqrt{2(1+b_1^2)}$	.1397
y(zy)z	QT	1.127	$.5201 (1+b_4) p_{44} / \sqrt{2(1+b_3^2)}$	.0445
y(xy)z	TA	1.347	$.291 \quad p_{66} / \sqrt{2}$	.0321
x(yy)z	QL	2.624	$.6577 (b_{21} + b_{51} p_{23}) / \sqrt{2(1+b_5^2)}$	.1030
x(zx)	TA	1.298	$.321 \quad p_{66} / \sqrt{2}$	.0300
salol #3				
-x+z(VV)x+z	LA	2.207	.8128 p_{21}	.1070
-x+z(HH)-x+z	LA	2.205	.378 $(p_{11} + p_{31})$	.0824
-x-z(VV)-x+z	LA	2.317	.929 p_{23}	.1284
-x-z(HH)-x+z	LA	2.325	.477 $(p_{32} + p_{33}) / 2$	.1097
salol #8				
x+y(VV)x-y	LA	2.655	.4306 p_{32}	.0971
salol #7				
-y-z(VV)y-z	LA	2.978	.578 p_{12}	.1932
-y-z(HH)y-z	LA	2.867	.556 $(p_{22} + p_{32}) / 2$	.1155

From table 8-7, computation of the Pockel's coefficients can be readily completed. The constants b_1, b_2, b_3, b_4 , and b_5 which are function of the C_{ij} 's can be calculated from the first set of C_{ij} 's shown in table 8-2 [for exact dependence of b 's on C_{ij} , see table 5-5 in chapter 5].

As can be seen from table 8-7, certain Pockel's coefficients are directly deducible from columns five and six. They are given by:

$$\begin{aligned}
 p_{66} &= 0.0438 \\
 p_{44} &= 0.0420 \\
 p_{55} &= 0.0501 \\
 p_{21} &= 0.1070 & (8-20) \\
 p_{23} &= 0.1284 \\
 p_{32} &= 0.0971 \\
 p_{12} &= 0.1932
 \end{aligned}$$

The rest of the Pockel's coefficient are determined by solving the following equations for the P_{ij} 's appearing in combined form in column five of table 8-7 with the help

of equation 8-20

$$\begin{aligned}
 P_{31} + 1.04 P_{32} &= 0.1714 \\
 P_{12} + 1.236 P_{13} &= 0.3140 \\
 P_{21} + 1.508 P_{23} &= 0.2636 \\
 P_{11} + P_{31} &= 0.1648 \\
 P_{23} + P_{33} &= 0.2194 \\
 P_{22} + P_{32} &= 0.2310
 \end{aligned}
 \tag{8-21}$$

The values of the Pockel's coefficients represented in matrix form are given in table 8-8.

Table 8-8

Pockel's coefficients of salol determined by isotropic consideration of the crystal and the mode intensity calibrated against quartz via benzene.

$$\begin{bmatrix}
 P_{11} & P_{12} & P_{13} & 0 & 0 & 0 \\
 P_{21} & P_{22} & P_{23} & 0 & 0 & 0 \\
 P_{31} & P_{32} & P_{33} & 0 & 0 & 0 \\
 0 & 0 & 0 & P_{44} & 0 & 0 \\
 0 & 0 & 0 & 0 & P_{55} & 0 \\
 0 & 0 & 0 & 0 & 0 & P_{66}
 \end{bmatrix}
 =
 \begin{bmatrix}
 .0944 & .1932 & .0977 & 0 & 0 & 0 \\
 .0698 & .1378 & .1284 & 0 & 0 & 0 \\
 .0704 & .0971 & .0910 & 0 & 0 & 0 \\
 0 & 0 & 0 & .042 & 0 & 0 \\
 0 & 0 & 0 & 0 & .0501 & 0 \\
 0 & 0 & 0 & 0 & 0 & .0438
 \end{bmatrix}$$

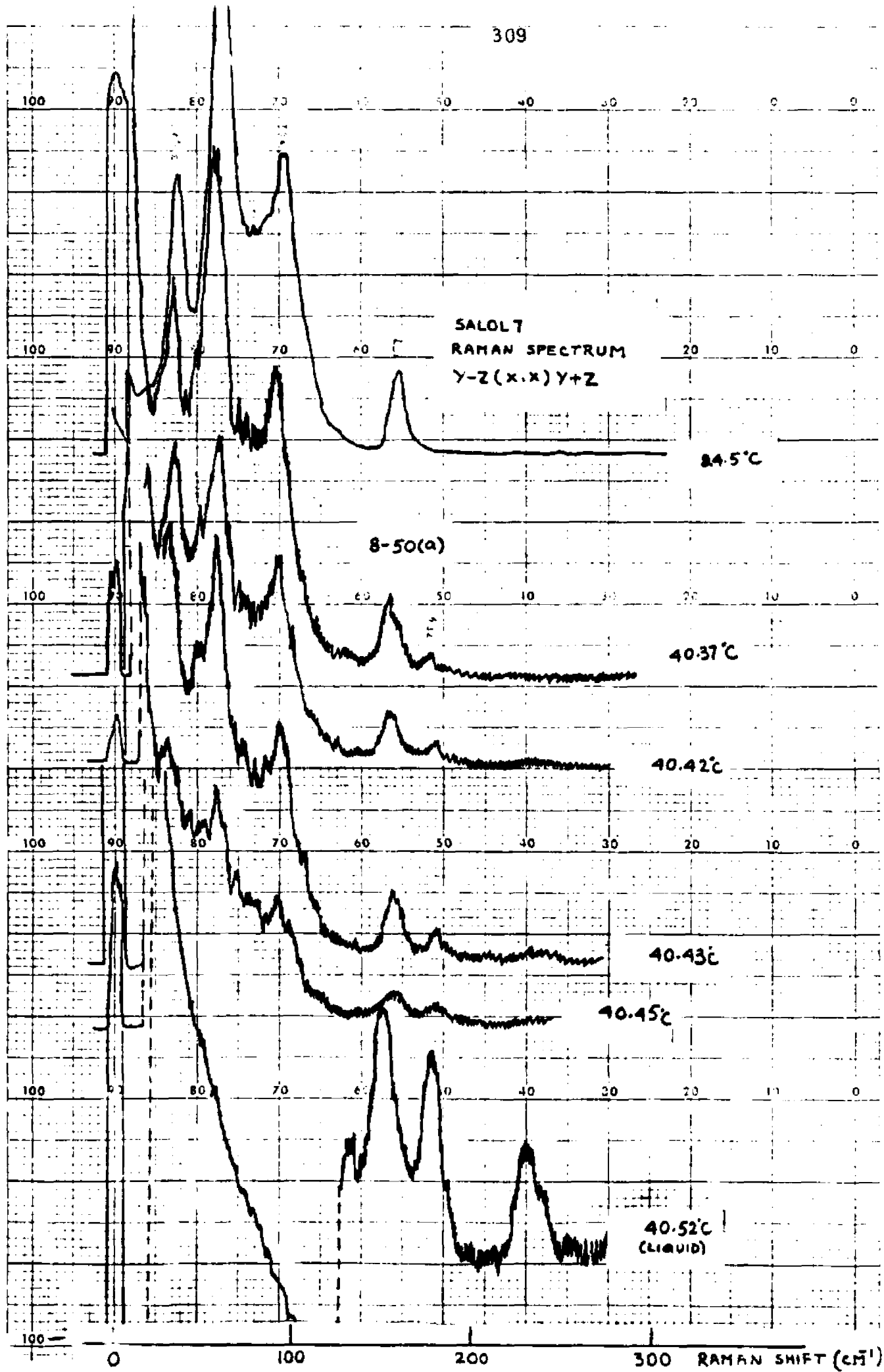
D. Results of Raman scattering experiments

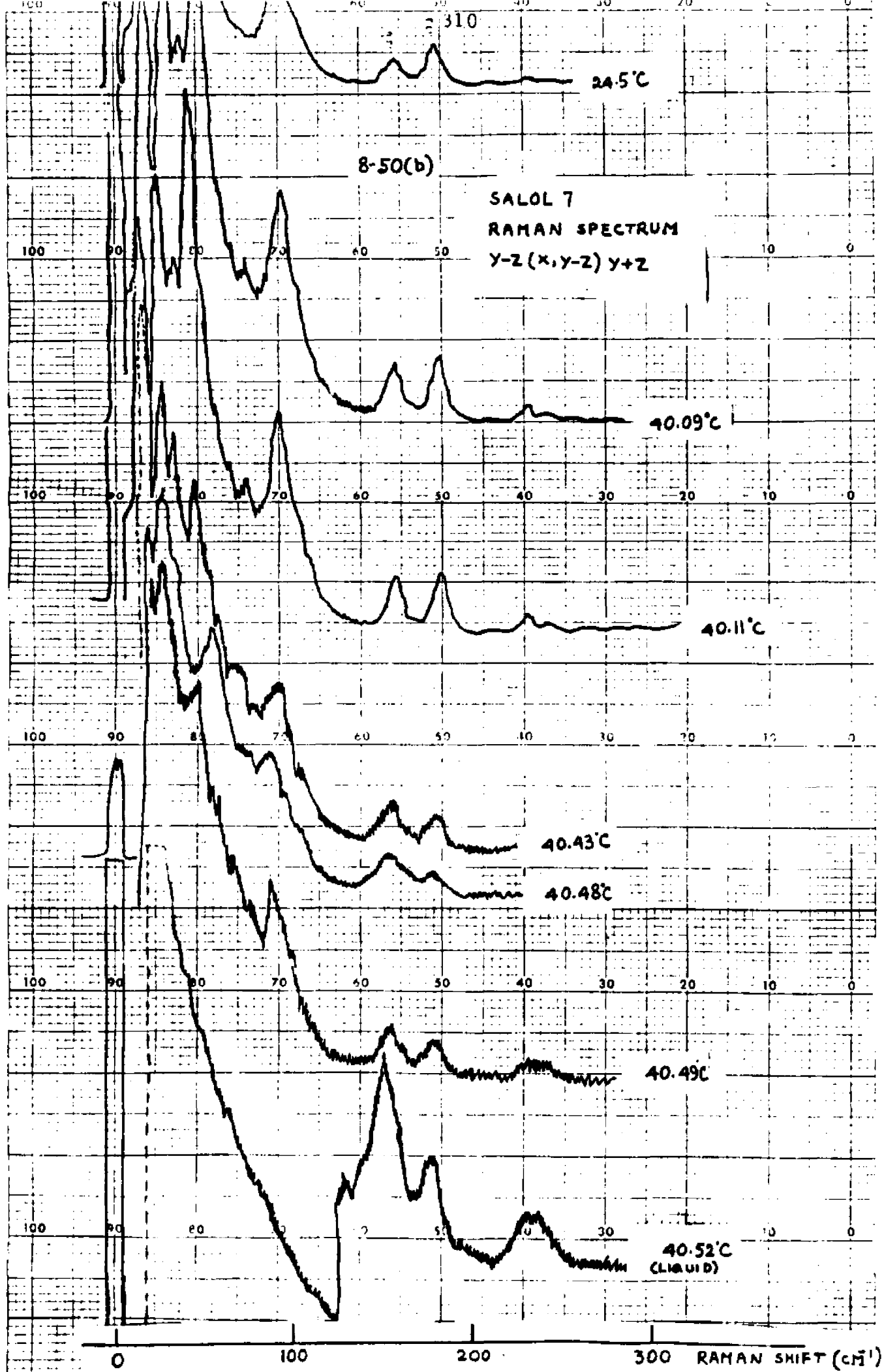
In chapter 7, I have summarized the Raman scattering experiments performed in the course of this work. No significant broadening of the optic modes was observed. The most notable feature of the Raman experiment was the temperature dependence of the relative intensity of different modes and the appearance of several new modes very close to T_m which will be described below. Although Raman experiments were performed on four different samples with similar results, I chose Salol 7 for the presentation of results since those changes were most distinct in it.

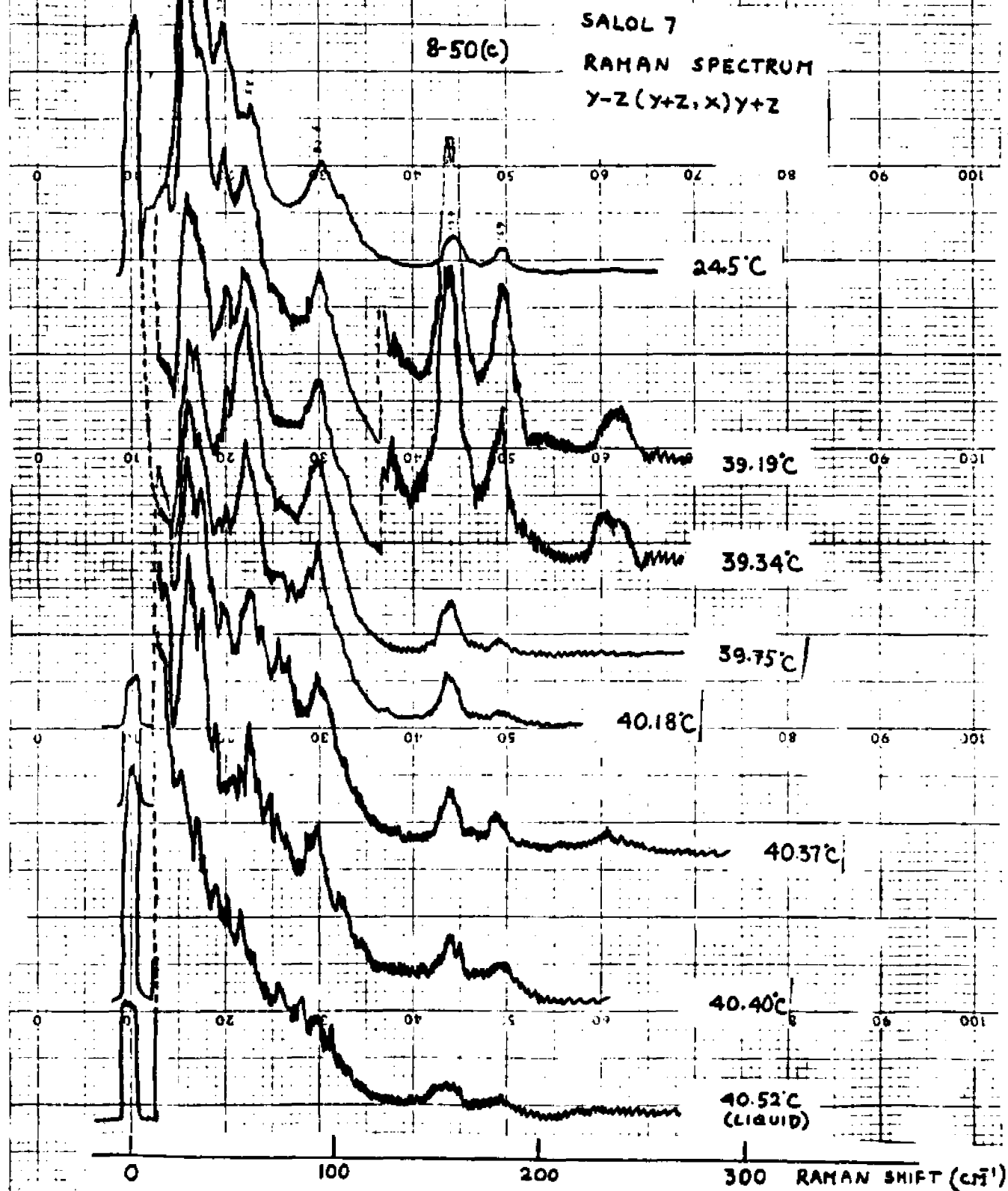
(1) Temperature dependence of relative intensities

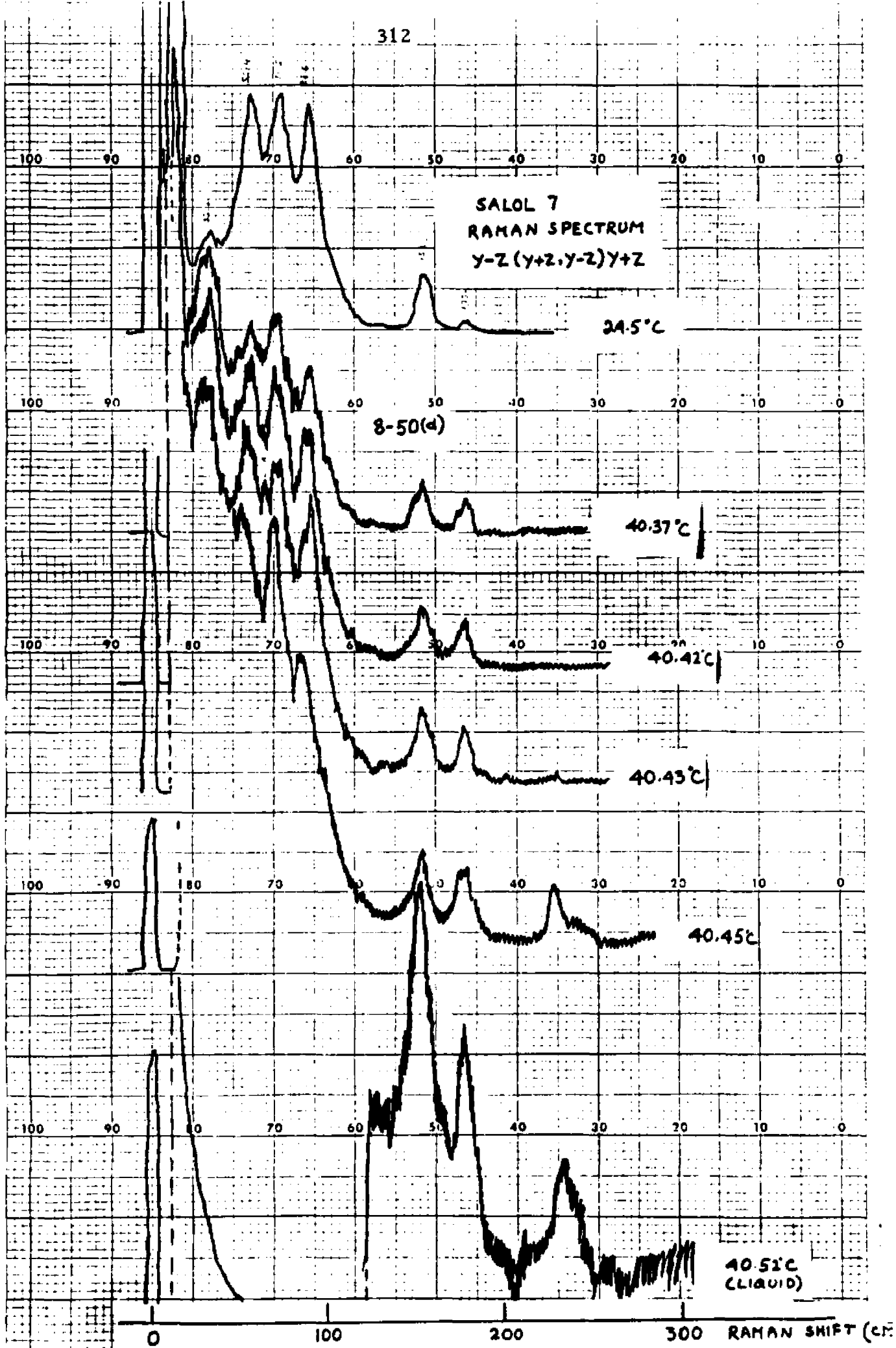
The temperature dependence of the relative intensities of various optic modes can be visualized from figures 8-50 (a), (b), (c) and (d), each of which shows a slow scanned ($50 \text{ cm}^{-1} / \text{min}$) Raman spectrum of Salol 7 in scattering configurations: $X-Y(ZZ)X+Y$, $X-Y(Z,X-Y)X+Y$, $X-Y(X+Y,Z)X+Y$ and $X-Y(X+Y,X-Y)X+Y$. respectively. The Raman spectra from room temperature to T_m as well as one liquid spectrum in the vicinity of T_m are shown in each of those figures. Except for this qualitative visualization of the changes in relative intensities of Raman modes, no further analysis was attempted. Figure 8-50(b) shows that the 16.6 cm^{-1} Raman mode, almost invisible at room

Fig. 8-50: Summary of the Raman experiment results on salol 7. A qualitative comparison between the various mode strengths is obtained by plotting the low frequency Raman modes on the same scale for various scattering configurations: (a) $Y-Z(X,X)Y+Z$ (b) $Y-Z(X,Y-Z)Y+Z$ (c) $Y-Z(Y+Z,X)Y+Z$ (d) $Y-Z(Y+Z,Y-Z)Y+Z$ $T_m = 40.45^\circ\text{C}$ (due to laser melting). The changes of the relative intensities in the Raman modes as the crystal is brought to melting is clearly visible. For comparison, a liquid spectrum near T_m is also shown. From inspection of the mode structure, the solid seem to transform into the melt continuously. (5145 Å argon ion laser. $P = 135$ mW. Spectra recorded on a strip chart recorder).









temperature, gradually becomes the dominant mode as the crystal was heated to melt. Also, sharp changes in the relative intensities of the 26.8 cm , 33.7 cm and 44.8 cm modes can be observed in fig. 8-50(b) between room temperature and T_m . The changes of lineshapes of the modes from solid to liquid looked like a continuous process. A gradual decrease of the 88.6 cm mode intensity with increasing temperature is shown in fig. 8-50(b).

The changes of relative intensity may also be interpreted as due the generation of defects close to melting, modifying the usual selection rules. That could make it possible to detect some modes in VH polarization which are normally observable only in (VV). The temperature dependence of the depolarized intensity is shown in fig. 8-51.

(2) Defect activated Raman modes

The generation of defects close to T_m may also give rise to some totally new Raman modes by breaking the local symmetry of the crystal[16]. Several such Raman modes were observed in the melting experiment. By comparing the room temperature crystal spectrum and the liquid spectrum of salol 7 in the same plot, the appearance of such new modes can be observed in figs. 8-52, 8-53 and 8-54.

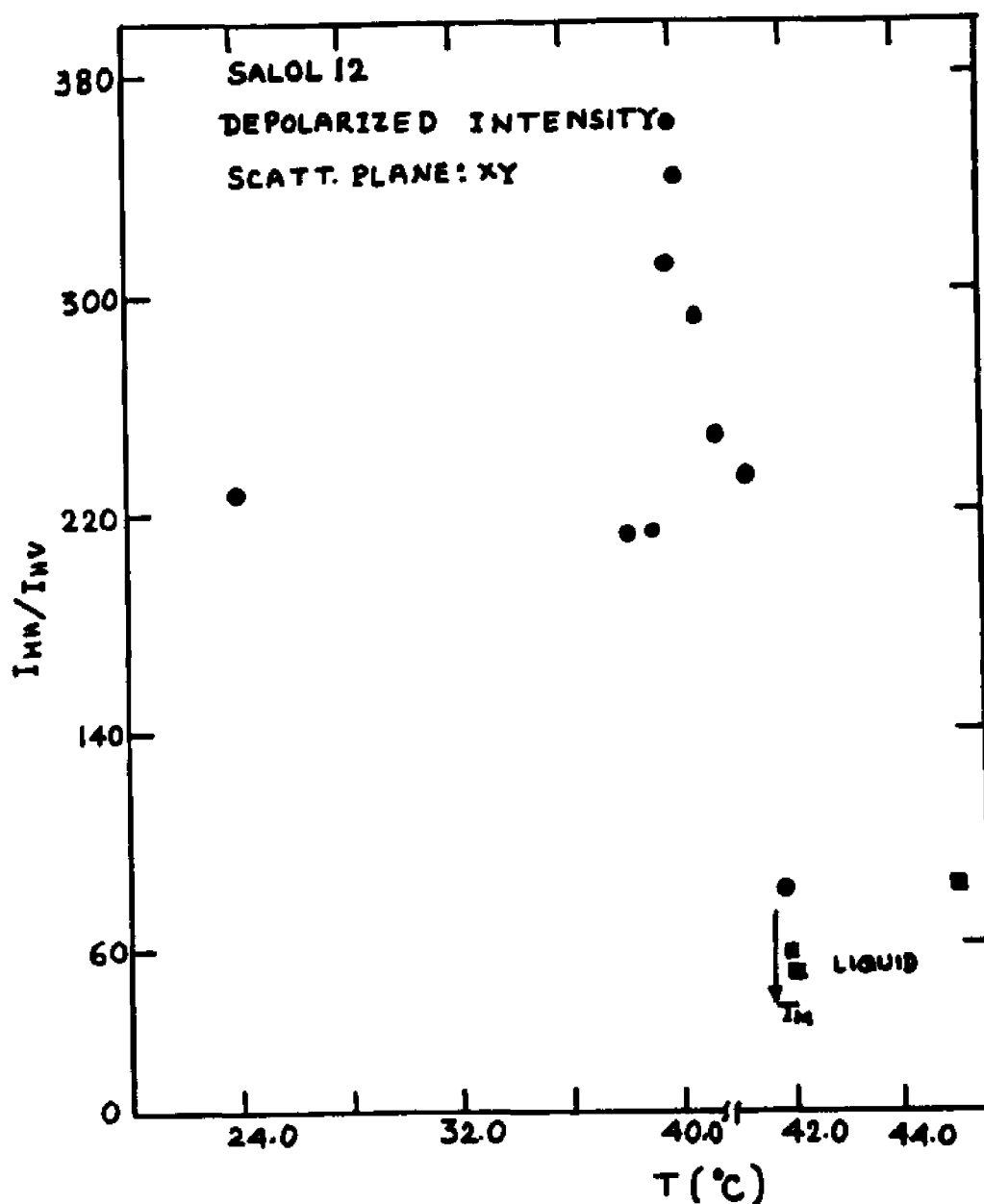


Fig. 8-51

Depolarized intensity salol 7 vs temperature. The temperature dependence of the ratio I_{HV}/I_{HH} shown in the figure increases rapidly near T_m , where I_{HV} is the intensity of the transmitted light (through crystal) with incident polarization in the yz plane and transmitted polarization along x. The sudden increase of I_{HV}/I_{HH} near T_m suggests of rotations of the atoms near T_m and polarization rotation.

Fig. 8-52: Raman spectra of salol 7, scattering configuration $Y-z(x,x)y+z$ recorded up to 2000 cm^{-1} , at three temperatures of including spectra in both the solid and liquid close to T_m . The defect activated modes which appear near T_m in the solid (shown by arrows) supports the hypothesis of defect mediated melting.

Fig. 8-53: Defect activated modes in salol 7 in scattering configuration $Y-Z(Y+Z,X)Y+Z$ [HV]. The new modes which were present neither in the low temperature solid nor in the liquid near T_m , are shown by arrow.

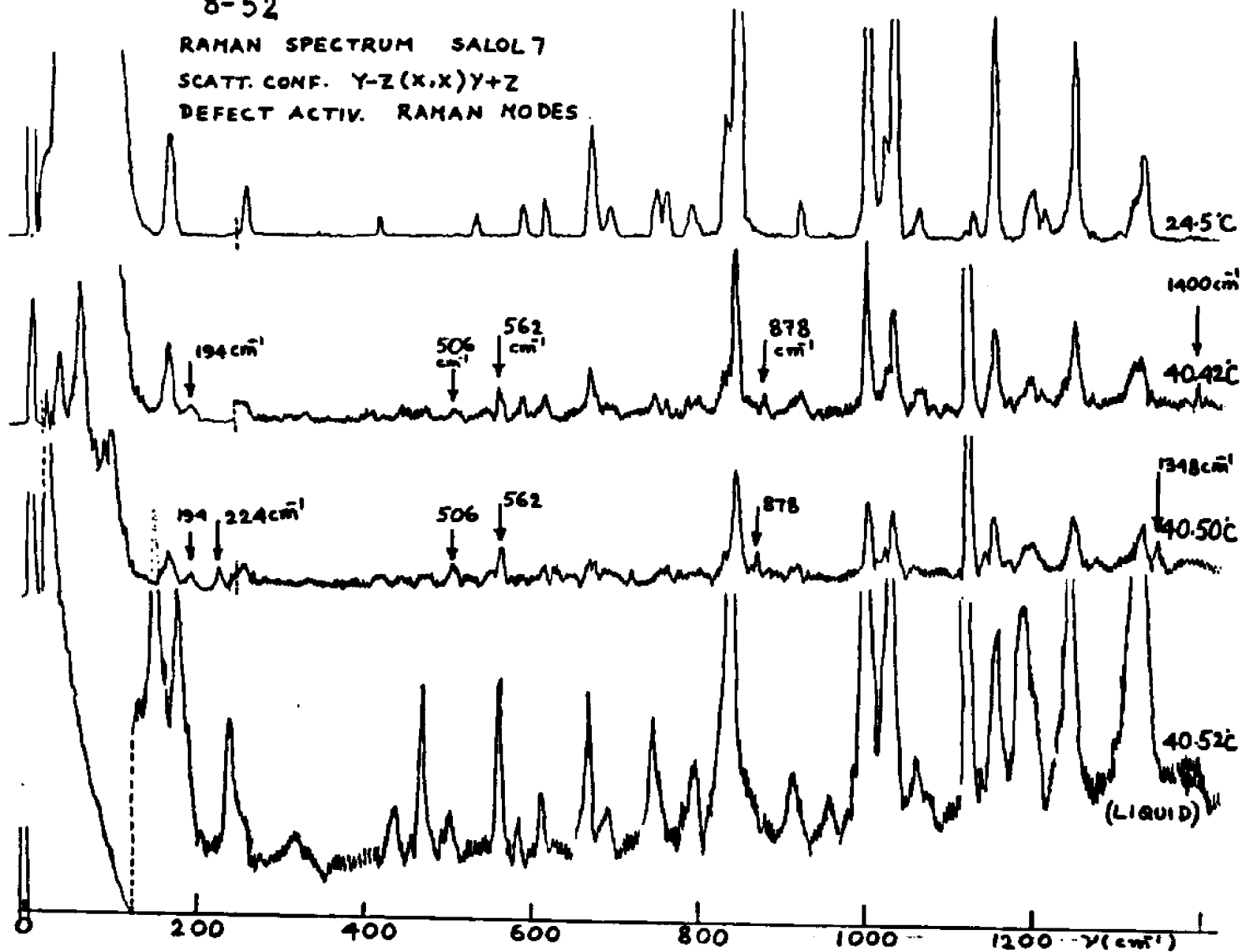
Fig. 8-54: Defect activated modes observed by Raman scattering measurements on salol 7 in $Y-Z(Y+Z,Y-Z)Y+Z$ [HH] configuration. The new modes are shown by arrows.

8-52

RAMAN SPECTRUM SALOL 7

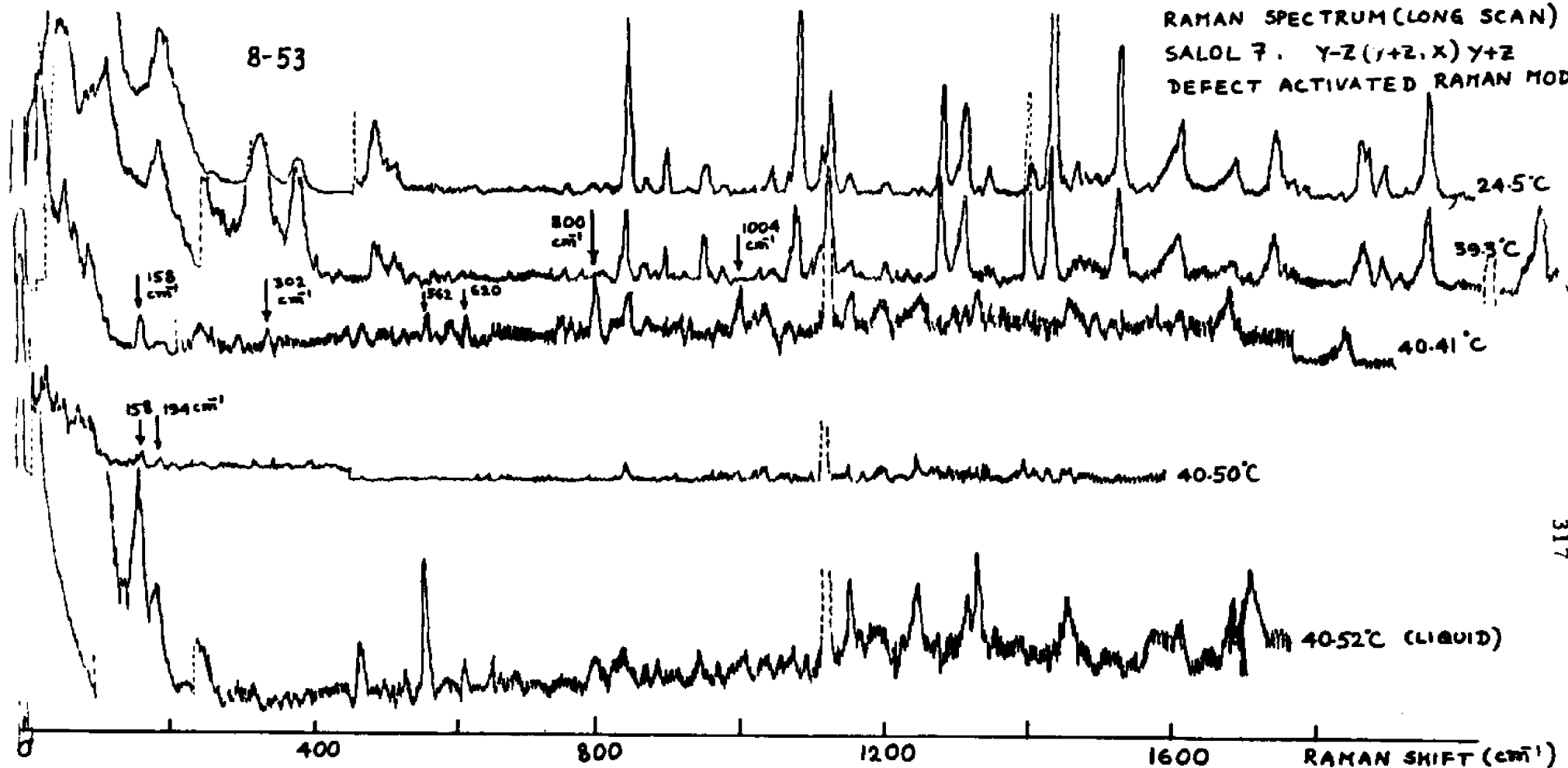
SCATT. CONF. Y-Z (X,X) Y+Z

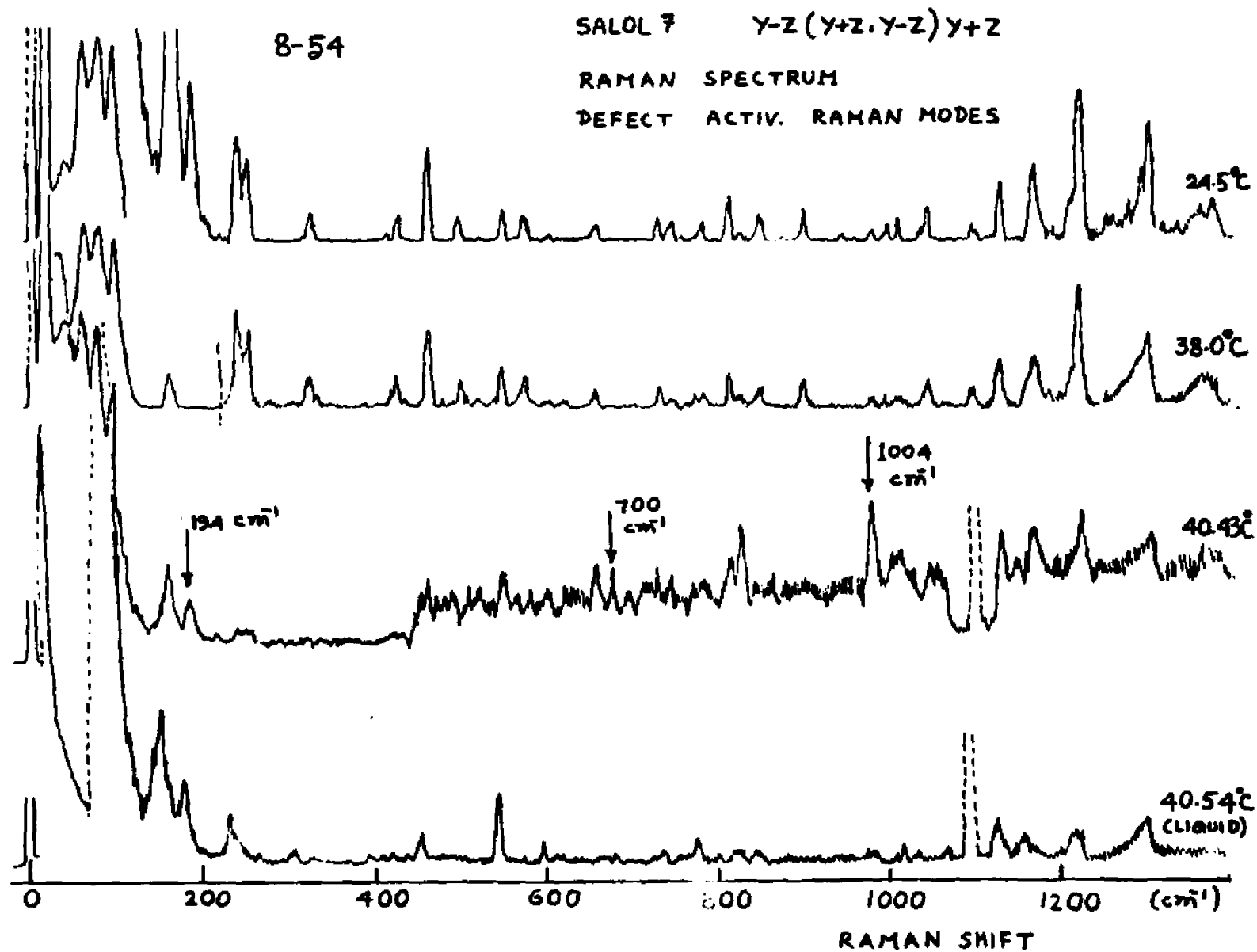
DEFECT ACTIV. RAMAN MODES



8-53

RAMAN SPECTRUM (LONG SCAN)
SALOL 7. γ -Z (γ +Z, X) γ +Z
DEFECT ACTIVATED RAMAN MODES





These spectra are fast scanned ($100 \text{ cm}^{-1} / \text{min}$) and contain Raman modes up to 2000 cm^{-1} . Modes at 224 cm^{-1} , 878 cm^{-1} and 1348 cm^{-1} in figure 8-52 in $Y-Z(X,X)Y+Z$ at 40.50°C which are totally absent in both room temperature and liquid spectra are believed to be defect activated lattice modes. The other new Raman modes observable close to T_m which were also absent at room temperature were continuously growing liquid modes. Table 8-9 summarizes the results of figs. 8-52, 8-53 and 8-54. From the table, it can be seen that the eight new modes (totally absent in room temperature and liquid) assumed to be activated by defect generation are 224 cm^{-1} , 878 cm^{-1} , 700 cm^{-1} , 134 cm^{-1} , 1004 cm^{-1} , 800 cm^{-1} and 1400 cm^{-1} . A detailed theoretical discussion of defect activated Raman scattering can be found in [16].

Table 8-9

Defect activated Raman modes for various scattering configurations of salol 7 are shown close to the melting point

Temperature Observable modes at specific locations
[in units of cm^{-1}]

("none" indicates the absence of the Raman mode at the specified location at temperature shown)

scattering configuration Y-Z(VV)Y+Z:

24.5°C	none	none	none	none	none	none	none
40.50°C	194	224	506	562	878	1348	1400
40.52°C	none	none	506	562	none	none	none (liq.)

scattering configuration Y-Z(VH)Y+Z:

24.5°C	none	none	none
40.43°C	194	700	1004
40.54°C	194	none	none (liquid)

scattering configuration Y-Z(HV)Y+Z:

24.5°C	none	none	none	none	none	none	none
40.41°C	158	194	302	562	620	800	1004
40.52°C	158	194	none	562	620	none	none(liquid)

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CHAPTER IX

DISCUSSION OF RESULTS AND CONCLUSIONS

(A). Introduction

This thesis involved a study of the melting transition in crystalline salol by Raman and Brillouin scattering spectroscopy. In the Brillouin scattering experiments, the frequency shift and linewidth were measured accurately to within 0.005°C of the melting point of the crystal. The velocity and attenuation of the propagating hypersound waves were determined from those values. The resulting temperature dependent attenuation of the hypersound waves was analyzed in the context of the dislocation theory of melting and the results were presented in both graphic and tabular form in chapter 8. The anomalies observed in the velocity of sound as well in the elastic constants near T_m were also presented in chapter 8, and discussed qualitatively in the context of Born's theory of melting.

Due to the absence of any fully structured theory of melting, I could not compare my results with quantitative theoretical predictions. This is the main reason for the

qualitative interpretations of the results presented here. In the first part of this chapter I shall mention various current experimental and theoretical work on melting whose results may show a close similarity with different parts of my results. In section C I shall point out experimental improvements and modification for future investigations of the melting problem. I shall present conclusions of my work in section D.

(B) Discussion and Interpretation of results

There are four parts of the results. The first two parts consist of the Brillouin frequency shift (or hypersonic velocity) and linewidth (or attenuation of hypersound) measurements on four different samples. The third part consists of the determination of elastic and elasto-optic constants of salol by the Brillouin scattering technique. Discussion on the Raman scattering results of the melting experiment will be presented in part four.

(1) Brillouin Shift

(a) Changes in elastic modulus: Born's instability criteria

The temperature dependence of the Brillouin shifts from room temperature up to T_M for various samples are

presented in graphical form in chapter 8. Though similar results were already reported for ultrasonic measurements on molecular crystals [1,2], the continuous downward bending of the longitudinal and transverse sound velocities in salol up to T_M , determined by Brillouin scattering measurements, is reported here for the first time. Born's stability criteria for orthorhombic structure salol are:

$$C_{44} > 0, C_{55} > 0, C_{66} > 0 \text{ and } C_{22}C_{23} - C_{23}^2 > 0 \quad (9-1)$$

According to Born's conjecture, the crystal would melt if any of those shear elastic moduli vanishes. Since none of those elastic constants decreased to zero near T_M , Born's melting criteria could not be verified in this work. However, the downward bending of the Brillouin shifts in figs. 8-9 through 8-12 shows that none of the velocities decreases by more than 20% to within 0.01°C of T_M . In order to satisfy Born's conjecture, the remaining 80% decrease of velocity would have to occur within the last 0.01°C before melting, which is at best a remote possibility. With this result, Born's picture of the melting phenomenon as a continuous transition with order parameter C_{44} can be effectively ruled out.

A similar decrease of the elastic constants of BaF_2 was reported by Catlow et al [3] (see fig 2-3) who measured the temperature dependence of C_{11} , $C_{11}-C_{12}$ and C_{44} . The measured linear decrease below T_c (region I) was attributed to the 3% lattice expansion and the additional decrease near T_c (region II) was attributed to formation of about 25% interstitial fluorines near T_m . Such an approach could also be followed to explain the 20% reduction of the elastic constants of salol in order to determine the contribution of generated defects (dislocations) near T_m in lowering the sound velocity of all three modes.

Though the shear modulus is not zero at T_m , one should note that melting may still involve shearing deformations caused by generated defects. Dislocations could be generated by thermal activation near T_m and could produce shear if they had the appropriate Burger's vector. Theories that are related to that of Born have invoked dynamic instability in certain vibrational modes. As the temperature increases, the interatomic interaction leads to thermal expansion, a decrease in the strength of the coupling forces and to a lowering of the vibrational frequencies. It was suggested with the concept of "vibrational" elongation that beyond a certain point, no

further energy can be fed into the vibrations, so it goes into producing disorder[4]. Alternatively there is a possibility that certain vibrational frequencies became imaginary beyond T_m thereby overdamping the oscillations and producing permanent displacements that may give rise to melting.

As can be seen in figures 8-16 through 8-20, the temperature dependence of $\nu_{BGD} - \nu_B$ has a close similarity to that of the Brillouin linewidths shown in figures 8-21 through 8-27. The $\nu_{BGD} - \nu_B$ data were obtained by subtracting ν_B from the change in ν due to thermal expansion (ν_{BGD}), and thus represents the temperature dependence of the frequency shift over and above that due to thermal expansion. The previous discussion suggests a reduction in the frequency shift due to the effect of defects. Since the increase of Brillouin linewidth (to be discussed later) was attributed to the phonon-dislocation interaction, one can compare the temperature dependent behavior of both linewidth and $\nu_{BGD} - \nu_B$ in order to explore the relation between them.

(2) Brillouin linewidth

Several recent direct experimental studies of the melting process through x-ray and high voltage electron

microscope techniques [5,6] have established the fact that melting is mediated by the growth of the dislocation density near T_m . Since the dislocations, by their collisions with the propagating elastic waves in the solid, may affect the lifetime of those modes remarkably, a study of the attenuation of such modes as a function of temperature up to T_m should also reveal some facts about the role of dislocations in the melting process.

Therefore, the observed temperature dependent ultrasonic attenuation of all the modes up to T_m were interpreted by a simple dislocation model of melting in this work.

The first suggestion of a dislocation theory capable of describing part of the internal friction and modulus changes in metals due to the motion of dislocations came from Read in 1941 [7]. Later on, a quantitative theory of the damping and modulus changes due to motion of dislocations was developed by Granato and Lucke [8], with a model analogy between the motion of a dislocation line segment pinned down by an impurity, and that of a forced damped vibration of a string. In the present work, the temperature dependent ultrasonic attenuation of the acoustic modes was interpreted by a simpler dislocation model. In that model, the increasing number of dislocations causes a proportional increase in the

attenuation of the propagating sound waves, represented as

$$\Gamma(\tau) \sim \mathcal{S}_D(T) = \mathcal{S}_0 \exp(-E_D(T)/k_B T) \quad (9-2)$$

The right hand side of equation (9-2) represents the temperature dependence of the dislocation density $\mathcal{S}_D(T)$, with $E_D(T)$ being the temperature dependent formation energy. From equation (9-2), one can easily extract the temperature dependent behavior of the formation energy $E_D(T)$ from the measured $\Gamma(T)$ (shown in figs 8-21 through 8-27) by assuming a constant phonon-dislocation scattering cross-section $\mathcal{S}$. The temperature dependence of the dislocation formation energy $E_D(T)$ determined by this model is shown in figs. 8-31 through 8-43 for various assumed values of the background linewidth. The plotted energies show a continuous decrease with increasing temperature. Quantitatively, a decrease in $E_D(T)$ of 60% from its room temperature value could be recorded within 0.02°C of T_m , indicating the onset of a significant growth of dislocation concentration close to T_m , which is the essence of the dislocation theory of melting suggested by Mizushima, Nabarro, Cotteril, Kuhlman-Wilsdorf and many others.

In calculating the formation energy E_D , the only

parameter which could not be independently determined was the background linewidth Γ_B (due to other anharmonic interactions). However, lower and upper limits of Γ_B could be estimated from the temperature dependent linewidth measurement. Therefore, energy plots were shown for three different assumed Γ_B 's which were 0%, 50% and 70% of the average room temperature linewidth. It is seen in figs. 8-31 through 8-35 that the choice of Γ_B does not affect the qualitative behavior of $E_D(T)$, although its absolute magnitude is clearly affected by the choice.

Although the present dislocation model procedure used to deduce the defect formation energy from the measured Brillouin linewidth had not been employed previously, similar approaches have been reported by many authors. In the elastic neutron scattering study of the melting of submonolayers absorbed on Grafoil, Feile, Wiechert and Lauter [9] interpreted the temperature dependence of the nearest neighbor distance by a simple model assuming the melting transition to be driven by thermally created lattice defects. They extracted the vacancy formation energy $E_D(T)$ by assuming the change in nearest neighbor distance Δa_{NN} to be proportional to the defect concentration given by :

$$\frac{\Delta a_{NN}}{a} \sim C(T) = C_0 \exp [S - E_D(T)] / k_B T \quad (9-3)$$

In another work, Iwasa and Suzuki [10] interpreted their observed decrease in hypersonic velocity v by a simple defect-phonon interaction model given by:

$$\frac{\Delta v}{v} \sim \exp [\bar{\Phi}(T) / k_B T] \quad (9-4)$$

where $\bar{\Phi}(T)$ is the vacancy formation energy.

(3) Dependence due to sample, crystal purity and mode

The parameters measured in this experiment seem to show a dependence on samples, their degree of purity and growth condition as well as on the Brillouin modes from which they were determined. Following is a discussion of such dependence.

(a) Defect formation energy

From the $E_D(T)$ vs T plots one can see that the behavior (curvature) of the defect formation energy around T_m deduced from the Brillouin linewidth is not substantially different between Salol A,B or 18. Only the absolute values of the energies seem to show a sample dependence which could be related to differences in factors such as growth condition, crystal purity, presence of other defects etc. The apparent mode dependence of the magnitude of the defect formation energy for the same

sample is shown in figs. 8-37(a), (b) and (c) . The absolute magnitudes of the energies seem to diverge from each other for LA, TA1 and TA2 modes significantly for $T_B > 0.5 T(RT)$, when the assumed background value of the linewidth exceeds 50% of that of its room temperature value. The least amount of decrease in the formation energy is observed in the case of LA modes of all the samples, specially in salol A, indicating the scattering cross section of dislocation-LA Phonon collision to be the smallest. The average magnitude of the formation energy which is on the order of 100 meV seems to be consistent with the theory of defects.

(b) Brillouin shift

Following the study of McFarlane, Courtens and Bischofberger[11] who studied the refractive index n of succinonitrile near T_M and found a discontinuous drop in n for a very pure crystal, whereas a downward bending was observed in n with a small residual impurity concentration present, I also performed a melting experiment with three different samples of succinonitrile grown with two, five and ten zone refining passes, respectively. No apparent differences could be observed in the temperature dependence of the Brillouin shifts (see fig. 8-15) for SUCC D5, SUCC D3 and SUCC ED5 samples.

(c) Melting point T_m

The melting temperature showed an observable change in different samples, at different purity and sample location. In an experiment which determined T_m accurately with samples immersed in various materials (air, water, glycerol, paraffin oil and ethylene glycol), the T_m in one fluid (glycerol) was found to be 0.06°C higher than that in air. The pressure dependence (pressure of the liquid column) of T_m must have caused this variation. Besides, the melting point T_m for salol A (solution grown) was also found to differ from the others. The melting point in succinonitrile was found to be consistently higher for the samples grown with a larger number of zone refining passes.

(4) Effect of misorientation

Since salol is a highly anisotropic crystal, the effect of a slight misorientation of the sample ($\approx 11^\circ$) was very apparent in the number of Brillouin modes observed. As can be seen in fig.8-48 (a), (b) and (c), the raw spectra of salol 16, salol 1 and salol 11 at $y(ZT)x$ configuration, one can count the total number of Brillouin modes to be five, four and three respectively. The extra

modes are due to the misorientation of salol 16 and salol 1 by $\Psi = 11^\circ$ (error during sample cutting), where the third spectrum was taken from a correctly oriented sample, salol 1. All the spectra were obtained with the same scattering configuration and FPP plate spacing, $d=15.40$ mm. The extra modes of salol 16 and 1 were explained by a calculation in section 5-c(3) where the Brillouin scattering tensor was calculated for all the modes at $y(z,z)x$ and $y(zy)x$ scattering configuration with anisotropic considerations. It was found that up to six different Brillouin modes may be observed at $Y(ZT)X$ [$=Y(ZZ)X+Y(ZY)X$] scattering configuration for such a misoriented crystal.

(5) Room temperature results

From the measured Brillouin shift and linewidth of the three observed acoustic modes of Salol 11, 3 and 7, I determined the complete set of room temperature elastic and elasto-optic constants of salol. The results are presented in matrix form in chapter 8 (tables 8-2 through 8-8). A second set of elastic constants was also determined from the measured Brillouin spectra recorded at VV, VH and HH scattering configuration, where the eigenvalue for the elastic constants was calculated with

the anisotropic optical properties of salol included as described in chapter 5. The C_{ij} values obtained by anisotropic consideration were found to be significantly different than those obtained by isotropic consideration (see table 8-7), specially the C_{12} component.

Another effect of the crystal anisotropy is shown in table 8-6. The observation of a Brillouin mode which was not predicted by an isotropically calculated selection rule, was shown to originate from the crystal anisotropy, as was predicted by the anisotropic calculation for salol 3 and salol 8.

(6) Results of Raman scattering experiments

(a) Defect activated Raman modes

The observation of defect activated Raman modes has been reported by many experimentalists. By breaking the local symmetry of crystals, the generation of defects may make it possible to observe some new modes which are usually forbidden by the Raman selection rules. These are called defect-activated Raman modes. A detailed discussion can be found in Loudon and Hayes's recent book on the scattering of light by crystals.

Such defect-activated Raman modes observed very close

to melting in the present experiment were shown by arrows in figs. 8-52 through 8-54. By comparing the spectra of fig. 8-52 at T_m with those at room temperature and of the melt near T_m , one can clearly see that the indicated components are only observed close to T_m in the solid. This observation also suggests a rapidly increasing defect generation close to T_m which further supports the defect theory of melting. Disorder-activated Raman scattering in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys was reported by Saint Cricq et al [12]. A detailed investigation of the effect of disorder on Raman scattering by fluorite crystals can be found in the recent work of Elliot et al [13].

(b) Relative Intensity change: Molecular rotation

The most distinctive result in the Raman scattering experiment on the melting of salol was the observed changes in the relative intensity of the low frequency Raman modes. We assume that these changes are due to rotations of the molecules at or near T_m . The sharp increase in the intensity of depolarized light near T_m shown in fig. 8-51 is also evidence of rotation of polarization of the incident light by the molecules. In order to visualize these changes in the relative

intensity, the single plot diagrams at a particular scattering configuration but at various temperatures up to melting are shown in fig. 8-50(a), (b), (c) and (d).

Such an observation of molecular rotation near T_m is not new. Ichishima [14] in his Raman experiment in benzene crystals through the melting transition, showed evidence of molecular rotation. Tohji and Murata [15] in their x-ray diffraction study of premelting and melting of benzene, reported intensity changes of Bragg peaks at the pre-melting stage due to changes in the average molecular motions of the atoms. They also found that the molecular structure of the solid just below T_m is similar to that of a liquid. The last two salol Raman spectra (fig. 8-50), one in the solid just below T_m and the other in the melt, look similar. No continuous line broadening or gradual softening of the Raman modes was observed.

(C) Conclusions

Brillouin scattering experiments on the melting transition in salol were reported for the first time in the present work. A plane Fabry Perot interferometer was used both in single pass and triple pass in the experiment providing a finesse of 50 and 80 respectively. In the melting experiment with salol, Brillouin and Raman spectra

were obtained at temperatures within 0.005°C of T_m . The Brillouin spectra were analyzed by a nonlinear least square fitting program to determine the frequency shifts and linewidths of the Brillouin components. The observed linewidth was analyzed by a simple model, assuming the melting process to be driven by thermally activated dislocations whose concentration grows very rapidly near T_m , and brings about melting by disrupting the crystalline structure.

The observed Brillouin shifts were compared qualitatively with Born's instability criterion of crystals, which states that a solid melts when its shear modulus vanishes. Though the frequency shifts did not go to zero near T_m , clear evidence of continuous decrease of the elastic constants was observable. The least amount of change was observed for the elastic constants associated with the pure LA or Quasi-LA modes. A short discussion was also given of the possibility of phonon-defect interactions in reducing the sound velocity, as was done by Catlow [3].

With a simple dislocation model of melting, assuming the observed hypersonic attenuation to be proportional to the phonon concentration (the scattering cross section of dislocation-phonon collisions was assumed constant), the

dislocation formation energy was determined from the temperature dependent data of the observed linewidth. The temperature dependence of the formation energy which was determined by that model showed strong decreases near T_m . The dislocation formation energy $E_D(T)$ was found to be continuously decreasing function of the temperature with a large downward bending around T_m for all three samples and all of their modes. This clearly showed the possibility of a sudden growth of dislocations near T_m (because of substantial reduction in formation energy). Growth of dislocations near T_m has also been seen by high voltage electron microscopy[19,20]. A qualitative correlation was attempted between the temperature dependence of $\Gamma(\text{linewidth})$ and that of $\nu_{BGD} - \nu_B$, where ν_{BGD} includes the temperature dependent frequency shift due to thermal expansion. A comprehensive review of past experimental and theoretical studies of the melting transition was given which shows that the current analysis of the observed Brillouin linewidth in the context of the dislocation model of melting is one of the first of its type. In short, the present experimental results test both the Born theory of melting (partially) and the dislocation theory of melting.

A complete set of Brillouin spectra from six different samples were also taken at room temperature to determine the full set of elastic and elastooptic constants of salol. The Brillouin scattering tensor for each of the experimental scattering configuration was calculated both by isotropic and anisotropic considerations. The extra modes observed in some samples which could not be explained by isotropic considerations were explained by anisotropic considerations. The values of C_{ij} and P_{ij} for salol were determined for the first time by the Brillouin scattering technique (ultrasonic data have not been reported so far, which precluded a comparison). The highly anisotropic properties of salol could be observed in the Brillouin spectra of slightly misoriented ($\Psi=11^\circ$) samples which showed as many as six different modes. Melting experiments on succinonitrile samples grown with various purity levels were also performed. The continuous decrease of hypersonic velocities for three different samples with different orders of purity were observed to be similar.

In the Raman experiments the changes observed in relative mode intensities resembled x-ray studies of Tohji where changes in relative intensities of Bragg peaks were observed near T_m [15] in benzene. Only a qualitative analysis of Raman data was made in a single plot to

visualize those changes in relative intensities which indicate an internal molecular rotation near T_m . Several defect-activated Raman modes were also observed very close to T_m which were totally absent in both the solid at room temperature and in the melt. This observation also supports the defect mediated theory of melting.

(D) Considerations for future melting experiments

In the present study we indirectly deduced information about the effect of defect-phonon scattering on the hypersonic attenuation and velocity by the Brillouin scattering technique. Another possible approach to the study of the melting transition is through direct scattering of light, neutrons or electrons by vacancies or defects. A calculation on the scattering process between phonons and dislocations was initiated by Liebfried [16] in 1956. A theory on the scattering of light by crystal imperfections including dislocations was discussed by Theimer and Plint [17]. For a more detailed discussion on the scattering of dislocation by light, x-ray, electron or neutron beams, the reader should consult the most recent edition of Nabarro's theory of dislocations [18]. Glass,

Boff. and Bilello [19] calculated the cross section for inelastic neutron scattering by dislocation associated modes in crystals.

Martin, Parodi and Parshan [20] have discussed the general hydrodynamics of crystals and have shown that a crystal must have eight hydrodynamic modes; three pairs of sound waves, a heat transport mode and a vacancy diffusion mode. Flemming and Cohen [21] have shown that in the light scattering spectrum of crystals there will be a contribution to the Brillouin linewidth due to coupling with the vacancy diffusion mode. They also suggested that the light scattering spectrum of a crystal near T_m where the vacancy concentration is high should have a quasi-elastic line separable into components described by the thermal diffusion and vacancy diffusion constants respectively. If there is a very rapid buildup in defect concentration near T_m (as predicted by the defect theory of melting), then the intensity of the quasi-elastic line due to vacancy diffusion should increase rapidly as T_m is approached while its linewidth could give the temperature dependence of the vacancy diffusion constant directly.

Another preliminary investigation of both the intensity and correlation function of light scattered by NaCl was reported by Pike and Vaughan [22]. They found that the total scattered intensity decreases with increasing temperature in NaCl, presumably because the radius of the charge cloud (to which light couples) surrounding the dominant anion vacancy decreases with temperature faster than the vacancy concentration increases. This extremely interesting preliminary result indicates the need for additional experiments very close to T_m where one might expect the rapid increase in vacancy concentration to dominate.

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APPENDIX A

CALCULATION OF BRILLOUIN SCATTERING TENSOR FOR QUARTZ IN $X(ZZ)\bar{Y}$ CONFIGURATION AND ELASTIC AND ELASTO-OPTIC TENSORS OF SALOL

The calculation follows the general procedure described in chapter V. For the scattering configuration $X(ZZ)\bar{Y}$,

$$\hat{q} = \frac{1}{\sqrt{2}}(110).$$

Using the elastic tensor (C_{ij}) and Pockel's tensor (P_{ij}) of Quartz:

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & C_{66} \end{bmatrix}$$

$$\begin{bmatrix}
 P_{11} & P_{12} & P_{13} & P_{14} & 0 & 0 \\
 P_{12} & P_{11} & P_{13} & P_{14} & 0 & 0 \\
 P_{13} & P_{31} & P_{33} & 0 & 0 & 0 \\
 P_{41} & -P_{41} & 0 & P_{44} & 0 & 0 \\
 0 & 0 & 0 & 0 & P_{44} & P_{41} \\
 0 & 0 & 0 & 0 & P_{14} & P_{66}
 \end{bmatrix}$$

where all the C_{ij} 's and P_{ij} 's are known [1,2] namely:

$$C_{11} = 86.87 \times 10^{10} \text{ dynes/cm}^2$$

$$C_{12} = 7.09 \times 10^{10} \quad "$$

$$C_{13} = 11.92 \times 10^{10} \quad "$$

$$C_{14} = 18.04 \times 10^{10} \quad "$$

$$C_{44} = 58.18 \times 10^{10} \quad "$$

$$C_{33} = 10.57 \times 10^{10} \quad "$$

$$C_{66} = 39.89 \times 10^{10} \quad "$$

and

$$P_{11} = 0.138 \quad P_{12} = 0.250 \quad P_{13} = 0.259$$

$$P_{14} = 0.029 \quad P_{41} = 0.042 \quad P_{31} = 0.258$$

$$P_{33} = 0.098 \quad P_{44} = 0.065 \quad P_{66} = 0.056$$

one can determine the three eigenvalues and the corresponding displacement vectors for each of the QL, QT1, and QT2 modes belonging to $\hat{q} = \frac{1}{\sqrt{2}}(110)$ from eqn. (5-7). The summary of the results including the Brillouin scattering tensor for each of those modes is tabulated below:

I. Mode QL: $\rho v_{QL}^2 = 92.12 \times 10^{10} \text{ dynes/cm}^2$
 $\hat{u}_{QL} = (0.72, 0.59, 0.38)$

The scattering tensor is given by:

$$\begin{bmatrix} .72p_{11} + .59p_{12} + .38p_{14} & .38p_{14} + 1.31p_{66} & .38p_{44} + 1.31p_{41} \\ .38p_{14} + 1.31p_{66} & .72p_{12} + .59p_{11} - .38p_{14} & .34p_{41} + .38p_{44} \\ .38p_{44} + 1.31p_{41} & .34p_{41} + .38p_{44} & 1.31p_{31} \end{bmatrix}$$

From the selection rule, one may observe this mode in X(ZZ)Y configuration, and the observed intensity should be:

$$I \sim T_{33}^2 = (1.31p_{31})^2$$

II. Mode QT1: $\xi^{V_{QT1^2}} = 60.11 \times 10^{10} \text{ dynes/cm}^2$

$$\hat{u}_{QT1} = (0.09, 0.61, 0.78)$$

The scattering tensor is given by:

$$\begin{bmatrix} .09p_{11} + .61p_{12} + .78p_{14} & .78p_{14} + .7p_{66} & .78p_{44} + .7p_{41} \\ .78p_{14} + .7p_{66} & .09p_{12} + .61p_{11} - .78p_{14} & .52p_{41} + .78p_{44} \\ .78p_{44} + .7p_{41} & -.52p_{41} + .78p_{44} & .7p_{31} \end{bmatrix}$$

III. Mode QT2: $\xi^{V_{QT2^2}} = 32.65 \times 10^{10} \text{ dynes/cm}^2$

$$\hat{u}_{QT2} = (0.6 - 0.53, -0.49)$$

$$\begin{bmatrix} .6p_{11} - .53p_{12} - .49p_{14} & -.49p_{14} + .07p_{66} & -.49p_{44} + .07p_{41} \\ -.49p_{14} + .07p_{66} & .6p_{12} - .53p_{11} + .49p_{14} & .07p_{41} - .49p_{44} \\ .49p_{44} + .07p_{41} & .07p_{41} - .49p_{44} & .07p_{31} \end{bmatrix}$$

The selection rules also allow one to observe QT1 and QT2 in the $X(Z,Z)\bar{Y}$ configuration with relatively low intensity.

Experimentally, all three modes were observed with relative intensities of the same order as predicted by the selection rules as

$$I_{QL} : I_{QT1} : I_{QT2} = 1.312 : 0.72 : 0.072$$

other necessary Quartz data:

$$\rho = 2.65 \text{ g/cm}^3$$

$$n_o = 1.5482, n_e = 1.5575$$

(II) Elastic and Pockel's tensor of salol

The elastic and Pockel's coefficient tensor (used in chapter V and chapter VIII) are given by [1]:

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$$

and

$$\begin{bmatrix} P_{11} & P_{12} & P_{13} & 0 & 0 & 0 \\ P_{21} & P_{22} & P_{23} & 0 & 0 & 0 \\ P_{31} & P_{32} & P_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & P_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & P_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & P_{66} \end{bmatrix}$$

(III) Determination of the Rayleigh ratio of quartz for the QL-mode.

The Rayleigh ratio of the j -th mode of a crystal for incident light polarized along $\hat{k}$ and scattered light along $\hat{z}$ is given by:

$$R^j = \frac{\pi^2 k_B T \epsilon_k^2 \epsilon_z^2}{2 \lambda_s^4 g_j v_j^2} \left[\hat{e}_z \cdot T^j \hat{e}_k \right]^2 \quad (A-1)$$

where T^j is the Brillouin scattering tensor for the j -th mode. In our particular case, we plan to determine the Rayleigh ratio for the QL mode of quartz for the scattering configuration $X(ZZ)\bar{Y}$. The Rayleigh ratio in terms of Pockel's coefficients, substituting the component of the Brillouin scattering tensor of the QL-mode from

section (I) is given by:

$$R_{\text{QTZ}}^{\text{QL}} = \frac{\pi^2 k_B T \epsilon_z^4}{2 \lambda_s^4 \rho_{\text{QTZ}} v_{\text{QL}}^2} (1.31 p_{31})^2 \quad (\text{A-2})$$

which can further be simplified by substituting the sound velocity v_{QL} from the observed spectrum, the Pockel's coefficient p_{31} from ref. [2], and the density and refractive index of quartz:

$$R_{\text{QTZ}}^{\text{QL}} = 7.39 \times 10^{-13} \text{ bl} \quad (\text{A-3})$$

where $\text{bl} = \frac{\pi^2 k_B T}{2 \lambda_s^4}$ is the same for benzene and quartz.

Substituting $R_{\text{QL}}^{\text{QTZ}}$ from (3), experimentally determined linewidths and peak heights of benzene and quartz spectra and other known parameters in eqn. (8-3a) one gets the absolute value of the Rayleigh ratio of benzene:

$$R_{\text{BEN}}^{\text{VV}} = 3.9 \times 10^{-11} \text{ bl} \quad (\text{A-4})$$

which can be further simplified for $\lambda = 5145 \text{ \AA}$ and $T = 300^\circ \text{K}$ to:

$$R_{\text{BEN}} = 5.648 \times 10^{-6}$$

The superscript (VV) means that the one to one comparison between benzene and salol spectra can be made only if both are obtained for incident and scattered light polarized perpendicular to the scattering plane. Otherwise the proper k_F factor in eqn. (8-4) must be used for true comparison.

References

1. J.F. Nye, Physical properties of crystals, Oxford University press, 1967
2. S.M. Shapiro, PhD Thesis, Johns Hopkins University, 1969