

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 9510694

Ultrafast optical pulse studies of metallic layers and particles

Mihailidi, Margarita, Ph.D.

City University of New York, 1994

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

+

Ultrafast Optical Pulse Studies of Metallic Layers and Particles

by

Margarita Mihailidi

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

1994

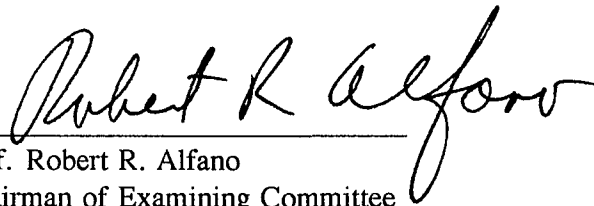
This manuscript has been read and accepted for the Graduate Faculty in Engineering
in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy

Date

9/21/94

Prof. Robert R. Alfano

Chairman of Examining Committee

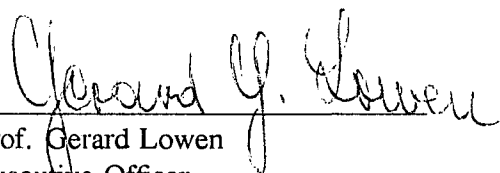


Date

9/26/94

Prof. Gerard Lowen

Executive Officer



Prof. M. Lax

Prof. P. P. Ho

Prof. R. Dorsinville

Prof. S. K. Gayen

Supervisory Committee

The City University of New York

Abstract

Ultrafast Optical Pulse Studies of Metallic Layers and Particles

by

Margarita Mihailidi

Advisor: Professor R. R. Alfano

In this thesis, time resolved measurements of the transmissivity change in niobium has been performed with 100-fs resolution, using the pump-probe technique. The temperature dependence of the electron-phonon relaxation time in a niobium film was obtained for a range of temperatures below the Debye temperature. The temperature dependence of the electron-phonon coupling parameter, g , that governs the electron-phonon relaxation time, has been derived for temperatures below the Debye temperature. The time dependence of g has been calculated and experimentally verified for temperatures below the Debye temperature. In the picosecond time domain, temporal measurements of the transmissivity change in niobium in the transition from the superconducting to the normal state have confirmed the existence of a postulated subnanosecond transient state. The effect of niobium particle absorption on the propagation of ultrashort light pulses in dense random media was also investigated.

The change in phonon temperature in the fs time scale has been measured for ambient (initial) temperatures ranging from 292 K to 7 K. From these results the time

it takes for the electrons to thermalize with phonons was extracted and it was found to decrease from 370 fs at 292 K to 250 fs at 7 K. The time dependence of the electron-phonon coupling parameter governing the electron-phonon relaxation process was determined for temperatures ranging from 292 K to 7 K, showing a complex behavior in agreement with Allen's theory.

Measurements of the transient thermotransmittance decay in the ps time scale, for ambient temperatures ranging from room to superconducting temperatures, have been performed for a niobium film and have been attributed to cooling due to heat diffusion. A change in the transient decay dynamics of thermotransmittance in the visible has been detected in the transition from the normal to the superconducting phase and was related to the onset of nonequilibrium superconductivity.

The temporal profile of an ultrafast laser pulse incident on to a dense mixture of dielectric and niobium particles, has also been investigated. The pulse duration of the outgoing light was found to decrease as the concentration of metallic particles was increased. This process was modeled with diffusion theory taking into account the phase correlation among scattered waves.

To my dearest parents, Agapi and Mihailo Mihailidi.

Acknowledgments

I greatly appreciate the guidance and help of my thesis advisor, Robert Alfano, Distinguished Professor of Science and Engineering, during the course of my thesis work. His critical reviewing of all my work, and most of all his creative discussions and suggestions have brought my research to a successful completion. I also thank the members of the Institute of Ultrafast Spectroscopy and Lasers for their help during the course of this work. Special thanks to Professor Nenad Marinovic for his help with the computational work for this thesis and to Professor Melvin Lax and Quen-Zhen Wang for their help with problems in scattering through random media. I wish to express my sincere thanks to Professor Roger Dorsinville for his advice, support and valuable discussions and all the other committee members for their valuable time. I also thank Megan Gibbs for her understanding and help in the administrative work.

This thesis study was made possible from the educational and financial support provided in part by the Department of Electrical Engineering of the City College of the City University of New York, the Air Force Office of Scientific Research, and Hamamatsu Photonics K. K.

Contents

Abstract	iii
Acknowledgments	vi
I Introduction	1
1. Background	1
2. Thesis Statement	5
3. Thesis Organization	7
Bibliography	10
II Thermophysical and Electron-Phonon Interaction Parameters	11
1. Introduction	11
2. The Éliashberg Coupling Function and Moments	12
3. Thermal Conductivity	16
3.1. Lattice Contribution to the Thermal Conductivity	17
3.2. Electronic Contribution to the Thermal Conductivity . .	19
4. The Heat Capacity	22
4.1. Lattice Heat Capacity	22
4.2. Electronic Heat Capacity	25
4.3. Heat Capacity of a Typical Transition Metal	29
5. Thermal Diffusivity	34
Bibliography	35

III	Thermomodulation Spectroscopy and Laser Heating	36
1.	Introduction	36
2.	Thermomodulation Spectroscopy	37
3.	Ultrafast Thermomodulation Measurements of Electron-Phonon Relaxation	41
3.1.	The Transient Transmissivity Method	41
3.2.	The Physical Model - Energy Rate Equations	44
3.3.	Review of Subpicosecond Thermomodulation Experiments	51
4.	Ultrafast Thermomodulation Measurements of Heat Diffusion	54
4.1.	The Transient Transmissivity Method	54
4.2.	The Physical Model – Fourier Equation	54
4.3.	Review of Recent Subnanosecond Thermomodulation Experiments	55
	Bibliography	58
IV	Measurements of the Temperature Dependence of the Electron-Phonon Relaxation Time in Nb	60
1.	Introduction	60
2.	Experimental Set-Up	62

3.	Description of the Experiment	71
4.	Experimental Results	73
5.	Conclusion	81
	Bibliography	82
V	The Time Evolution for the Electron-Phonon Coupling Parameter g	84
1.	Introduction	84
2.	Allen's Theory of Thermal Relaxation of Electrons in Metal	88
3.	Time Evolution of the Temperature-Dependent Electron-Phonon Coupling Parameter g	94
4.	Numerical Solution of the Time Evolution of g and the Electron-Phonon Relaxation Time	97
5.	Conclusion	108
	Bibliography	111
VI	Measurements of Diffusion Related Thermotransmittance in Niobium from Room Temperature to Below Superconducting Temperature	113
1.	Introduction	113
2.	Description of Experiment	115
3.	Results	117
3.1.	Experimental Results	117
3.2.	Numerical Results	120

4.	Discussion	134
5.	Conclusion	140
	Bibliography	142
VII	Scattering Through Metallic Particles in Dense Dielectric Media	144
1.	Introduction	144
2.	Theoretical Background	145
3.	Experimental Method	149
4.	Results	152
5.	Discussion	165
6.	Conclusion	169
	Bibliography	171
VIII	Summary	172
	Bibliography	177
IX	Future Research Directions	178
	Bibliography	180
A	Appendix	181
1.	Programs for Electron-Phonon Relaxation . . .	181
2.	Programs for Heat Transfer by Diffusion	185
3.	Simplified Heat Diffusion Model	195
3.1.	Solution for Niobium	197
3.2.	Solution for Quartz	200
	Bibliography	202

II	Thesis Bibliography	203
1.	Bibliography-Ch. I	203
2.	Bibliography-Ch. II	204
3.	Bibliography-Ch. III	205
4.	Bibliography-Ch. IV	207
5.	Bibliography-Ch. V	209
6.	Bibliography-Ch. VI	211
7.	Bibliography-Ch. VII	213
8.	Bibliography-Ch. VIII	214
9.	Bibliography-Ch. IX	215
10.	Bibliography-Appendix	216

I Introduction

I.1. Background

The advent of ultrafast lasers permits the investigation of nonequilibrium dynamics in condensed matter. Many studies of electron-phonon processes have concentrated on semiconducting materials with spectral features accessible by currently available laser sources. Few attempts have been made to investigate nonequilibrium processes in metals [1], [2], [3]. The earliest experiment on this topic was the generation of transient black body radiation spectra by heating Cu, Ag and Au targets with intense, 20-picosecond YAG laser pulses [2]. Other experiments investigated nonequilibrium heating based on the phenomenon of multiphoton photoemission from metals illuminated by high-intensity laser pulses [1] [4]. Fujimoto et al. [3] first recorded nonequilibrium heating in tungsten using femtosecond laser pulses to produce multiphoton photoemission.

Nonequilibrium superconductivity plays an important role in high-speed superconducting devices such as high speed electronic sampling oscilloscopes, computer chips, and ultrafast, wide-bandwidth electromagnetic detectors from x-ray to microwave regions. Niobium is a superconducting metal widely used for fabrication of superconducting devices because of its relatively high superconducting temperature for a metal. The operation of these devices is based on driving the superconductor into the nonequilibrium state. Determining the speed of the nonequilibrium processes

involved in niobium will provide the necessary information to establish the speed limit of these devices.

The speed of superconducting devices is limited by the relaxation times in the materials, such as the electron-phonon scattering time, the phonon-Cooper pair breaking time, the quasiparticle recombination time, and the phonon escape time via diffusion. The dynamics of these processes have been studied in the past by driving the Josephson junction into the nonequilibrium state using ultrafast laser excitation [5]. However, in these experiments the detection technique was not in the femtosecond time scale. Special purpose fast switches, like those used for noise discrimination in digital circuits, primarily demand fast switching even if power levels have to remain large. Laser-induced electron heating with ultrafast pulses, provides unique possibilities for fast switching from the superconducting to the normal state. To investigate fast, nonequilibrium transient properties that govern the transition process at lower temperatures, ultrafast laser pulses have to be used, with pulse durations shorter than these transition processes.

With the development of picosecond and femtosecond lasers, ultrafast laser pulses have been used to produce fast transient nonequilibrium temperatures and investigate ultrafast relaxation processes [6]. By generating transient nonequilibrium temperatures in metals with femtosecond laser pulses, the electron-phonon relaxation times of Cu, Au [7] and other metals have been determined. Recently, time-resolved thermomodulation measurements have been performed on various metals in order to determine the electron-phonon mass enhancement parameter λ [8]. Using femtosecond pump-and-probe spectroscopy electron-phonon relaxation times of hundreds of femtoseconds have been measured in Cu, Au, Cr, Ti, W, Nb, V and Pb. This work achieved 100 fs time resolution but has been restricted to

characterizing the nonequilibrium electron-phonon interactions at room temperature, where most parameters may be considered to be independent of temperature.

In this thesis, the relaxation times of elementary excitations in niobium metal in the normal and the superconducting states are investigated by pump-probe methods in the *femtosecond* scale using femtosecond laser pulses for high speed resolution. Various derivations of these times as well as certain analytic results and some numerical calculations exist in the literature [9] [10]. We seek to provide experimental evidence and theoretical models describing the dynamic nature of these processes. The thermal relaxation rate γ_T of electron-phonon heat transfer can be related to the Éliashberg coupling function $\lambda\langle\omega^2\rangle$ which is related to the electron-phonon parameter g . The temperature dependence and the time evolution of the electron-phonon parameter g , as the electron and phonon temperatures change dynamically for an ultrafast pump-probe experiment, have been measured.

The importance of the research performed here is that subpicosecond nonequilibrium processes are investigated at a range of temperatures from room temperature to below the superconducting transition temperature ($\Theta_c=8.8$ K for niobium) with 100 fs resolution. For temperatures below the Debye temperature ($\Theta_D=272$ K for niobium) the parameters of the nonequilibrium interactions become temperature dependent and are affected by the change in the electron and phonon temperature due to heating by the pump pulse. Thus, measurements for temperatures below the Debye temperature need be performed and appropriate theoretical models developed. The knowledge of these parameters, that govern the processes on the fs time scale, is a first step towards better understanding of nonequilibrium superconductivity and thus the ultimate speed of the superconducting devices.

The dynamics of subnanosecond processes, like heat diffusion in thin metal

films, can be investigated by thermotransmittance spectroscopy. For this purpose, thermotransmittance measurements for ambient temperatures above and below the superconducting temperature for niobium film are performed in the *picosecond* time scale.

When niobium in the superconducting state is heated by a femtosecond pulse the transition from superconducting to normal state is reflected in the diffusion process measured. The change in the thermotransmittance relaxation time is measured in the 250-ps time range and related to heat diffusion and the nonequilibrium processes in the transition from the superconducting to the normal state. It will be shown that measurements of thermal transport in a metal in the normal and superconducting state at different time delays after heating a superconducting film, confirm that the transition from the superconducting to the normal state occurs in the ps time range.

Time resolved experimental studies of ultrafast laser pulse scattering have been performed in dielectric medium in the past to investigate the ability to see through a highly scattering random wall. Different techniques have been used for this purpose, such as time of flight [11] and image enhancement using absorbing dyes [12]. In this thesis, the temporal profile of an ultrafast laser pulse scattered in random media, consisting of a mixture of dielectric particles and metallic particles, has been investigated in the ps time scale. Diffusion theory is used to model the light pulse after undergoing multiple random scattering in a dense mixture of dielectric and metallic particles. It is shown that correlation effects in photon transport can not be ignored in this dense random system. The results show that the diffuse scattered light, that arrives at later times and travels over a longer distance, is attenuated more with an increased presence of metallic particles.

I.2. Thesis Statement

In this thesis, the fundamental relaxation processes in a niobium film in its normal and superconducting nonequilibrium states are experimentally and theoretically studied using ultrafast laser pulses in a pump-and-probe configuration for ultrafast time resolved detection. The transmitted laser pulse profile through a slab of random media with niobium particles is also investigated, using ps time resolution.

This research involved taking part in a group which designed and built an experimental set-up, including a colliding pulse mode-locked (CPM) dye laser and amplifier that would generate femtosecond pulses using known and novel techniques. These fs pulses were applied in the investigation of ultrafast processes in niobium metal in the normal and the superconducting states using transient thermotransmittance spectroscopy. This research investigates processes (1) in niobium film in the femtosecond time scale, (2) in niobium film in the picosecond time scale, and (3) in random media with niobium particles in the picosecond time scale.

The goal of this work is:

- (1) To apply ultrafast laser pulses in investigating femtosecond processes in niobium in the normal and the superconducting states. In particular:
 - (i) To generate transient nonequilibrium temperatures of the electron gas in the metal lattice to investigate the dynamics of electron-phonon interaction.
 - (ii) To determine the temperature dependence of the electron-phonon relaxation time in the subpicosecond time scale for temperatures ranging from room temperature to below the critical superconducting temperature.

- (iii) To determine the time evolution and temperature dependence of the electron phonon coupling constant.
- (2) To apply ultrafast laser pulses in investigating picosecond processes in niobium in the normal and superconducting state. In particular:
- (i) To investigate heat diffusion in a niobium film in the normal state for different film temperatures.
 - (ii) To investigate nonequilibrium superconductivity in a niobium film as reflected in the transient optical properties in the visible.
- (3) To investigate the transmitted laser pulse through a slab of random media with a mixture of dielectric and niobium particles using picosecond time resolution. In particular:
- (i) To investigate the temporal profile of the diffuse light in a mixture of dielectric and niobium particles as the concentration of niobium particles is increased.
 - (ii) To confirm the presence of the correlation effect in photon transport in dense random systems by modeling the process with the diffusion equation.

I.3. Thesis Organization

The thesis is organized into seven chapters. An introduction is given in chapter I. Chapter II presents the theory needed to understand the physical processes investigated in niobium film. In ch. III, the theory behind the experimental methods used in the niobium film measurements is discussed. The chapters V and IV cover the theoretical model and the experimental measurements of the electron-phonon interaction and heat transfer in metals. Chapter VI deals with heat diffusion and nonequilibrium superconductivity in niobium metal film. In chapter VII an experimental and theoretical investigation of a transmitted laser pulse through a slab of random media with a mixture of dielectric and niobium particles is presented. A summary of the work presented in this thesis is given in chapter VIII. In the last chapter, ch. IX, a discussion of possible future directions is provided. These chapters are now summarized.

In chapter II, we first present a brief review of some basic electron-phonon parameters and the thermophysical parameters that are influenced by electron-phonon interaction. The electron-phonon interaction is described by the Éliashberg coupling function $\alpha^2 F(\omega)$, or its anisotropic version $\alpha^2 F(\omega; \mathbf{k})$ and its integrals. The zero moment of $\alpha^2 F(\omega)$, which is the electron-phonon mass enhancement parameter, λ , is explained with respect to the electron-phonon heat transfer coefficient γ_T , the electron-phonon coupling parameter g , and the expressions for determining the superconducting transition temperature. This is needed in order to explain the close relation between the electron-phonon interaction parameters, the thermophysical parameters and the physics behind the thermomodulation measurements presented in the following section.

In chapter III, thermomodulation measurements in general and as applied to thermomodulation experiments based on ultrafast laser heating are discussed. First we present the physical concept of thermomodulation spectroscopy. The possible applications of thermomodulation spectroscopy to investigate electron-phonon relaxation (fs-time scale) and heat diffusion (ps-time scale) in metal are presented. We explain how ultrafast laser pulses have been used to produce fast transient temperatures and investigate ultrafast relaxation processes [6], [13]. The two temperature model is described as the one usually used to ultrafast laser heating in the fs-time scale, and the heat diffusion model, appropriate in the ps-time scale. At the end, a brief review of work done so far on ultrafast thermomodulation measurements is also presented.

Measurements of the temperature dependence of the electron-phonon relaxation time in niobium are presented in chapter IV. First, we briefly review the basic concept of the experiment. Then, the experimental set-up is presented: A brief description is presented of the colliding pulse mode locked dye laser used as the source for the pump-probe experiment [14]. The dye amplifier and the pump-probe set-up are also described. The experimental results are presented for temperatures ranging from 292 K down to 7 K (below critical superconducting temperature).

The focus of chapter V is the time evolution of the electron-phonon parameter g , as the electron and phonon temperatures change dynamically in case of ambient temperatures below the Debye temperature for an ultrafast pump-probe experiment. First, we present Allen's theory, where the thermal relaxation rate γ_T is related to $\lambda\langle\omega^2\rangle$ for $\Theta > \Theta_{\text{Debye}}$. Then, we present the derivation of the electron-phonon coupling parameter g based on Allen's theory [15] for $\Theta > \Theta_{\text{Debye}}$, when g is constant, and more importantly for the case of $\Theta \leq \Theta_{\text{Debye}}$, when g becomes temperature, and thus time dependent. A numerical solution of the time dependence of $g(\Theta_e(t)\Theta_l(t))$

with parameters corresponding to our experiments is given and the electron-phonon relaxation time for different ambient temperatures is calculated. These theoretically obtained results of the electron-phonon relaxation time are compared with the experimentally measured electron-phonon relaxation time (from chapter IV) for different temperatures. A good agreement of theory and experiment can be seen for temperatures $\Theta=292$ K down to $\Theta=30$.

In chapter VI we describe the pump-probe experiment performed to investigate the diffusion in niobium metal in the transition from superconducting to normal state. Experimental results are compared with results obtained from numerical modelling. The measured faster decay of the thermotransmittance change, when illuminating a superconducting film at temperatures below superconducting temperature ($\Theta_0 < \Theta_c$), was related to increased diffusivity due to nonequilibrium processes in Nb in the transition from superconducting to normal state.

An investigation of the temporal profile of a ps-laser pulse, after passing through a slab of dense random media, made of a mixture of dielectric particles and metallic particles, is presented in chapter VII. Diffusion theory was used to model the light after undergoing multiple random scattering. It is shown that the presence of metallic particles decreases the duration of the temporal profile and that correlation effects in photon transport can not be ignored in this dense random system.

Chapter VIII contains a summary of work performed in this thesis. Chapter IX provides a discussion of possible future research directions. In the appendix, the derivation of a simplified diffusion model is presented and the programs used throughout the thesis are listed.

Bibliography

- [1] R. Yen, J. M. Liu, and N. Bloembergen *Opt. Commun.* **35**, p. 277, 1980.
- [2] M. B. Agranat, A. A. Benditskii, and G. M. Gandelman *Zh. Eksp. Theor. Fiz.* **79**, p. 55, 1980.
- [3] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen *Phys. Rev. Lett.* **53**, p. 1837, 1984.
- [4] S. I. Anisimov, V. A. Bendetskii, and G. Farkas *Sov. Phys. —Usp.* **20**, p. 467, 1977.
- [5] C. Chi, M. T. Loy, and D. Cronmeyer *Phys. Rev. B* **23**, p. 124, 1981.
- [6] S. D. Brorson, J. G. Fujimoto, and E. P. Ippen *Phys. Rev. Lett.* **59**, p. 1962, 1987.
- [7] G. L. Eesley, B. M. Clemens, and C. A. Paddock *Appl. Phys. Lett.* **50**, p. 717, 1987.
- [8] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus *Phys. Rev. Lett.* **64**, p. 2172, 1990.
- [9] K. E. Gray, *Superconductive Particle Detectors*. World Scientific, Singapore, 1988.
- [10] K. E. Gray *J. Phys. F* **1**, p. 290, 1971.
- [11] J. G. Fujimoto, S. D. Silversti, E. P. Ippen, R. Margolis, and A. Oseroff *Opt. Lett.* **11**, p. 150, 1986.
- [12] K. M. Yoo, F. Liu, and R. R. Alfano *Opt. Lett.* **16**, p. 1068, 1991.
- [13] B. M. Clemens, G. L. Eesley, and C. A. Paddock *Phys. Rev. B* **37**, p. 1085, 1988.
- [14] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano *Opt. Lett.* **13**, p. 987, 1988.
- [15] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.

II Thermophysical and Electron-Phonon Interaction Parameters

II.1. Introduction

In this chapter, a brief review of some basic electron-phonon parameters and the thermophysical parameters that are influenced by electron-phonon interaction is given. This is needed in order to explain the physics behind the thermomodulation measurements. Many important phenomena in solids are based on the electron-phonon interaction. The electron-phonon interaction is usually described by the Éliashberg coupling function $\alpha^2 F(\omega)$, or its anisotropic version $\alpha^2 F(\omega; \mathbf{k})$ and its integrals. To describe transport phenomena in solids Éliashberg has also introduced the transport coupling function $\alpha_{tr}^2 F(\omega; \mathbf{k})$. This function is present in the expressions for heat capacity, C , and thermal conductivity, κ , in metals.

The zero moment of $\alpha^2 F(\omega)$ is the electron-phonon mass enhancement parameter, λ , which appears in the electron-phonon heat transfer coefficient γ_T and in the expressions for determining the superconducting transition temperature. It will be shown that the zero moment of $\alpha^2 F(\omega)$ is present in the expression for the electron-phonon coupling parameter g .

II.2. The Éliashberg Coupling Function and Moments

Knowledge of the phonon density of states, $F(\omega)$, where ω is the phonon frequency, is sufficient to calculate some thermophysical properties without any detailed knowledge of the phonon dispersion curves and the phonon eigenvectors. If $F(\omega)$ is expressed in terms of the dispersion relation $\omega(\mathbf{q}, \eta)$, where $\mathbf{q}$ is the phonon wave vector, and η is the phonon branch index, then

$$\begin{aligned} F(\omega) &= \frac{1}{N} \frac{V}{(2\pi)^3} \sum_{\eta} \int d^3\mathbf{q} \delta(\omega(\mathbf{q}, \eta) - \omega) \\ &= \frac{1}{N} \frac{V}{(2\pi)^3} \sum_{\eta} \int_{S_{\mathbf{q}}} \frac{dS}{|\nabla_{\mathbf{q}} \omega(\mathbf{q}, \eta)|}. \end{aligned} \quad (\text{II.2.1})$$

Here N is the number of atoms in volume V . The integration is performed over the surface $S_{\mathbf{q}}$ on which $\omega(\mathbf{q}, \eta) = \omega$. $NF(\omega)d\omega$ represents the phonon states that have frequencies in the interval $[\omega, \omega + d\omega]$. The normalization is usually taken to be

$$\int_0^{\omega_{\max}} F(\omega) d\omega = 3, \quad (\text{II.2.2})$$

because the vibrational degree of freedom for each atom is three.

To consider the scattering of electrons with energy $\varepsilon_{\mathbf{k}}$ from state $\mathbf{k}$, to all state $\mathbf{k}'$ which have an energy $\varepsilon_{\mathbf{k}'} = \varepsilon_{\mathbf{k}} \pm \hbar\omega(q, \eta)$ Éliashberg has introduced the coupling function $\alpha^2 F(\omega; \mathbf{k})$ which describes the electron-phonon coupling between an initial state $\mathbf{k}$ on the Fermi surface S_F and all other states $\mathbf{k}'$ on S_F that differ from the initial state by $\hbar\omega$. This electron-phonon coupling function is defined as [1]

$$\alpha^2 F(\omega; \mathbf{k}) = \frac{V}{\hbar(2\pi)^3} \sum_{\eta} \int_{S_F} \frac{d^2 \mathbf{k}'}{v_{\mathbf{k}'}} |g(\mathbf{k}, \mathbf{k}'; \eta)|^2 \delta(\hbar\omega(\mathbf{q}, \eta) - \hbar\omega). \quad (\text{II.2.3})$$

where $|g(\mathbf{k}, \mathbf{k}'; \eta)|$ is the coupling function that refers to scattering from a point $\mathbf{k}$ to a point $\mathbf{k}'$ in the $\mathbf{k}$ space for branch η . The function describes the material in question and is independent of volume. The average of $\alpha^2 F(\omega; \mathbf{k})$ over all $\mathbf{k}$ on S_F is

$$\alpha^2 F(\omega) = \frac{\frac{V}{\hbar(2\pi)^3} \sum_{\eta} \int_{S_F} \frac{d^2 \mathbf{k}}{v_{\mathbf{k}}} \int_{S_F} \frac{d^2 \mathbf{k}'}{v_{\mathbf{k}'}} |g(\mathbf{k}, \mathbf{k}'; \eta)|^2 \delta(\hbar\omega(\mathbf{q}, \eta) - \hbar\omega)}{\int_{S_F} \frac{d^2 \mathbf{k}}{v_{\mathbf{k}}}}. \quad (\text{II.2.4})$$

$\alpha^2 F(\omega)$ is called the Éliashberg coupling function [1]. This function describes the electron-phonon coupling and is a property of the material. It gives, as will be shown below, the second moment of the phonon frequencies, which in turn appears in the electron-phonon heat transfer coefficient γ_T , the electron-phonon coupling parameter g , and can also be found in the expressions for determining the superconducting transition temperature.

In describing transport phenomena it is important to know in which direction the electron goes after the scattering, since for example, the largest contribution to the resistivity comes from backscattering. This is the reason Eliashberg has introduced the transport coupling function $\alpha_{tr}^2 F(\omega; \mathbf{k})$ which is defined as [2]

$$\alpha_{tr}^2 F(\omega; \mathbf{k}) = \frac{V}{\hbar(2\pi)^3} \sum_{\eta} \int_{S_F} \frac{d^2 \mathbf{k}'}{v_{\mathbf{k}'}} \left(1 - \frac{\mathbf{v}_{\mathbf{k}} \mathbf{v}_{\mathbf{k}'}}{|\mathbf{v}_{\mathbf{k}}|^2} \right) |g(\mathbf{k}, \mathbf{k}'; \eta)|^2 \delta(\hbar\omega(\mathbf{q}, \eta) - \hbar\omega). \quad (\text{II.2.5})$$

The factor $\left(1 - \frac{\mathbf{v}_\mathbf{k} \mathbf{v}_{\mathbf{k}'}}{|\mathbf{v}_\mathbf{k}|^2}\right)$ takes into account the direction the electron goes after the scattering. This factor is the only difference between $\alpha^2 F(\omega; \mathbf{k})$ and $\alpha_{tr}^2 F(\omega; \mathbf{k})$. In free-electron-like metals the approximation

$$\left(1 - \frac{\mathbf{v}_\mathbf{k} \mathbf{v}_{\mathbf{k}'}}{|\mathbf{v}_\mathbf{k}|^2}\right) = 1 - \cos \theta_{\mathbf{k}\mathbf{k}'} \quad (\text{II.2.6})$$

is usually introduced, where $\theta_{\mathbf{k}\mathbf{k}'}$ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. The Éliashberg transport coupling function $\alpha_{tr}^2 F(\omega)$ is the average over all directions and is defined as

$$\alpha_{tr}^2 F(\omega) = \frac{\frac{V}{\hbar(2\pi)^3} \sum_{\eta} \int_{S_F} \frac{d^2 \mathbf{k}}{v_{\mathbf{k}'}} \int_{S_F} \frac{d^2 \mathbf{k}'}{v_{\mathbf{k}'}} \left(1 - \frac{\mathbf{v}_\mathbf{k} \mathbf{v}_{\mathbf{k}'}}{|\mathbf{v}_\mathbf{k}|^2}\right) |g(\mathbf{k}, \mathbf{k}'; \eta)|^2 \delta(\hbar\omega(\mathbf{q}, \eta) - \hbar\omega)}{\int_{S_F} \frac{d^2 \mathbf{k}}{v_{\mathbf{k}'}}} \quad (\text{II.2.7})$$

When back scattering of electrons is present, like in resistivity problems, the transport coupling function, $\alpha_{tr}^2 F(\omega)$, is used. It is present in the expression for thermal conductivity, κ , presenting in the next section.

The above described Éliashberg coupling functions $\alpha^2 F(\omega; \mathbf{k})$ and $\alpha_{tr}^2 F(\omega; \mathbf{k})$ will prove to be very helpful in expressing basic thermophysical and electron-phonon coupling parameters. The moments of $\alpha^2 F(\omega; \mathbf{k})$ and $\alpha_{tr}^2 F(\omega; \mathbf{k})$ appear in the theory of resistivity, electronic specific heat and in superconducting theory. The moments of $\alpha^2 F(\omega; \mathbf{k})$ are defined as

$$\lambda \langle \omega^n \rangle = 2 \int_0^\infty d\omega [\alpha^2 F(\omega)/\omega] \omega^n \quad (\text{II.2.8})$$

where

$$\langle \omega^n \rangle = \int_0^\infty \omega^n F(\omega) d\omega. \quad (\text{II.2.9})$$

The zero moment of $\alpha^2 F(\omega)$ is called the electron-phonon mass enhancement parameter λ , and is defined as

$$\lambda = 2 \int_0^{\infty} d\omega [\alpha^2 F(\omega)/\omega]. \quad (\text{II.2.10})$$

It appears in the electron-phonon heat transfer coefficient γ_T and the electron-phonon coupling parameter g . λ can also be found in the expressions for determining the superconducting transition temperature. Since the coupling function $\alpha^2 F(\omega)$ is in general not known, an approximate relation between the superconducting transition temperature, Θ_c , and some average value of $\alpha^2 F(\omega)$, such as the mass enhancement parameter, λ , is found. One of the basic versions of this formula is the McMillan formula [3]:

$$\Theta_c = \frac{\Theta_D}{1.45} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right] \quad (\text{II.2.11})$$

where Θ_D is the Debye temperature and μ^* represents the repulsive electron-electron interaction parameter. In practice, Θ_c is known but not λ , and thus Eq. (II.2.11) is a way to estimate the electron-phonon mass enhancement parameter λ .

Similarly λ_{tr} is defined as

$$\lambda_{tr} = \int_0^{\omega_{max}} \frac{2\alpha_{tr}^2 F(\omega)}{\omega} d\omega. \quad (\text{II.2.12})$$

and appears in the expression for electron thermal conductivity presented in section II.3.2.

II.3. Thermal Conductivity

Because the heat in metals is carried mainly by conduction electrons, they usually have high thermal conductivity, κ . The temperature dependence of thermal conductivity in pure materials has a maximum well below room temperature. This maximum shifts to higher temperatures and becomes less pronounced as the lattice disorder increases. For very disordered or impure materials the maximum completely disappears.

The thermal conductivity is actually a tensor with components κ_{ij} ($i, j = x, y, z$). If the lattice has cubic symmetry, $\kappa_{ii} = \kappa$ when $i = 1, 2, 3$ and $\kappa_{ij} = 0$ when $i \neq j$. In that case, the heat flow, Q , in a temperature gradient $\nabla\Theta$ is described with Fourier's Law

$$Q = -\kappa(\nabla\Theta). \quad (\text{II.3.1})$$

Here, the heat conductivity, κ , is a scalar and describes heat flow parallel to the temperature gradient. Often, the inverse of the heat conductivity, $W = 1/\kappa$, is used, where W represents the thermal resistivity.

Thermal conductivity in metals can be considered as the sum of two independent terms [1],

$$\kappa = \kappa_c + \kappa_{ph}, \quad (\text{II.3.2})$$

where κ_c is the lattice thermal conductivity and κ_{ph} is the electronic thermal conductivity. This means that two separate Boltzmann equations for electrons and phonons may be considered while still not neglecting the electron-phonon interaction.

II.3.1. Lattice Contribution to the Thermal Conductivity

Phonons are characterized by a momentum $\hbar q$ and an energy $\hbar\omega(q, \eta)$ where $\hbar$ is the Planck constant. Phonon mean free path is limited by collisions and in that process phonons may be annihilated or created.

The thermal conductivity in solids may be given by an expression for the classical gas [4]

$$\kappa = (1/3)nc_V\bar{v}l \quad (\text{II.3.3})$$

when a summation over all phonon modes is performed. In the above expression $C_V = nc_V$ represents the heat capacity per volume, $\bar{v}$ is the average velocity of gas particle in thermal equilibrium and l is the mean free path. However, c_V , $\bar{v}$ and l in solids depend on $(\mathbf{q}, \eta)$, and the expression for the lattice thermal conductivity is

$$\kappa_{ph} = (1/3) \sum_{\mathbf{q}, \eta} C_V(\mathbf{q}, \eta) v_g(\mathbf{q}, \eta) l(\mathbf{q}, \eta). \quad (\text{II.3.4})$$

where $\bar{v}$ is replaced by the group velocity, v_g . The phonon mean free path l is limited by various kinds of lattice defects and by collisions with other phonons. Different mechanisms prevail at different temperatures and the discussion of the temperature dependence of the lattice thermal conductivity is greatly simplified if only one mechanism is assumed to be dominant. Having that in mind we proceed to analyze the temperature dependence of the lattice thermal conductivity for different temperature ranges.

For temperatures, $\Theta \ll \Theta_D$, $\kappa_{ph} \sim \Theta^n$, where n is typically ~ 3 . At these low temperatures there are few phonons and the scattering is dominated by collisions between phonons and lattice defects. If l is limited by the finite sample size or grain boundary scattering, then l is independent of $(\mathbf{q}, \eta)$ and Θ . For crystalline solids in this temperature range $C_V \sim \Theta^3$ which makes $\kappa_{ph} \sim \Theta^3$.

In the region where Θ is close to Θ_D , κ_{ph} approaches its maximum value usually just below $0.1\Theta_D$, where $l_{ph-def} \sim l_{ph-ph}$. Because of this, the details in this temperature range depend on each specific sample.

For $\Theta > \Theta_D$, the Bose-Einstein distribution that determines the number of phonons in thermal equilibrium is [1]

$$n(\mathbf{q}, \eta) = \frac{1}{\exp\left[\frac{\hbar\omega(\mathbf{q}, \eta)}{k_B\Theta}\right] - 1} \approx \frac{k_B\Theta}{\hbar\omega(\mathbf{q}, \eta)} \quad (\text{II.3.5})$$

where only the leading term of the series expansion may be retained. At these temperatures phonon-phonon scattering is dominant and it is governed mainly by three phonon processes. In this case the mean free path $l \sim 1/\Theta$ because $n \sim \Theta$ at high temperatures. Since the heat capacity, $C_V \sim 3k_B$, the lattice heat conductivity, $\kappa_{ph} \sim 1/\Theta$.

The last temperature region to be discussed is where $\Theta \gg \Theta_D$. In this region, although the mean free path l decreases as Θ increases, l is limited by the distance between two neighboring atoms. Therefore, κ_{ph} can not be smaller than $1/3(3Nk_B/V)v_D a \sim k_B v_D / a^2$ where a is the distance between the neighboring atoms, $a^3 \sim N/V$, and v_D is the sound velocity in the Debye approximation. This qualitatively explains why κ_{ph} becomes weakly temperature dependent at high Θ .

Equation (II.3.4) may be modified to express κ_{ph} as a function of phonon frequencies ω if the phonon density of states $F(\omega)$ is known. Replacing the sum over (q, η) with an integral we get

$$\kappa_{ph} = (n/3)\bar{v}_g \int_0^{\omega_{max}} C_E(\omega) l(\omega) F(\omega) d\omega \quad (\text{II.3.6})$$

where

$$C_E = k_B \frac{x^2 e^x}{(e^x - 1)^2} \quad (\text{II.3.7})$$

is an Einstein heat capacity with $x = \frac{\hbar\omega(q,\eta)}{k_B\Theta}$. $\bar{v}_g$ is an average phonon group velocity and n is the number of atoms per unit volume. The normalization convention here is $\int F(\omega)d\omega = 3$. Substituting $l(q, \eta) = \bar{v}_g(q, \eta)\tau(q, \eta)$ in Equation (II.3.6), the lattice heat capacity becomes

$$\kappa_{ph} = (n/3)\bar{v}_g^2 \int_0^{\omega_{\max}} C_E(\omega)\tau(\omega)F(\omega)d\omega. \quad (\text{II.3.8})$$

II.3.2. Electronic Contribution to the Thermal Conductivity

One may use the fundamental relation for the thermal conductivity of a classical gas as a starting point in describing the electronic contribution κ_e as well;

$$\kappa_e = \frac{1}{3}nC_e v_e l_e \quad (\text{II.3.9})$$

where n is the number of conduction electrons per unit volume, C_e is the electronic heat capacity per electron, v_e the electron velocity, and l_e is the electron mean free path. Using the free-electron model, the electronic heat capacity may be expressed as

$$C_e = \frac{\pi^2 k_B^2 \Theta}{m v_F^2} \quad (\text{II.3.10})$$

where v_F is the Fermi velocity. If the mean free path in Equation (II.3.9) is substituted by $l_e = v_F \tau_e$ the electronic thermal conductivity becomes

$$\kappa_e = \frac{\pi^2 n k_B^2 \Theta \tau_e}{3m}. \quad (\text{II.3.11})$$

Introducing the electrical conductivity $\sigma = ne^2\tau_e/m$ in the above equation, we get

$$\kappa_e = \frac{\sigma\pi^2k_B^2}{3e^2} \quad (\text{II.3.12})$$

which is the Wiedemann-Franz-Lorentz law. The Lorentz number L_e for metals is defined as $L_e = \kappa_e/\sigma\Theta$ and is almost independent of temperature for $\Theta > \Theta_D/2$.

The expression (II.3.11) for κ_e has also been obtained from a more fundamental approach, when the electron energy ε , and the wave vector $\mathbf{k}$, is taken into consideration. Then τ becomes the electron lifetime $\tau_e(\varepsilon, \mathbf{k})$, which depends on both, ε and $\mathbf{k}$. Thus, κ_e becomes

$$\kappa_e = \frac{nk_B^2\Theta}{m_b} \left\langle \left(\frac{\varepsilon_{\mathbf{k}} - E_F}{k_B\Theta} \right)^2 \tau_e(\varepsilon, \mathbf{k}) \right\rangle \quad (\text{II.3.13})$$

where E_F is the Fermi level energy and m_b is the effective electron band mass. The averaging is performed over all electron states with a weight factor $-\frac{\partial f(\varepsilon_{\mathbf{k}})}{\partial \varepsilon_{\mathbf{k}}}$ where $-\frac{\partial f}{\partial \varepsilon_{\mathbf{k}}} = (1/k_B\Theta)f(1-f)$.

Yet another way to express κ_e is in terms of electron-phonon coupling functions; the transport Éliashberg coupling function $\alpha_{tr}^2 F(\omega)$ and the ordinary Éliashberg coupling function $\alpha^2 F(\omega)$. It was derived in a more convenient form as thermal resistivity [1] $W_e = 1/\kappa_e$,

$$\begin{aligned} \frac{1}{\kappa_e} = & \frac{1}{L_0\Theta} \frac{(4\pi^2)}{\omega_{pl}} \int_0^{\omega_{max}} \frac{\hbar\omega/k_B\Theta}{[\exp(\hbar\omega/k_B\Theta) - 1][1 - \exp(-\hbar\omega/k_B\Theta)]} \\ & \times \left\{ \left[1 - \frac{1}{2\pi^2} \left(\frac{\hbar\omega}{k_B\Theta} \right)^2 \right] \alpha_{tr}^2 F(\omega) + \frac{3}{2\pi^2} \left(\frac{\hbar\omega}{k_B\Theta} \right)^2 \alpha^2 F(\omega) \right\} d\omega. \end{aligned} \quad (\text{II.3.14})$$

Here L_0 is the Lorentz number for a free electron model in which the lifetime τ_e , is taken to be the same for electrical and thermal transport, and $\omega_{pl} = 4\pi ne^2/m$. At the high temperature limit, $\hbar\omega_{max}/k_B\Theta \gg 1$, and the expression for $1/\kappa_e$ becomes

$$\frac{1}{\kappa_e} = \frac{2\pi mk_B}{L_0 ne^2 \hbar} \int_0^{\omega_{max}} \frac{2\alpha_{tr}^2 F(\omega)}{\omega} d\omega = \frac{2\pi mk_B \lambda_{tr}}{L_0 ne^2 \hbar} \quad (\text{II.3.15})$$

The above equation represents the Wiedemann-Franz-Lorentz law. In metals the Wiedemann-Franz-Lorentz law does not reflect any saturation effects because the electrons are the ones mainly responsible for thermal conductivity.

II.4. The Heat Capacity

The total heat capacity for solids at constant pressure C_p is made of the lattice contribution to the heat capacity C_l and the electron contribution to the heat capacity C_e . An analytic approach to each contribution is presented separately in the following sections. An example of the temperature dependance of the total heat capacity is shown at the end for a typical transition metal. For different temperature regions, the relative magnitude of different contributions to the total heat capacity are analyzed.

II.4.1. Lattice Heat Capacity

The simplest description of the lattice vibrations is achieved when it is assumed that the atoms vibrate as independent harmonic oscillators. In this case, when only harmonic vibrations are involved, the heat capacity at constant pressure equals the heat capacity at constant volume, and is defined as

$$C_{har} = \left(\frac{\partial E_{har}}{\partial \Theta} \right) = \Theta \left(\frac{\partial S_{har}}{\partial \Theta} \right), \quad (\text{II.4.1})$$

where S_{har} is the entropy when harmonic vibrations are assumed.

For a single phonon mode, the heat capacity $C_{har}(\mathbf{q}, \eta)$ is

$$C_{har}(\mathbf{q}, \eta) = k_B \left(\frac{\hbar \omega(\mathbf{q}, \eta)}{k_B \Theta} \right)^2 \frac{\exp[\hbar \omega(\mathbf{q}, \eta)/k_B \Theta]}{\{\exp[\hbar \omega(\mathbf{q}, \eta)/k_B \Theta] - 1\}^2}. \quad (\text{II.4.2})$$

Then, the total heat capacity of a solid is

$$C_{har}(\Theta) = Nk_B \int_0^{\omega_{max}} \left(\frac{\hbar\omega}{k_B\Theta} \right)^2 \frac{\exp[\hbar\omega/k_B\Theta]}{\{\exp[\hbar\omega/k_B\Theta] - 1\}^2} F(\omega) d\omega. \quad (\text{II.4.3})$$

If the Debye model is introduced the density of states is

$$F_D(\omega) = \frac{3V\omega^2}{2\pi^2 N v_D^3} \quad (\text{II.4.4})$$

where v_D is the sound velocity taken constant for each polarization type. The Debye heat capacity is then

$$C_D(\Theta) = 9Nk_B \left(\frac{\Theta}{\Theta_D} \right)^3 \int_0^{\frac{\Theta_D}{\Theta}} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{II.4.5})$$

where $\Theta_D = \frac{\hbar v_D}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3}$ and $x = \frac{\Theta_D}{\Theta}$.

The Low Temperature Limit of C_l

In the low temperature limit, Θ_D/Θ may be taken as ∞ . The integral in Equation (II.4.5) is then $4\pi^4/15$ and C_D becomes

$$C_D(\Theta) = \frac{12\pi^4 Nk_B}{5} \left(\frac{\Theta}{\Theta_D} \right)^3. \quad (\text{II.4.6})$$

The lowest order correction term may be obtained if the integral $\int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx$ is added and subtracted from Equation (II.4.5). Then the integrals result in a term equal to $4\pi^4/15$ minus an integral from Θ_D/Θ to ∞ , where the leading term is obtained from integration by parts [1];

$$C_D(\Theta) = Nk_B \left[\frac{12\pi^4}{5} \left(\frac{\Theta}{\Theta_D} \right)^3 - 9 \frac{\Theta_D}{\Theta} \exp \left(-\frac{\Theta_D}{\Theta} \right) \right]. \quad (\text{II.4.7})$$

To obtain higher order correction terms, one has to note that the density of states $F(\omega)$ can be expended in a series which only contains even powers of ω $F(\omega) = c_1\omega^2 + c_2\omega^4 + \dots$ and substitute this expression in Equation (II.4.3). Since terms of the order of $\exp[\hbar\omega_{max}/k_B\Theta]$ may be neglected in the low temperature limit, becomes

$$C_D(\Theta) = Nk_B \left[\frac{4\pi^4}{15} c_1 \left(\frac{k_B\Theta}{\hbar} \right)^3 + \frac{16\pi^6}{21} c_2 \left(\frac{k_B\Theta}{\hbar} \right)^5 + \dots \right]. \quad (\text{II.4.8})$$

The High Temperature Limit of C_l

In the high temperature limit Thirring [5] has derived an expression for the heat capacity per mode for a solid

$$C_{har} = k_b \left\{ 1 + \sum_{n=1}^{\infty} (-1)^n \frac{(2n-1)B_{2n}}{(2n)!} \left(\frac{\hbar\omega_{q\eta}}{k_B\Theta} \right)^{2n} \right\} \quad (\text{II.4.9})$$

where B_{2n} are constants. In terms of frequency moments $\omega(n)$ the high temperature limit for the lattice heat capacity is

$$C_{har}(\Theta) = 3Nk_b \left\{ 1 - \frac{1}{12} \left(\frac{\hbar\omega(2)}{k_B\Theta} \right)^2 + \frac{1}{240} \left(\frac{\hbar\omega(4)}{k_B\Theta} \right)^4 - \dots \right\}. \quad (\text{II.4.10})$$

The heat capacity per mass multiplied by the atomic weight is an almost constant number for most solids at room temperature. Dulong and Petit measured this value to be about 6.5 cal/mole. The high temperature limit in the harmonic approximation

gives 5.96 cal/mol ($3Nk_B$). The difference is due to the fact that Dulong and Petit measured the real C_p which includes anharmonic effects as well.

II.4.2. Electronic Heat Capacity

The electronic heat capacity like most other thermophysical properties that are related to the electronic structure of metals, depend on the electronic density of states $N(E)$ at the Fermi level E_F . For simple free-electron-metals and for transition metals the simplest approximation for the electronic heat capacity C_e is the Sommerfield formula

$$C_e = \gamma\Theta = \frac{2\pi^2 k_B^2}{3} N(E_F)\Theta. \quad (\text{II.4.11})$$

Here it is assumed that the energy density may be considered constant and equal to $N(E_F)$ which, for some transition metals, results in a factor of two error at very high temperatures. Also at low temperatures an electron-phonon many body enhancement factor should be present that can be as large as 2.5. In this Sommerfield model the electrons are treated as a gas of Fermions having energies E_k and density of states $N(E)$. The energy distribution is described by the Fermi-Dirac distribution function

$$f(E) = \frac{1}{\exp[(E - \mu)/k_B\Theta] + 1} \quad (\text{II.4.12})$$

where $\mu(\Theta)$ is the chemical potential determined from the condition that the total number of conduction electrons is conserved;

$$\int_{-\infty}^{\infty} 2N(E)f(E)dE = N_e. \quad (\text{II.4.13})$$

The Fermi level E_F is defined as the chemical potential at zero temperature, $E_F = \mu(0)$.

The total conduction-electron energy is

$$E_{el} = \int_{-\infty}^{\infty} 2EN(E)f(E)dE, \quad (\text{II.4.14})$$

and the heat capacity is

$$C_{el} = \int_{-\infty}^{\infty} 2(E - E_F)N(E)\frac{\partial f(E)}{\partial \Theta}dE, \quad (\text{II.4.15})$$

or after subtracting $\frac{\partial(E_F N_F)}{\partial \Theta} = 0$,

$$C_{el} = k_B^2 \Theta \int_{-\infty}^{\infty} 2\frac{(E - E_F)^2}{k_B \Theta} N(E)\frac{\partial f}{\partial E}dE. \quad (\text{II.4.16})$$

If near the Fermi level $N(E)$ is slowly varying with E , $N(E)$ may be considered constant (i.e. equal to $N(E_F)$) and C_{el} yields

$$C_{el} = \frac{2}{3}\pi^2 N(E_F)k_B^2 \Theta = \gamma \Theta. \quad (\text{II.4.17})$$

Since γ usually includes the electron-phonon many body correction, it is more precise that in the Sommerfeld result the notation γ_b is used where the index b indicates that the band structure effects are included. The expression for C_{el} is then

$$C_{el} = \gamma_b \Theta. \quad (\text{II.4.18})$$

If the density of states $N(E)$ near the Fermi level is not assumed constant (i.e. equal $N(E_F)$) it may be expressed by a series expansion around the temperature independent Fermi level E_F

$$N(E) = N(E_F) + (E - E_F)\frac{dN(E)}{dE}\bigg|_{E=E_F} + \frac{1}{2}(E - E_F)^2\frac{d^2N(E)}{dE^2}\bigg|_{E=E_F} + \dots, \quad (\text{II.4.19})$$

and the electronic heat capacity becomes

$$C_{el} = \frac{2}{3}\pi^2 N(E_F) k_B^2 \Theta \left\{ 1 - \frac{\pi^2}{2} (k_B \Theta)^2 \left[\left(\frac{N'}{N} \right)^2 - \frac{7}{5} \frac{N''}{N} \right] \right\}. \quad (\text{II.4.20})$$

In the above equation

$$N' = \frac{dN(E)}{dE} \Big|_{E=E_F} \text{ and } N'' = \frac{d^2 N(E)}{dE^2} \Big|_{E=E_F}. \quad (\text{II.4.21})$$

In the free-electron model, the density of states $N(E) \sim \sqrt{E}$, so that the higher order terms in Equation (II.4.20) become

$$\left(\frac{N'}{N} \right)^2 = \frac{1}{4E_F^2} \text{ and } \frac{N''}{N} = -\frac{1}{4E_F^2}. \quad (\text{II.4.22})$$

Now Equation (II.4.20) obtains the well known form

$$C_{el} = \frac{2}{3}\pi^2 N(E_F) k_B^2 \Theta \left[1 - \frac{3\pi^2}{10} \left(\frac{\Theta}{\Theta_F} \right) \right] \quad (\text{II.4.23})$$

where $\Theta_F = E_F/k_B$.

Equation (II.4.20), obtained for C_{el} according to Sommerfield model, does not show quantitatively good agreement with experiment. The main reason for this is that the electron-phonon many body correction is not included in the Sommerfield electron theory.

An important expression for the electron entropy S_{el} has been derived by Éliashberg [6] and Grimvall [7] that includes the electron-phonon many body effects by including the electron-phonon self energy [2]. This expression for S_{el} results in

an integral over electron energies that in turn, results into an expression connecting the Sommerfield model;

$$S_{el} = \frac{2}{3}\pi^2 N(E_F)(1 + \lambda)k_B^2 \Theta. \quad (\text{II.4.24})$$

where $(1 + \lambda)$ is the electron-phonon many-body correction. λ , which is temperature dependent, will turn out to be the second moment of the Éliashberg electron-phonon coupling function. For $\Theta \gtrsim \Theta_D$ λ becomes zero, and the Sommerfield model is retrieved. Therefore it is logical to split S_{el} into two parts

$$S_{el} = S_b + S_{ep}, \quad (\text{II.4.25})$$

where S_b is the electron bend theory (or Sommerfield) result and S_{ep} is the correction due to electron-phonon many-body interaction. For low temperatures

$$S_{el} = \lambda S_b. \quad (\text{II.4.26})$$

From S_{el} one can obtain the electronic heat capacity at constant volume

$$C_{el} = \Theta \left(\frac{\partial S_{el}}{\partial \Theta} \right)_V. \quad (\text{II.4.27})$$

and at low temperatures ($\Theta \ll \Theta_D$) S_{el} becomes

$$C_{el} = \gamma_b(1 + \lambda)\Theta = \frac{2}{3}\pi^2 N(E_F)(1 + \lambda)k_B^2 \Theta. \quad (\text{II.4.28})$$

The electronic heat capacity C_{el} may also be split into two part;

$$C_{el} = [\gamma_b + \gamma_{ep}(\Theta)]\Theta, \quad (\text{II.4.29})$$

where $\gamma_{ep}(\Theta = 0) = \lambda(\Theta = 0)\gamma_b$. For $\Theta \gtrsim \Theta_D$ γ_b becomes zero. In metals the value of λ is of the order of 1. For a given Debye temperature, one may approximate

$$\gamma_{ep}(\Theta)/\gamma_b = \lambda \text{ for } \Theta < \Theta_D/4 \text{ and } \gamma_{ep}(\Theta) = 0 \text{ for } \Theta > \Theta_D/3. \quad (\text{II.4.30})$$

The temperature dependence of $\gamma_{ep}(\Theta)$ and $S_{ep}(\Theta)$ is shown in Fig. II.4.1 [2] calculated with the Einstein model for the lattice vibration. $(1 + \gamma_{ep}(\Theta)/\gamma_b)$ represents $(1+\lambda)$ and shows that λ is temperature dependent. The temperature dependence of $\gamma_{ep}(\Theta)$ and $S_{ep}(\Theta)$ calculated with a true phonon spectrum gives very similar results.

II.4.3. Heat Capacity of a Typical Transition Metal

A brief discussion on the relative magnitude of the different terms contributing to the total heat capacity is presented here. Since in insulators the electronic part of the heat capacity does not exist, it is interesting to look at the various contributions to the total heat capacity in metals. We chose to discuss the total heat capacity of a transition metal because the focus of this work is niobium, a transition metal. In nontransition metals the electronic contribution to the heat capacity is much smaller. To get a qualitative picture, the relative magnitude of the various contributions in a typical transition metal are discussed for different temperature ranges with reference to Fig. II.4.2

Heat Capacity at Low Temperatures

The total heat capacity of a Typical transition metal is presented in Fig. II.4.2 as a function of temperature. Various contributions are shown marked with letters A-H. Contributions A and B refer to low temperatures;

Contribution A: In Fig. II.4.2 A represents the electronic contribution, and it is the dominant one for $\Theta < \Theta_D$. The electronic contribution at low temperatures has

the form

$$C_{el} = \gamma_b(1 + \lambda)\Theta \quad (\text{II.4.31})$$

where $\gamma_b\Theta$ is the standard electronic heat capacity derived from the electron-band theory, with $\gamma_b = (2\pi^2/3)k_B^2N(E_F)$. The electron-phonon enhancement factor $(1 + \lambda)$ is temperature dependent as shown in Fig. II.4.1 ($(1 + \gamma_{ep}(\Theta)/\gamma_b)$ represents $(1+\lambda)$). The magnitude of λ is a characteristic of a material and may acquire values from .1 to 3.

Contribution B: Contribution B to the heat capacity represents the low temperature limit of the Debye law. This is the phonon contribution, which holds for all solids and has the form

$$C_p = \frac{12\pi^4}{5}Nk_B\left(\frac{\Theta}{\Theta_D}\right)^3. \quad (\text{II.4.32})$$

Very small contributions to the total heat capacity are possible from the vibration of dislocations, vibrations from heavy impurities or surface effects in very small samples. These effects are of some importance only for $\Theta < 0.01\Theta_D$.

Heat Capacity at Intermediate Temperatures

Contribution C: In Fig. II.4.2, C represents the contribution due to harmonic vibrations. At intermediate temperatures C_{har} represents the main contribution to C_p and is well described by an Einstein model or a Debye model.

Heat Capacity at High Temperatures

Contribution D: At high temperatures the harmonic vibrational heat capacity is no longer C_p and needs to be corrected by $C_p - C_V$. This term is usually obtained by a quasiharmonic model [9] and is linear in Θ , to leading order,

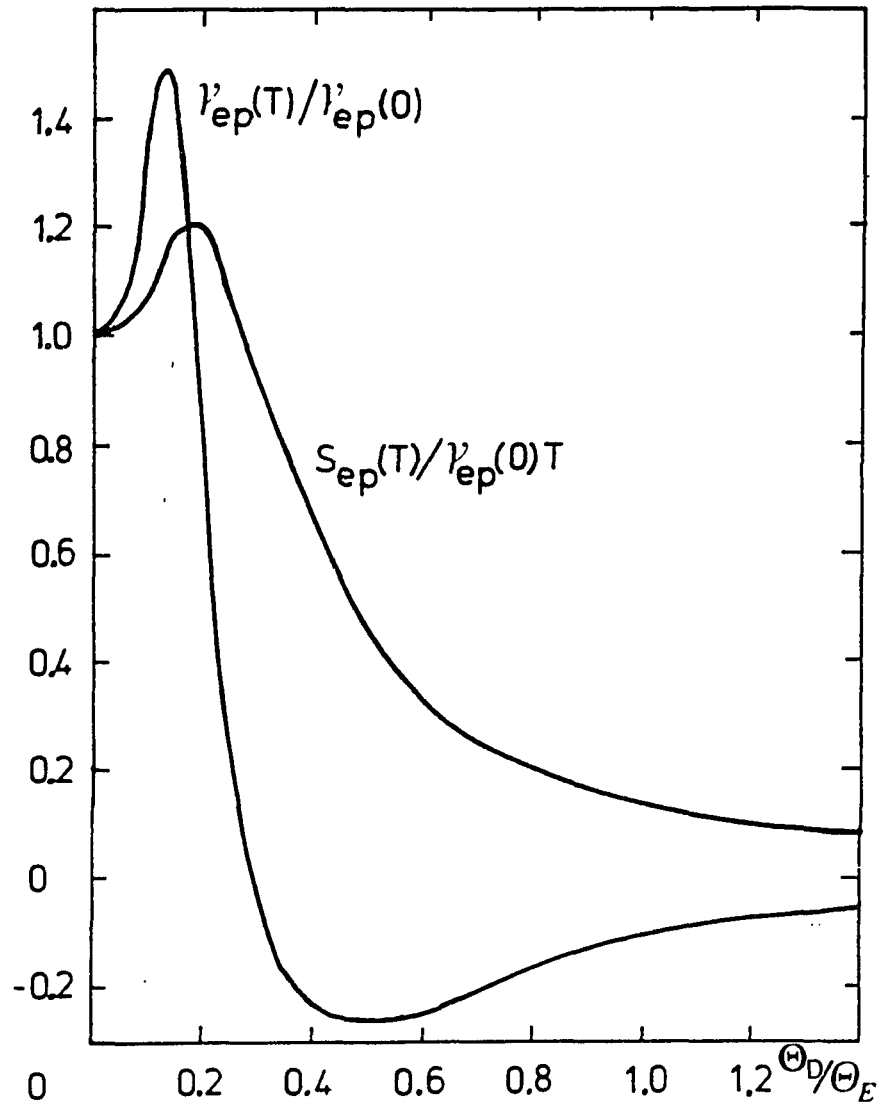


Figure II.4.1 The temperature dependence of the correction to the electronic heat capacity, $\gamma_{ep}(\Theta)$, and of the correction to the electronic entropy, $S_{ep}(\Theta)$, caused by electron-phonon many-body interaction [8].

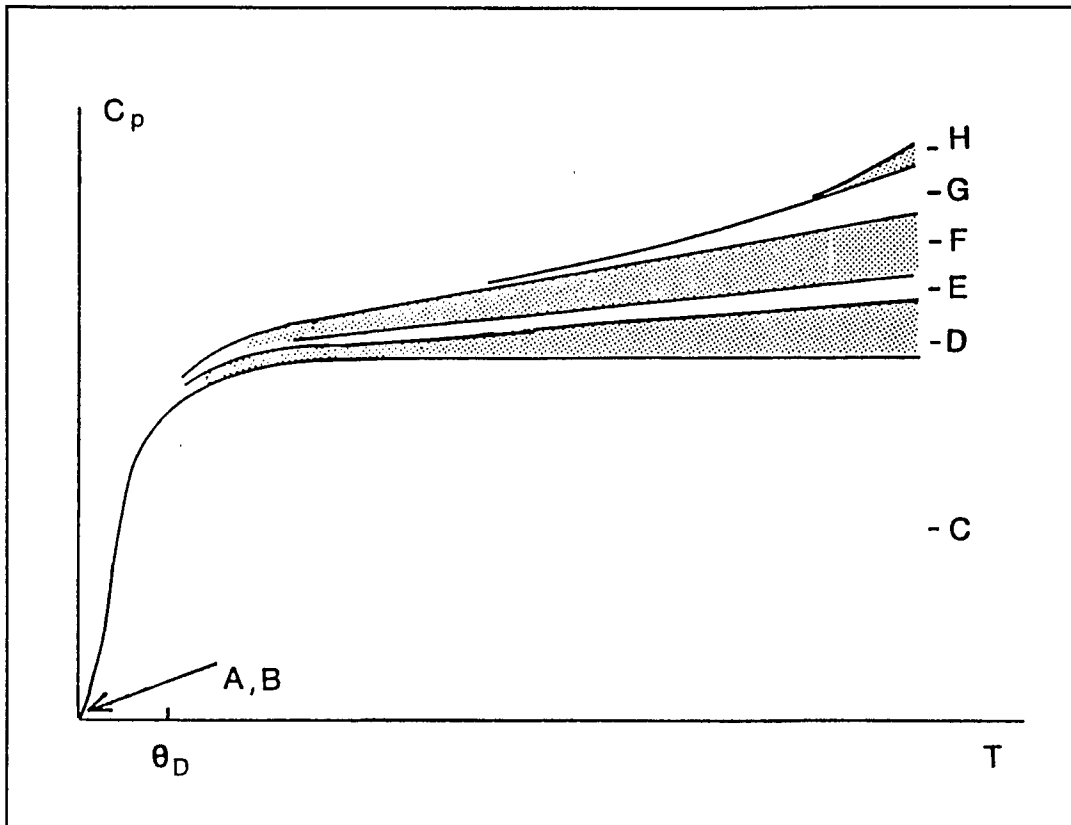


Figure II.4.2 The temperature dependence of the total heat capacity for a typical transition metal. The relative magnitude of the various contributions in a typical transition metal for different temperature ranges are marked with letters A-H, and are explained in the text in detail [2].

$$C_p - C_V = \frac{V\beta^2 K_T}{C_p^2} C_p^2 \Theta = a C_p^2 \Theta, \quad (\text{II.4.33})$$

where K_T is the isothermal bulk modulus $(K_T)^{-1} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$ and β is the cubic expansion coefficient. Parameter a is often approximately constant for a wide range of temperatures $\Theta > \Theta_D$. A is also a small contribution to $C_p - C_V$ from higher order anharmonic effects.

Contribution E: E represents the explicit anharmonic contribution to C_V and may have any sign. It is linear in Θ to leading order.

Contribution F: Contribution F represents the electronic heat capacity at high temperature $C_{el} = \gamma_b \Theta$. At high temperatures $\lambda = 0$, and the electron-phonon enhancement factor $(1 + \lambda)$ is missing.

Contribution G: This contribution is pronounced at very high temperatures and is due to the fact that the approximation $N(E) = N(E_F)$ is not good any more. Then there is a correction up to $\pm 50\%$ to the electronic heat capacity C_{el} .

Contribution H: Near maximum temperature heat capacity due to lattice defects become significant, especially in non-metals. This contribution varies exponentially with Θ_m/Θ .

II.5. Thermal Diffusivity

The conductivity κ is of primary interest to the scientist, while measurements often give the thermal diffusivity D . The thermal diffusivity is related to thermal conductivity by

$$D = \frac{\kappa}{C_p} \quad (\text{II.5.1})$$

where C_p is the heat capacity at constant pressure. The Fourier's equation that describes the heat diffusion process is

$$\frac{\partial \Theta}{\partial t} - D(\nabla^2 \Theta) = 0. \quad (\text{II.5.2})$$

When κ is spatially varying, i.e. not uniform throughout the sample Fourier's equation takes the form

$$C_p \frac{\partial \Theta}{\partial t} - \nabla(\kappa \nabla \Theta) = 0. \quad (\text{II.5.3})$$

It should be mentioned that κ may be spatially varying because κ is temperature dependent and the sample is in a temperature gradient.

One may approximate the relative magnitude of thermal conductivity and diffusivity when $\Theta > \Theta_D$ [1]. If N is the total number of atoms, M the average mass of an atom in a material, V the volume of the sample, and approximating C_p by $3k_B$ per atom, we obtain

$$\frac{\kappa}{D} = C_p \approx \left(\frac{3k_B}{M} \right) \left(\frac{M}{V/N} \right) = \frac{3k_B}{V/N}. \quad (\text{II.5.4})$$

For $\Theta > \Theta_D$ V/N varies much less than κ for different materials, the material with higher thermal conductivity usually has higher thermal diffusivity too.

Bibliography

- [1] G. Grimvall, *Thermophysical Properties of Materials*. North-Holland, Amsterdam, 1986.
- [2] G. Grimvall, *The Electron-Phonon Interaction in Metals*. North-Holland, Amsterdam, 1981.
- [3] W. L. McMillan *Phys. Rev.* **167**, p. 331, 1968.
- [4] C. Kittel, *Introduction To Solid State Physics*. John Wiley, New York, 1986.
- [5] H. Thirring *Phys. Zeitschrift* **14**, p. 867, 1913.
- [6] G. M. Éliashberg *Sov. Phys. — JETP* **16**, p. 780, 1963.
- [7] G. Grimvall *Phys. Stat. Sol.* **32**, p. 383, 1969.
- [8] G. Grimvall *Phys. Kondens. Materie* **9**, p. 283, 1969.
- [9] D. C. Wallace, *Thermodynamics of Crystals*. John Wiley, New York, 1972.

III Thermomodulation Spectroscopy and Laser Heating

III.1. Introduction

The method of modulation spectroscopy consists of applying a perturbation on a material that causes a change in the reflected or transmitted light. From measuring the change in the reflected or transmitted light useful information about the location of critical points in the interband absorption of solids [1] has been extracted.

Thermomodulation measurements have been used in the past to obtain information about the structure of metals [2]. In thermomodulation measurements a temperature wave may be applied to the sample and the resulting ac component of the reflected or transmitted light at different wavelength may be obtained. This has proven especially useful for obtaining thermotransmission and thermoreflectance spectra of metals (for example Au, Cu and Al) [3,4]. With the development of the picosecond and femtosecond lasers, ultrafast laser pulses have been used to produce fast transient nonequilibrium temperatures and investigate ultrafast relaxation processes [5].

In the following sections, an introduction to the thermomodulation spectroscopy method is provided, together with the physical explanation of the thermomodulation signal. A brief review of work done so far on ultrafast thermomodulation measurements is also presented.

III.2. Thermomodulation Spectroscopy

Transient thermorefectance and thermotransmittance spectroscopy is based on producing a small change in reflectance or transmittance by changing the temperature of the material [6,7]. The heated electrons and phonons alter the dielectric constant which in turn changes the transmissivity T , as shown in the equation below:

$$\frac{\Delta T}{T} = \frac{1}{T} \left[\frac{\partial T}{\partial \varepsilon_1} \Delta \varepsilon_1 + \frac{\partial T}{\partial \varepsilon_2} \Delta \varepsilon_2 \right] \quad (\text{III.2.1})$$

where $T = T(\hat{n})$ and $\hat{n} = \sqrt{\varepsilon_1 + i\varepsilon_2}$. The change in the dielectric constant is known to be proportional to the change in both electric and lattice temperature [6], and therefore

$$\frac{\Delta T}{T} = b_1 \Delta \Theta_l + b_2 \Delta \Theta_e \quad (\text{III.2.2})$$

where $\hat{n}$ is the complex index of refraction, b_1 and b_2 are constant coefficients, ε_1 and ε_2 are the real and imaginary part of the dielectric constant, and Θ_e and Θ_l are the electron and lattice temperature, respectively.

The three dominant contributions to the thermomodulation signal are:

- Electron-phonon collisions which result in phonon population increase, and this shifts and warps the energy bands through electron-phonon interaction. The change in transmissivity (or reflectivity) due to phonon population increase, ΔT_l , is

$$\Delta T_l = \sum_q \frac{\partial T}{\partial n_q} \frac{\partial n_q}{\partial \Theta_l} \Delta \Theta_l \quad (\text{III.2.3})$$

where T stands for transmissivity, n_q is the phonon distribution, and q is the phonon quantum number.

• Lattice expansion causes shifts and warping in the electron energy bands through changes in one-electron potential, which in turn causes the Fermi level to shift. This volume thermal expansion also decreases the plasma frequency. The change in transmissivity due to lattice expansion, ΔT_{exp} , is

$$\Delta T_{exp} = \frac{\partial T}{\partial a} \Delta a \quad (\text{III.2.4})$$

where Δa represents the lattice expansion.

• Fermi level smearing - as the electron temperature rises, the tails of the Fermi level distribution spread out in energy and open states below the Fermi level for transition. Only interband transitions that originate or terminate on states near Fermi level are affected [8]. The change in transmissivity due to Fermi level smearing, ΔT_e , is

$$\Delta T_e = \sum_k \frac{\partial T}{\partial f_k} \frac{\partial f_k}{\partial \Theta_e} \Delta \Theta_e \quad (\text{III.2.5})$$

where f_k is the electron distribution and k is the electron quantum number. This is the free electron contribution which depends on the electronic subsystem only. The free electron contribution is present in metals when transitions of electrons from the top of the d-band to the Fermi level occur. When temperature modulation is applied the distribution of occupied electronic states near the Fermi level,

$$\rho = \frac{1}{(1 + \exp \{[\hbar\omega - (E_F - E_d)]/k_B\Theta_e\})} \quad (\text{III.2.6})$$

changes. The absorption of photons with energies, $\hbar\omega$, corresponding to the transition from E_d to E_F is directly effected by this change. That is, when heating is applied, the conduction-electron temperature increases and the Fermi distribution of occupied states decreases or increases depending on whether $\hbar\omega$ is less or greater than $E_F - E_d$ [2]. When $\hbar\omega < E_F - E_d$, $\frac{\partial \rho}{\partial \Theta_e} < 0$, i. e. the number of occupied states in

the conduction band decreases and there are more available states for promotion of the d-band electrons into the conduction band. Therefore, the absorption of light with energies slightly less than $E_F - E_d$ increases. On the other hand, for photon energies $\hbar\omega > E_F - E_d$, $\frac{\partial \rho}{\partial \Theta_e} > 0$. The change in the conduction electron temperature decreases the number of conduction band states available for transitions from the d-band. This results in a decrease in absorption of phonons with energies slightly greater than $E_F - E_d$.

The temperature derivative of the Fermi level distribution ρ , versus energy difference between the top of the d-band and the Fermi level in copper is presented in Fig. III.2.1. For copper $E_F - E_d = 2.15\text{eV}$. The derivative is evaluated at 100 and 300 K, demonstrating spectral broadening as temperature increases. One can see from Fig. III.2.1 that when the photon energy $\hbar\omega = E_F - E_d$ there is no change in ρ due to electron temperature. There is also no Fermi smearing for photon energies that are not close to $E_F - E_d$. Therefore, there will be no change in absorption and transmissivity other than the one resulting from volume expansion and increased electron-phonon collision frequency for photon energies not close to $E_F - E_d$.

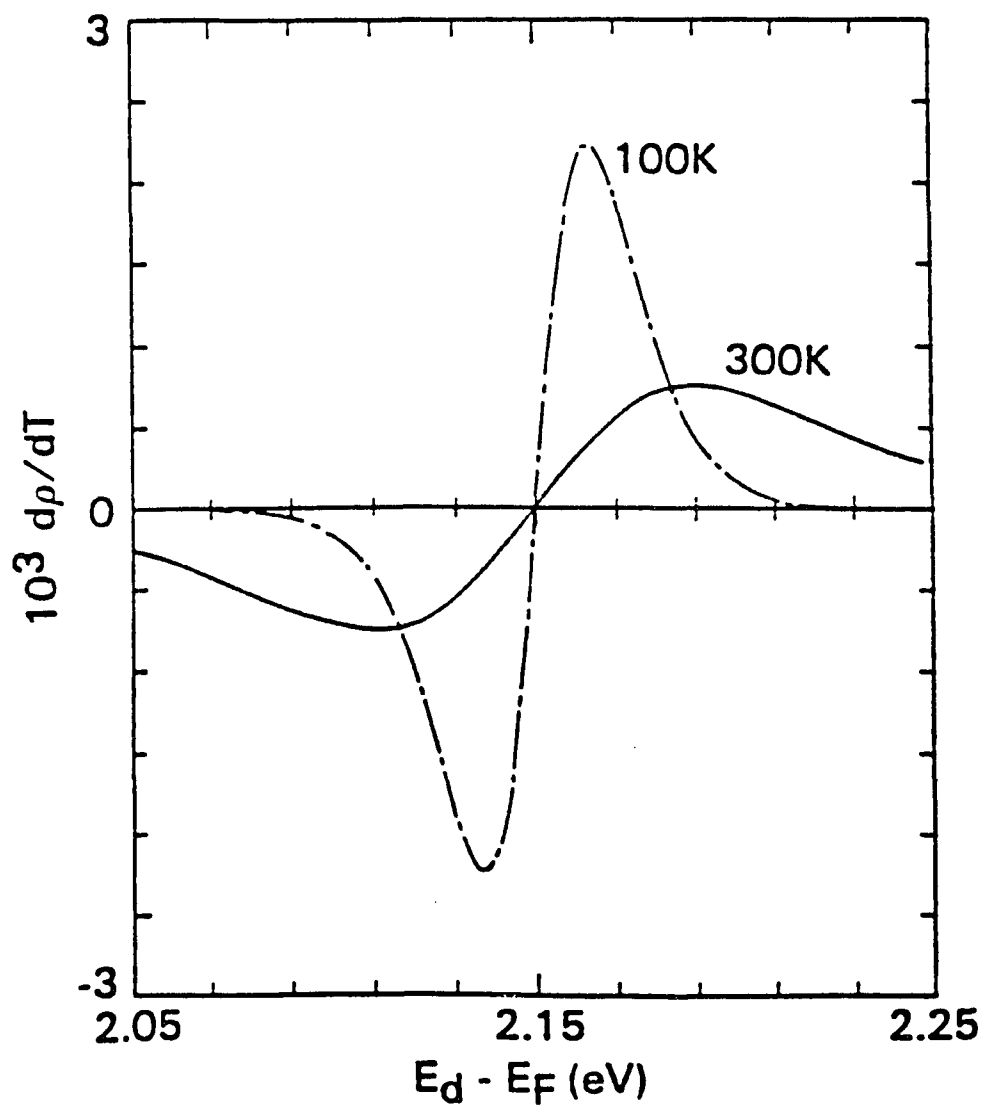


Figure III.2.1 The temperature derivative of the Fermi level distribution ρ , versus energy difference between the top of the d-band and the Fermi level in copper is presented [8]. For copper $E_F - E_d = 2.15$ eV. The derivative is evaluated at 100 and 300 K, demonstrating spectral broadening with temperature.

III.3. Ultrafast Thermomodulation Measurements of Electron-Phonon Relaxation

III.3.1. The Transient Transmissivity Method

At present, no measurements could give direct information of the electron relaxation times in metals since they have to be performed in the femtosecond time domain. However, indirect methods like the techniques of transient reflectivity and transient transmissivity have been made feasible with the advent of high-repetition-rate ultrafast lasers. These are pump-and-probe experiments that have the capability to investigate the dynamics of the electron-phonon interaction in the femtosecond time domain.

The pump and probe technique consists of introducing a perturbation in the material by a “pump” light pulse and then investigating the resulting change by a “probe” light pulse. The probe pulse is of much lower intensity than the pump pulse so that the perturbation it introduces is negligible. The probe beam is delayed with respect to the pump beam by requiring it to traverse a greater distance than the pump beam before reaching the target. In this way, changes due to the pump pulse are detected by the probe pulse at times shortly after they have been induced. The delay time may be varied by varying the excess distance the probe pulse has to travel with respect to the pump pulse.

The transient reflectivity and transient transmissivity techniques are pump-probe techniques, based on the temperature dependence of the complex dielectric constant. First heat is deposited by the pump pulse in the material. The deposition is distributed,

since there is a penetration depth for the light of about 10–20 nm for metals. After the electrons are excited they thermalize rapidly through electron-electron scattering [9] [10] [11]. Then, energy is transferred to the lattice via electron-phonon scattering. This interpretation is based on the quadratic energy dependence of the cross-section of electron-electron collisions close to the Fermi energy [12], and the fact that the energy a phonon can typically accommodate is about 0.02 eV, that is, the major part of the electronic excitation is transferred to the electronic subsystem. Because of its temperature dependence, the dielectric constant of the material is modified by the heat deposition. This modification changes the optical properties of the material which is detected by the probe pulse. There are two contributions to the change in the dielectric constant; i) the free electron contribution and ii) the bound electron contribution. These contributions as previously explained, are effected by temperature and volume changes in different ways [13] [1] [14].

The free electron contribution to the transmissivity change, which is proportional to electron temperature, is a common optical property of the noble-metal elements. There is a sign reversal of the reflectivity or transmissivity change when the phonon energy is tuned to equal the energy required for interband transitions from d-band to Fermi level, as shown in Fig. III.3.2. The arrow represents optical transitions from the top of the d-band to unoccupied states in the conduction band (p-band) near the Fermi level for Au. The transition energy for Au is 2.4 eV. The sign reversal of the thermorefectance of thermotransmittance signal occurs due to Fermi distribution smearing, i.e. the increase of unoccupied states below the Fermi level due to heating induced by the pump pulse. The free electron contribution is usually called the electron contribution, as opposed to bound electron contribution which is called lattice contribution, because the bound electrons have to be in thermal equilibrium

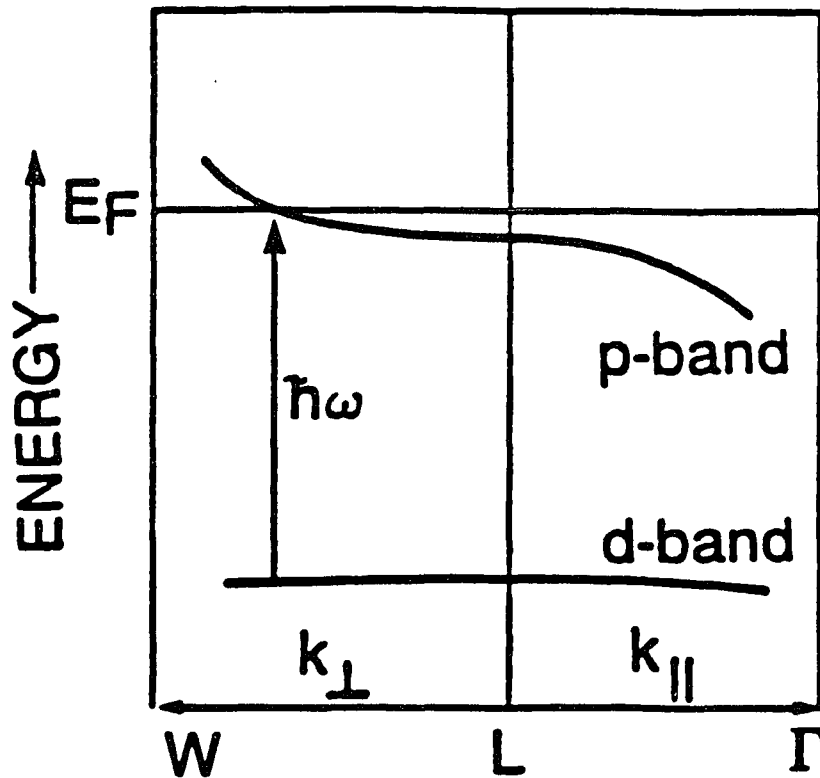


Figure III.3.2 Schematic diagram of the noble-metal band structure responsible for the optical transitions that cause the electronic contribution to the thermotransmittance or thermorefectance [8]. The arrow represents optical transitions from the top of the d-band to unoccupied states in the conduction band (p-band) near the Fermi level for Au. The transition energy for Au is 2.4 eV.

with lattice. The sign reversal due to electron contribution is shown in Fig. III.3.3 for cooper as measured by Eesley [8]. The time resolved thermorefectance signal was obtained by incrementally increasing the delay of the probe pulse with respect to the pump pulse. The measurement was repeated for different probe energies from 2.10 to 2.16 eV. As can be seen, there is an increase in the absorption (decrease in reflectivity) for $\hbar\omega < 2.15$ and a decrease in absorption (increase in reflectivity) for $\hbar\omega > 2.15$. At $\hbar\omega = 2.15$ there is no Fermi level smearing. This is because when the conduction temperature increases during the heating pulse, the fermi distribution of occupied states decreases slightly ($\frac{\partial \rho}{\partial T} < 0$) for $\hbar\omega < E_F - E_d$ and more d-band electrons are promoted into the conduction band by the absorption of probe photons at these energies. This results in a decrease in the reflectivity for $\hbar\omega < E_F - E_d$. For $\hbar\omega > E_F - E_d$ the opposite happens. For $\hbar\omega = 2.15$ there is no temperature modulation of the unoccupied states sampled; to first order $\frac{\partial \rho}{\partial T} = 0$.

It is important to note that besides the fast transient which represents the electron contribution, there is the slow transient, which is the contribution to thermorefectance change due to increase in phonon temperature, i.e. the lattice contribution. This contribution is also present for energies that are not close to $E_F - E_d$. The important point to realize is that close to the Fermi level (except for $\hbar\omega = 2.15$) both contributions to the change of the dielectric constant are present, while away from $E_F - E_d$ we can attribute the change of the optical properties to the phonon temperature only.

III.3.2. The Physical Model - Energy Rate Equations

In the above discussion of the different contributions to the transient

thermomodulation signal in metals, in a pump and probe experiment, it has been implicitly assumed that the electron and phonon temperatures are different. When a femtosecond pump pulse is used the conduction electrons absorb the energy of the heating pulse and thermalize rapidly through electron-electron scattering and via electron-phonon interaction. Since the rate of energy absorption by the electrons is larger than the rate of energy transfer to the lattice, different transient electron and lattice temperatures will be generated. It is possible to obtain transient electron

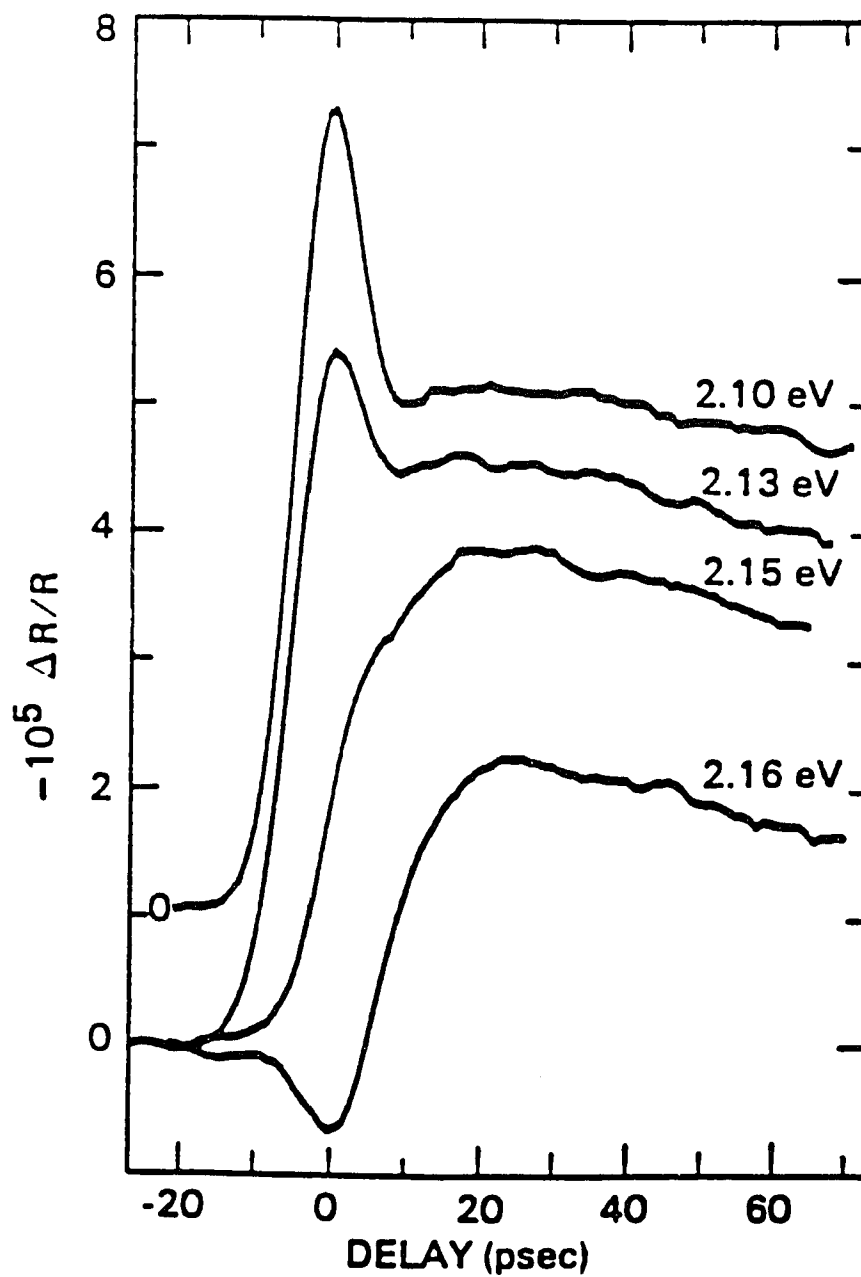


Figure III.3.3 The sign reversal of ΔR due to electron contribution is shown for copper as measured by Eesley [8]. The measurement was repeated for different probe energies from 2.10 to 2.16 eV. The transition energy for Cu is 2.15 eV.

temperature far in excess of the lattice temperature because the electron heat capacity is much smaller than the lattice heat capacity. The magnitude of the excess electron temperature strongly depends on the intensity and duration of the heating pulse and on the coupling between the electrons and the phonons.

Since the electrons achieve local equilibrium among themselves much faster than it takes to achieve equilibrium between the electron and the lattice [15] [16], the electron gas may be considered to be in a state of local equilibrium described by the ordinary Fermi distribution function:

$$\rho = \frac{1}{(1 + \exp \{[\hbar\omega - (E_F - E_d)]/k_B\Theta_e\})} \quad (\text{III.3.1})$$

where Θ_e is the electron temperature, different from the lattice temperature Θ_l . At the same time the phonons may be considered to be in local equilibrium themselves, described by the Bosse-Einstein distribution at Θ_l [17]. Subsequently, the return to equilibrium, i.e. the transfer of energy takes place, governed solely by electron-phonon processes [10] [18] [19] [15]. Other collision processes, such as electron-electron (Coulomb) and phonon-phonon (anharmonic) are active in maintaining the local equilibrium of the electrons at Θ_e and phonons at Θ_l . So on the time scale of few picoseconds (depending on a particular material) the electrons thermalize with phonons and then a slower relaxation process, governed by heat diffusion takes over and the system returns to ambient temperature.

In many previous publications [10] [18] [19], where the establishment of thermal equilibrium between the electrons and the phonons was considered, it was shown that this relaxation process must be modeled as a two temperature system. Two coupled energy balance equations were used and the electron-phonon coupling coefficient was calculated [6] [7]. These energy balance equations, that describe the establishment

of equilibrium between the electrons and the phonons in a metal absorbing the laser pulse, are

$$C_e \frac{\partial \Theta_e}{\partial t} = \kappa \nabla^2 \Theta_e - g(\Theta_e - \Theta_l) + S(r, t) \quad (\text{III.3.2})$$

and

$$C_l \frac{\partial \Theta_l}{\partial t} = g(\Theta_e - \Theta_l), \quad (\text{III.3.3})$$

where $S(r, t)$ is the heat source term, C_e is the heat capacity of the electrons, C_l is the heat capacity of the phonons, g is the electron-phonon coupling parameter, and κ is the heat conductivity for electrons. The first term in Equation (III.3.2) represents the energy absorbed by the electrons, the second term represents the energy lost by electrons because of diffusion out of the film by heat conduction, the third term represents the energy given by the electrons to the phonons, and the last term is the heat source term. The diffusion term $\kappa \nabla^2 \Theta_e$ in Equation (III.3.2) may be neglected in the 1 ps time scale for the transmission geometry, because the diffusion in thin films (thickness - wavelength) is about three orders of magnitude slower process than the electron-phonon thermalization. For room temperatures and above, more precisely for temperatures $> \Theta_D$, $C_e = \gamma \Theta_e$, and C_l and g may be considered constant.

To show how the electron-phonon relaxation time depends on g the energy equation is solved numerically for a given laser pulse profile and energy. The calculated time evolution of the electron and lattice temperature for Nb film at room temperature [20] (initial temperature $\Theta_0 = 292 \text{ K}$) is displayed in Fig. III.3.4. The heating pulse is assumed Gaussian, 100 fs FWHM and 110 nJ per pulse and the electron phonon parameter g is taken to be $20 \times 10^{17} \text{ Wm}^{-3} \text{ K}^{-1}$ and $14 \times 10^{17} \text{ Wm}^{-3} \text{ K}^{-1}$. Initially, the electron temperature increases with time as the electrons absorb the energy of the laser pulse. Then, as the electrons thermalize with phonons, the electron temperature

decreases and the lattice temperature increases. The time it takes for the electrons to thermalize with phonons becomes shorter with stronger electron-phonon coupling i.e. for higher values of g . Lowering the pumping power $S(r,t)$ also makes this electron-

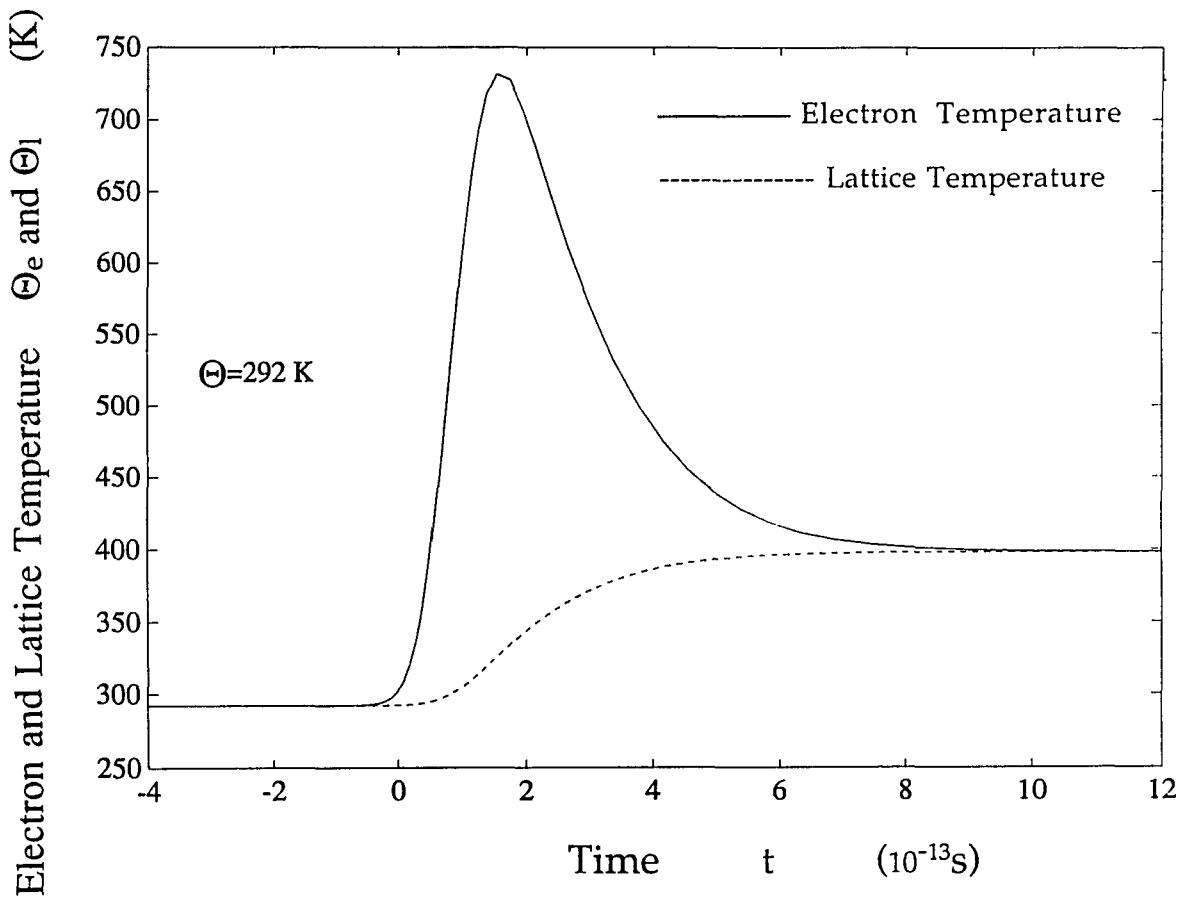


Figure III.3.4 The calculated time evolution of the electron and lattice temperature for Nb film at room temperatures [21] is displayed above. The time it takes for the electrons to thermalize with phonons becomes shorter with stronger electron-phonon coupling i.e. for higher values of g .

phonon phonon relaxation time shorter but this effect is much less pronounced.

To illustrate the influence of the values of C_e , C_l , the computed electron and lattice temperature for same pump intensity (50 nJ per pulse at 120 fs) for Nb and Cu are plotted in Figs. III.3.5(a) and III.3.5(b) [7]. The electron-phonon coupling parameter g is taken from literature [18] [7] to be $g_{Nb}=17 \times 10^{17} \text{Wm}^{-3}\text{K}^{-1}$ and $g_{Cu}=1 \times 10^{17} \text{Wm}^{-3}\text{K}^{-1}$. The electronic heat capacity for niobium is 7.5 times higher than it is for copper which reduces the peak electron temperature for niobium. At the same time the lattice heat capacity for niobium is 0.67 times that of copper, which increases the peak phonon temperature for niobium compared to copper. The electron-phonon coupling parameter for niobium is much higher than for copper which effectively reduces the peak electron temperature for niobium and shortens the electron-phonon relaxation time.

It should be emphasized here that the above calculation are greatly simplified by the assumption that the electron-phonon coupling parameter g is constant, which is a valid assumption only for temperatures above Debye temperature. As will be shown later, the electron-phonon coupling parameter g becomes temperature dependent for temperatures less than Debye temperature. For most metals Θ_{Debye} is less than or close to room temperature (e. g. $\Theta_{Debye,Nb} = 272 \text{ K}$) so $g=\text{const.}$ is a valid assumption for room temperature measurements.

III.3.3. Review of Subpicosecond Thermomodulation Experiments

By generating transient nonequilibrium temperatures in metals with femtosecond laser pulses, the electron relaxation time of Cu, Au, Nb [16] [7] and other metals has been determined. The first observation of nonequilibrium electron heating was

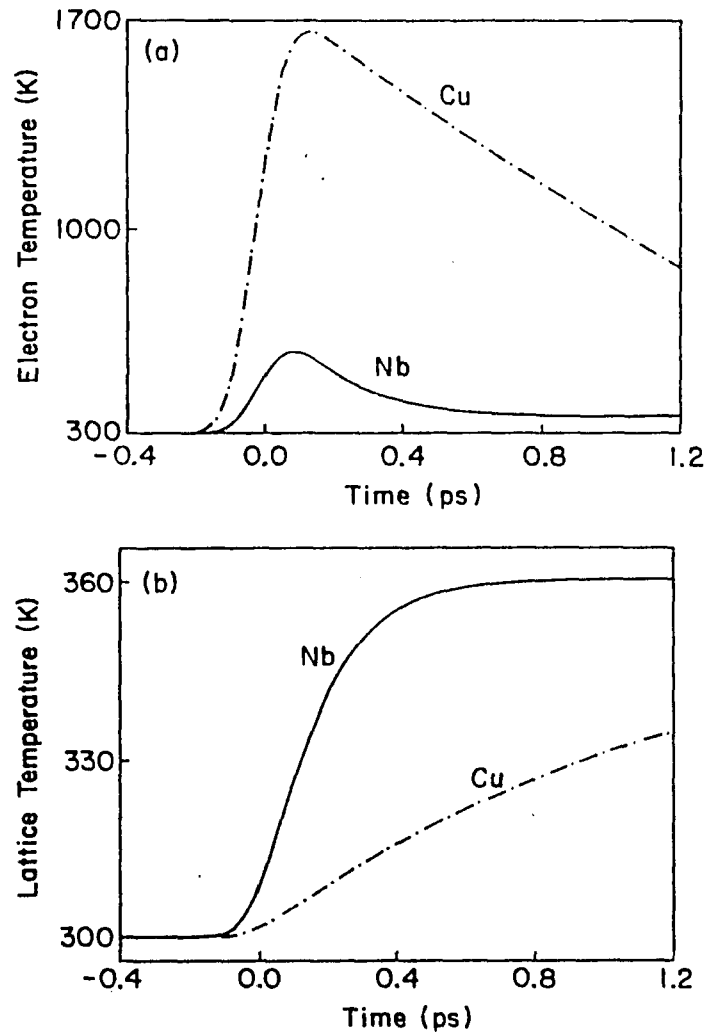


Figure III.3.5 The computed electron and lattice temperature for Nb and Cu are plotted in (a) and (b) respectively [7]. The $C_{e,Nb}$ is 7.5 times higher than $C_{e,Cu}$ which reduces the peak electron temperature for Nb. At the same time the $C_{l,Nb}$ is 0.67 times $C_{l,Cu}$, which increases the peak phonon temperature for Nb compared to Cu.

demonstrated by Eesley in 1983 [22] in a thermomodulation experiment. He used picosecond laser pulses to sequentially heat and probe the thermally induced reflectivity transient in copper, and the nonequilibrium heating of electrons to a temperature above the lattice.

With the development of the femtosecond laser pulses, the process of electron-phonon energy transfer was time resolved and was observed to be 1–4 ps for copper [18]. In this experiment, laser-heating-induced transmissivity of a copper film of thickness comparable to the skin depth was measured in order to minimize the hot electron diffusion effect. Room temperature measurements have also been performed for many metals [10] [7] to determine the electron-phonon coupling parameter g by fitting the results of Equation (III.3.2) and (III.3.3) to the experimental data. Recently Brorson et al. [6] have performed room temperature femtosecond pump-probe measurements in thin metallic superconductor films to determine the electron-phonon coupling constant λ used in the Éliasberg [23] generalization of BCS theory. They have used Allen's theory [17], and the relation between the electron-phonon coupling parameter g and the electron-phonon coupling constant λ at room temperature. Using g as a fitting parameter they determined $\lambda\langle\omega^2\rangle$, and by using values of $\langle\omega^2\rangle$ published in the literature they demonstrated that excellent measurements of the electron-phonon coupling can be obtained with this technique.

III.4. Ultrafast Thermomodulation Measurements of Heat Diffusion

III.4.1. The Transient Transmissivity Method

The transient reflectivity and transmissivity methods for heat diffusion measurements are technically the same pump-probe technique based on the temperature dependence of the dielectric constant, as explained in section III.3.1, with one essential difference; The time resolved thermotransmittance (or thermoreflectance signal) is obtained by incrementally increasing the delay of the probe pulse in steps 1–10 ps long. In this time range the electrons and the lattice have reached thermal equilibrium ($\tau_{\text{el-ph}} < 0.5$ ps) and the signal obtained represents the lattice temperature change as the sample is cooling down to its initial temperature.

III.4.2. The Physical Model – Fourier Equation

In a ultrafast transient thermotransmittance experiment the metal film is heated via a short optical pulse (pump) absorbed by metal electrons. The pump pulse is usually focuses onto a spot $\sim 30 \mu\text{m}$ in diameter. The electrons, after rapidly (~ 1 ps) thermalizing with the lattice diffuse a distance $d \sim \sqrt{Dt}$ where t is the time after the arrival of the pump pulse and D is the thermal diffusivity. The distance traveled in a typical metal ($D \sim 1 \times 10^{-5} \text{ m}^2/\text{s}$) per 100 ps is ~ 30 nm. This means that radial diffusion may be neglected. Therefore, a one-dimensional model may be used in the subnanosecond time scale. Assuming a Gaussian heat pulse, the equation that

describes the one-dimensional heat conduction process is [24]

$$C \frac{\partial \Theta(x, t)}{\partial t} = \kappa \frac{\partial^2 \Theta(x, t)}{\partial x^2} + I(1 - R)\alpha e^{-\alpha x} e^{-(t/\tau)^2}, \quad (\text{III.4.1})$$

where $\Theta(x, t)$ is the temperature, x is the dimension normal to the metal film, t is time, I is the laser intensity, C is the metal heat capacity, κ is the metal heat conductivity, R is reflectivity, α is the absorption coefficient and τ is the pulse width. One approach to solving the Fourier equation (Eq. III.4.1) is to obtain a solution for a point source and then to obtain the solution for an arbitrary source using the principle of superposition [24]. Another approach, more appropriate when C and κ are temperature dependent is the finite difference method presented in more detail in chapter VI.

The change in the relative transient thermotransmittance signal, $\Delta T/T$, is (as explained in section III.2) proportional to the change in the film temperature. For films with thickness $\sim$ skin depth measurements of transmissivity show better results, since the average effect over film thickness is measured. For films with thickness $>$ skin depth measurements of reflectivity are more appropriate, and in that case the change in reflectivity is related to the temperature at the film surface. Fig. III.4.1 shows results of typical transient thermoreflectance measurements performed by Paddock et al [25]. These results were obtained with a pump-and-probe experiment performed in the ps-time scale in order to measure the thermal diffusivity of a metal film. The calculated change in film temperature was fitted to the measured change in reflectivity using thermal diffusivity as a fitting parameter.

III.4.3. Review of Recent Subnanosecond Thermomodulation Experiments

By measuring the optically induced thermoelastic deformation of the film surface Opsal et al. [26] have used photothermal defectometry to determine the thermal

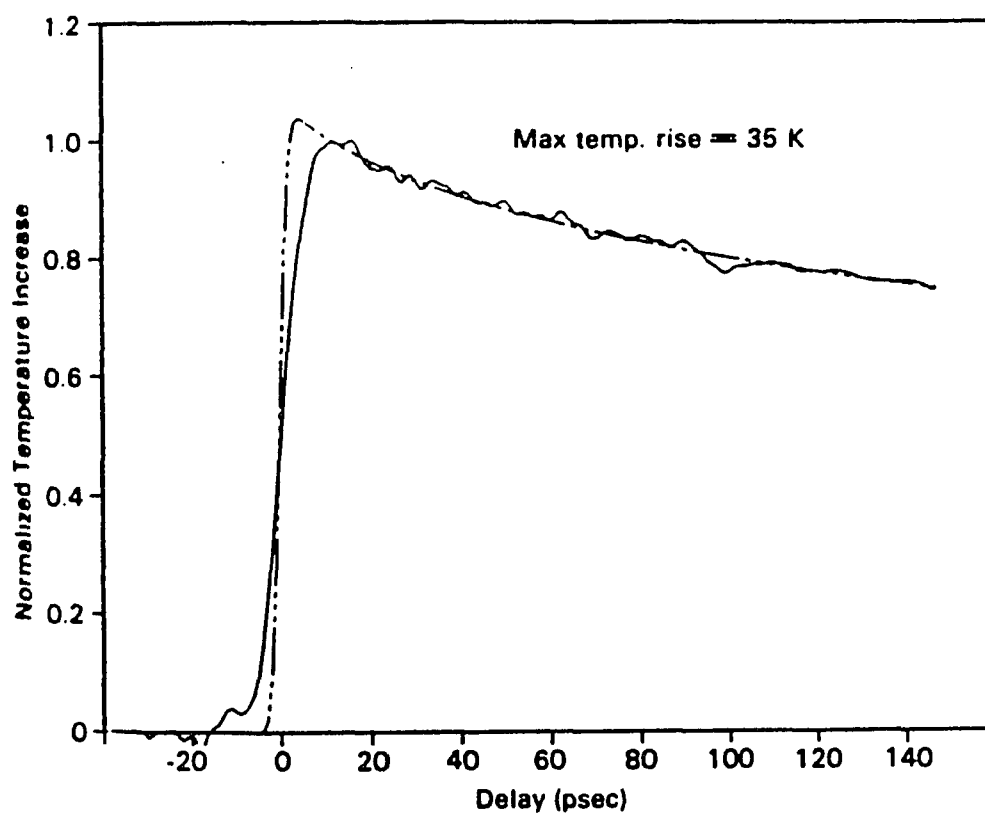


Figure III.4.1 Transient Thermorefectance measurement and fitted temporal profile for sputtered NiTi composite films obtained by Paddock et al. [25]. The hatched line represents the theoretical temperature profile, and the solid line is the normalized measured change in reflectivity

properties of a thin film. Recently, Rosencweig et al. [27] have demonstrated that one can use thermomodulation measurements for the same purpose and with equal success as the deformation technique. The set-back for all these techniques was a relatively low time resolution and the fact that a thorough knowledge of the thermal properties of the substrate was required. With the improvement of the ultrafast laser technology picosecond laser pulses became readily available, and experiments could be performed with picosecond time resolution [25]. In these experiments measurements of thermal diffusivity for sputtered and evaporated single element metal films were performed as well as measurements of thermal transport in compositionally modulated metal films in the direction perpendicular to the film plane. It was found that thermal transport in multilayer metal films exhibits a substantial decrease in thermal diffusivity relative to that measured in the constituent single element.

New material structures with compositional modulation on the atomic scale, that have resulted from material growth processes such as molecular beam epitaxy and ion sputter deposition, have new thermal and electrical processes. Clemens et al. [28] have used the thermomodulation technique to devise an optical noncontacting method of measuring the thermal impedance on a metallic interface. The importance of their technique is evident if one assumes that the multilayer structures obey the Weidemann-Franz relationship so that the electrical properties can be inferred.

The fact that the heat diffusion process can be measured with the thermomodulation technique is used in the experiments described in chapter VI to investigate the thermal behavior in niobium in the transition from the superconducting phase to the normal phase.

Bibliography

- [1] W. J. Scouler *Phys. Rev. Lett.* **18**, p. 455, 1967.
- [2] R. Rosei and D. W. Lynch *Phys. Rev. B* **5**, p. 3883, 1972.
- [3] N. E. Christensen and B. O. Seraphin *Phys. Rev. B* **4**, p. 3321, 1971.
- [4] G. P. Pella and M. Shiga *J. Phys. C* **2**, p. 1835, 1969.
- [5] S. D. Brorson, J. G. Fujimoto, and E. P. Ippen *Phys. Rev. Lett.* **59**, p. 1962, 1987.
- [6] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus *Phys. Rev. Lett.* **64**, p. 2172, 1990.
- [7] K. M. Yoo, X. M. Zhao, M. Siddique, R. R. Alfano, D. P. Osterman, M. Radparvan, and J. Cunniff *Appl. Phys. Lett.* **56**, p. 1908, 1990.
- [8] G. L. Eesley *Phys. Rev. B* **33**, p. 2144, 1986.
- [9] S. I. Anisimov, B. L. Kapelovich, and T. L. Perel'man *Zh. Eksp. Theor. Fiz.* **66**, p. 776, 1974.
- [10] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen *Phys. Rev. Lett.* **53**, p. 1837, 1984.
- [11] M. Cordona, *Modulation Spectroscopy*. Academic, New York, 1969.
- [12] C. Kittel, *Quantum Theory of Solids*. John Wiley, New York, 1963.
- [13] A. Miklós, Z. Bozókl, and A. Lörincz *J. Appl. Phys.* **66**, p. 2968, 1989.
- [14] C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc *Opt. Commun.* **60**, p. 55, 1986.
- [15] M. I. Kaganov, I. M. Lifshitz, and L. V. Tanatarov *Sov. Phys. JETP* **4**, p. 173, 1957.
- [16] G. L. Eesley, B. M. Clemens, and C. A. Paddock *Appl. Phys. Lett.* **50**, p. 717, 1987.
- [17] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.

- [18]H. E. Elsayed-Ali, T. B. Norris, M. A. Pessot, and G. A. Mourou *Phys. Rev. Lett.* **58**, p. 1212, 1987.
- [19]R. W. Schoenlein, W. Z. Lin, J. G. Fujimoto, and G. L. Eesley *Phys. Rev. Lett.* **58**, p. 1680, 1987.
- [20]M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [21]M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.
- [22]G. L. Eesley *Phys. Rev. Lett.* **51**, p. 2140, 1986.
- [23]G. M. Éliashberg *Sov. Phys. — JETP* **16**, p. 780, 1963.
- [24]J. H. Bechtel *J. Appl. Phys.* **46**, p. 1585, 1975.
- [25]C. A. Paddock and G. L. Eesley *J. Appl. Phys.* **60**, p. 285, 1986.
- [26]J. Opsal, A. Rosencwaig, and D. L. Willenborg *Appl. Opt.* **22**, p. 3169, 1983.
- [27]A. Rosencwaig, J. Opsal, W. L. Smith, and D. L. Willenborg *Appl. Phys. Lett.* **46**, p. 1013, 1985.
- [28]B. M. Clemens, G. L. Eesley, and C. A. Paddock *Phys. Rev. B* **37**, p. 1085, 1988.

IV Measurements of the Temperature Dependence of the Electron-Phonon Relaxation Time in Nb

IV.1. Introduction

As discussed in the previous chapter and demonstrated by past research [1] [2] [3] [4], the ultrafast pump-probe experiments generate nonequilibrium conditions in metals such that the electron and phonon temperatures do not track each other on the fs time scale. For room temperature experiments, assuming constant pump energy, the electron-phonon relaxation time (i.e. the time it takes for the two temperatures to equalize) depends on constant parameters such as the lattice heat capacity and the electron-phonon coupling parameter g mentioned in Equations V.3.11 and V.3.12. For temperatures $>\Theta_D$ this topic has been well researched [1] [2] [3] [4]. At temperatures below Debye temperature (and below room temperature for most metals) the parameters that determine the electron-phonon relaxation time τ become temperature dependent and change dynamically as the electron and the lattice temperatures change in time [5] [6]. It is the conditions at ambient temperatures $\Theta \leq \Theta_{\text{Debye}}$ (for Nb $\Theta_{\text{Debye}}=275$ K), that are of interest to this research.

The goal of this work is to measure the electron-phonon relaxation process in niobium for different sample (initial) temperatures; from 7 K (below Nb superconducting temperature) to 292 K (room temperature). This range of temperatures will provide conditions $\Theta \leq \Theta_{\text{Debye}}$, where the electron-phonon coupling parameter is temperature dependent and thus changes in time with the change in electron and lattice temperatures. The experimental results will be compared with theory and the

numerical model, presented in chapter V. The electron-phonon relaxation time, τ_{Nb} , is measured using 100 fs laser pulses since τ_{Nb} is expected to be < 1 ps [4].

To obtain the electron-phonon relaxation time, pump-probe experiments are performed for the range of temperatures, $\Theta=7 - 292$ K, and the relative change of the thermotransmittance signal in time is related to the relative change in the lattice temperature in time. From there, the rise time of the lattice temperature, Θ_l , which corresponds to the electron-phonon relaxation time, τ , is found for a range of different sample (initial) temperatures, $\Theta=7 - 292$ K. Thus the dependence of the electron-phonon relaxation time, τ , on sample (initial) temperature is obtained.

IV.2. Experimental Set-Up

The experimental arrangement used for the transient thermotransmittance spectroscopy is presented in Fig. IV.2.1. It consists of a pump-probe set-up and a source of femtosecond laser pulses centered at 625 nm. The source of laser pulses is a colliding pulse mode-locked dye laser and an amplifier pumped with a copper vapor laser operating at 6.5 KHz. An additional configuration, made of four prisms, was used for pulse compression after the amplifier. The change of the transmissivity due to heating by the pump pulse was recorded with the data-collection system made of a photodiode, a lock-in amplifier, a stepping-motor controller and a personal computer. A description of each of the main elements of the set-up follows.

The Source of Femtosecond Pulses

The source of femtosecond pulses used for thermotransmittance spectroscopy is a system that consists of two parts; a) A quasi-linear colliding pulse mode locked (CPM) dye laser pumped by an argon laser and b) A femtosecond dye amplifier pumped by a copper vapor laser (CVL).

CPM Dye Laser We have built a quazilinear CPM dye laser containing four prisms and an almost linear ring cavity for maximum chirp reduction [7] [8]. In the CPM dye lasers designed before [9] [10], the number of dielectric mirrors used has been reduced to six in order to minimize mirrors' contribution to cavity dispersion. However, the incidence angles have remained considerably large. We solved this problem by a new

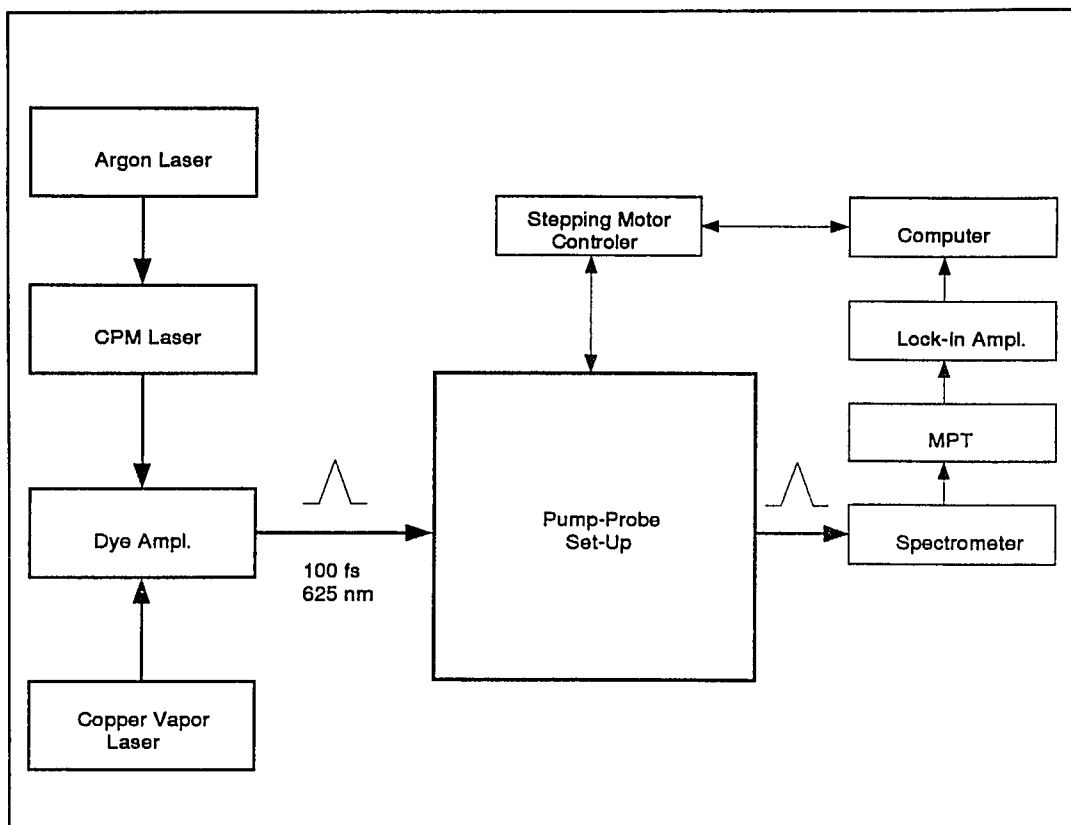


Figure IV.2.1 Set-up for transient thermotransmittance subpicosecond measurements.

The source of laser pulses is a colliding pulse mode-locked dye laser and an amplifier pumped with a copper vapor laser operating at 6.5 KHz. The change of the transmissivity was measured with a pump-probe technique and was recorded with the data-collection system made of a photodiode, a lock-in amplifier, a stepping-motor controller and a personal computer

design, an almost linear ring cavity configuration for the CPM laser. Thus, we have avoided astigmatic distortions introduced by oblique angles of incidence that limit the performance of the system. The schematic diagram of the near linear six mirror ring cavity (the angles are not to scale) is shown in Fig. IV.2.2. Two Z folds are employed around the saturable absorber jet and gain jet with angles of incidence of less than 2° . The radius of curvature of the absorber jet mirrors is 5 cm. For the gain jet a combination of one 1.27 cm (0.5 in) diameter mirror and two halfmirrors, each with a radius of curvature of 10 cm, is employed to obtain minimum incidence angle. The incidence angles at the end mirrors M_1 and M_2 are less than 0.5° .

DODCI was used as a standard saturable absorber dye and Ethylene Glycol as the solvent. Rhodamine 590 dissolved in Ethylene Glycol was used in the gain jet. The typical concentration of DODCI was 1×10^{-3} mol/liter and the concentration of Rhodamine 590 was 1.6×10^{-3} mol/liter. CPM was pumped by cw Argon laser at 514 nm. The pulse duration was monitored by a standard autocorrelator with a 0.1 mm KDP crystal for second harmonic generation, and a pellicle beam splitter. Typical laser operation gave -50 fs pulses at FWHM, with repetition rate of 82 MHz and 10 mW output power for Argon laser pump power of -2.0 W. It was possible to produce 27 fs laser pulses if a mixture of Rhodamine 590 and Kiton Red was used in the gain jet. The resulting short pulse is explained by the fact that high concentration of DODCI was not necessary to shift the lasing spectrum to the red since this was achieved by using Kiton Red in Rhodamine 590. Thus the part of the uncompensatable chirp from the DODCI jet was reduced. Both, the design and the binary-energy-transfer gain dye mixture contributed to reducing the multiple sources of chirp, while at the same time considerably broadening the spectral width and therefore resulting in a shorter pulse [7].

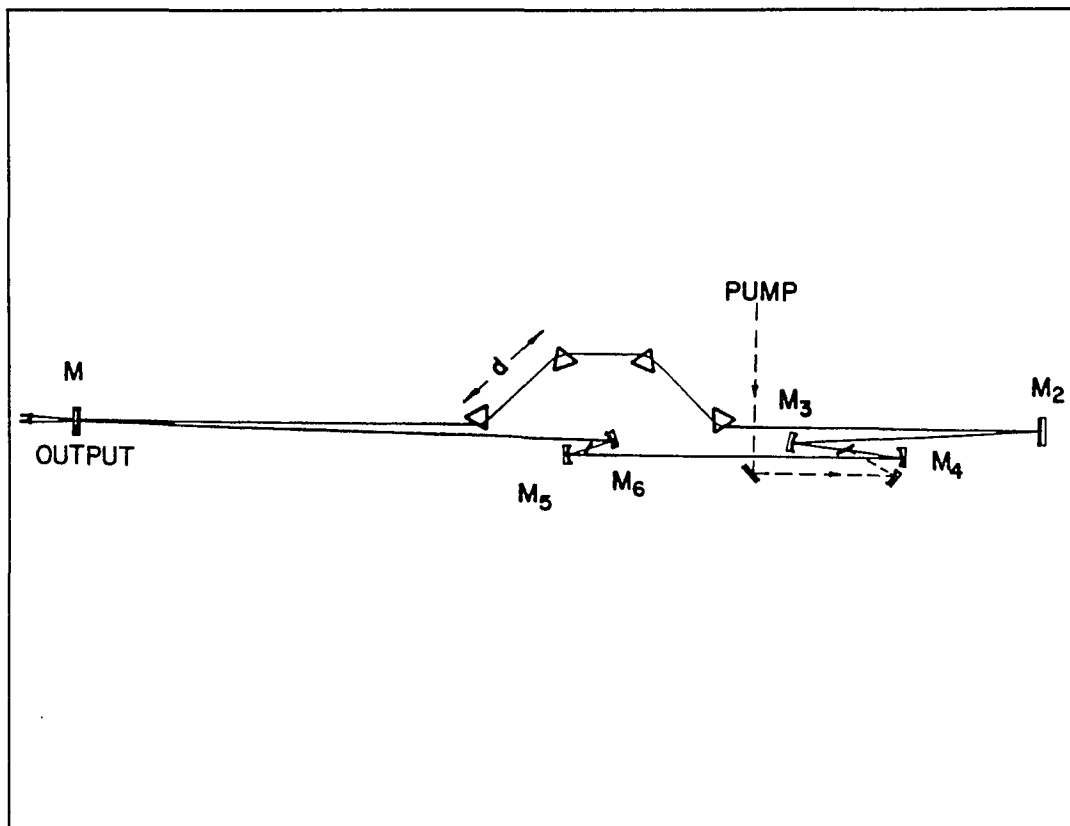


Figure IV.2.2 The schematic diagram of the near linear six mirror ring cavity (the angles are not to scale) designed for maximum chirp reduction. Astigmatic distortion introduced by oblique angles of incidence was avoided by the small incidence angles.

The Argon laser used for pumping the CPM laser is made by Spectra Physics. It is used in the cw mode at 514 nm, and can produce power of up to 6.5 W.

Dye Amplifier The experimental arrangement for amplification of CPM laser pulses is shown in Fig. IV.2.3. It consists of two confocal mirrors. Mirror one (M_1) has a 6 in focal length with a 3 in diameter, and mirror two (M_2) has a 4 in focal length with 2 in diameter. A small mirror M is used to select the output from the amplifier, i.e. to obtain output from different passes of the amplifier. The spot distribution of the laser beam on mirror (M_1) and the focal point is shown in Fig. IV.2.4. Apertures on mirrors are used to reduce the amplified spontaneous emission (ASE) background.

A copper vapor laser (CVL) CU40 from Oxford Corporation is used as the pumping energy source. The CVL beam is split into green and yellow wavelength by a beam splitter. The green wavelength beam is focused to ~1 m diameter at dye jet by an AR coated 25 cm focal length lens. The gain medium is SulfaRhodamine 640 in Ethylene Glycol solvent. The solution passes through a 300-mm thick Lexel jet at the common focal point of the two mirrors. Normal SulfaRhodamine 640 concentration is of 5.0×10^{-3} mol/liter.

Typical output after the amplifier was 100 fs pulses for input pulse duration 50–100 fs. The output power was $0.5 \mu\text{J/pulse}$ at 6.5 KHz repetition rate, for 4–6 W of green. ASE to signal ratio was 2–10 %.

The CVL pulse has a pulse width of 10 ns FWHM at repetition rate of 6.5 KHz. The CVL can deliver a total of 17 W average power : 9 W in the green (511 nm), and 7 W in the yellow (578 nm). The CVL laser is synchronously triggered by the CPM laser pulse through a special electronic circuit, so that the CVL pulses and CPM pulses coincide.

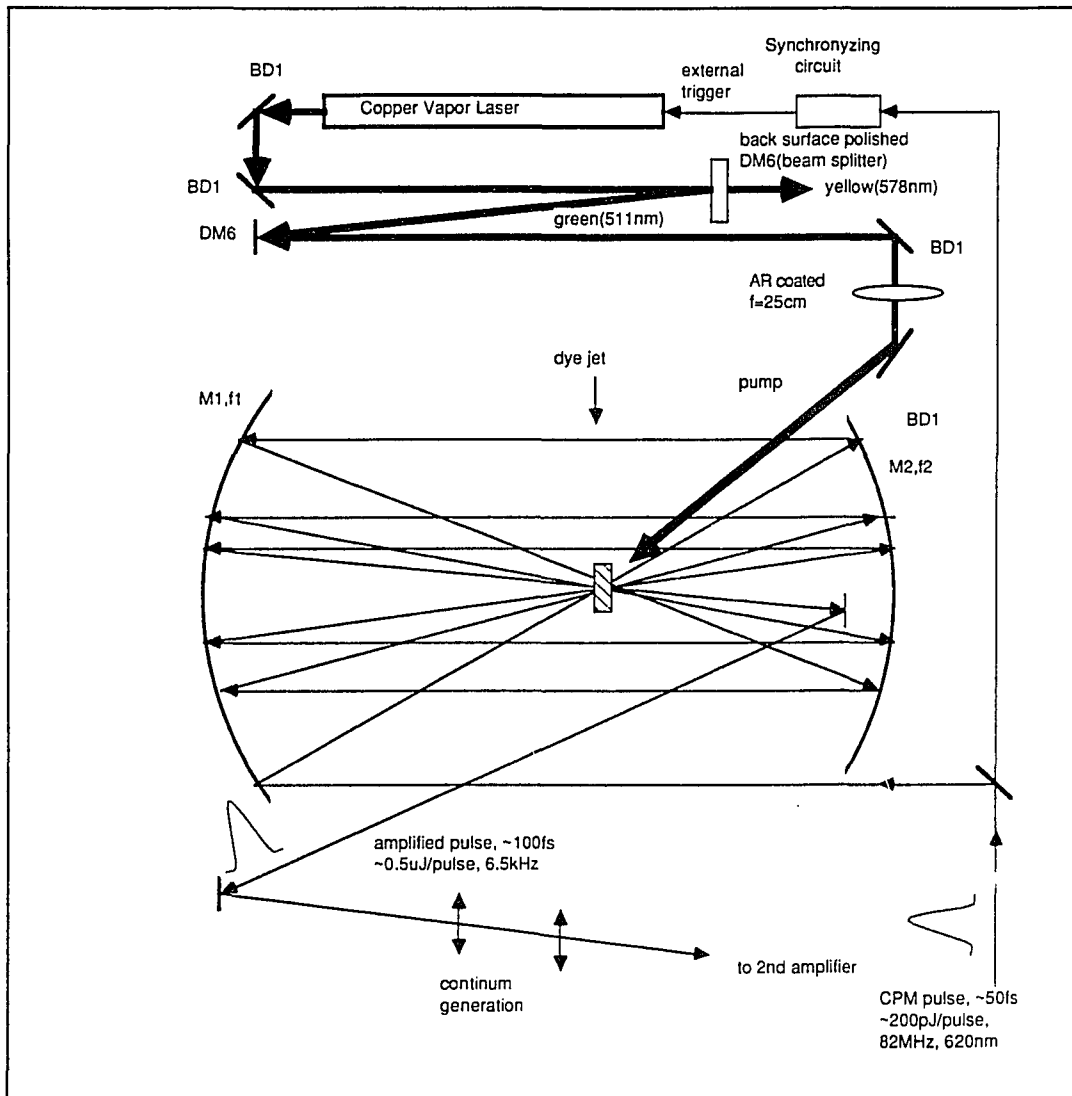


Figure IV.2.3 The Confocal Femtosecond Pulse Amplifier consists of two mirrors: Mirror one (M_1) has a 6 in focal length with a 3 in diameter, and mirror two (M_2) has a 4 in focal length with 2 in diameter. A small mirror M is used to select the output from the amplifier, i.e. to obtain output from different passes of the amplifier.

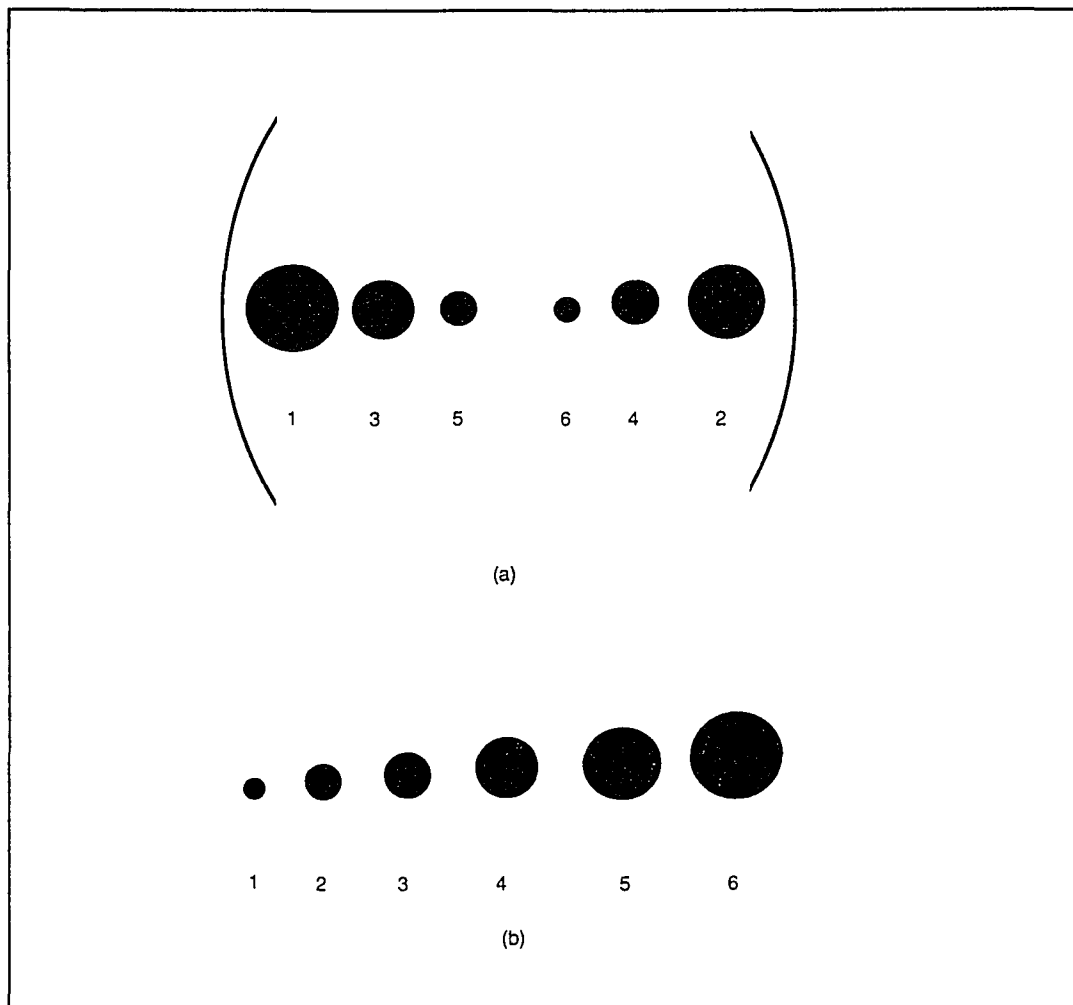


Figure IV.2.4 Laser beam spot distribution in the dye amplifier on : (a) mirror M1, (b) focal point. Apertures on mirrors are used to reduce the amplified spontaneous emission (ASE) background.

The Pump-Probe Configuration

The pump and probe technique consists of introducing a perturbation in the material by a light pulse called the pump pulse, and then investigating the resulting change by another pulse, called the probe pulse, of much lower intensity than the pump pulse so that the perturbation it introduces is negligible. The probe beam is delayed with respect to the pump beam by requiring it to traverse a greater distance than the pump beam before reaching the target. In this way, changes due to the pump pulse are detected by the probe pulse at times shortly after they have been induced. The delay time may be varied by varying the excess distance the probe pulse has to travel with respect to the pump pulse.

The pump-probe configuration used for our transient thermotransmittance spectroscopy is shown in Fig. IV.2.5. For the lock-in detection the pump beam was chopped in order to detect the difference in the transmitted intensity of the probe beam caused by the pump. The probe beam was detected by a photodiode connected to the lock-in amplifier. The data from the lock-in amplifier was collected into a personal computer. A motorized translation stage with 1μ accuracy was used to delay the probe pulse with respect to the pump pulse. The niobium film used was placed in a helium dewar whose temperature could be controlled.

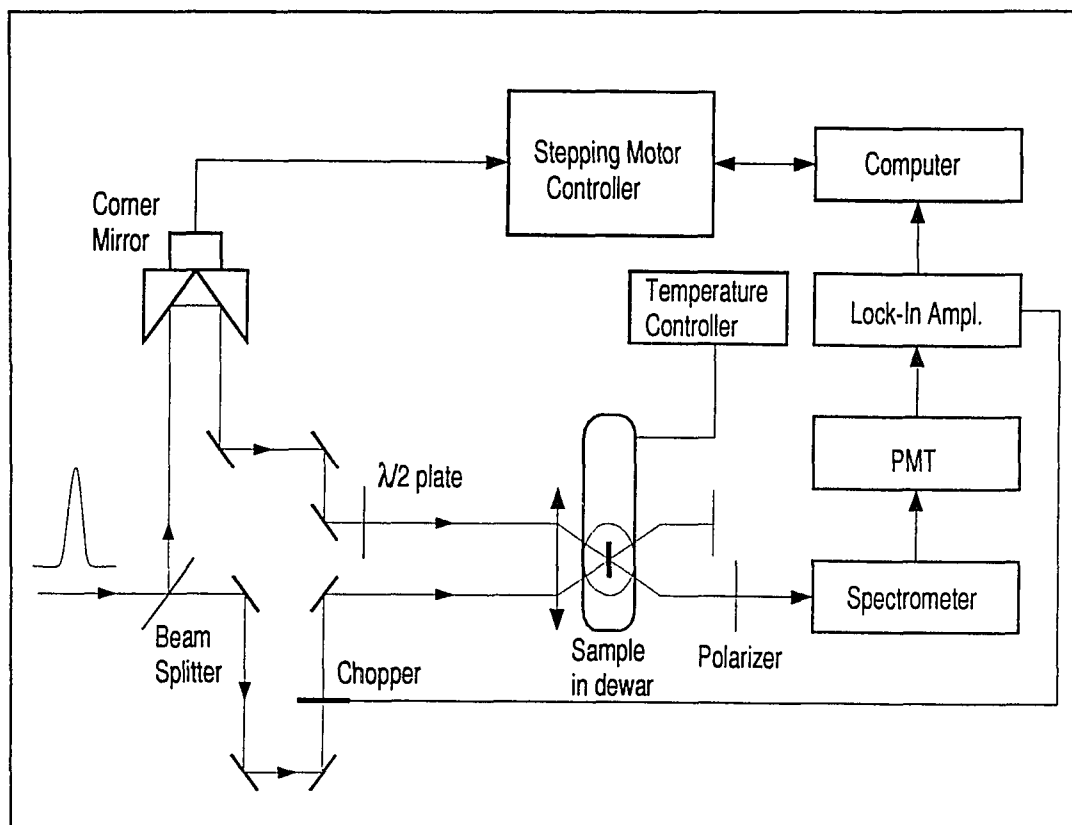


Figure IV.2.5 The pump-probe set-up used for transient thermotransmittance spectroscopy. For the lock-in detection the pump beam was chopped in order to detect the difference in the transmitted intensity of the probe beam caused by the pump. The probe beam was detected by a photodiode connected to the lock-in amplifier. The niobium film used was placed in a helium dewar whose temperature could be controlled.

IV.3. Description of the Experiment

In this experiment, the pulse train coming out of the CPM dye laser at 82 MHz repetition rate, of ~ 10 mW, was amplified in the dye amplifier to obtain ~ 0.5 μ J pulses at 6.5 KHz repetition rate. After compressing the pulses in a four-prism configuration, the pulse used in the transmissivity measurements was 100 fs FWHM. The pulse energy was 110 nJ and was focused onto a spot 35 μ m in diameter. The probe spot radius was about five times smaller than the pump spot radius in order to minimize diffusion effects. The probe beam was polarized perpendicular to the polarization of the pump beam to avoid the large coherence artifact which occurs when the probe beam is polarized parallel to the pump beam.

The niobium film used was 20 nm thick, deposited on a fused quartz plate. It was attached to a heat sink whose temperature could be varied and was located inside a helium dewar. The experimentally determined absorptivity was found to be $\sim 5\%$ of the incident laser energy.

The change in the transmitted probe intensity was measured for time delays from 0 to 1.5 ps of the probe pulse with respect to the pump. The relative transmissivity change was measured by measuring the change in the transmitted intensity of the probe pulse. This was measured by chopping the pump pulse, thus modulating the part of the probe pulse that changes due to the pump. The lock-in detector detects only the modulated signal, i.e. only the modulated part of the probe pulse thus effectively measuring only the change of the transmitted probe signal. The pump beam, which is also modulated, was easily blocked since it was not colinear with the

probe beam. Any left over pump leakage was filtered out with a polarizer, since the pump was polarized perpendicularly to the probe. The maximum change was 8% and was linearly dependent on the laser fluence.

These measurements were performed using the output directly from the amplifier, so that the center wavelength of the pulse was 625 nm. Room temperature measurements were also performed using the configuration for supercontinuum generation and subsequent pulse compression, so that the center wavelength ranged from 590 nm to 680 nm. This was done in order to try and detect the fast purely electronic component discussed in Section III.2. The measured transmissivity change was the same regardless of probe wavelength and no fast component was observed. Therefore the experiment was performed using 625 nm pulses. The pulse width was always maintained at 100 fs FWHM.

IV.4. Experimental Results

The change in the transmitted probe intensity was measured for ten different ambient temperatures (temperatures of the sample in the dewar) ranging from 292 K to 7 K for time delays from 0 to 1.5 ps of the probe pulse with respect to the pump. In these measurements, the fast purely electronic component was not observed because the probe wavelength was away from the electronic transition to the Fermi level. Therefore, the observed transmission change is attributed to the change in the lattice temperature and is assumed to be linearly proportional [1] [4].

Typical results of the measured relative transmission change are displayed for five different ambient temperatures, $\Theta=292$ K (Fig. IV.4.1), $\Theta=100$ K (Fig. IV.4.2), $\Theta=50$ K (Fig. IV.4.3), $\Theta=20$ K (Fig. IV.4.4), $\Theta=7$ K (Fig. IV.4.5), for delays from -0.4 to 1.2 ps. The measured electron-phonon relaxation time, i.e. the experimentally obtained transmissivity rise time (measured from 10% to 90% of the total rise), τ_{exp} , is 370 fs, 290 fs, 300 fs, 270 fs, and 250 fs respectively. The solid line represents the experimental data and the dash-dot line represents the best fit to the experimental data. The relative transmissivity change was measured by measuring the change in the transmitted intensity of the probe pulse with the lock-in detection technique. The rise time of this signal corresponds to the rise time of the lattice temperature before the electrons reach thermal equilibrium with the lattice.

Fig. IV.4.6 shows the measured transmissivity rise time (the time required to establish temperature equilibrium between the electrons and the phonons) as a function of sample (ambient) temperature. The rise time (measured from 10% to 90%

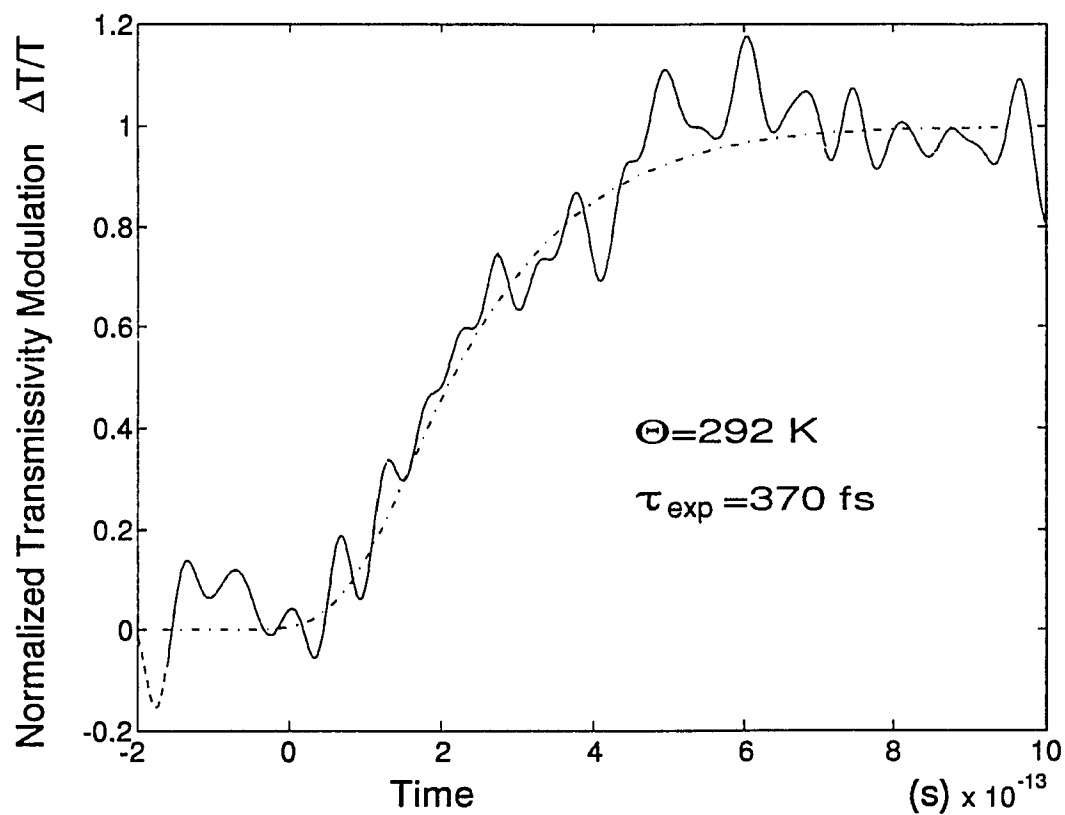


Figure IV.4.1 Typical results of the measured relative transmission change is displayed for ambient temperature, $\Theta = 292 \text{ K}$ for delays from -0.4 to 1.2 ps. The experimentally obtained electron-phonon relaxation time, i.e. the transmissivity rise time, $\tau_{\text{exp}} = 370 \text{ fs}$. The solid line represents experimental data, and the dash-dot line represents the best fit to the experimental data.

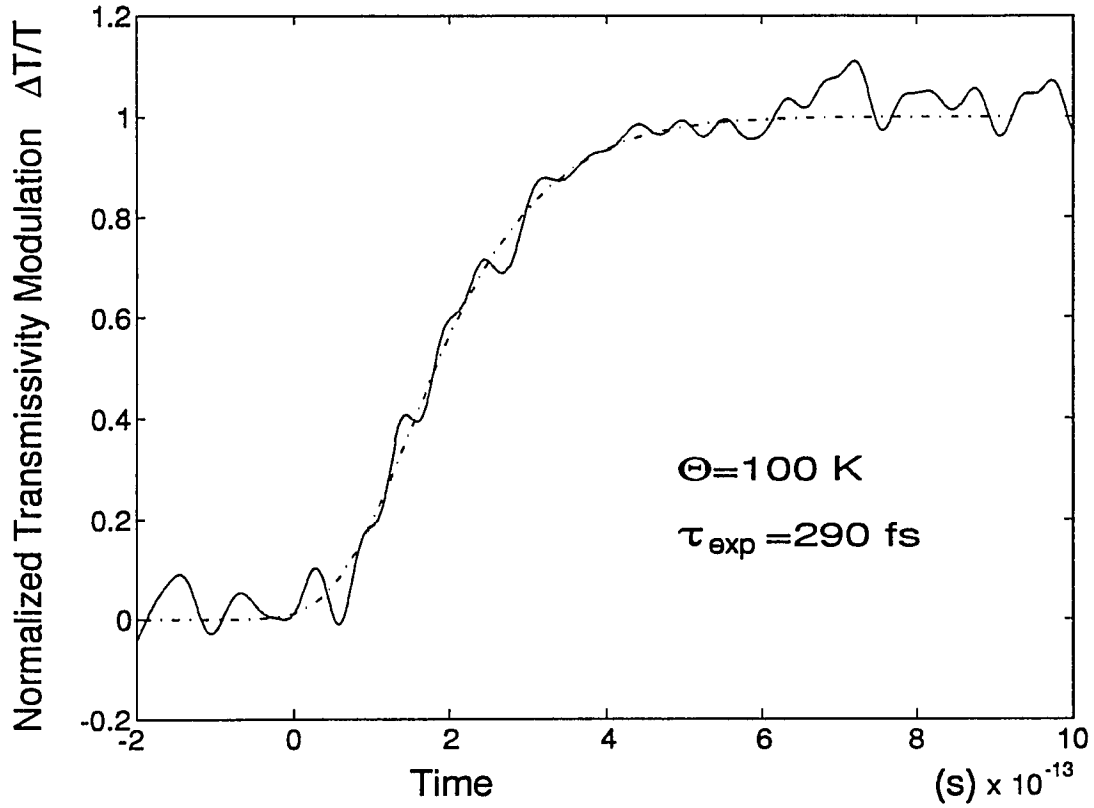


Figure IV.4.2 Typical results of the measured relative transmission change is displayed for ambient temperature, $\Theta=100 \text{ K}$ for delays from -0.4 to 1.2 ps. The experimentally obtained electron-phonon relaxation time, i.e. the transmissivity rise time, $\tau_{\text{exp}}=290 \text{ fs}$. The solid line represents experimental data, and the dash-dot line represents the best fit to the experimental data.

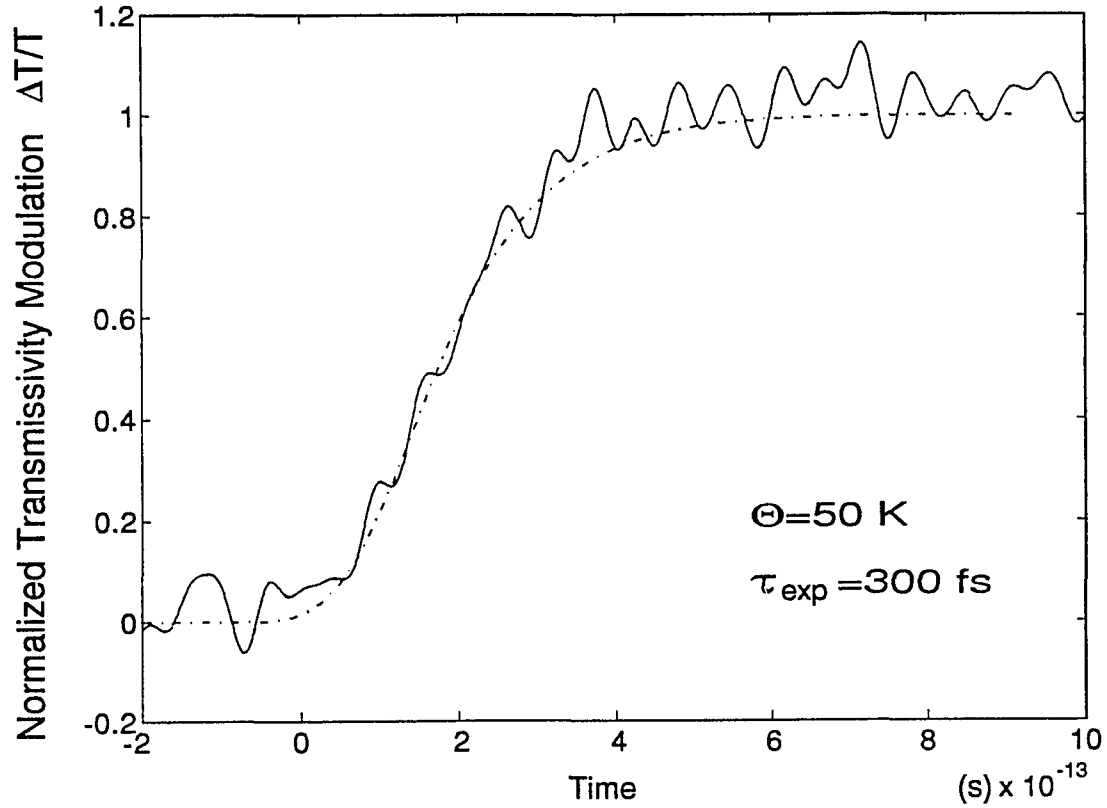


Figure IV.4.3 Typical results of the measured relative transmission change is displayed for ambient temperature, $\Theta = 50 \text{ K}$ for delays from -0.4 to 1.2 ps . The experimentally obtained electron-phonon relaxation time, i.e. the transmissivity rise time, $\tau_{\text{exp}} = 300 \text{ fs}$. The solid line represents experimental data, and the dash-dot line represents the best fit to the experimental data.

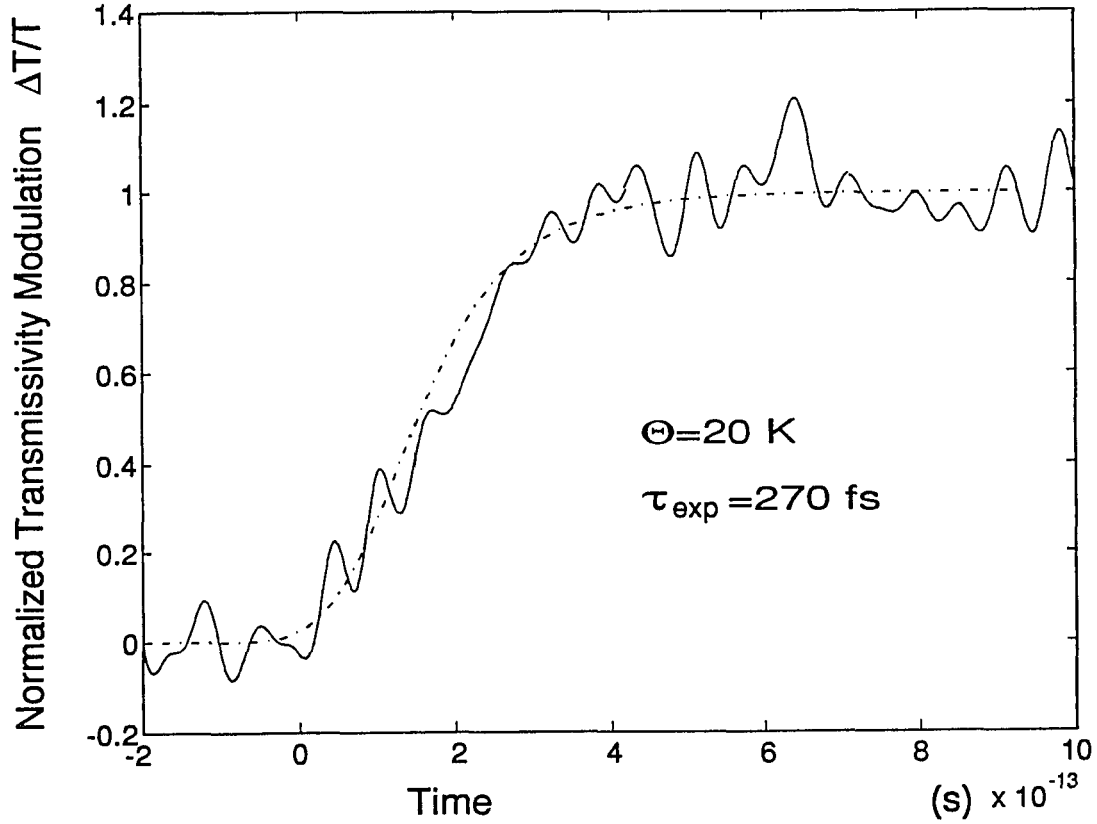


Figure IV.4.4 Typical results of the measured relative transmission change is displayed for ambient temperature, $\Theta = 20 \text{ K}$ for delays from -0.4 to 1.2 ps . The experimentally obtained electron-phonon relaxation time, i.e. the transmissivity rise time, $\tau_{\text{exp}} = 270 \text{ fs}$. The solid line represents experimental data, and the dash-dot line represents the best fit to the experimental data.

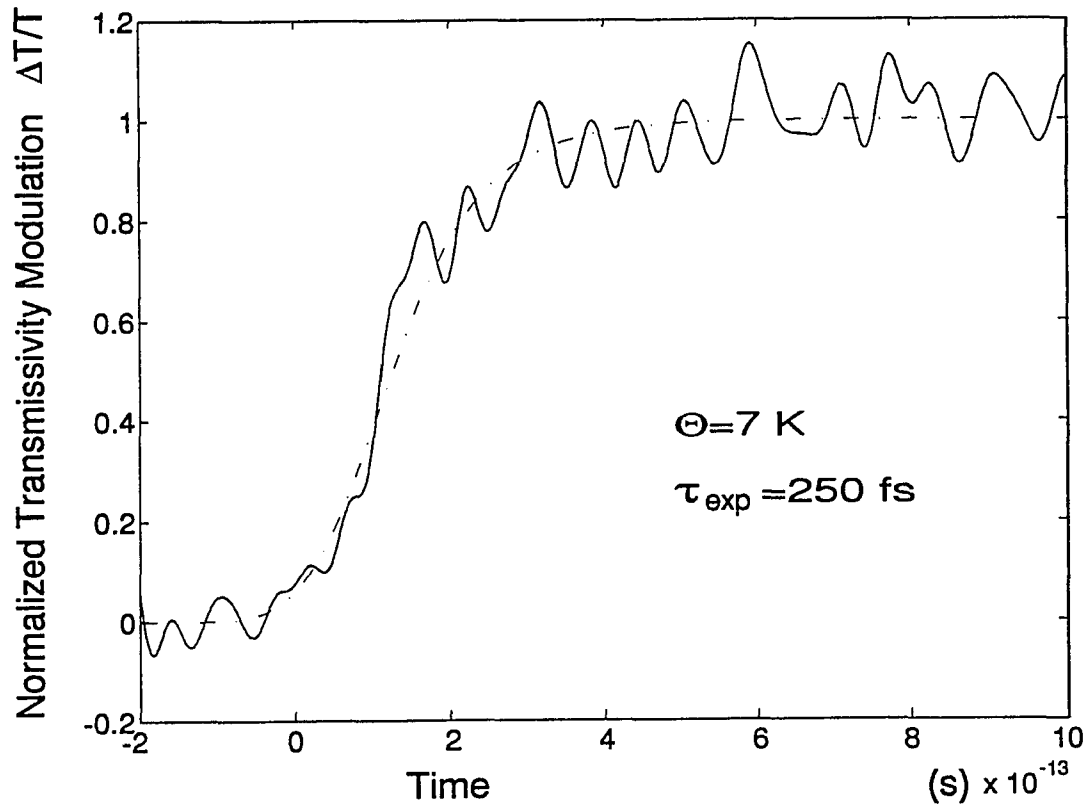


Figure IV.4.5 Typical results of the measured relative transmission change is displayed for ambient temperature, $\Theta = 7 \text{ K}$ for delays from -0.4 to 1.2 ps . The experimentally obtained electron-phonon relaxation time, i.e. the transmissivity rise time, $\tau_{\text{exp}} = 250 \text{ fs}$. The solid line represents experimental data, and the dash-dot line represents the best fit to the experimental data.

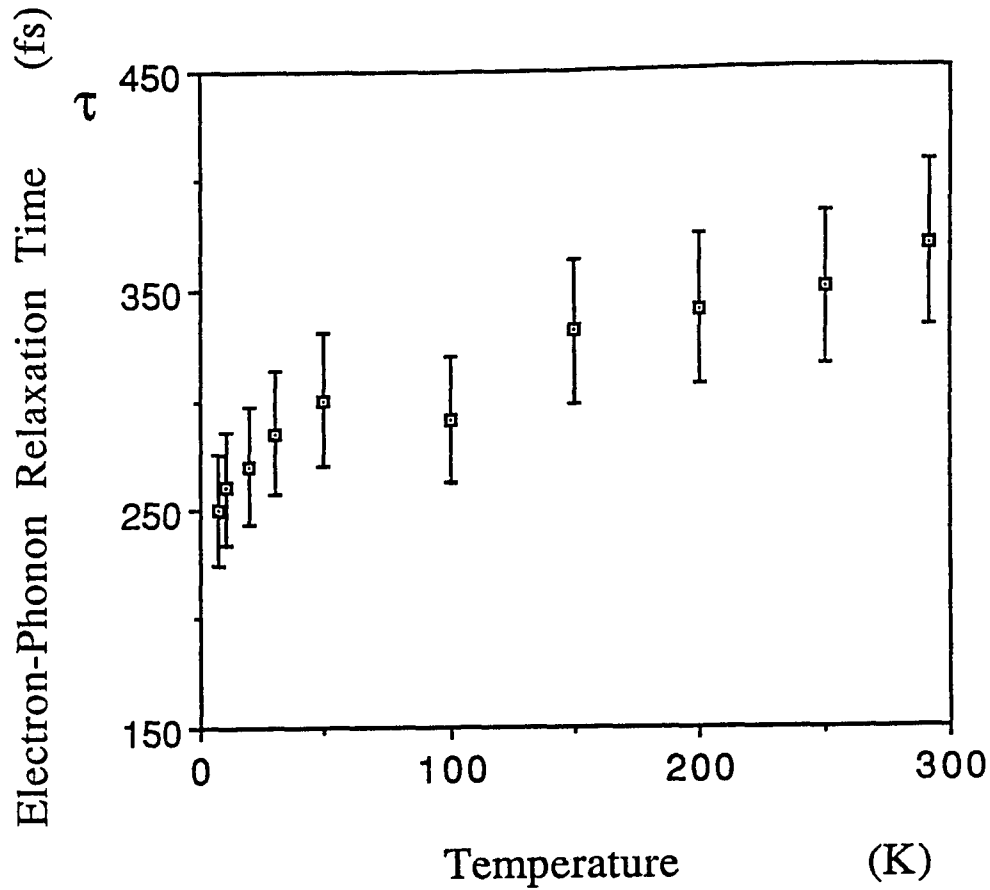


Figure IV.4.6 Measured transmissivity rise time as a function of sample temperature. The results show that the time it takes for the electrons to thermalize with phonons decreases from 370 fs to 250 fs, as the ambient temperature is decreased from 292 K to 7 K. No special features are detected as the sample (initial) temperature is lowered from 10 K (above critical superconducting temperature, $\Theta_{c, Nb}=8.8$ K) to 7 K (superconducting temperature).

of the total rise) decreases from 370 fs at 292 K to 250 fs at 7 K. The results show that the time it takes for the electrons to thermalize with phonons decreases from 370 fs to 250 fs, as the ambient temperature is decreased from 292 K to 7 K. It should be noted that the experimentally obtained rise time shows a steady decrease with decreasing temperature within the experimental error. The error bars reflect the standard deviation. No special features are detected as the sample (initial) temperature is lowered from 10 K (above critical superconducting temperature, $\Theta_{c, Nb}=8.8$ K) to 7 K (superconducting temperature).

In work performed in the past [3] [11] [12] g used in the Eqs. III.3.2 and III.3.3 has been referred to as the electron-phonon coupling constant and has been temperature independent since experiments were performed at room temperature. However, for temperatures $<\Theta_D$, when g becomes temperature dependent (and thus dependent on the intensity of the pump pulse) one should be aware that g is actually the coefficient of heat transfer between the electrons and the lattice [13]. τ_{exp} measured in this experiment is actually the thermalization time, and it is governed by the magnitude of g and the decreasing specific heat. This explains the decreasing of τ_{exp} with decreasing temperature obtained in this experiment; for temperatures $<\Theta_D$ both electron and lattice heat capacity decrease fast with temperature so the thermalization time diminishes as the temperature is lowered.

IV.5. Conclusion

In summary, the temporal behavior of the electron-phonon relaxation process (electron-phonon relaxation time) has been measured under nonequilibrium conditions for temperatures ranging from room temperature to superconducting temperatures. It was found that the experimentally obtained electron-phonon relaxation time, τ_{exp} , decreases from 370 fs at 292 K to 250 fs at 7 K. When the convolution with the probe pulse is taken into account the actual τ_{exp} would be 5–10 % smaller than displayed in Fig. IV.4.6. This effect is greater for shorter τ_{exp} i.e. at smaller temperatures. Experimental results show [14] [15] that the electrons thermalize with phonons faster at smaller ambient temperatures. No special features have been observed below superconducting temperature ($\Theta_{\text{c,Nb}}=8.8$ K) on this time scale.

One would expect, since the electron-phonon thermalization time, τ , is shorter for stronger electron-phonon coupling, i. e. higher g , and since it was found that τ_{exp} decreases with decreasing temperature, that g must be increasing with decreasing temperature. However, it is logical to expect weaker electron-phonon coupling at lower temperatures. Indeed, as will be shown in the next chapter, g decreases with decreasing temperature. Electrons thermalize with phonons faster at smaller temperatures because τ decreases with increasing g and decreasing specific heat, which in turn, decreases fast with temperature at lower temperatures. In the following chapter, a theoretical model of the electron-phonon interaction below Debye temperature, that explains the temperature dependence of the electron-phonon relaxation time, will be developed.

Bibliography

- [1] G. L. Eesley *Phys. Rev. B.* **33**, p. 2144, 1986.
- [2] S. D. Brorson, J. G. Fujimoto, and E. P. Ippen *Phys. Rev. Lett.* **59**, p. 1962, 1987.
- [3] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus *Phys. Rev. Lett.* **64**, p. 2172, 1990.
- [4] K. M. Yoo, X. M. Zhao, M. Siddique, R. R. Alfano, D. P. Osterman, M. Radparvan, and J. Cunniff *Appl. Phys. Lett.* **56**, p. 1908, 1990.
- [5] M. Mihailidi and R. R. Alfano *Appl. Phys. Lett.* (accepted for publication), 1994.
- [6] M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [7] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano *Opt. Lett.* **13**, p.987, 1988.
- [8] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano, *Ultrafast Phenomena VI*, vol. 48 of *Springer Series in Chemical Physics*. Springer-Verlag, Berlin, Heidelberg, 1988.
- [9] J. C. Diels, J. J. Fontaine, I. C. McMichael, B. Wilhelmi, W. Dietel, and D. Kuhlke *Sov. J. Quantum Electron.* **QE-13**, p. 12, 1983.
- [10] J. A. Valdmanis and R. L. F. nad J. P. Gordon *Opt. Lett.* **10**, p. 3, 1986.
- [11] P. B. Corkum, F. Brunel, and N. K. Sherman *Phys. Rev. Lett.* **61**, p. 2886, 1988.
- [12] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen *Phys. Rev. Lett.* **53**, p. 1837, 1984.

- [13]S. I. Asimov, B. L. Kopeliovich, and T. L. Perelman *Sov. Phys. JETP* **39**, p. 375, 1974.
- [14]R. H. M. Groeneveld, R. Sprik, and A. Lagendijk *Phys. Rev. B Rapid Comm.* **45**, p. 5079, 1992.
- [15]M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.

V The Time Evolution for the Electron-Phonon Coupling Parameter g

V.1. Introduction

In all the work performed so far on electron-phonon relaxation in metal using ultrafast thermomodulation spectroscopy the electron-phonon parameter g was assumed constant, namely temperature and time independent [1] [2] [3]. Most of this work was performed at room temperature. In room temperature measurements, one may use Allen's theory in the high temperature limit ($\Theta > \Theta_{\text{Debye}}$), where the electron-phonon coupling parameter g may be considered constant. In this case g may be related to the factor $\lambda \langle \omega^2 \rangle$ which is of crucial importance to the theory of superconducting transition temperature Θ_c [4] (λ plays a central role in determining Θ_c [5]). The factor $\lambda \langle \omega^2 \rangle$ is the first moment of $\alpha^2 F(\omega)$. McMillan [5] has shown that it is independent of the phonon spectra, and it may be expressed as

$$\lambda \langle \omega^2 \rangle = 2 \int_0^{\omega_{\max}} \alpha^2 F(\omega) \omega d\omega = N_a(E_F) \langle I^2 \rangle / M = \frac{\eta}{M} \quad (\text{V.1.1})$$

where $N_a(E_F)$ is the electron density of states per atom per spin, η is the McMillan-Hopfield parameter [5], M is the ion mass, and

$$\langle I^2 \rangle = \frac{\left[\frac{\Omega_a}{\hbar(2\pi)^3} \right]^2 \int \frac{d^2 \mathbf{k}'}{\mathbf{v}_{\mathbf{k}'}} \int \frac{d^2 \mathbf{k}}{\mathbf{v}_{\mathbf{k}}} |I(\mathbf{k}, \mathbf{k}')|^2}{N_a^2(E_F)}. \quad (\text{V.1.2})$$

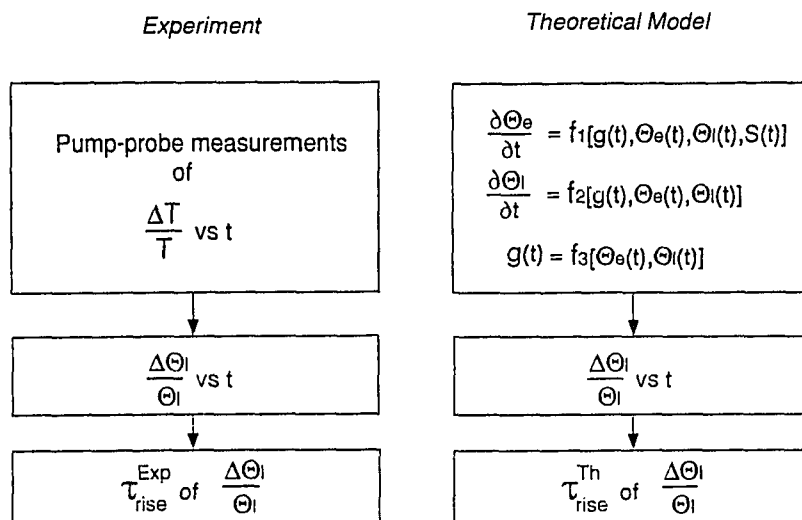
In the above equation, $I(\mathbf{k}, \mathbf{k}')$ is the Bloch matrix element and Ω_a is the atomic volume. The factor $\lambda \langle \omega^2 \rangle$ is also important because the simplicity of Equation (V.1.1) has made possible many microscopic calculations [6].

With room temperature ultrafast thermal relaxation experiments and using Allen's theory, scientists have been able to obtain good agreement between experimentally and theoretically obtained electron-phonon parameters: Elsayed-Ali et al. [2] have determined a value for copper of $g=1 \times 10^{17} \text{ W/m}^3\text{K}$. Khan et al. [7] have calculated $\lambda\langle\omega^2\rangle$ for copper to be 43 meV^2 which corresponds to accuracy of within $\pm 50 \%$ of the result obtained by Elsayed-Ali et al. The values of $\lambda\langle\omega^2\rangle$ for gold are also very accurate. Results obtained by Schoenlein et al. [3] for gold yield $\lambda\langle\omega^2\rangle=24 \text{ meV}^2$. This agrees with estimated values for $\lambda=0.15$ [8]. The results for tungsten obtained by Fujimoto et al. [1] give $\lambda\langle\omega^2\rangle=100\text{--}200 \text{ meV}^2$ and are also within 50% of theoretical estimates.

There have been very few ultrafast thermal relaxation experiments performed at temperatures $< \Theta_{\text{Debye}}$ in metal [9] [10]. In these experiments, performed for gold, the measured electron-phonon relaxation time shows a continuous decrease with decreasing temperature, in agreement with our results obtained for niobium. However, the theoretical model discussed does not show good agreement with experiment since the electron-phonon coupling parameter, g , is considered temperature independent. In this chapter the temperature and thus time dependence of the electron-phonon coupling parameter g will be derived based on Allen's theory for electron-phonon energy transfer. The goal is to obtain a theoretical model for the experiment presented in chapter IV i.e. for ultrafast thermal relaxation experiments performed at temperatures $< \Theta_{\text{Debye}}$.

The flowgraph presented in Fig. V.1.1 describes in detail the experimental and numerical procedure applied to obtain the electron-phonon relaxation time τ . The theoretical model, discussed in section V.3 is based on the coupled Eq.'s (V.3.10), (V.3.11) and (V.3.12) which produce solutions for Θ_l and Θ_e with no free parameters.

FOR ONE SAMPLE (INITIAL) TEMPERATURE Θ



REPEATED FOR A RANGE OF SAMPLE TEMPERATURES

$$7 \text{ K} \leq \Theta \leq 292 \text{ K}$$

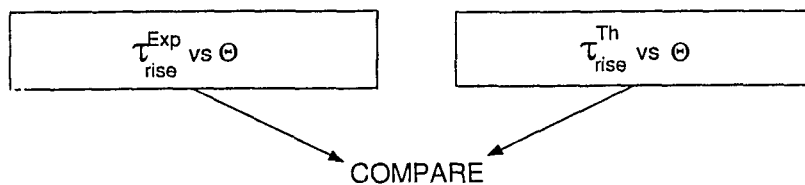


Figure V.1.1 The flowgraph presented describes the experimental and numerical procedure applied to obtain the electron-phonon relaxation time τ for sample (initial) temperatures ranging from 292 K to 7 K.

From here, the electron-phonon relaxation time, τ_{th} , which corresponds to the rise time of the lattice temperature, Θ_l , is found for a range of temperatures, Θ_0 , from 7 K to 292 K. This is presented in section V.4. To obtain the electron-phonon relaxation time, τ_{exp} , pump-probe experiments were performed for the range of temperatures, $\Theta=7 - 292$ K, and the relative change of the thermotransmittance signal in time was related to the relative change in the lattice temperature with time (ch. IV). From there, the rise time of the lattice temperature, Θ_l is found for the range of different sample (initial) temperatures, $\Theta=7 - 292$ K. Thus the dependence of the electron-phonon relaxation time, τ_{exp} , on sample (initial) temperature is obtained.

The theory behind the thermal relaxation experiments is presented in the following sections. Section V.2 presents Allen's theory, where the thermal relaxation rate γ_T is related to $\lambda\langle\omega^2\rangle$ for $\Theta>\Theta_{Debye}$. Section V.3 presents the derivation of the electron-phonon coupling parameter g based on Allen's theory [11] for $\Theta>\Theta_{Debye}$, and more importantly for the case of $\Theta\leq\Theta_{Debye}$, when g becomes temperature dependent. In section V.4 the numerical solution of the time dependence of $g(\Theta_e(t)\Theta_l(t))$ with parameters corresponding to our experiment is presented. At the end, the calculated electron-phonon relaxation time is shown and compared with the experimentally obtained one.

V.2. Allen's Theory of Thermal Relaxation of Electrons in Metal

As already described, in the picosecond pump-probe thermomodulation experiments the electrons are photoexcited and achieve local thermal equilibrium at temperature Θ_e above the lattice temperature Θ_l . In these experiments, as demonstrated by several authors [12] [13] [2], the time it takes for the electrons to thermalize with the lattice is governed solely by electron-phonon processes, as opposed to steady-state transport experiments, which always measure the combined rate caused by all available processes. These experiments were theoretically analyzed by P. B. Allen [11] and the theory is briefly presented in this section.

The Bloch-Boltzman-Peierls formulas [14] for the rate of change of electron and phonon distributions F_k and N_Q due to electron-phonon collision are

$$\begin{aligned} \left[\frac{\partial F_k}{\partial t} \right]_{ep} = & -\frac{2\pi}{\hbar N_c} \sum_Q |M_{kk'}|^2 \{ F_k(1 - F_{k'})[(N_Q + 1)\delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_Q) \\ & + N_Q\delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_Q)] - (1 - F_k)F_{k'}[(N_Q + 1)\delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_Q) \\ & + N_Q\delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_Q)] \} \end{aligned} \quad (\text{V.2.1})$$

$$\begin{aligned} \left[\frac{\partial N_Q}{\partial t} \right]_{ep} = & -\frac{\pi^4}{\hbar N_c} \sum_k |M_{kk'}|^2 F_k(1 - F_{k'})[N_Q\delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_Q) \\ & - (N_Q + 1)\delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_Q)] \end{aligned} \quad (\text{V.2.2})$$

where k is short for electron quantum number $(\mathbf{k}, n)$ and Q is short for phonon quantum number $(\mathbf{Q}, j)$ and $\mathbf{Q}$ is always $\pm(\mathbf{k}-\mathbf{k}')$. N_c is the number of cells in the sample, the factor 2 in Eq. (V.2.2) accounts for electron degeneracy, and the electron-phonon matrix element $M_{\mathbf{k}\mathbf{k}'}$ is normalized to the unit cell and has magnitude $((E_F \hbar \omega)^{1/2})$. It may easily be shown [11] that the rates represented by Equations (V.2.1) and (V.2.2) conserve total energy:

$$2 \sum_k \varepsilon_k \left[\frac{\partial F_k}{\partial t} \right]_{ep} + \sum_Q \hbar \omega_Q \left[\frac{\partial N_Q}{\partial t} \right]_{ep} = 0. \quad (\text{V.2.3})$$

Equations (V.2.1) and (V.2.2) determine the evaluation of the distributions $F_k(t)$ and $N_Q(t)$ provided (a) $F_k(t)$ and $N_Q(t)$ is known at $t=0$; (b) one may neglect diffusion due to spatial inhomogeneity; (c) one may neglect acceleration due to external and internal fields; and (d) one may neglect any other collision processes.

The physical model that describes the ultrafast pump-probe experiment is as follows: (1) The distributions $F_k(t)$ and $N_Q(t)$ equal to local equilibrium distributions

$$F_k(t) = \frac{1}{1 + \exp [(\varepsilon_k - \mu)/k_B \Theta_e(t)]} \quad (\text{V.2.4})$$

$$N_Q(t) = \frac{1}{\exp [\hbar \omega_Q / k_B \Theta_l(t)] - 1} \quad (\text{V.2.5})$$

characterized by separate electron and lattice temperatures, Θ_e and Θ_l . This local equilibrium is achieved by electron-electron (Coulomb) collisions and by phonon-phonon anharmonic interaction. (2) one may neglect diffusion because of constrained geometry and short time scale. Under the above assumptions Equations (V.2.1) and (V.2.2) completely determine the subsequent energy distribution. The assumption that

$F_k(t)$ and $N_Q(t)$ are in local thermal equilibrium is of course incorrect at some level. However, all known experimental results are consistent with the notion that even if F and N are athermal, they are still adequately characterized by a thermal distribution at equivalent energy. In fact, the energy relaxation described by Equations (V.2.1) and (V.2.2) may not be much influenced by the deviation of F and N from local equilibrium.

To calculate the rate of energy exchange Allen starts with the expressions for electron and lattice energy, E_e and E_l ,

$$E_e = 2 \sum_k \varepsilon_k F_k \approx E_0 + \frac{1}{2} \Theta_e^2 \quad (\text{V.2.6})$$

and

$$E_l = \sum_Q \hbar \omega_Q N_Q \approx 3 N_a k_B \Theta_l, \quad (\text{V.2.7})$$

and the expression for the rate of energy exchange [15]

$$\left[\frac{\partial E_e}{\partial t} \right]_{ep} = \left(\frac{4\pi}{\hbar N_c} \right) \sum_{kk'} \hbar \omega_Q |M_{kk'}|^2 [S(k, k')] \delta(\varepsilon_k - \varepsilon_{k'} + \hbar \omega_Q). \quad (\text{V.2.8})$$

In the above equation, the thermal factor $S(k, k')$ is

$$S(k, k') = (F_k - F_{k'}) N_Q - F_{k'} (1 - F_k). \quad (\text{V.2.9})$$

For further derivation, Equations (V.2.8) and (V.2.9) require relabelling of dummy variables and inserting three factors of 1 in Eq. (V.2.8) in the form of $\int d\varepsilon \delta(\varepsilon_k - \varepsilon)$, $\int d\varepsilon' \delta(\varepsilon_{k'} - \varepsilon')$, $\int d\Omega \delta(\omega_Q - \Omega)$. Now Eq. (V.2.8) may be written in terms of the electron-phonon spectral function $\alpha^2 F$ [4],

$$\alpha^2 F(\varepsilon, \varepsilon', \Omega) \equiv \left(\frac{2}{\hbar N(\varepsilon_F) N_c^2} \right) \sum_{kk'} |M_{kk'}|^2 \delta(\omega_Q - \Omega) \delta(\varepsilon_k - \varepsilon) \delta(\varepsilon_{k'} - \varepsilon'). \quad (\text{V.2.10})$$

In the above expression for $\alpha^2 F$, Ω -variations are on a scale ω_D while ε -variations and ε' -variations are only the much larger energy scale $1/N(\varepsilon_F)$. Therefore, it is customary [4] to consider $\alpha^2 F$ independent of ε and ε' , i. e. $\alpha^2 F(\varepsilon, \varepsilon', \Omega) \equiv \alpha^2 F(\Omega)$. Eq. (V.2.8) now becomes

$$\frac{\partial E_e}{\partial t} = 2\pi N_c N(\varepsilon_F) \int_0^\infty d\Omega \alpha^2 F(\Omega) \hbar \Omega \int d\varepsilon d\varepsilon' \delta(\varepsilon - \varepsilon' + \hbar \Omega) \{ [f(\varepsilon) - f(\varepsilon')] N(\Omega, \Theta_l) - f(\varepsilon') [1 - f(\varepsilon)] \} \quad (\text{V.2.11})$$

where $N(\Omega, \Theta_l)$ is the Bose-Einstein distribution at $\Theta = \Theta_l$ and $f(\varepsilon)$ is the Fermi-Dirac function at $\Theta = \Theta_e$. The integrals containing ε and ε' can now be solved, and Eq. (V.2.11) becomes

$$\frac{\partial E_e}{\partial t} = 2\pi N_c N(\varepsilon_F) \int_0^\infty d\Omega \alpha^2 F(\Omega) (\hbar \Omega)^2 [N(\Omega, \Theta_l) - N(\Omega, \Theta_e)]. \quad (\text{V.2.12})$$

The above formula is the most important result of Allen's thermal relaxation theory because it expresses the energy exchange in terms of modern terminology appropriate to arbitrary electronic spectra. Expression (V.2.12) is valid for all Θ_e and Θ_l given the accuracy of the underlying assumptions.

Now a simple formula of the thermal relaxation rate may be derived for $\Theta_e \gg \Theta_{\text{Debye}}$ and $\Theta_l \gg \Theta_{\text{Debye}}$, i. e. assuming $\hbar \Omega / k_B \Theta_e$ and $\hbar \Omega / k_B \Theta_l$ are small, so that the Taylor expansion in terms of $\hbar \Omega / k_B \Theta$ may be used. First, the term $e^{\frac{\hbar \Omega}{k_B \Theta}}$ in $N(\Omega, \Theta)$ is expanded

$$N(\Omega, \Theta) = \left(e^{\frac{\hbar \Omega}{k_B \Theta}} - 1 \right)^{-1} = \left(\frac{\hbar \Omega}{k_B \Theta} \right)^{-1} \left(1 + \frac{1}{2} \frac{\hbar \Omega}{k_B \Theta} + \frac{1}{6} \left(\frac{\hbar \Omega}{k_B \Theta} \right)^2 + \dots \right)^{-1} \quad (\text{V.2.13})$$

and Eq. (V.2.12) becomes

$$\frac{\partial E_e}{\partial t} = 2\pi N_c N(\varepsilon_F) \int_0^\infty d\Omega \alpha^2 F(\Omega) \hbar \Omega$$

$$\left[k_B \Theta_l \left(1 + \frac{1}{2} \frac{\hbar \Omega}{k_B \Theta_l} + \frac{1}{6} \left(\frac{\hbar \Omega}{k_B \Theta_l} \right)^2 \right)^{-1} - k_B \Theta_e \left(1 + \frac{1}{2} \frac{\hbar \Omega}{k_B \Theta_e} + \frac{1}{6} \left(\frac{\hbar \Omega}{k_B \Theta_e} \right)^2 \right)^{-1} \right]. \quad (\text{V.2.14})$$

Further, replacing

$$\left(1 + \frac{1}{2} \frac{\hbar \Omega}{k_B \Theta} + \frac{1}{6} \left(\frac{\hbar \Omega}{k_B \Theta} \right)^2 + \dots \right)^{-1} \quad (\text{V.2.15})$$

with

$$\left(1 - \frac{1}{4} \frac{\hbar \Omega}{k_B \Theta} + \frac{1}{12} \left(\frac{\hbar \Omega}{k_B \Theta} \right)^2 + \dots \right) \quad (\text{V.2.16})$$

(using Taylor expansion $\frac{1}{1+\Delta x} \simeq 1 - \frac{1}{2}\Delta x$) in V.2.14, yields

$$\frac{\partial E_e}{\partial t} = 2\pi N_c N(\varepsilon_F) \int_0^\infty d\Omega \alpha^2 F(\Omega) \hbar \Omega \left(1 - \frac{1}{12} \frac{(\hbar \Omega)^2}{k_B^2 \Theta_e \Theta_l} \right) k_B (\Theta_l - \Theta_e). \quad (\text{V.2.17})$$

Now, using the expression (Eq. (II.2.8)),

$$\lambda \langle \omega^n \rangle = 2 \int_0^\infty d\Omega [\alpha^2 F(\Omega) / \Omega] \Omega^n \quad (\text{V.2.18})$$

Eq. (V.2.17) may be expressed in terms of moments of $\alpha^2 F$

$$\frac{\partial E_e}{\partial t} = \pi \hbar N_c N(\varepsilon_F) \lambda \langle \omega^2 \rangle \left[1 - \frac{\hbar^2 \langle \omega^4 \rangle}{12 \langle \omega^2 \rangle k_B^2 \Theta_e \Theta_l} \right] k_B (\Theta_l - \Theta_e). \quad (\text{V.2.19})$$

Here the higher order terms of the Taylor expansion were truncated. Now using

$$\frac{\partial E_e}{\partial t} = \gamma \Theta_e \frac{\partial \Theta_e}{\partial t} \quad (\text{V.2.20})$$

where $\gamma = \pi^2 N_c N(\varepsilon_F) k_B^2 / 3$, and

$$\frac{\partial \Theta_e}{\partial t} = \gamma_T (\Theta_l - \Theta_e), \quad (\text{V.2.21})$$

where γ_T is the thermal relaxation rate, $\frac{\partial \Theta_e}{\partial t}$ may be expressed as

$$\frac{\partial \Theta_e}{\partial t} = \frac{1}{\gamma \Theta_e} \frac{\partial E_e}{\partial t} = \frac{3 \hbar \lambda \langle \omega^2 \rangle}{\pi k_B \Theta_e} \left[1 - \frac{\hbar^2 \langle \omega^4 \rangle}{12 \langle \omega^2 \rangle k_B^2 \Theta_e \Theta_l} \right] (\Theta_l - \Theta_e). \quad (\text{V.2.22})$$

Therefore, the thermal relaxation rate in the high temperature limit, γ_T , as derived by Allen (obtained by comparing Eq. (V.2.22) and Eq. (V.2.21)) is

$$\gamma_T = \frac{3 \hbar \lambda \langle \omega^2 \rangle}{\pi k_B \Theta_e} \left[1 - \frac{\hbar^2 \langle \omega^4 \rangle}{12 \langle \omega^2 \rangle k_B^2 \Theta_e \Theta_l} \right]. \quad (\text{V.2.23})$$

This expression is used by experimentalist [1] [2] [13] to calculate λ from the experimentally obtained electron-phonon coupling parameter g in room temperature measurements. In these room temperature measurements g is obtained by fitting the thermomodulation data to the numerical model using Eq.'s (III.3.2) and (III.3.3) where g is used as a constant fitting parameter.

V.3. Time Evolution of the Temperature-Dependent Electron-Phonon Coupling Parameter g

Since

$$\frac{\partial E_e}{\partial t} = \gamma \Theta_e \frac{\partial \Theta_e}{\partial t} = -g(\Theta_e - \Theta_l), \quad (\text{V.3.1})$$

it is evident from Eq. (V.3.1) and Eq. (V.2.22) that the electron-phonon coupling parameter g may be expressed as

$$g = \frac{3\hbar\gamma\lambda\langle\omega^2\rangle}{\pi k_B} \left[1 - \frac{\hbar^2\langle\omega^4\rangle}{12\langle\omega^2\rangle k_B^2 \Theta_e \Theta_l} \right]. \quad (\text{V.3.2})$$

In all the ultrafast pump-probe experiments so far g has been considered constant because for room temperature measurements the first thermal correction factor

$$\frac{\hbar^2\langle\omega^4\rangle}{12\langle\omega^2\rangle k_B^2 \Theta_e \Theta_l} \quad (\text{V.3.3})$$

is negligibly small under most experimental conditions, and it was possible to directly relate g to $\lambda\langle\omega^2\rangle$.

We investigate the temperature dependence of the electron-phonon coupling for ambient temperature from 7 K to 292 K. Since Θ_D for niobium is 275 K, the assumption $\Theta \gg \Theta_D$ does not hold any more, and the integral

$$\int_0^\infty d\Omega \alpha^2 F(\Omega) (\hbar\Omega)^2 [N(\Omega, \Theta_l) - N(\Omega, \Theta_e)] \quad (\text{V.3.4})$$

in Eq. (V.2.12) may not be simplified using Taylor expansion. Moreover, as will be shown, the electron-phonon parameter g may not be assumed constant anymore

since now it becomes temperature dependent. Both Θ_e and Θ_l change in time as the electrons are heated, and then transfer their energy to the lattice (Fig. III.3.4) and thus the electron-phonon parameter g also changes in time. Equation (V.3.1) now contains a temperature dependent g

$$\frac{\partial E_e}{\partial t} = \gamma \Theta_e \frac{\partial \Theta_e}{\partial t} = -g(\Theta_e, \Theta_l)(\Theta_e - \Theta_l). \quad (\text{V.3.5})$$

Using Eq. (V.2.12) and $\frac{\partial E_e}{\partial t} = g(\Theta_e, \Theta_l)(\Theta_l - \Theta_e)$, one gets for $g(\Theta_e, \Theta_l)$

$$g(\Theta_e, \Theta_l) = \frac{2\pi N_c N(\varepsilon_F)}{(\Theta_l - \Theta_e)} \int_0^\infty d\Omega \alpha^2 F(\Omega) (\hbar\Omega)^2 [N(\Omega, \Theta_l) - N(\Omega, \Theta_e)]. \quad (\text{V.3.6})$$

Since

$$\gamma = \pi^2 N_c N(\varepsilon_F) k_B^2 / 3 \quad (\text{V.3.7})$$

the product $2\pi N_c N(\varepsilon_F)$ in Eq. (V.3.6) may be expressed as

$$2\pi N_c N(\varepsilon_F) = \frac{6\gamma}{\pi k_B^2}, \quad (\text{V.3.8})$$

and the expression for temperature dependent g becomes

$$g(\Theta_e, \Theta_l) = \frac{6\gamma}{\pi k_B^2 (\Theta_l - \Theta_e)} \int_0^\infty d\Omega \alpha^2 F(\Omega) (\hbar\Omega)^2 [N(\Omega, \Theta_l) - N(\Omega, \Theta_e)]. \quad (\text{V.3.9})$$

Substituting the Bose-Einstein distribution Eq. (V.2.5) for $N(\Omega, \Theta_l)$ and $N(\Omega, \Theta_e)$ $g(\Theta_e, \Theta_l)$ becomes

$$g(\Theta_e, \Theta_l) = \frac{6\gamma}{\pi k_B^2 (\Theta_l - \Theta_e)} \int_0^\infty d\Omega \alpha^2 F(\Omega) (\hbar\Omega)^2 \left\{ [\exp(\hbar\Omega/k_B\Theta_l) - 1]^{-1} - [\exp(\hbar\Omega/k_B\Theta_e) - 1]^{-1} \right\}. \quad (\text{V.3.10})$$

The time evolution of g occurs through the time dependence of $\Theta_e(t)$ and $\Theta_l(t)$, which is governed by the coupled Equations (III.3.2) and (III.3.3) where g is now temperature dependent

$$C_e \frac{\partial \Theta_e}{\partial t} = -g(\Theta_e, \Theta_l)(\Theta_e - \Theta_l) + S(r, t) \quad (\text{V.3.11})$$

and

$$C_l \frac{\partial \Theta_l}{\partial t} = g(\Theta_e, \Theta_l)(\Theta_e - \Theta_l), \quad (\text{V.3.12})$$

and the diffusion term $\kappa \nabla^2 \Theta_e$ in Equation (III.3.2) is again neglected in the 1 ps time scale for the transmission geometry, because the diffusion in thin films (thickness - wavelength) is about three orders of magnitude slower process than the electron-phonon thermalization.

The coupled Eq.'s (V.3.10), (V.3.11) and (V.3.12) are simultaneously solved for the whole range of ambient temperatures, Θ_0 , from 292 K to 7 K. The fluence used (represented in $S(r, t)$) is somewhat higher than the one usually used for noble metals, but the achieved rise of $\Theta_e(t)$ and $\Theta_l(t)$ are similar since the electron heat capacity of niobium is substantially higher than in noble metals (for example $C_{e\text{Nb}} \sim 10 \times C_{e\text{Au}}$ [16]).

V.4. Numerical Solution of the Time Evolution of g and the Electron-Phonon Relaxation Time

The electron-phonon coupling parameter $g(\Theta_e(t), \Theta_l(t))$ for niobium is calculated as a function of $\Theta_e(t)$ and $\Theta_l(t)$ according to Eq. (V.3.10) using numerical integration. Values for the electron-phonon coupling function $\alpha^2 F(\omega)$ for niobium are taken from literature [17] and are based on tunneling experiments. (In the tunneling experiment, the normalized density of states $\sigma(E)$ is fit to the experimental tunneling characteristics and $\alpha^2 F(\omega)$ is found from the derivative of $\sigma(E)$.) The value for the electronic constant used is $\gamma=719 \text{ Jm}^{-3}\text{K}^{-2}$ [18].

A 3D plot of the electron-phonon coupling parameter g as a function of Θ_e and Θ_l is displayed in Fig. V.4.1. It is evident that when both $\Theta_e \gg \Theta_D$ and $\Theta_l \gg \Theta_D$ ($\Theta_e=275 \text{ K}$ for Nb), g becomes temperature independent [19] [20], which is why g has been considered constant in prior, room temperature experiments [13] [21] [3].

In a case of pulsed heating, when both Θ_e and Θ_l are not $\gg \Theta_D$, the electron-phonon coupling parameter $g(\Theta_e(t), \Theta_l(t))$ changes in time as Θ_e and Θ_l change according to Eq.'s (V.3.11) and (V.3.12). The coupled Eq.'s (V.3.10), (V.3.11) and (V.3.12) are simultaneously solved using the Runge-Kutta method in time while integrating for g in the phonon frequency domain for each step in time. C_e is calculated from

$$C_e = \gamma(1 + \lambda)\Theta_e \quad (\text{V.4.1})$$

where $(1+\lambda)$ is the temperature dependent many-body enhancement factor. For $\Theta_e > \Theta_D/3$ one may set λ to be equal to zero while for $\Theta_e < \Theta_D/4$ it resumes its

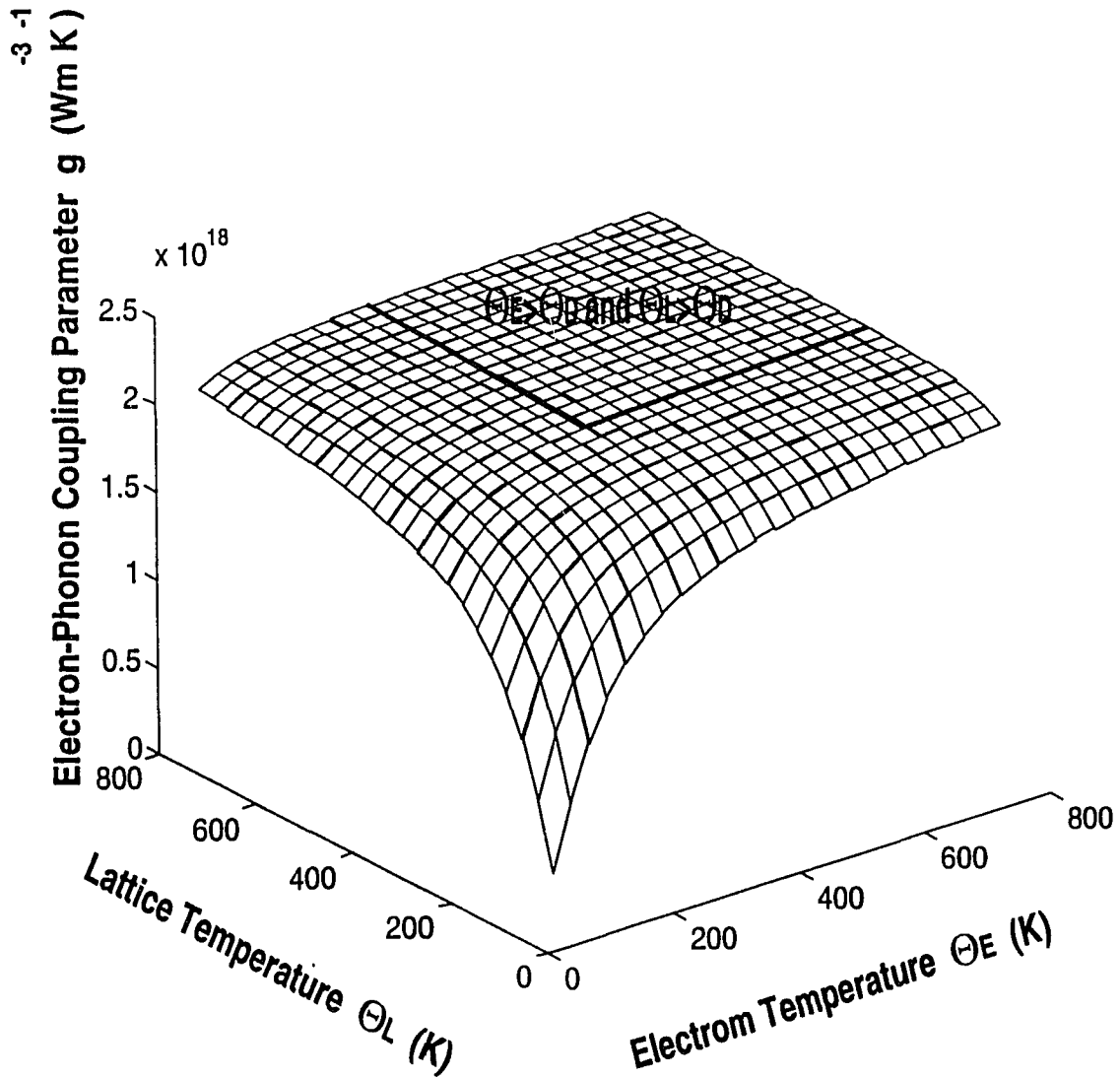


Figure V.4.1 The electron-phonon coupling parameter $g(\Theta_e, \Theta_l)$ for niobium is calculated as a function of Θ_e and Θ_l . It is evident that only when both $\Theta_e \gg \Theta_D$ and $\Theta_l \gg \Theta_D$ ($\Theta_D = 275$ K for Nb), g becomes temperature independent.

full value [22]. The value for the dimensionless electron-phonon mass enhancement parameter used is $\lambda=0.82$ [5]. The Debye approximation is used to calculate C_l at temperatures where there is good agreement with experimentally obtained C_l values for Nb. Otherwise, the experimentally obtained C_l values given in literature are directly used [18]. $g(\Theta_e(t), \Theta_l(t))$ has been calculated, as values of Θ_e and Θ_l change in time due to heating with a 110 nJ pulse. Results of this kind of calculation are shown for ambient (initial) temperature $\Theta_0=20$ K ($\Theta_0 \ll \Theta_D$), in Fig.V.4.2.

The calculated time evolution of temperatures Θ_e and Θ_l are displayed in Fig. V.4.3 for sample (ambient) temperatures $\Theta_0= 292$ K and $\Theta_0=100$ K. Initially, Θ_e increases with time as the electrons absorb the energy of the laser pulse. Then, as the electrons thermalize with phonons, Θ_e decreases and Θ_l increases. In ~ 0.5 ps the electrons and phonons acquire a constant value, after the electrons have thermalized with phonons.[23] [24]. The open circles represent experimental data and show good agreement with theory. The time it takes for the electrons to thermalize with the lattice, τ (i.e. the lattice temperature rise time) is governed by the temperature dependent electron-phonon coupling parameter g .

The calculated time evolution of the electron-phonon coupling parameter $g(\Theta_e(t), \Theta_l(t))$ is displayed in Fig. V.4.4 for ambient temperatures 7 K, 20 K, 100 K, and 292 K. The time evolution of $g(t)$ is due to the change in Θ_e and Θ_l in time as the electrons are first heated by the pump pulse and then transfer the heat to the lattice according to (V.3.11) and (V.3.12). During the first 100 fs $g(\Theta_e, \Theta_l)$ increases with time as the electrons are heated by the laser pulse, i.e. as Θ_e increases. Then, as the electrons transfer their energy to the phonons, $g(\Theta_e, \Theta_l)$ slightly decreases. Finally, the flat region represents $g(\Theta_e, \Theta_l)$ for times >500 fs at temperatures when the electrons have thermalized with the lattice. The negative time in Fig. V.4.4

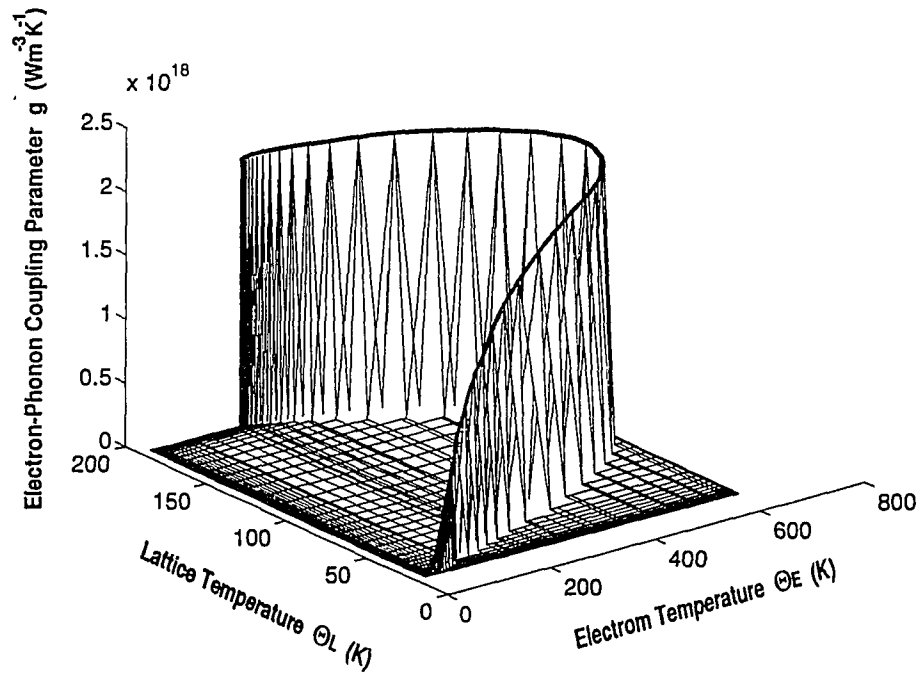


Figure V.4.2 $g(\Theta_e(t), \Theta_l(t))$ displayed as a function of Θ_e and Θ_l for ambient (initial) temperature $\Theta_0=20$ K ($\Theta_0 \ll \Theta_D$). $g(\Theta_e(t), \Theta_l(t))$ is calculated as values of Θ_e and Θ_l change in time due to heating by a 110 nJ pulse.

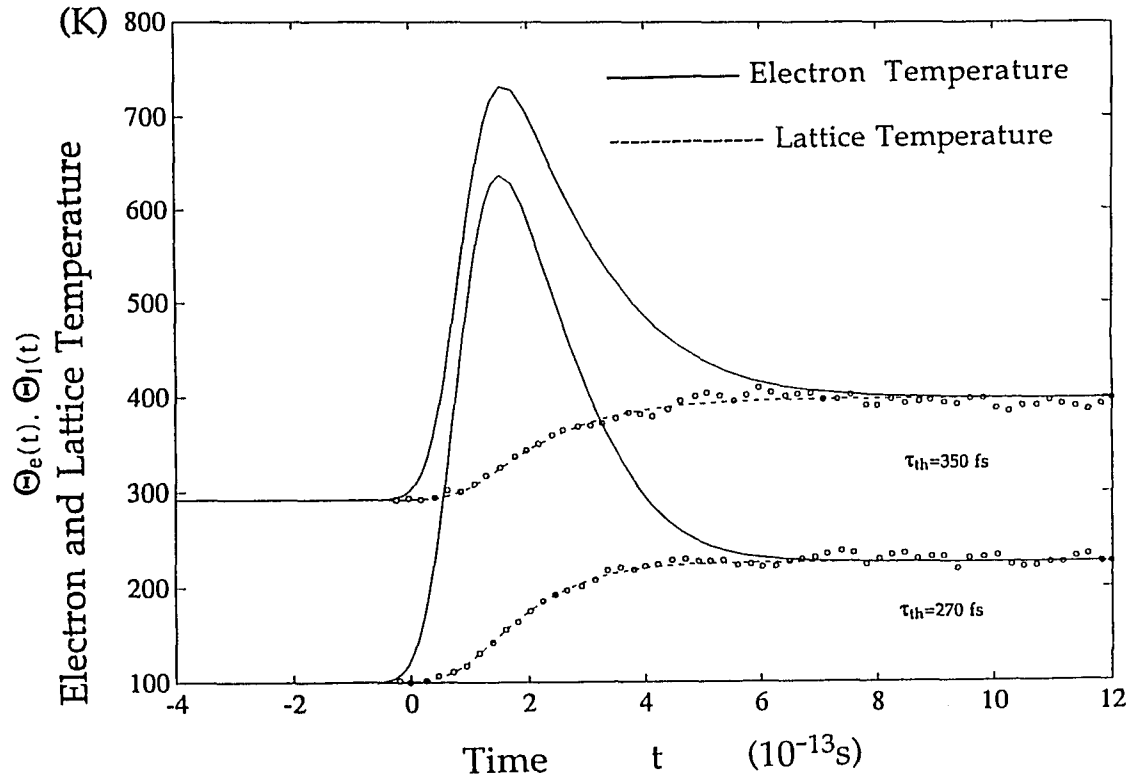


Figure V.4.3 The calculated time evolution of temperatures Θ_e and Θ_l are displayed for sample (ambient) temperatures $\Theta_0 = 292\text{ K}$ and $\Theta_0 = 100\text{ K}$. Initially, Θ_e increases with time as the electrons absorb the energy of the laser pulse. Then, as the electrons thermalize with phonons, Θ_e decreases and Θ_l increases. The circles represent experimental data.

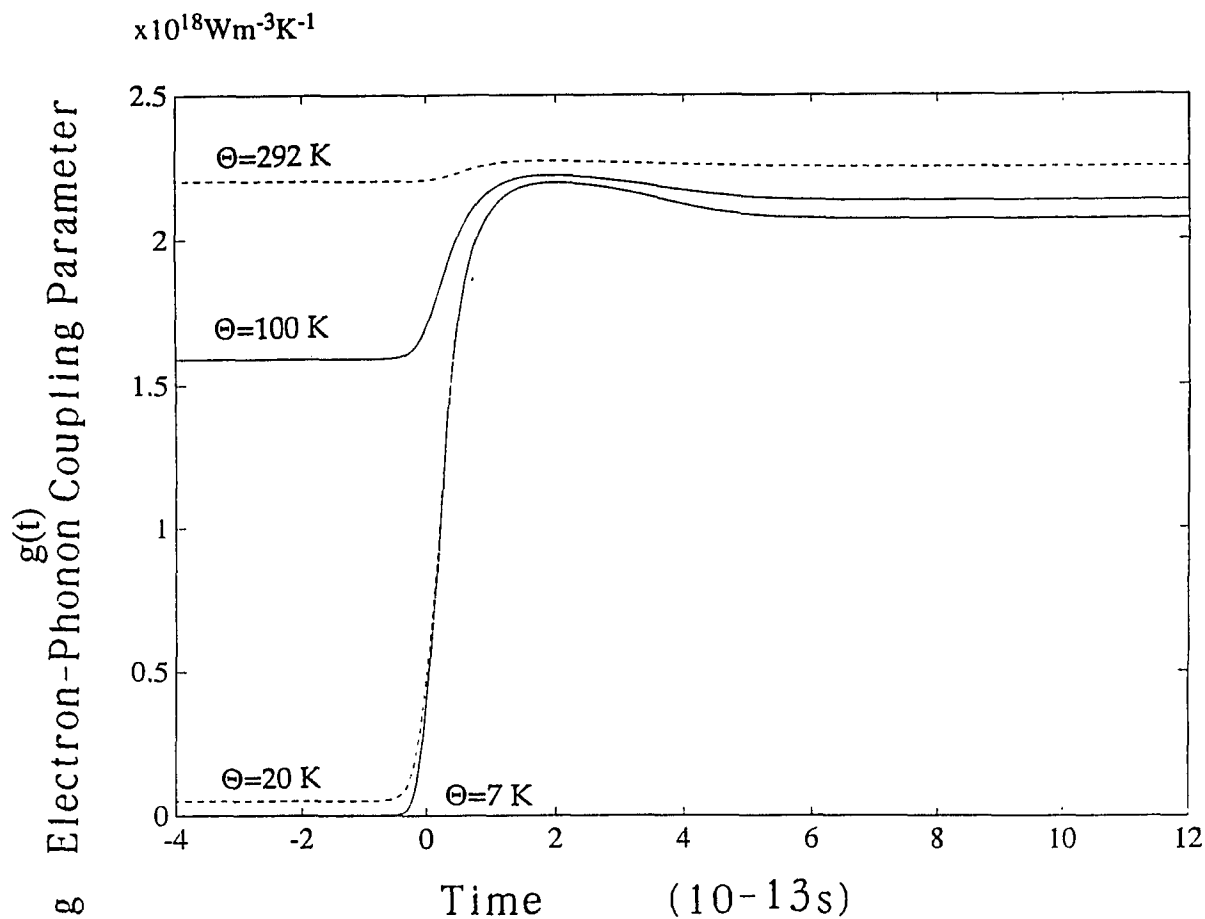


Figure V.4.4 The calculated time evolution of the electron-phonon coupling parameter $g(\Theta_e(t), \Theta_l(t))$ is displayed as a function of time as values of Θ_e and Θ_l change in time due to heating with a 110 nJ pulse. $g(\Theta_e(t), \Theta_l(t))$ is shown for ambient (initial) temperatures 7 K, 20 K, 100 K, and 292 K. One should note that $g(\Theta_e, \Theta_l)$ becomes time dependent for temperatures below Debye temperature ($\Theta_D=275 \text{ K}$ for Nb).

represents the time before the electrons are heated by the pump pulse, the value of g in this time region being that of g at ambient temperature. One should note that, for the same pump energy, $g(\Theta_e, \Theta_l)$ becomes time dependent only for temperatures below Debye temperature ($\Theta_D=275$ K for Nb).

The rise time of the calculated time evolution of the lattice temperature (i.e. the electron-phonon relaxation time) obtained as 10 % to 90 % of the total rise is shown in Fig. V.4.5 for three ambient (initial) temperatures $\Theta_0=50$ K, $\Theta_0=100$ K, and $\Theta_0=292$ K. As can be seen, τ decreases with decreasing temperature.

The normalized time evolution of the measured relative transmissivity change $\Delta T/T$ (circles) is presented in Fig. V.4.6 together with the corresponding time evolution of the lattice temperature Θ_l (solid line) for four different ambient (initial) temperatures, 7, 10, 20, and 50 K. The dashed line represents the best fit to the experimental data. Below 30 K the experimental results show a continuous decrease in the electron phonon relaxation time, while according to theory the relaxation time starts slightly increasing.

In Fig. V.4.7 values of the calculated electron-phonon relaxation time, τ_{th} , obtained as in Fig. V.4.5 are plotted for a range of ambient (initial) temperatures from $\Theta_0=7$ K to $\Theta_0=292$ K (solid circles). The time it takes for the electrons to thermalize with phonons, τ_{th} , decrease with decreasing temperature for all but the lowest ambient temperatures. At low temperatures, $\Theta_0 \leq 20$ K, τ starts slightly increasing with increasing temperature. For comparison, the experimentally obtained electron-phonon relaxation time, τ_{exp} is also plotted.

Although most experiments measuring the electron-phonon relaxation time were performed at room temperature, recently some experiments attempt to measure the electron-phonon relaxation time at temperatures below Θ_D . In the work by Groeneveld

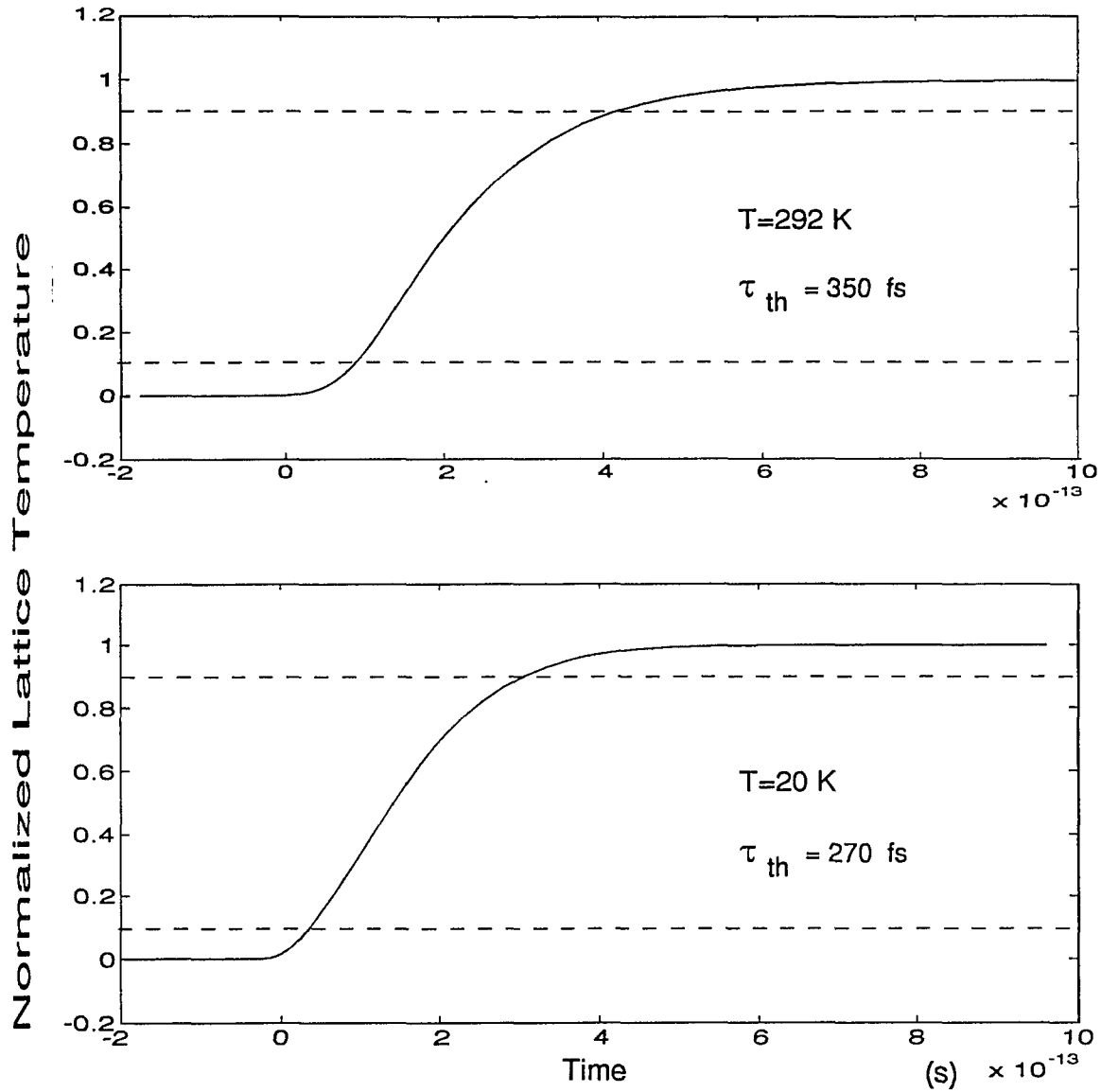


Figure V.4.5 The rise time of the calculated time evolution of the lattice temperature (i.e. the electron-phonon relaxation time) measured as 10 % to 90 % of the total rise is shown for two ambient (initial) temperatures; $\Theta_0=20$ K, and $\Theta_0=292$ K. As can be seen, τ decreases with decreasing temperature.

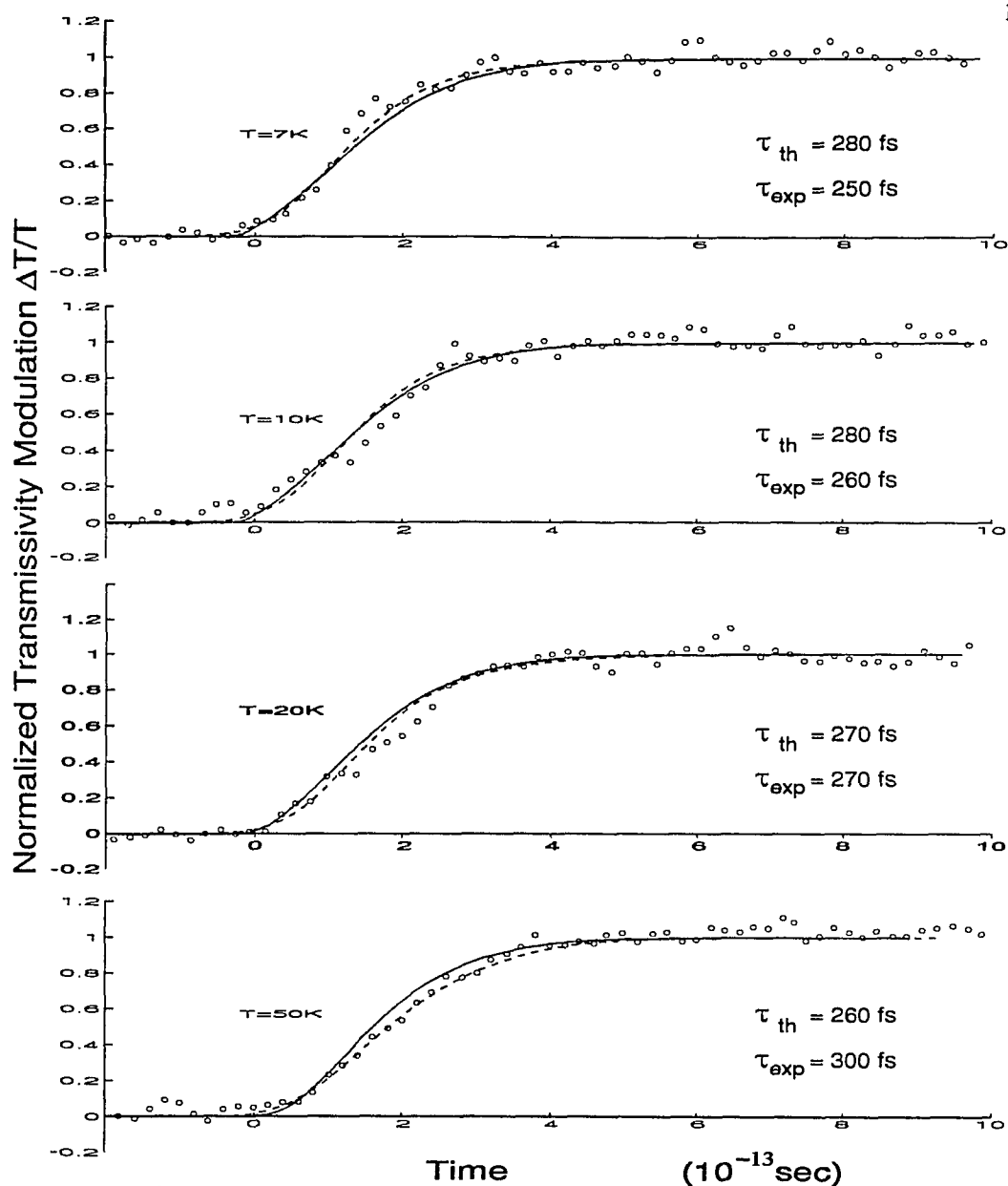


Figure V.4.6 The normalized time evolution of the measured relative transmissivity change $\Delta T/T$ (circles) is presented together with the corresponding time evolution of the lattice temperature Θ_l (solid line) for four different ambient (initial) temperatures, 7, 10, 20, and 50 K. The dashed line represents the best fit to the experimental data.

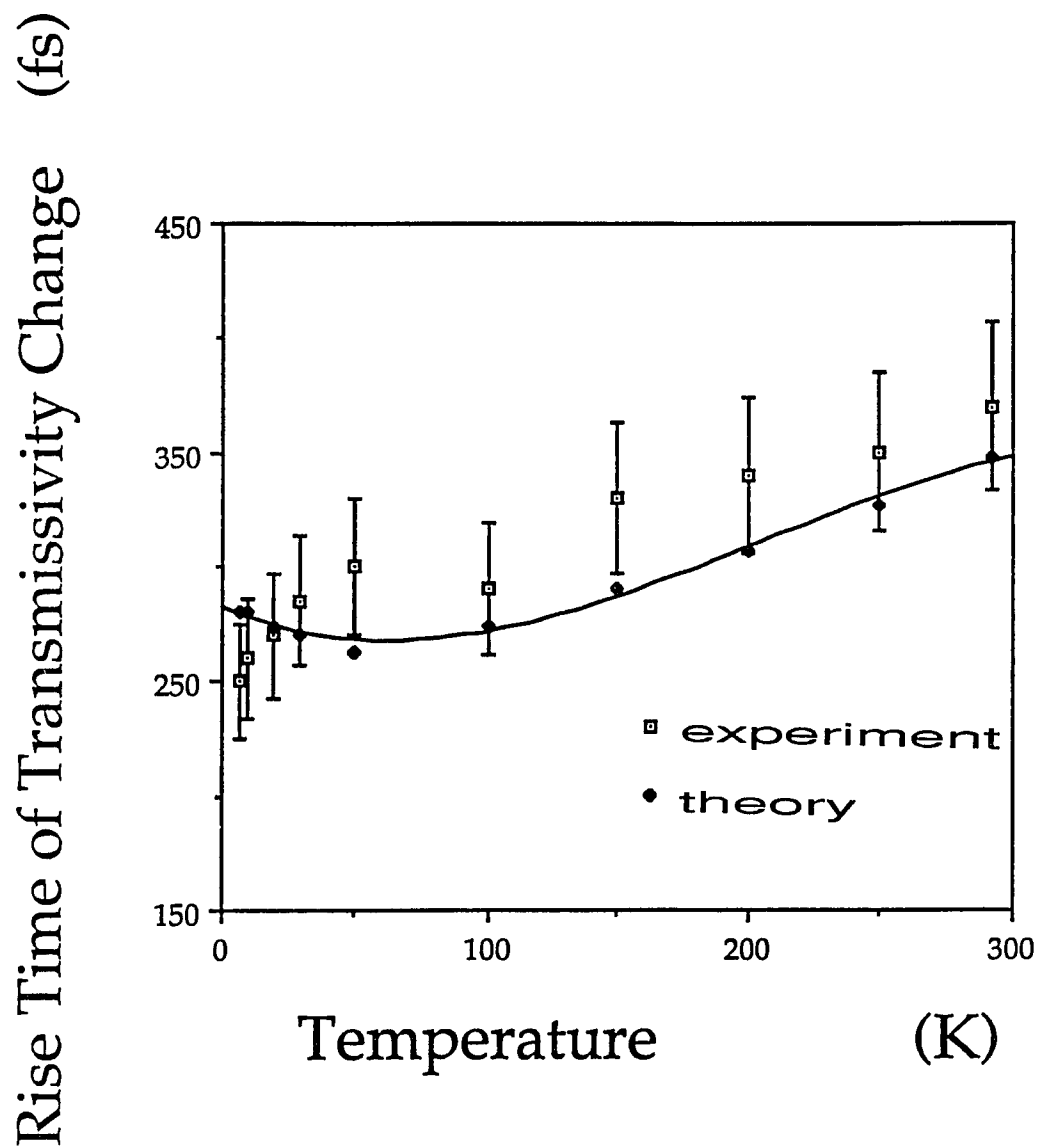


Figure V.4.7 The calculated values of the electron-phonon relaxation time, τ_{th} , obtained as in Fig. V.4.5 are plotted for a range of ambient (initial) temperatures from $\Theta_0=7$ K to $\Theta_0=292$ K. For comparison, the experimentally obtained electron-phonon relaxation time, τ_{exp} is also plotted.

et al. [9], performed below Θ_D , the measured electron-phonon thermalization time for Au was found to be longer than the one predicted by TTM, the discrepancy increasing with decreasing temperature. However in the TTM model used in this work, constant room temperature value was used for g . Since, as we have shown, g decreases with decreasing temperature, a smaller value for g would give longer electron-phonon thermalization time in agreement with experimental results.

V.5. Conclusion

Calculations based on Allen's theory for electron-phonon energy exchange show that when temperatures are decreased below Θ_D , the electron-phonon coupling parameter is not constant any more. Namely, it becomes dependent on both electron temperature and phonon temperature. g is found to decrease with decreasing temperature. Since during the electron-phonon interaction, i.e. during the time it takes for the electrons to thermalize with phonons, both the electron and phonon temperature change in time, the value of the electron-phonon coupling parameter changes in time accordingly. Therefore in the two temperature model (TTM) based on Eqs. (V.3.11) and (V.3.12), the electron phonon coupling parameter g becomes a dynamic variable.

The calculated values of the electron-phonon relaxation time, τ_{th} show good agreement with measured experimental values, τ_{exp} (Fig. V.4.7), undershooting τ_{exp} by <10%, from room temperature to well below Debye temperature, ($\Theta_D=275$ K for niobium) at 20 K. However, for sample temperatures below 20 K the theoretical calculations give larger values of the transmissivity rise time than the experiment by 15% which means that the calculated coupling parameter $g(\Theta_e, \Theta_l)$ is too small at very low temperatures. When the convolution with the probe pulse is taken into account, the actual experimentally obtained τ_{exp} would be 5–10% smaller than displayed in Fig. IV.4.6, the effect being greater for shorter τ_{exp} , i.e. at smaller temperatures. This improves the agreement with theory at all but the lowest temperatures.

There is a discrepancy between theory and experiment at very low temperatures. For temperatures, $\Theta \leq 20$ K the theoretically obtained electron-phonon relaxation

time, τ_{th} , although within experimental error bars, shows an increasing trend with decreasing temperature, as opposed to the experimentally obtained value, τ_{exp} . The lower values and continuous decrease of the electron-phonon relaxation obtained by the experiment for $\Theta < \Theta_D/3$ are most likely due to a shake-off process taking place for $\Theta < \Theta_D/3$. Namely, at $\Theta < \Theta_D/3$ some part of the lattice energy is stored in a Fermi liquid, which is seen in the specific heat change from C_e to $(1 + \lambda)C_e$. The laser pump pulse heats the electrons quickly from $\Theta_e = \Theta_{amb} \ll \Theta_D$ to $\Theta_e > \Theta_D$. It causes a shake-off process [14] leading to a release of the lattice energy represented by λ . So the absorbed energy is shared by the electrons and the shake-off phonons. This is an additional and probably faster mechanism to heat the lattice phonons at $\Theta < \Theta_D/3$. Moreover, this effect is more pronounced at lower temperatures since λ increases with decreasing temperature, which explains the measured continuous decrease in electron-phonon relaxation time obtained in the experiment. The disagreement between theory and experiment at very low temperature may also be attributed to the uncertainty in the experimentally obtained value of the electron-phonon mass enhancement parameter λ used in the calculations, whose effect is much more important at low temperatures [22].

In summary, the temperature dependence and time evolution of the electron-phonon coupling parameter $g(\Theta_e, \Theta_l)$ has been determined based on Allen's theory. These values for $g(\Theta_e, \Theta_l)$ were used to obtain the numerically calculated rise time of the lattice temperature. The calculated electron-phonon relaxation time is in good agreement with the measured experimental values well below Debye temperature, down to 20 K. This confirms the validity of the theoretical model for $g(\Theta_e, \Theta_l)$ used for determining the time evolution of the electron-phonon coupling parameter.

Although the difference between the experimentally obtained electron-phonon

relaxation time and the theoretically calculated one is almost within the experimental error, it is clearly evident that for sample temperatures ≤ 20 K the experimental results show a continuous decrease in the electron-phonon relaxation time, while according to the theory the relaxation time starts increasing slightly with temperature for $\Theta < 30$ K. There is a strong indication that the theoretical model has to be improved for temperatures from 30 K to below Θ_c . The discrepancy seen at lower temperatures may be due to the fact that the exact temperature dependence of the electron-phonon mass enhancement parameter λ is not known. The effect of the shake-off process that arises at lower temperatures also may need to be taken into consideration.

Bibliography

- [1] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen *Phys. Rev. Lett.* **53**, p. 1837, 1984.
- [2] H. E. Elsayed-Ali, T. B. Norris, M. A. Pessot, and G. A. Mourou *Phys. Rev. Lett.* **58**, p. 1212, 1987.
- [3] R. W. Schoenlein, W. Z. Lin, J. G. Fujimoto, and G. L. Eesley *Phys. Rev. Lett.* **58**, p. 1680, 1987.
- [4] P. B. Allen, *Dynamic Processes in Solids*, Vol. **3**, p. 95. North-Holland, Amsterdam, 1980.
- [5] W. L. McMillan *Phys. Rev.* **167**, p. 331, 1968.
- [6] G. D. Gaspari and B. L. Gyorffy *Phys. Rev. Lett.* **29**, p. 801, 1972.
- [7] F. S. Khan, P. B. Allen, W. H. Butler, and F. J. Pinski *Phys. Rev. B* **26**, p. 1538, 1982.
- [8] P. B. Allen *Phys. Rev. B* **36**, p. 2920, 1987.
- [9] R. H. M. Groeneveld, R. Sprik, and A. Lagendijk *Phys. Rev. B Rapid Comm.* **45**, p. 5079, 1992.
- [10] T. Juhasz, H. E. Elsayed-Ali, X. H. Hu, and W. E. Bron *Phys. Rev. B* **45**, p. 13819, 1992.
- [11] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.
- [12] G. L. Eesley, B. M. Clemens, and C. A. Paddock *Appl. Phys. Lett.* **50**, p. 717, 1987.
- [13] K. M. Yoo, X. M. Zhao, M. Siddique, R. R. Alfano, D. P. Osterman, M. Radparvan, and J. Cuniff *Appl. Phys. Lett.* **56**, p. 1908, 1990.

- [14]J. M. Ziman, *Electrons and Phonons*. Oxford University Press, London, 1960.
- [15]P. B. Allen *Phys. Rev. B* **6**, p. 2577, 1972.
- [16]W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor *Phys. Rev. Lett.* **68**, p. 2834, 1992.
- [17]G. B. Arnold, J. Zasadzinski, J. W. Osmun, and E. L. Wolf *J. Low Temp. Phys.* **40**, p. 225, 1980.
- [18]R. C. Weast and D. R. Lide, *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida, 1989.
- [19]M. Mihailidi and R. R. Alfano *Appl. Phys. Lett.* (accepted for publication), 1994.
- [20]M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [21]G. L. Eesley *Phys. Rev. Lett.* **51**, p. 2140, 1986.
- [22]G. Grimvall, *The Electron-Phonon Interaction in Metals*. North-Holland, Amsterdam, 1981.
- [23]M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.
- [24]M. Mihailidi and R. R. Alfano in *9th Interdisciplinary Laser Science Conference (ILS-IX)*, 1993.

VI Measurements of Diffusion Related Thermotransmittance in Niobium from Room Temperature to Below Superconducting Temperature

VI.1. Introduction

A good number of superconducting devices base their performance on switching from superconductive to normal state and vice versa. This transition process is intrinsically nonequilibrium in nature. To improve the performance of such devices it is necessary to study the factors that affect the minimum switching time and that reduce the energy required for switching. Optimizing both the switching time and energy is one direction in improving the switching performance. Special purpose fast switches, like those used for noise discrimination in digital circuits, demand primarily fast switching even if power levels have to remain large. Laser induced electron heating with ultrafast pulses, provides unique possibilities for fast switching from superconducting to metal state. To investigate fast, nonequilibrium transient properties that govern the transition process, ultrafast laser pulses have to be used, with pulse duration shorter than these transition processes.

Mitsen et al. [1] [2] [3] were the first to make the hypothesis that a superconductor under nonequilibrium conditions caused by homogeneous excitation by a laser pulse, assumes a spatially-inhomogeneous state characterized by the simultaneous coexistence of the normal and superconducting phase. This hypothesis has also been supported by Elesin et al. [4] [5] who shows that for high enough pump there is nonstationary

coexistence of the normal and superconducting regions, when the regions of normal phase increase in volume and the superconducting regions decrease in volume.

In work by Janik et al. [6] a change in transmittance of a 20-nm aluminum film was measured under laser irradiation. The results were explained by assuming formation of a certain intermediate state which consists of alternating regions of normal and superconducting phases. The superconducting regions where the gap and the critical superconducting temperature, Θ_c , conserve their unperturbed values, while the volume of the normal phase increases in time.

In this work, to investigate the niobium metal in the transition from superconducting to normal state, thermotransmittance measurements for ambient temperatures above and below the superconducting temperature are performed for niobium film using 100 fs laser pulses in a pump-probe configuration. The measured change in the thermotransmittance relaxation time in the 250-ps time range is attributed to heat diffusion and the nonequilibrium processes in the transition from superconducting to normal state.

VI.2. Description of Experiment

Transient thermorefectance and thermotransmittance spectroscopy is based on producing a change in reflectance or transmittance by changing the temperature of the material. Measurements of the thermal transport in metal films based on the thermally induced change in reflectivity or transmissivity have been successfully performed before [7] [8]. Experimental thermotransmittance spectroscopy methods have been used to determine the temperature decay due to diffusion in several metal films (Ni, No, Ti, Zr, and Cu) [8] [9]. In these experiments, as in the experiments presented below, a transient thermorefectance technique is used to detect the change in metal temperature. Two synchronous laser pulses are used in a pump-probe configuration, one to heat the metal film and the other to measure the resulting relative change in transmissivity, which is proportional to the change in metal temperature.

Experiments were performed using a standard pump-probe configuration to measure the transient thermotransmittance in Nb film at a range of sample temperatures from 4.5 K (below superconducting temperature) to 292 K. The experimental set-up used is the same as the one described in detail in chapter IV. It consists of a colliding pulse mode-locked (CPM) dye laser and an amplifier pumped with a copper vapor laser operating at 6.5 kHz. The duration of the pulses generated was 100 fs full width at half maximum and the wavelength was centered at 625 nm. For the lock-in detection the pump beam was chopped in order to detect the difference in the transmittance intensity of the probe beam caused by the pump. The probe pulse used was 1% of the pump intensity. The energy of the pump was 110 nJ and was focused onto a

spot $35\text{ }\mu\text{m}$ in diameter. The diameter of the probe beam was 5 times smaller than the pump beam. A motorized translation stage was used to delay the probe pulse with respect to the pump pulse. The probe beam was polarized perpendicular to the polarization of the pump beam to avoid the large coherent artifact which occurs when the probe beam is polarized parallel to the pump beam. The sample was a 20 nm thick niobium film, deposited on a $100\text{-}\mu$ thick fused quartz, and was attached to a heat sink whose temperature may be varied. The skin depth of niobium is $\sim 20\text{ nm}$. The experimentally determined absorptivity was found to be $\sim 5\%$ of the incident laser energy. The change in transmitted probe intensity was measured for time delays from 0 to 250 ps of the probe pulse with respect to the pump. The maximum change was 8% and was linearly dependent on the laser fluence.

VI.3. Results

VI.3.1. Experimental Results

The measured temporal response of the thermotransmittance signal is directly related to the film temperature [7] [8] [10]. The temperature decay time depends on the sample geometry and the diffusivity $D=k/C_p$. The geometry of the sample is that of a semifinite bilayer made of 20 nm thick Nb film, deposited on fused quartz. The Nb film is placed in a helium dewar with a temperature controller. One face of the 20 nm Nb film is isolated by vacuum, while the other side is connected to the 100 μm quartz plate the film was deposited on. The sample is placed in vacuum, between two copper plates attached to a cold finger. The volume heated by the laser pulse is 20 nm thick and 35 μm in diameter. Due to large aspect ratio of the heated volume, diffusion across the film will dominate in the 250 ps time scale, and the experimental data obtained for Nb in the normal state represent the cooling of the Nb film in time due to thermal diffusion across the bilayer.

Typical results on the transient thermotransmittance for sample (initial) temperatures 10 K (above Θ_c) and 4.5 K (below Θ_c) are displayed in Fig. VI.3.1. The relaxation of the thermotransmittance signal below Θ_c shows a considerably faster decay than above Θ_c ($\Theta_c=8.8$ K). The thermotransmittance relaxation time, $\tau_{\Delta T}$, (measured from 10% to 90% of the total rise) is obtained by extrapolation, approximating the temperature decay to be linear, as suggested by both the experimental results and the theoretical model presented below. Fig. VI.3.2 shows measured relaxation time for sample at initial temperatures ranging from 292 K

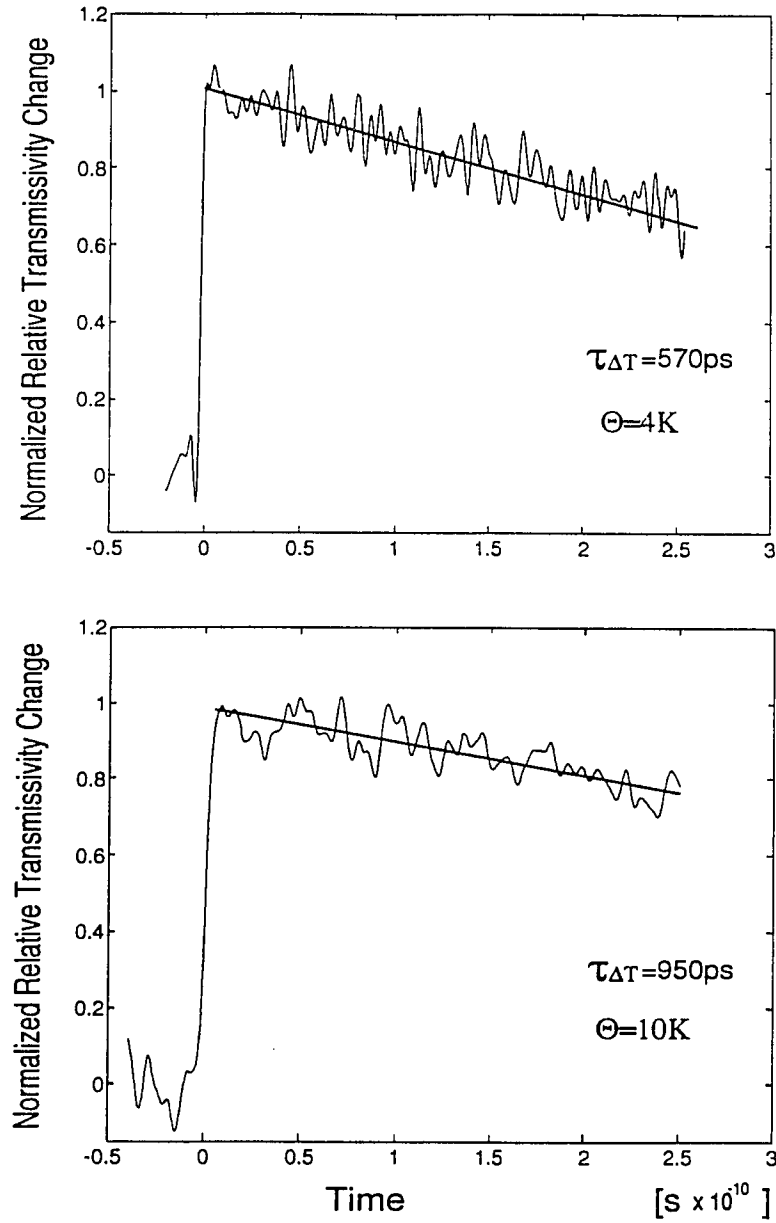


Figure VI.4.1 The experimentally obtained results of the transient thermotransmittance are shown for sample (initial) temperature 10 K (above Θ_c) and 4.5 K (below Θ_c). The relaxation time, $\tau_{\Delta T}$, is measured to be 950 ps for temperatures above Θ_c , while below Θ_c it decreases to 570 ps.

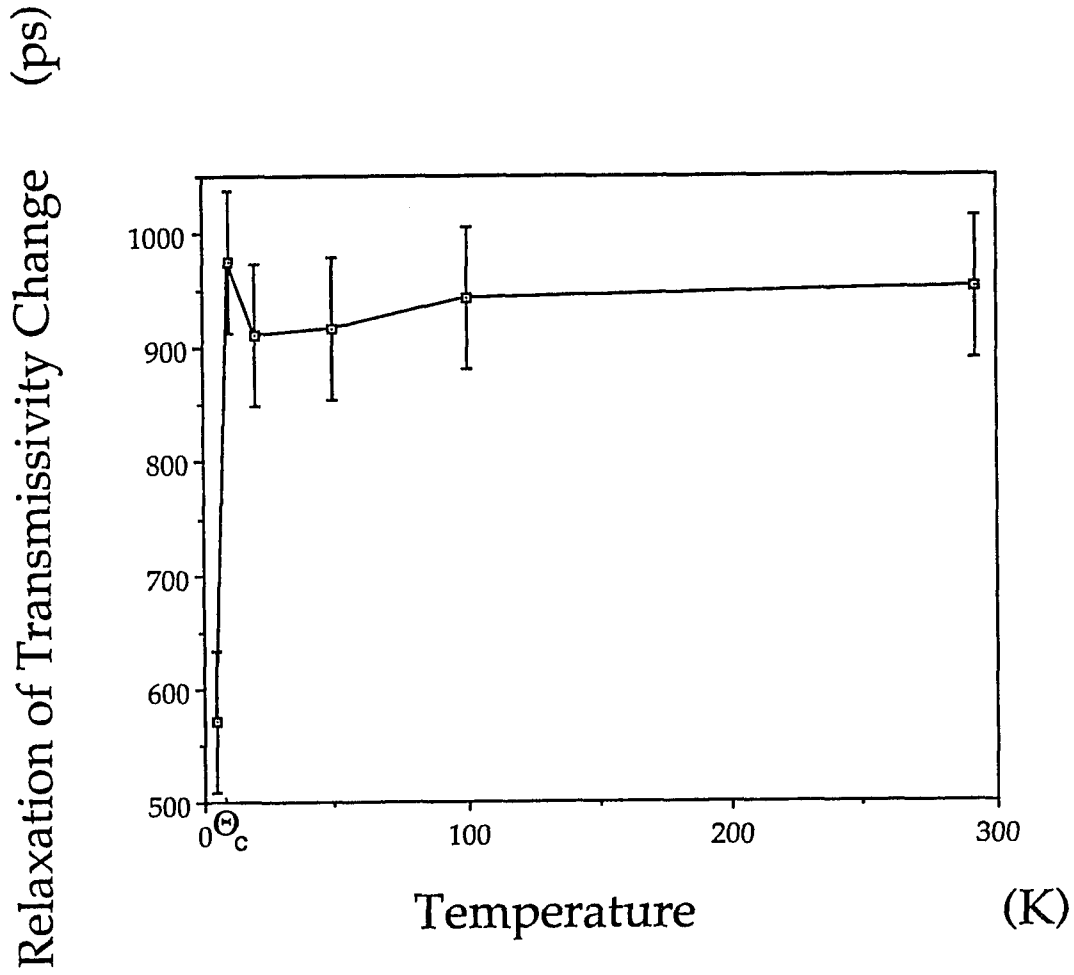


Figure VI.3.2 The measured thermotransmittance relaxation time is shown for sample (initial) temperatures ranging from 292 K to 4.5 K. The relaxation time, $\tau_{\Delta T}$, (measured from 10% to 90% of the total rise) is obtained by extrapolation, approximating the temperature decay to be linear. $\tau_{\Delta T}$ was found to remain the same for all temperatures above Θ_c and was measured to be 950 ± 70 ps. For temperatures below critical temperature, Θ_c , $\tau_{\Delta T}$ decreases to 570 ± 70 ps.

and 4.5 K. It was found that the thermotransmittance decay time remains about the same for all temperatures above Θ_c which was measured to be -950 ± 70 ps. For temperatures below critical temperature, Θ_c , the thermotransmittance decay time decreases to -570 ± 70 ps.

VI.3.2. Numerical Results

Mathematical Model

The mathematical calculations are based on modeling the following process that takes place in the metal film. Part of the laser pulse energy is absorbed by the thin metal film. This energy rises the temperature of the metal film and is subsequently transferred to the substrate. The transport of heat through this layer can be described by Eq. VI.3.1, which is a standard heat diffusion equation, and Eq. VI.3.2 that describes conservation of thermal flux at the interface. The temperature as a function of time and depth is given by

$$C_i \frac{\partial \Theta(x, t)}{\partial t} = k_i \frac{\partial^2 \Theta(x, t)}{\partial x^2} + \alpha_i I_0 \exp(-\alpha_i x) \exp\left(-\frac{1}{2} \left(\frac{t - t_0}{\sigma}\right)^2\right), \quad i = 1, 2 \quad (\text{VI.3.1})$$

where $i=1$ stands for the upper layer (Nb film) and $i=2$ stands for the lower layer (quartz substrate). Here Θ denotes the change in temperature as a function of depth, x , and time, t . k_i is heat conductivity, C_i is heat capacity, α_i is the absorption coefficient and I_0 is the amplitude of the input laser intensity (assumed Gaussian). The heat conductivity, k_i , and the heat capacity, C_i , are temperature dependent. The boundary condition at the interface, representing the conservation of thermal flux, is

$$-\kappa_1 \frac{\partial \Theta(d^-, t)}{\partial x} = \frac{\Theta(d^-, t) - \Theta(d^+, t)}{\rho} = -\kappa_2 \frac{\partial \Theta(d^+, t)}{\partial x} \quad (\text{VI.3.2})$$

where ρ is the interfacial thermal impedance. There are two additional boundary conditions; for the surface and sufficiently deep in the underlayer. They represent the assumption that the heat flow is negligible both out of the surface and deep in the underlayer;

$$\left. \frac{\partial \Theta(x, t)}{\partial x} \right|_{x=0} = 0 \quad (\text{VI.3.3})$$

and

$$\left. \frac{\partial \Theta(x, t)}{\partial x} \right|_{x=x_{max}} = 0. \quad (\text{VI.3.4})$$

The boundary conditions VI.3.3 at the surface holds because the sample is in vacuum. For boundary condition VI.3.4, sufficiently deep in the underlayer mens that for the duration of our measurements (250 ps) some points, sufficiently deep in the underlayer, have not been heated yet. For quartz, $x=0.2 \mu\text{m}$ is sufficiently deep. And the last two conditions represent the fact that there is no change in temperature at sufficient depth or prior to the heating pulse:

$$\Delta \Theta(x_{max}, t) = 0 \quad (\text{VI.3.5})$$

and

$$\Delta \Theta(x, t < -4FWHM) = 0 \quad (\text{VI.3.6})$$

For the sake of better physical insight, lets consider a simplified model by introducing two approximations; (i) the parameters k_i and C_i are assumed temperature independent, thus making the diffusivity, D_i constant and (ii) the conservation of thermal flux at the interface (described by Eq. VI.3.2) is assumed to result in boundary conditions at the interface being represented with some function $B(t)$. Then, having in mind the boundary conditions at the front surface of Nb and at the back

surface of quartz specified by Equations VI.3.3 and VI.3.4 the diffusion Equations VI.3.1 for Nb film and quartz substrate may be solved in a closed form. The solution is of the form

$$\Theta_i(x, t) = A_i B(t) + \sum_{n=0}^{\infty} C_{in} \exp(-D_i \lambda_{in} t) \phi(\sqrt{\lambda_{in}} x) \quad (\text{VI.3.7})$$

The transient part of the solution describing the time dependence of the temperature distribution is proportional to both, the boundary condition function $B(t)$ and the exponential terms $\exp(-D_i \lambda_{in} t)$, where $i=1$ means niobium and $i=2$ means quartz. $\lambda_{in} = \left[\frac{(2n+1)\pi}{2L_i} \right]^2$, where L_i is the thickness of the niobium film ($i=1$) and the quartz substrate ($i=2$). The above simplified model shows that, as expected, the temperature decay time (i.e. cooling time) decreases with increasing diffusivity D_i ($D_i = \frac{k_i}{C_i}$). The approximated temperature at the interface, $B(t)$, will also decrease faster for greater flux at the interface (i.e greater conductivity k_i as seen from Eq. VI.3.2). If this simplified model is not assumed, there is no closed solution for temperature as a function of time and depth because of increased complexity due to the existence of an interface and due to the temperature dependence (and thus time dependence) of parameters k_i and C_i .

Application of the DuFort-Frankel Difference Method

To solve this problem accurately, we proceed with a numerical method and without the above mentioned assumptions (i) and (ii). Numerical modeling is performed to obtain temperature solutions as a function of time and sample depth. The solutions result in a 3D picture of the temperature distribution in time and depth of the bilayer. The calculated relative change in film temperature is fitted to the measured relative change in thermotransmittance. The interfacial thermal impedance, ρ , which is used

as a fitting parameter, is determined to be $3 \times 10^{-9} \text{ m}^2 \text{ K/W}$. ρ depends on the relative lattice mismatch between the film and the underlayer and the fabrication conditions[8].

The numerical approach was based on the unconditionally stable DuFort-Frankel explicit method [11]. This model was modified to account for temperature dependent C_i and k_i [12] [13]. The temperature dependent values for k_i and C_i are changed dynamically [12] [13] in the DuFort-Frankel mesh for each point in space as temperature changes with time. The temperature dependence of diffusivity $D(\Theta)$, where

$$D(\Theta) = \kappa(\Theta)/C(\Theta) \quad (\text{VI.3.8})$$

is obtained from literature [12] [13], and is presented in Fig. VI.3.3 for niobium and quartz. α_1 in the Eq. VI.3.1 was calculated to be $5.8 \times 10^7 (\text{m}^{-1})$ using the expression $\alpha = 4\pi n_i / \lambda$, where n_i is the imaginary part of the refractive index and λ is the wavelength of the laser light. α_2 in the Eq. VI.3.1 represents the absorption of visible light in the Quartz substrate and is taken to be zero.

The following describes the numerical modeling. As previously mentioned, in order to calculate the change in Nb film temperature in the ps time scale, a heat flow model was applied based on standard heat diffusion equations

$$C_i \frac{\partial \Theta(x, t)}{\partial t} = k_i \frac{\partial^2 \Theta(x, t)}{\partial x^2} + Q_i, \quad i = 1, 2 \quad (\text{VI.3.9})$$

where $i=1$ stands for the upper layer (Nb film) and $i=2$ stands for the underlayer (quartz substrate). Q_i is the forcing function that represents the pump pulse. The numerical method was based on the DuFort-Frankel explicit approximation which is unconditionally stable [11]. It is derived using the approximation

$$\Theta_j^n \simeq \left(\Theta_j^{n+1} + \Theta_j^{n-1} \right) \quad (\text{VI.3.10})$$

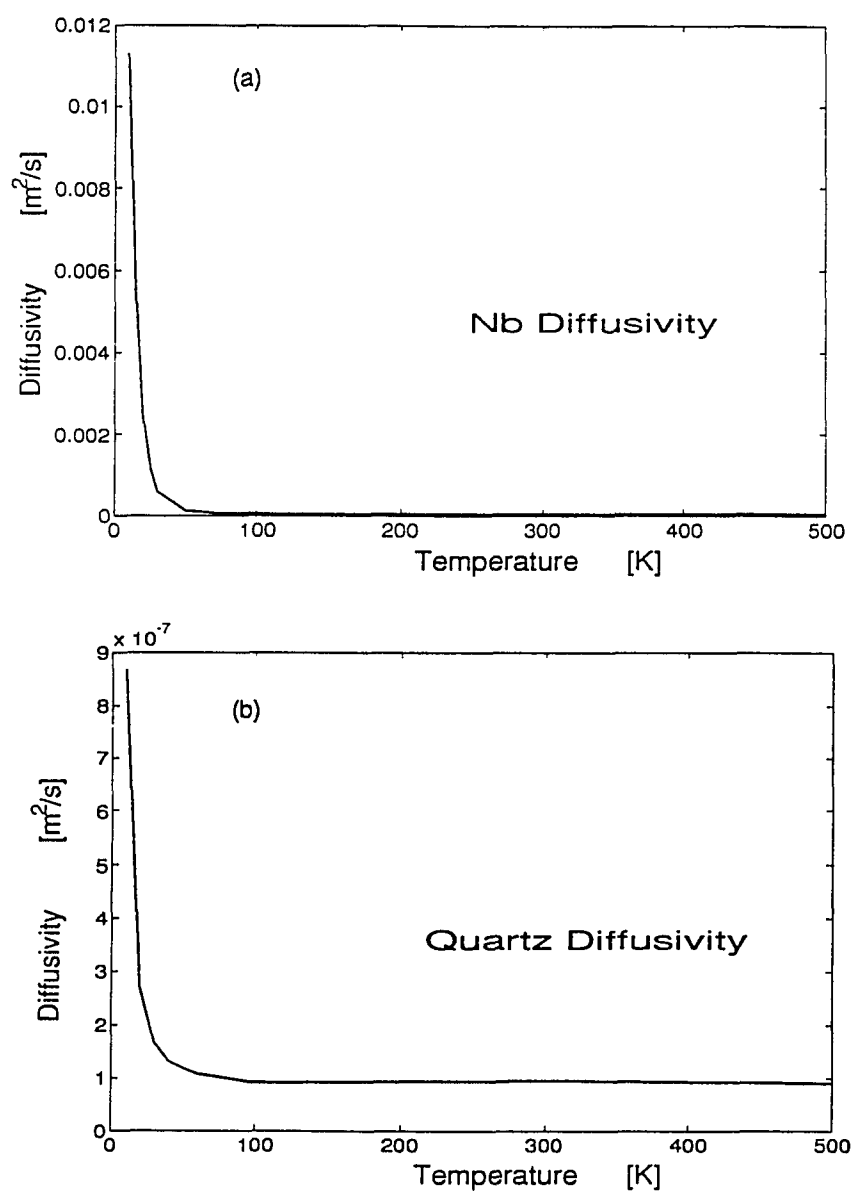


Figure VI.4.3 The temperature dependence of diffusivity $D=k/C$ for niobium (a) and quartz (b).

and the leap-frog method,

$$C_i \frac{(\Theta_j^{n+1} - \Theta_j^{n-1})}{2\Delta t} = \kappa_i \frac{\frac{\Delta \Theta_j^n}{\Delta x} - \frac{\Delta \Theta_{j-1}^n}{\Delta x}}{\Delta x} + Q_{i,j}^{n+1} \quad j = 1, 2, \dots, J-1; \quad n = 1, 2, \dots, N-1 \quad (\text{VI.3.11})$$

where j and n are points in distance and time respectively. The computational molecule for the Du Fort-Frankel method is shown in Fig. VI.3.4. The value of Θ at time $(n+1)\Delta t$ at position $j\Delta x$ is effected by Θ one time step ago at position $(j-1)\Delta x$ and position $(j+1)\Delta x$, and by Θ two time steps ago at position $j\Delta x$.

Writing VI.3.11 as

$$C_i \frac{(\Theta_j^{n+1} - \Theta_j^{n-1})}{2\Delta t} = \kappa_i \frac{\Theta_{j+1}^n - 2\Theta_j^n + \Theta_{j-1}^n}{(\Delta x)^2} + Q_{i,j}^{n+1} \quad j = 1, 2, \dots, J-1; \quad n = 1, 2, \dots, N-1 \quad (\text{VI.3.12})$$

and substituting VI.3.10 for Θ_j^n we get

$$\begin{aligned} (\Theta_j^{n+1} - \Theta_j^{n-1}) &= 2 \frac{\kappa_i}{C_i} \frac{\Delta t}{(\Delta x)^2} (\Theta_{j+1}^n - \Theta_j^{n+1} - \Theta_j^{n-1} + \Theta_{j-1}^n) + 2 \frac{\Delta t}{C_i} Q_{i,j}^{n+1} \\ j &= 1, 2, \dots, J-1 \quad n = 1, 2, \dots, N-1 \end{aligned} \quad (\text{VI.3.13})$$

From here the DuFort-Frankel Difference formula for Θ_j^{n+1} is

$$\Theta_j^{n+1} = \frac{(1 - \beta_i)}{(1 + \beta_i)} \Theta_j^{n-1} + \frac{2\beta_i}{(1 + \beta_i)} (\Theta_{j+1}^n - \Theta_{j-1}^n) + \frac{2\Delta t}{C_i(1 + \beta_i)} Q_{i,j}^{n+1} \quad (\text{VI.3.14})$$

where

$$\beta_i = \frac{\kappa_i \Delta t}{C_i (\Delta x)^2}. \quad (\text{VI.3.15})$$

The forcing function in the metal film and quartz substrate are

$$Q_{1,j}^{n+1} = \alpha_1 I_0 \exp(-\alpha_1(j-1)\Delta x) \exp\left(-\frac{1}{2} \left(\frac{(n-1)\Delta t - t_0}{\sigma}\right)^2\right) \quad (\text{VI.3.16})$$

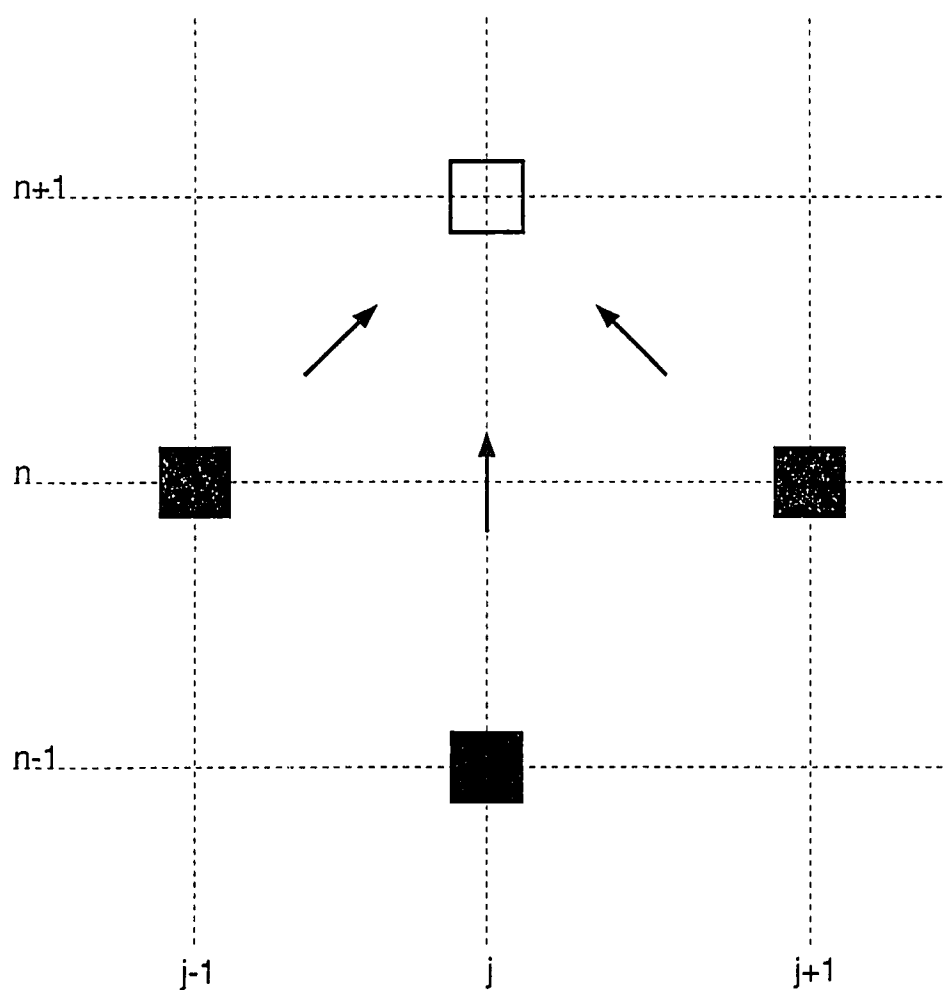


Figure VI.3.4 The computational molecule for the Du Fort-Frankel method.

n represents the time nodes and j the space nodes.

$$Q_{2,j}^{n+1} = 0. \quad (\text{VI.3.17})$$

The difference form of the boundary conditions at the interface is

$$-\frac{\kappa_1}{\Delta x}(\Theta_{d-1}^{n+1} - \Theta_{d-2}^{n+1}) = -\frac{\kappa_2}{\Delta x}(\Theta_{d+1}^{n+1} - \Theta_d^{n+1}) \quad (\text{VI.3.18})$$

$$-\frac{1}{\rho}(\Theta_{d-1}^{n+1} - \Theta_d^{n+1}) = -\frac{\kappa_2}{\Delta x}(\Theta_{d+1}^{n+1} - \Theta_d^{n+1}) \quad (\text{VI.3.19})$$

In Fig. VI.3.5 the finite difference scheme [8] [11] for the interface between Nb film and quartz substrate is shown. d is the node in the underlayer that is closest to the interface and $d-1$ is the node in the metal film that is closest to the interface. The nodes closest to the interface are effected by the nodes next to them as shown in Fig. VI.3.5. We proceed to derive the expressions for the temperature at the interface

$$\Theta_d^{n+1} = f_1(\Theta_{d+1}^{n+1}, \Theta_{d-2}^{n+1}) \quad (\text{VI.3.20})$$

$$\Theta_{d-1}^{n+1} = f_2(\Theta_{d+1}^{n+1}, \Theta_{d-2}^{n+1}) \quad (\text{VI.3.21})$$

from boundary conditions VI.3.18 VI.3.19. From VI.3.19 we have

$$\Theta_d^{n+1} = \frac{\Theta_{d-1}^{n+1} + \frac{\rho\kappa_2}{\Delta x}\Theta_{d+1}^{n+1}}{1 + \frac{\rho\kappa_2}{\Delta x}} \quad (\text{VI.3.22})$$

and from VI.3.18,

$$\Theta_{d-1}^{n+1} = -\frac{\kappa_2}{\kappa_1}(\Theta_{d+1}^{n+1} - \Theta_d^{n+1}) + \Theta_{d-2}^{n+1}. \quad (\text{VI.3.23})$$

Substituting Θ_d^{n+1} in Eq. VI.3.23 with Eq. VI.3.22 yields

$$\Theta_{d-1}^{n+1} = \frac{\kappa_2\Delta x}{(\kappa_2 + \kappa_1)\Delta x + \rho\kappa_1\kappa_2}\Theta_{d+1}^{n+1} + \frac{\kappa_1\Delta x + \rho\kappa_1\kappa_2}{(\kappa_2 + \kappa_1)\Delta x + \rho\kappa_1\kappa_2}\Theta_{d-2}^{n+1}. \quad (\text{VI.3.24})$$

Now, substituting Θ_{d-1}^{n+1} in Eq. VI.3.22 with Eq. VI.3.24 results in

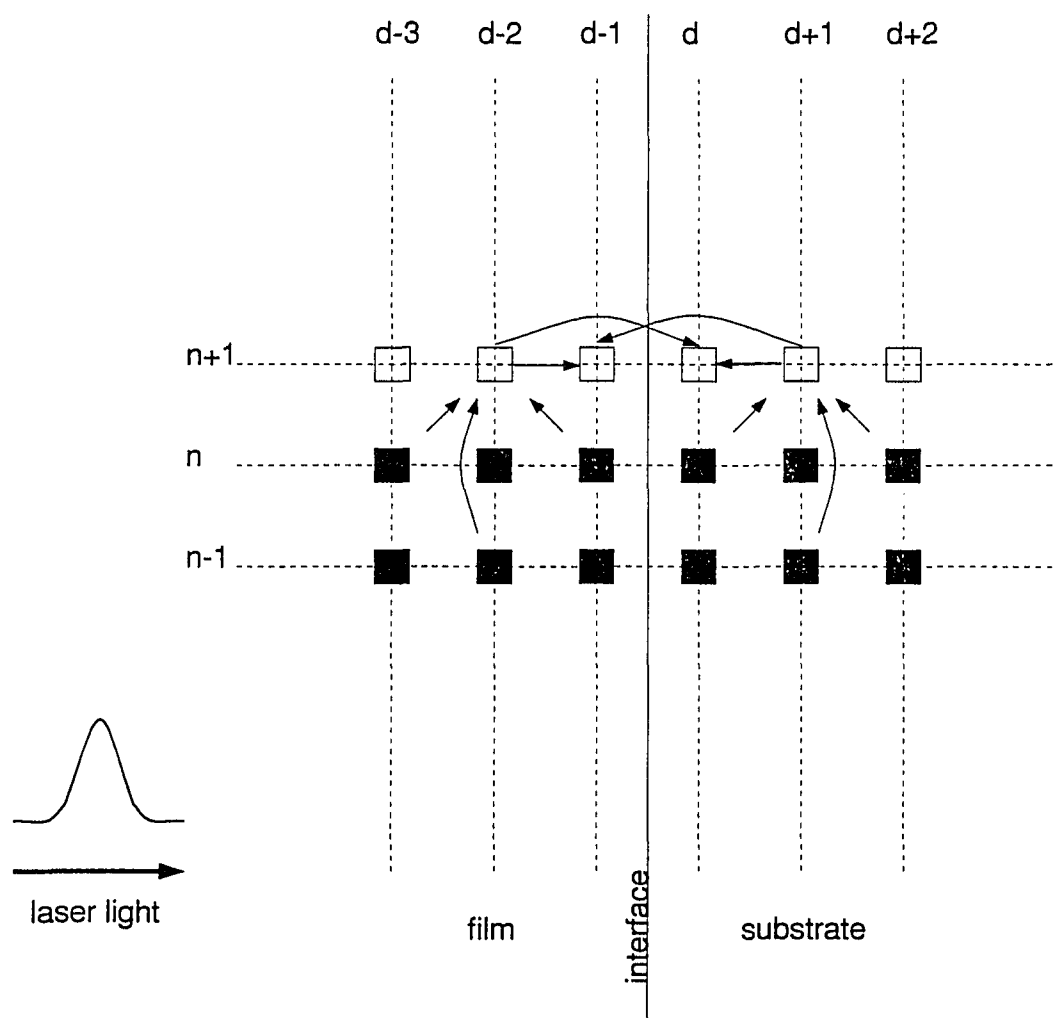


Figure VI.3.5 The mesh for the DuFort-Frankel method at the interface between two different materials. There are d spatial nodes in the film ($j=0,1,\dots,d-1$) and $J-d+1$ nodes in the substrate ($j=d, d+1, \dots, J$).

$$\Theta_d^{n+1} = \frac{\kappa_2 \Delta x + \rho \kappa_1 \kappa_2}{(\kappa_2 + \kappa_1) \Delta x + \rho \kappa_1 \kappa_2} \Theta_{d+1}^{n+1} + \frac{\kappa_1 \Delta x}{(\kappa_2 + \kappa_1) \Delta x + \rho \kappa_1 \kappa_2} \Theta_{d-2}^{n+1}. \quad (\text{VI.3.25})$$

Equations VI.3.14, VI.3.24 and VI.3.25 were used to determine the temperature distribution in the Nb film and quartz substrate in 1D space (normal to the film surface) and time. A variable mesh was used to be able to reduce the number of nodes needed in the area where the thermal gradient was no longer changing rapidly. The total number of nodes used in the calculations was 3,000,000. The temporal profile of the film temperature, averaged over the film thickness was fitted to the transmissivity data by adjusting the interfacial impedance ρ . A scaling factor was used to match the calculated temperature to the obtained data.

Results

The results of the numerical modeling are shown in Fig. VI.3.6, Fig. VI.3.7 and Fig. VI.3.8. The 3D plot in VI.3.6 shows the dynamics of the heat diffusion process when the ambient (initial) temperature is $\Theta_0=100$ K. The temperature, Θ , is shown at different time, t , and depth, x . The zero of the x -axis is at the front surface of the niobium film and the zero of the time axis is when the heating pulse strikes the surface. At first, as the laser pulse is absorbed by the film, the temperature at the front of the film increases more than at the back, because exponential absorption of the heating pulse is assumed. The temperature difference across the film thickness equalizes within ~ 1 ps since the metal conductivity is high. Then, the film temperature resumes an almost linear temperature decay due to cooling into the substrate governed by $D_{\text{Nb}}(\Theta)$ and $D_{\text{quartz}}(\Theta)$.

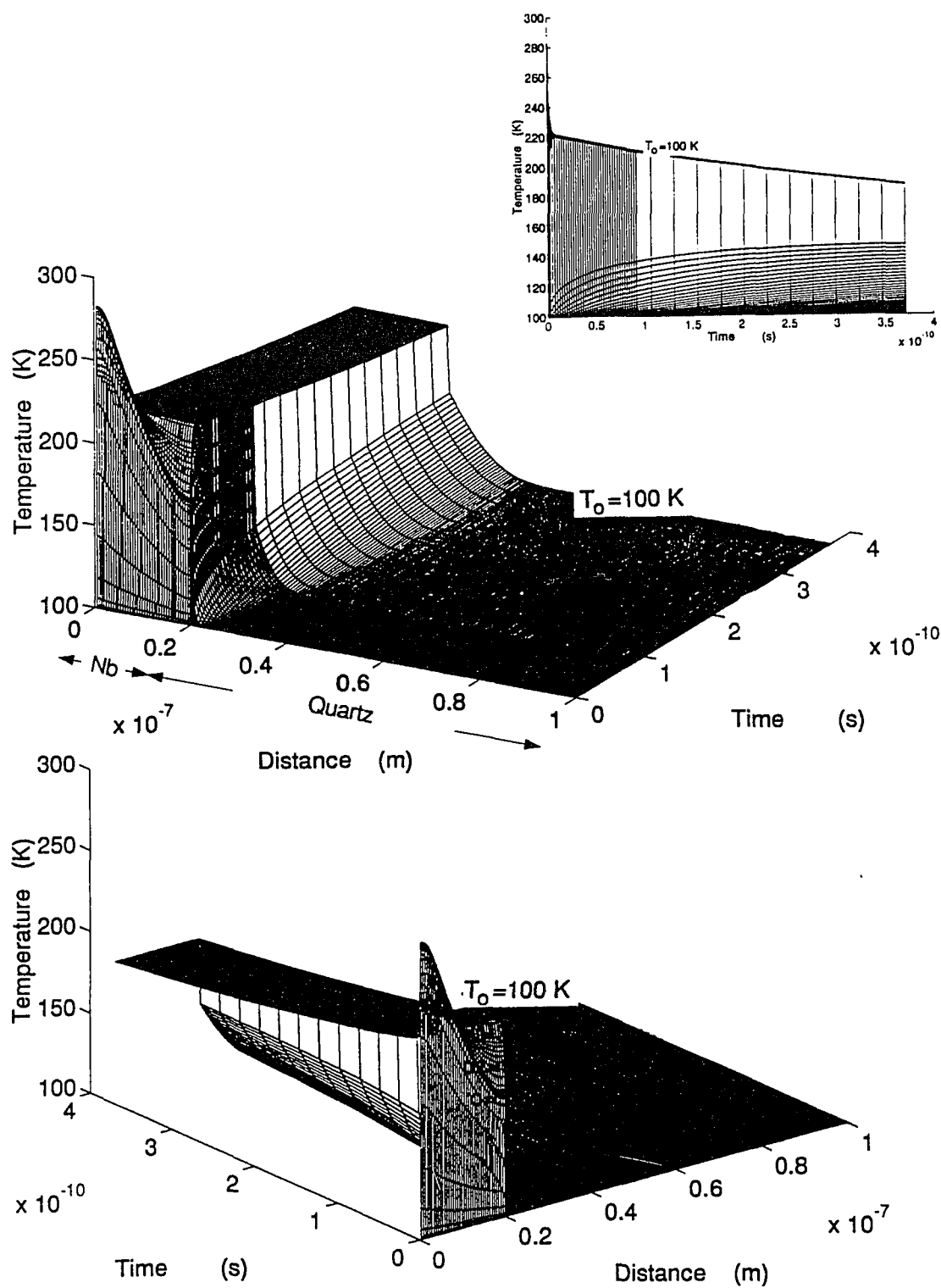


Figure VI.4.6 The 3D plot shows the dynamics of the heat diffusion process.

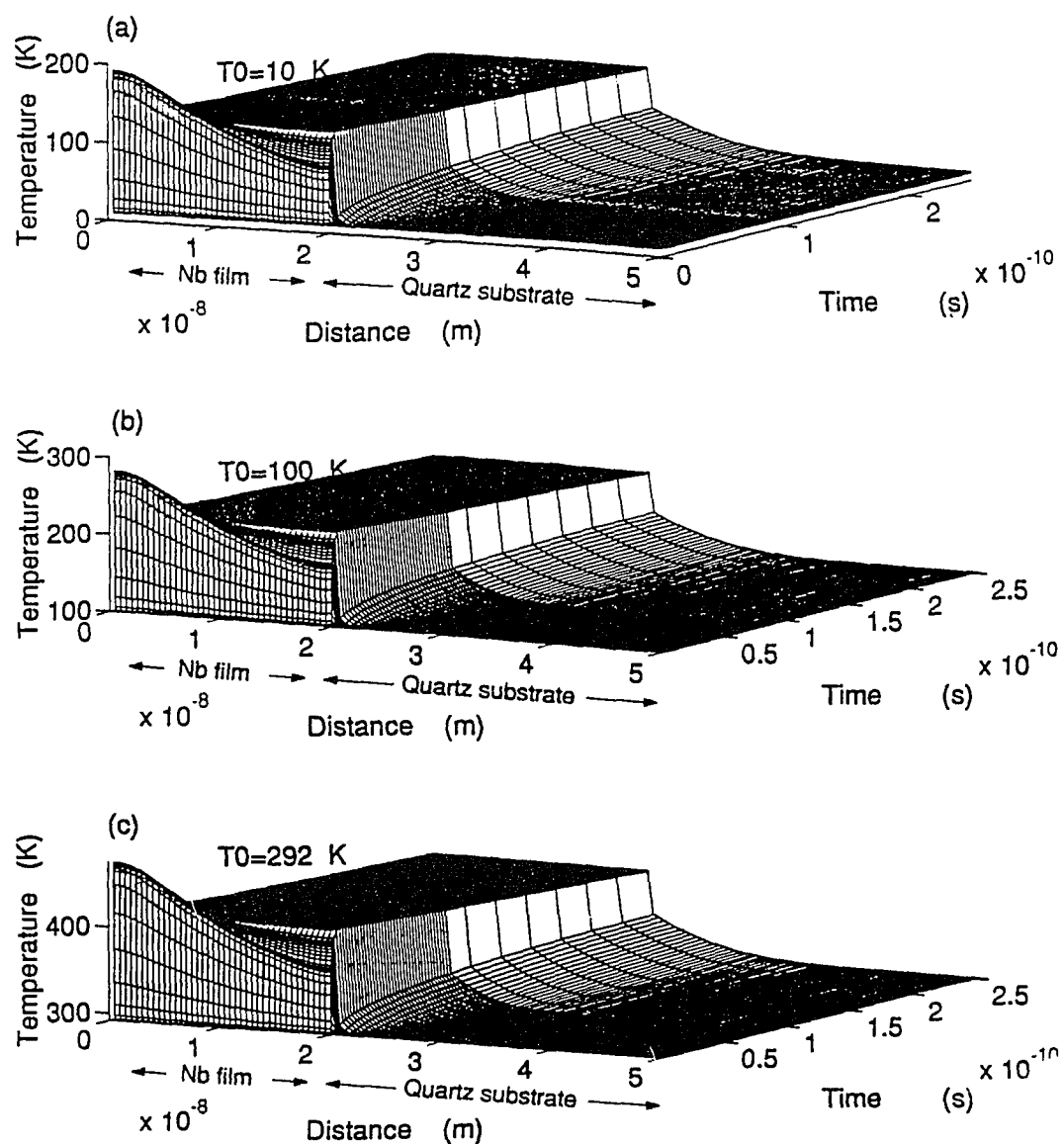


Figure VI.4.7 The results of the numerical modeling for normal metal state are shown for three sample (initial) temperatures (a) $\Theta_0 = 10$ K, (b) $\Theta_0 = 100$ K, and (c) $\Theta_0 = 292$ K. The calculated temperature decrease, $\Delta\Theta$, in time is the same for all initial temperatures during the first 250 ps.

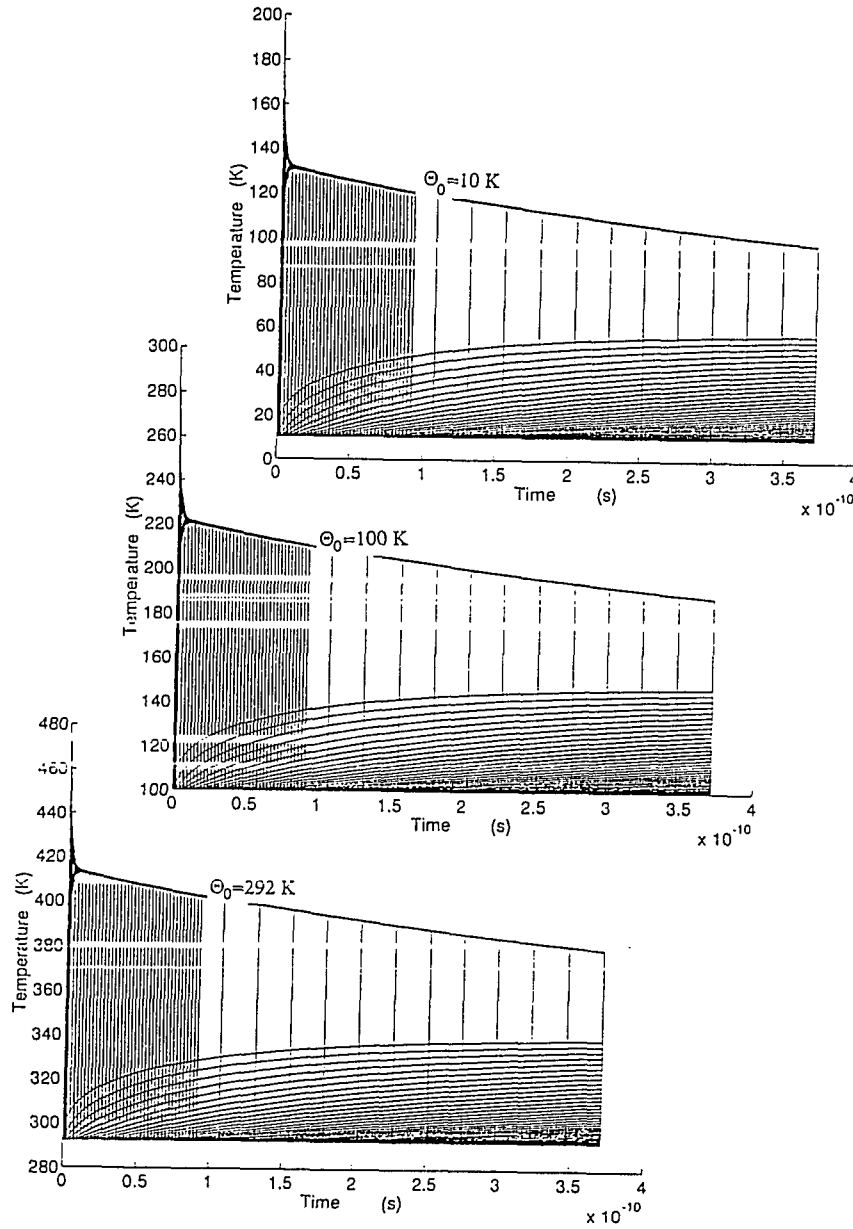


Figure VI.3.8 The results of the numerical modeling (as seen from the front) for normal metal state are shown for three sample (initial) temperatures (a) $\Theta_0=10$ K, (b) $\Theta_0=100$ K, and (c) $\Theta_0=292$ K. The calculated temperature decrease, $\Delta\Theta$, in time is the same for all initial temperatures during the first 250 ps.

In Fig. VI.3.7 the temperature, Θ , is plotted as it changes in time, t , and depth, x , when the niobium film is in normal metal state. Results are shown for three sample (initial) temperatures (a) $\Theta_0=10$ K, (b) $\Theta_0=100$ K, and (c) $\Theta_0=292$ K. As shown in Fig. VI.3.7, the calculated temperature change, $\Delta\Theta$, during the first 250 ps is the same for all initial temperatures. This agrees with the measured thermotransmittance decay time, which remains the same during the 250-ps duration of our measurements, for $\Theta_0=10$ –292 K.

In Fig. VI.4.1 the experimentally obtained normalized transmissivity change (same for all $\Theta_0>\Theta_c$) in the normal metal state is presented together with the best fit of the normalized film temperature increase (also same for all $\Theta_0>\Theta_c$) obtained from the heat-flow model. The film temperature is taken as the average temperature across the film since the thermotransmittance measurements probe the whole depth of the 20 nm film.

VI.4. Discussion

The temperature decay time depends on the cooling through the Nb-quartz interface, which depends on the diffusivity $D=k/c_p$, which (as shown in Fig. VI.3.3) may be considered constant (independent of temperature) for temperatures >30 K [13]. As shown by the numerical results, the sample temperature is always >100 K during the first 250 ps of the temperature decay time for all measurements in the normal metal state [12] [13]. Therefore, the diffusivity at the interface (which in turn results in temperature decrease $\Delta\Theta$) is the same for the 250 ps of the duration of our experiment, for all measurements in the normal metal state. This is consistent with

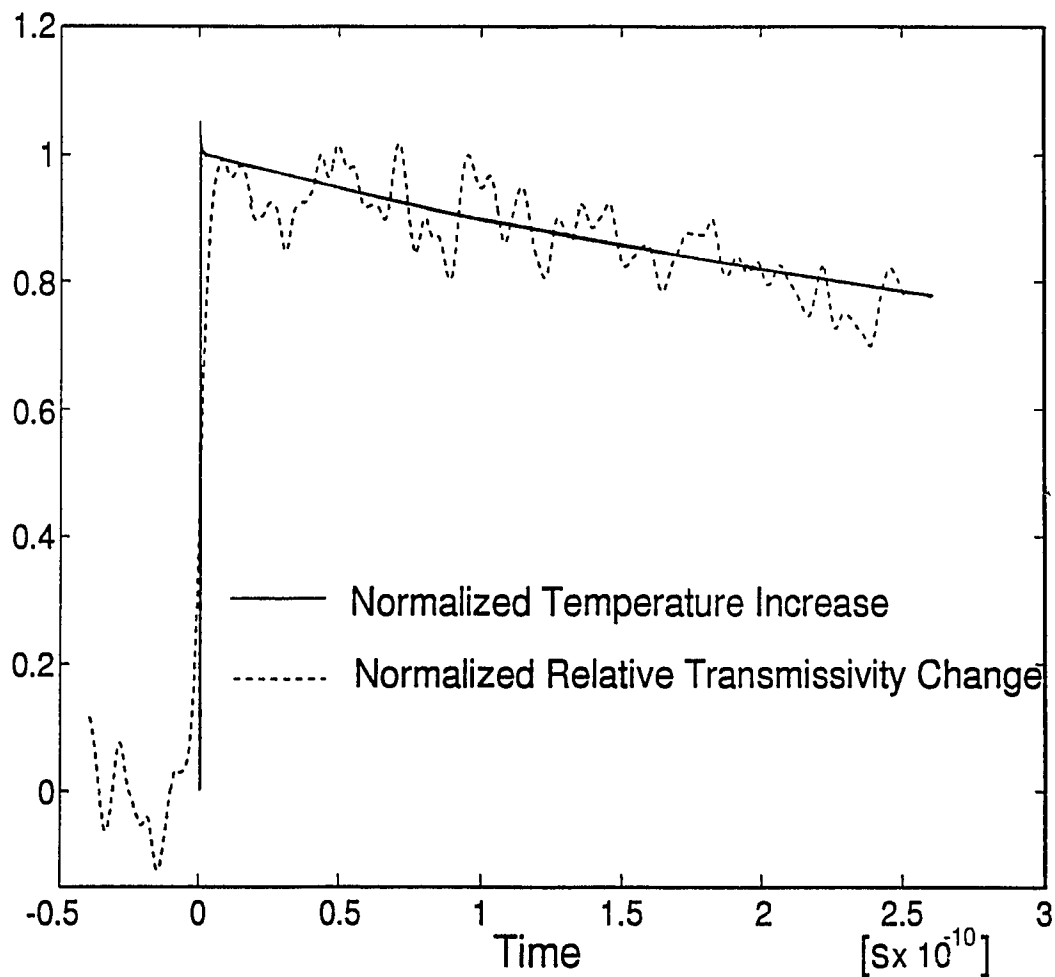


Figure VI.4.1 The experimentally obtained normalized transmissivity change in the normal metal state (dashed line) is presented together with the best fit of the normalized film temperature increase (solid line) obtained from the heat-flow model. The film temperature is taken as the average temperature across the film since the thermotransmittance measurements probe the whole depth of the 20 nm film. The best fit was obtained for $\rho=3 \times 10^{-9} \text{ m}^2 \text{ K/W}$.

our experimental observation that the measured change of $\Delta T/T$ in time, which is proportional to the temperature decay time, remains the same for all measurements in the normal metal state, i.e. for ambient temperature in the range from 10 K to 292 K.

In the above section it has been both experimentally and theoretically demonstrated that the decay of the transient signal is similar for the range of sample (initial) temperatures, from $\Theta_0=10$ K to 292 K. It would be reasonable to expect that it does not change if Θ_0 were decreased down to 4.5 K unless another physical process takes place. However, there is another process taking place when the sample (initial) temperature is decreased from 10 K to 292 K, since the critical superconducting temperature for niobium is 8.8 K.

For sample (initial) temperatures $\Theta_0 < \Theta_c$ (below critical superconducting temperature) it is questionable whether in the time scale of our experimental results (0–250 ps) the photoexcited metal is still in superconducting state, in normal state or in complex state. If the metal is in normal state, than it is possible to proceed with the calculations the same way as for $\Theta_0 > \Theta_c$. Calculations under this assumptions for $\Theta_0=4.5$ K give the same change of temperature in time as for $\Theta_0=10$ K. In this case, contrary to our experimental results, no change would be expected in the transient thermotransmittance decay time as the ambient temperature is lowered, since the conditions are the same as for $\Theta_0 > \Theta_c$, i.e. implies Nb film temperatures >100 K during the first 250 ps which in turn means same diffusivity. On the other hand, if one takes into account that Cooper pair breaking time is well into the ps time scale [14], and that the excited electrons take longer time to transfer their energy to the phonons than in the normal state [1], then the metal is still in superconducting state or in a complex spatially-inhomogeneous state characterized by the simultaneous coexistence of the normal and superconducting phase [1].

When measuring the transient thermotransmittance signal below Θ_c , we have observed that a shorter decay time of $|\Delta T/T|$ is obtained as the sample (initial) temperature is decreased from $\Theta_0=10$ K to $\Theta_0=4.5$, i.e. below critical superconducting temperature ($\Theta_c=8.8$ K). It is well known that the steady state optical properties of a metal in the visible and near infrared are unaffected by the transition to the superconducting state [15]. Since a shorter decay time of the transient thermotransmittance is observed below Θ_c , there is a good reason to believe that the thermotransmittance that is associated with the film lattice temperature [10] and the heat diffusion out of the sample [8] reflects the lower effective lattice temperature for ambient temperatures below Θ_c in the 250 ps after the pump pulse arrival. The transition from superconducting to normal state is a dynamic process requiring at least 10 – 100 ps and the faster decay of the transient thermotransmittance signal below Θ_c may be a result of nonequilibrium superconductivity. The so called “delayed” response of the superconductor to short pulses observed by Tesardi [16] and others [17] supports this argument. According to Tesardi, below Θ_c there is a bottleneck in the conversion of optical energy, absorbed by the electrons, to phonons ultimately sent to the heat sink, i.e. the electron-phonon relaxation time is much longer in the superconducting than in normal state. The simple heat diffusion model does not apply and the thermotransmittance signal is proportional to some effective sample temperature. In fact, as will be discussed below, there is no unique sample temperature for ambient temperature $\Theta_0 < \Theta_c$ in the 0–250 ps time range.

When a superconducting niobium film is illuminated by light pulses, the interaction between pairs, quasiparticles, and phonons is governed by the Rothwarf-Taylor coupled equations [18]. These equations are nonlinear and the time dependent problem is not analytically solvable unless quasiequilibrium conditions are satisfied so that the

sample remains in the superconducting state. In case of quasi equilibrium conditions the particles achieve a distribution close to thermal equilibrium in ~ 50 ps [19]. Because of quasi equilibrium conditions in his experiment with niobium film, Johnson [19] was able to obtain a model by linearizing the Rothwarf-Taylor equations in the weak perturbation limit (for low laser fluence). Using for the Cooper pair breaking time, $\tau_B \sim 8$ ps (calculated by Kaplan [19]), and for the time it takes a phonon to become unavailable for pair breaking, $\tau_\gamma \sim 55$ ps, Johnson was able to fit the experimentally obtained quasiparticle recombination time $\tau_{\text{eff}} \sim 430$ ps into the model. Other authors have argued that the Cooper pair breaking time, τ_B , is relatively large compared to τ_γ when phonons are generated at a greater rate [18]. As shown in Johnson's work, the magnitudes of τ_B and τ_γ are well in the ps region, so that for $\Theta_0 < \Theta_c$ the transmissivity change on the 250 ps time scale is affected by the nonequilibrium processes taking place in the transition from normal to superconducting state. In order to explain the faster transmissivity decay for $\Theta_0 < \Theta_c$ one needs to investigate the process that takes place when laser heating is applied to sample at $\Theta_0 < \Theta_c$.

Physically the following process takes place [19] : The absorbed photons excite electrons to energies ~ 2 eV after breaking Cooper pairs. The photoexcited electrons produce a number of high-energy quasiparticles with energy $\sim$ Debye energy and higher energy phonons. The high energy phonons themselves also proceed to break Cooper pairs and produce quasiparticles while at the same time transferring some of their energy to lower energy phonons. In their recent work, Johnson et al. [20] have shown that the modified heating theory approach is consistent with their experimental results for nonequilibrium conditions for Nb film illuminated by higher laser fluence. In this case, when higher fluence of optical radiation are used, the nonequilibrium phonon distribution is described by a temperature T^* [21]. In this "modified heating

theory” it is postulated that the optical radiation increases the number of phonons with energy $>2E_g$ and leaves the other phonons unchanged. The phonons of energy $<E_g$ are assumed to remain characterized by the ambient temperature.

All of the above is a strong indication that for $\Theta_0 < \Theta_c$ in the 250 ps time scale, the thermotransmittance signal obtained is associated with an effective temperature of the sample, which is a combination of T^* phonons and the phonons at low temperatures. The diffusion coefficient at low temperatures (<10 K) is ~ 10 times higher than the diffusion coefficient at $\Theta > 100$ K, which are the temperatures achieved for metal in normal state. The phonons at low temperature will effect the heat diffusion in such a way as to increase the resulting diffusivity. As a consequence, there will be a higher effective heat diffusion out of the probed area of the sample which will result in faster cooling. This faster decrease in metal temperature causes faster thermotransmittance decay since the change in the thermotransmittance is proportional to the temperature change. The dynamic nature of the process implies that this simple two fluid model can not be considered stationary for the duration of the heat diffusion process. Rather, it should be taken as a representation of a nonequilibrium process, where there are two groups of phonons, low and high energy phonons, that may not come to equilibrium before they diffuse out of the thin film. This picture is even more complicated since there is a nonstationary dynamic intermediate state present [22] [17] [1], where normal and superconducting areas coexist in the optically excited region, with normal metal areas increasing with time.

VI.5. Conclusion

Thermotransmittance measurements for ambient temperatures from room temperatures to below superconducting temperature have been performed for niobium film using 100 fs laser pulses in a pump-probe configuration. The thermotransmittance signal has been related to the temperature change in the niobium film caused by cooling due to heat diffusion. As shown by the mathematical model, the temperature difference across the film thickness equalizes within ~ 1 ps since the metal heat conductivity is high and the film is thin (thickness=20nm). After that, the film temperature decay is governed by the cooling through the film-substrate interface.

For sample (initial) temperatures above superconducting temperature ($\Theta_0 > \Theta_c$), the calculated temperature decay, $\Delta\Theta/\Delta t$, during the first 250 ps is the same for all initial temperatures. This is because the diffusivity is constant for temperatures > 100 K, and for all $\Theta_0 > \Theta_c$, the niobium film is heated and stays above 100 K in the first 250 ps of the diffusion process. The numerical results agree with the measured thermotransmittance decay time, $\tau_{\Delta T} = 950 \pm 70$ ps for $\Theta_0 > \Theta_c$, which remains the same during the 250-ps duration of our measurements, for $\Theta_0 = 10$ –292 K.

Although steady state optical properties in the visible spectral region remain the same when the temperature is decreased below superconducting temperature ($\Theta_0 < \Theta_c$), a change in the transient thermotransmittance decay in the visible during the first 250 ps has been detected in Nb in the transition from normal to superconducting phase. When niobium in superconducting state is illuminated by a 2eV, 100 fs laser pulse, it exhibits a faster decay of the transmissivity change ($\tau_{\Delta T} = 570 \pm 70$ ps for $\Theta_0 = 4.5$

$K < \Theta_c$), then when in the normal metal state. The measured faster decay of the thermotransmittance change, when illuminating a superconducting film at temperatures below superconducting temperature ($\Theta_0 < \Theta_c$), was related to increased diffusivity due to nonequilibrium processes in Nb in the transition from superconducting to normal state. A precise theory needs to be developed to explain in more detail the nonequilibrium superconducting processes taking place.

Bibliography

- [1] K. V. Mitsen, *Nonequilibrium Superconductivity*. Nova Science Publisher, 1986.
- [2] A. I. Golovashkin, K. V. Mitsen, and G. P. Motulevich in *The 18th All Union Conference in Low Temperature Physics* (Kiev, ed.), 1974.
- [3] A. I. Golovashkin, K. V. Mitsen, and G. P. Motulevich *ZhETF* **68**, p. 1408, 1975.
- [4] F. Elesin and Y. V. Kopaev *Sov. Phys. Usp.* **24**, p. 116, 1981.
- [5] F. Elesin *Sov. Phys. JETP* **46**, p. 185, 1977.
- [6] R. Janik, L. Morelli, and N. C. Cirillo *IEEE Trans. Magn.* **11**, p. 687, 1975.
- [7] G. L. Eesley *Phys. Rev. B.* **33**, p. 2144, 1986.
- [8] B. M. Clemens, G. L. Eesley, and C. A. Paddock *Phys. Rev. B* **37**, p. 1085, 1988.
- [9] C. A. Paddock and G. L. Eesley *J. Appl. Phys.* **60**, p. 285, 1986.
- [10] K. M. Yoo, X. M. Zhao, M. Siddique, R. R. Alfano, D. P. Osterman, M. Radparvan, and J. Cunniff *Appl. Phys. Lett.* **56**, p. 1908, 1990.
- [11] J. H. Ferziger, *Numerical Methods For Engineering Applications*. John Wiley & Sons, New York, 1981.
- [12] R. C. Weast and D. R. Lide, *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida, 1989.
- [13] Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Matter*. IFI/Plenum, New York, 1970.
- [14] S. B. Kaplan *Phys. Rev. B* **14**, p. 4854, 1976.
- [15] M. Tinkham and J. Clarke *Phys. Rev. Lett.* **28**, p. 1366, 1972.
- [16] L. R. Tesardi *Phys. Rev. B* **4**, p. 2159, 1971.

- [17]G. A. Sai-Halasz, C. C. Chi, A. Denestein, and D. Langenberg *Phys. Rev. Lett.* **33**, p. 215, 1974.
- [18]A. Rothwarf and B. N. Taylor *Phys. Rev. Lett.* **19**, p. 27, 1967.
- [19]M. Johnson *Phys. Rev. Lett.* **67**, p. 375, 1991.
- [20]M. Johnson *IEEE Trans. Magn.*, **27**, p. 1523, 1991.
- [21]W. H. Parker *Phys. Rev. B* **12**, p. 3667, 1975.
- [22]T. Gong, L. X. Zheng, X. Xiong, W. Kula, Y. Kostoulas, R. Sobolewski, and P. M. Fauchet *Phys. Rev. B* **47**, p. 14495, 1993.

VII Scattering Through Metallic Particles in Dense Dielectric Media

VII.1. Introduction

Recently, the problem of an electromagnetic wave scattering in random media has become an active field. When optical pulse is sent through random media it is considerably deteriorated due to scattering. The ballistic component of the propagating signal travels in a straight line path and carries the information, while the diffuse component, which develops due to scattering is noise. In a highly scattering medium the diffuse component is much stronger than the ballistic component and information can not be transmitted successfully. The “Signal noise” due to diffusion is the decreased visibility through atmosphere when clouds are present. To improve the ability to see through a highly scattering random wall one needs to study the cause of the decreased visibility, namely the diffuse component of a propagating light pulse.

In this chapter, the effect of metallic Nb spheres on propagation of pulse transmitted through dense media with randomly distributed dielectric is investigated. The experimental geometry is that of a plane wave incident on a slab of random media of thickness much greater than the transport mean free path. The temporal profile of the transmitted laser pulse is modeled with an existing analytic solution [1] of the diffusion equation and the phase correlation effect among scattered waves is included.

VII.2. Theoretical Background

Light propagating through disordered scattering medium is scattered randomly in all directions due to the spatial and time variation of the dielectric constant of the medium [2] [3]. The key parameters that describe light scattering in random medium are [3]: the scattering mean free path, l_s , the transport mean free path, l_t , and the absorption length, l_a . The scattering mean free path $l_s = \frac{1}{n\sigma_s}$, represents the mean distance between two scattering events. where σ_s is the scattering cross section of one particle and n is the number density of the scatterers. The cross section, σ_s is defined as

$$\sigma_s = \int \sigma(\theta, \phi) \sin\theta d\theta d\phi, \quad (\text{VII.2.1})$$

where $\sigma(\theta, \phi)$ is the differential cross section and represents the probability of light being scattered in the direction (θ, ϕ) . If the diameter, $d \ll \lambda$ (λ is the wavelength of light) the light is scattered almost uniformly in all directions (isotropic scattering). If $d \gg \lambda$ light is scattered mostly in the forward direction within an angle $1.2\lambda/d$ (anisotropic scattering). For particles of intermediate size, the scattering cross section fluctuates with θ and d .

The quantitative measure of light scattered away from the forward direction is given by the momentum transfer scattering cross section, σ_m

$$\sigma_m = \int \sigma(\theta, \phi) (1 - \cos\theta) \sin\theta d\theta d\phi. \quad (\text{VII.2.2})$$

Usually the mean cosine average of the scattering, called the anisotropic scattering parameter g can be calculated and the momentum transfer scattering cross section is

defined as $\sigma_m = (1 - g)\sigma_s$. This expression needs to be modified when absorption is present into $\sigma_m = (1 - wg)\sigma_s$, where w is the whiteness or albedo when diffraction is omitted. For big metal spheres ($d \gg \lambda$) $\sigma_m = (1 - wg)\pi \frac{d^2}{4}$ and $\sigma_{abs} = (1 - w)\pi \frac{d^2}{4}$. The mean distance of the random walk step of the multiply scattered phonon is called the transport mean free path, l_t , and is defined as $l_t = \frac{1}{n\sigma_m}$. $l_t > l_s$ when light is scattered anisotropically, i.e. for particles with $d \gg \lambda$. For particles of spherical shape $\sigma(\theta, \phi)$ can be obtained theoretically if the index of refraction, m , and the diameter, d of the particle are known using Mie theory [4].

Mie's theory holds under the classical assumption of independent scattering but breaks down if the number of scatterers per cubic wavelength, $n\lambda^3 > 1$. With increasing n , the spatial correlation among scatterers leads to phase correlation among scattered waves and weakens the effective cross section for scattering below that of an individual scatterer [5]. This effect becomes more pronounced with increasing d . Thus, in dense random media, due to correlation effects, the transport mean free path becomes much longer than expected from classical theory.

After an ultrashort laser pulse is transmitted through a slab of random medium it splits into two components; the coherent (ballistic) and the incoherent (diffuse). The ballistic components is attenuated by a factor $e^{-(w/l_a + w/l_s)}$, where w is the slab thickness and l_a is the mean distance that the light travels before being absorbed due to inelastic scattering in the medium. The ballistic component comes out first, while the diffuse component consists of multiple scattered phonons and is temporary broadened. When the medium is sufficiently strong in scattering, the diffuse component can be described using the diffusion theory [6]. If the slab thickness is many transport mean free path thick, i.e. $w/l_t \gg 1$, the medium is in the diffusion region.

Light scattering in random media can be described by the transport theory. In

case of a highly scattering medium the transport theory can be approximated by the diffusion theory [6]. The temporal profile of the scattered ultrashort laser pulse in a random medium is determined by the absorption length, l_a , the transport mean free path of the medium, l_t , the boundary conditions, and the distance between the source and the detector.

The analytic solution for the temporal profile of the photon density $n(\mathbf{r}, t)$, is obtained from the solution of the diffusion equation as follows [1] [6] [3]

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D \nabla^2 n(\mathbf{r}, t) - \frac{v}{l_a} n(\mathbf{r}, t) + \delta(\mathbf{r})\delta(t), \quad (\text{VII.2.3})$$

where $\mathbf{r}$ is the distance from the source, $D = vl_t/3$ is the diffusion constant (v is the speed of light in the scattering medium), and the δ -function term is the impulse photon source at time $t=0$. The first term on the right side of the above equation represents the diffusion and the second term the absorption. For an infinite slab of random media of thickness w , the temporal profile of the photon density at point (x, y, z) , when the impulse source is located at $(x'=0, y'=0, z')$ is obtained from the diffusion equation [7] [1] by the method of images and is given by:

$$n(\mathbf{r}, t) = \frac{e^{-R^2/4Dt}}{(4\pi Dt)^{3/2}} \sum_{m=-\infty}^{\infty} \left\{ e^{-(2md+z'-z)^2/4Dt} - e^{-(2md-z'-z)^2/4Dt} \right\} e^{-vt/l_a}, \quad (\text{VII.2.4})$$

where $z=z_0$ ($z_0=0.71l_t$, is the extrapolation length) is the location of the front surface of the slab, and $z=w+z_0$ is the location of the back surface of the slab. The boundary conditions are that the photon density vanishes at $z=0$ and $z=w+2z_0$. $R^2 = x^2 + y^2$ and $d=w+2z_0$. For $w=\infty$ the solution of Eq. VII.2.4 is

$$n(\mathbf{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-[R^2+(z-z')^2]/4Dt} e^{-vt/l_a}. \quad (\text{VII.2.5})$$

By using the Poisson sum formula, one may write Eq. VII.2.4 as the sum over the reciprocal space [8];

$$n(\mathbf{r}, t) = \frac{e^{-R^2/4Dt}}{(4\pi Dt)d} \sum_{m=-\infty}^{\infty} \left\{ \sin \frac{\pi m z'}{d} \sin \frac{\pi m z}{d} e^{-Dt(m\pi/d)^2} \right\} e^{-vt/l_a}. \quad (\text{VII.2.6})$$

For transmission through a slab, $z'=z_0$ and $z=w+z_0$, and Eq. VII.2.6 becomes

$$n_z(t) = \frac{e^{-R^2/4Dt}}{(4\pi Dt)d} \sum_{m=1}^{\infty} \left\{ (-1)^m \left(1 - \cos \frac{\pi m z_0}{d} \right) e^{-Dt(m\pi/d)^2} \right\} e^{-vt/l_a}. \quad (\text{VII.2.7})$$

The photon flux is related to the photon density by

$$\mathbf{j}(\mathbf{r}, t) \hat{s} = -D \hat{s} \nabla n(\mathbf{r}, t) \quad (\text{VII.2.8})$$

and the expression for the photon flux becomes [1]

$$j_z(t) = \frac{De^{-R^2/4Dt}}{\pi w^2(4\pi Dt)} \sum_{m=1}^{\infty} \left\{ \left(m \left(\frac{\pi w}{d} \right)^2 \sin \frac{\pi m w}{d} \right) e^{-Dt(m\pi/d)^2} \right\} e^{-vt/l_a}. \quad (\text{VII.2.9})$$

For a plane wave normally incident onto a slab (In our experiment we have a large beam diameter) the temporal profile of the pulse exiting at a point on the opposite side of the slab may be obtained from Eq. VII.2.9. It has been shown [9] that by integrating Eq. VII.2.9 over the whole surface of the slab one can get the expression for the measured scattered pulse profile in the diffusion region. This expression is

$$I_z(t) = \frac{D}{\pi w^2} \sum_{m=1}^{\infty} \left\{ \left(m \left(\frac{\pi w}{d} \right)^2 \sin \frac{\pi m w}{d} \right) e^{-Dt(m\pi/d)^2} \right\} e^{-vt/l_a}. \quad (\text{VII.2.10})$$

VII.3. Experimental Method

A schematic diagram of the experimental set-up utilizing the time-resolved detection technique used in this work to measure the time profile of the scattered pulse, is shown in Fig. VII.3.1. An ultrafast laser pulses of 8 ps in duration, average laser power of 100 $\mu\text{J}/\text{pulse}$, laser wavelength centered at 528 nm, were generated by a passively mode-locked Nd:Glass laser with one stage amplifier. Part of the laser beam was split to trigger the measurement instruments. The main part of the laser beam was expanded by two lenses to a beam diameter of 5 mm, and was incident on a 1mm slab or random medium. The random medium consists of a powder made of TiO_2 dielectric particles with $d=0.220 \mu\text{m}$ mixed with niobium particles with $d=11 \mu\text{m}$ as shown in Fig. VII.3.2. The temporal distribution of the photons emerging from the slab in the forward direction was time resolved by a streak camera. The horizontal input slit of the streak camera was placed at the focal plane of the collecting lens. The typical time response of this detecting system is about 10 ps.

The measured temporal profile can be approximated by Eq. VII.2.10 that models the plane wave incidence. The temporal profile of a medium made only of TiO_2 particles was measured first. From this measurements l_t was obtained by fitting the results to the curve represented by VII.2.10. Since this is a dense random medium ($\sim 4.2 \text{ particles}/\lambda^3$), a 1-mm thick glass cell was simply filled with TiO_2 powder, l_t was expected to be much longer due to correlation effects. However, the correlation effect in Nb particles was not present ($\text{number of particles}/\lambda^3 \ll 1$), and $l_{t,\text{Nb}}$ could be calculated classically.

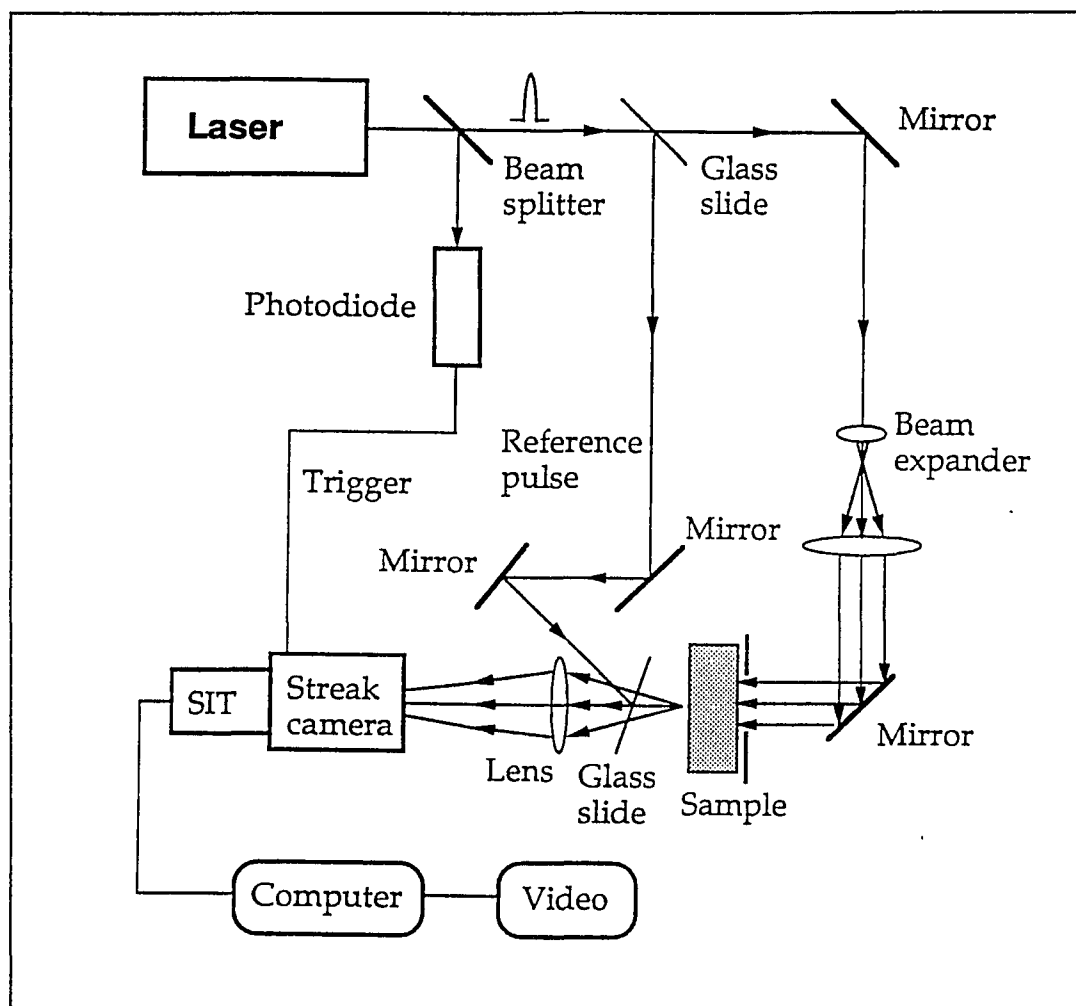


Figure VII.3.1 Schematic diagram of the experimental arrangement.

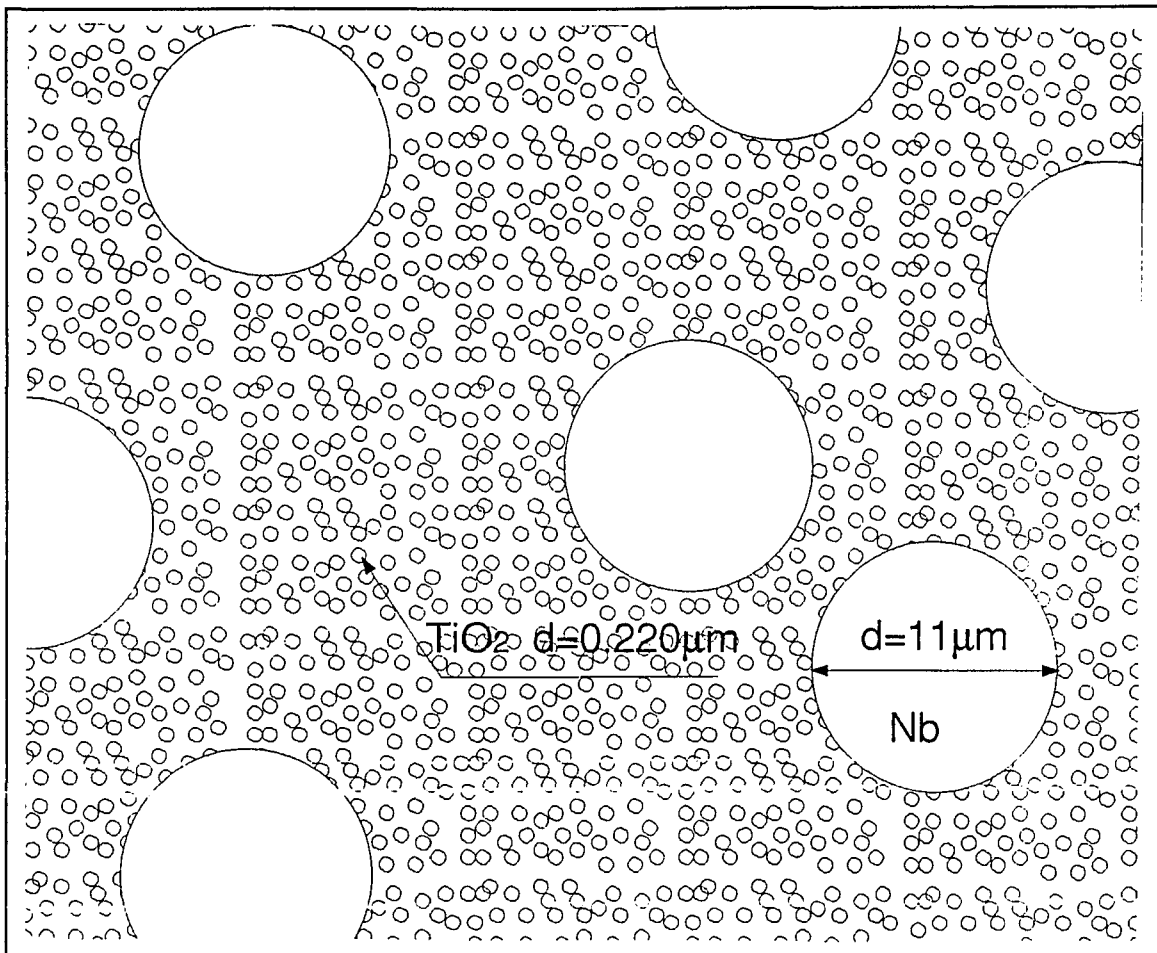


Figure VII.3.2 The sample is powder made of TiO_2 dielectric particles with $d=0.220 \mu\text{m}$ mixed with niobium particles with $d=11 \mu\text{m}$.

VII.4. Results

Measurements of the temporal profiles of the scattered transmitted pulse were performed for a mixture of TiO₂ and Nb particles, with the percentage of Nb particles varying from 0% to 66% by weight. The corresponding number density of TiO₂ and Nb particles is presented in Fig. VII.4.1. As Nb particles were added into TiO₂ powder, the number density of the TiO₂ changed from $4.26 \times 10^{13} \text{ cm}^{-3}$ to $3.50 \times 10^{13} \text{ cm}^{-3}$, while the number density of the Nb particles ranged from 0 – $2.64 \times 10^8 \text{ cm}^{-3}$. The packing density of pure TiO₂ powder and pure Nb powder was measured to be 4.2 and 6.5, respectively.

The measured temporal profiles of the scattered transmitted pulse and the corresponding curve fits (using Eq. VII.2.10) are presented in Figures VII.4.2–VII.4.8. In Fig. VII.4.2 the measured temporal profile of the pulse scattered through pure TiO₂ is presented. The corresponding curve fit was obtained when the expression VII.2.10 for the measured scattered pulse profile in the diffusion region,

$$I_z(t) = \frac{D}{\pi w^2} \sum_{m=1}^{\infty} \left\{ \left(m \left(\frac{\pi w}{d} \right)^2 \sin \frac{\pi m w}{d} \right) e^{-Dt(m\pi/d)^2} \right\} e^{-vt/l_a}. \quad (\text{VII.4.1})$$

was fitted to the measured data. The fitting was subject to two parameters, l_a and l_t . l_t is hidden in the diffusion constant $D = vl_t/3$. Since TiO₂ is a nonabsorbing medium, l_a was taken to be infinitely big so that l_t was the only fitting parameter in case of pure TiO₂. The best fit was achieved for $l_{t,\text{TiO}_2} = 26 \mu$. This approach to determining l_{t,TiO_2} was taken because TiO₂ powder is a dense medium (no. of particles/ $\lambda^3 \approx 4$) and the transport mean free path becomes much longer than expected from classical theory due to phase correlation among scattered waves [5].

When Nb particles are added the scattering medium becomes anisotropic. Although M. Lax [1] did not explicitly consider the anisotropy problem in the derivation of expression VII.2.10, the results remain valid as long as diffusion is valid. The anisotropy is buried in the calculation of the diffusion constant D ($D = vl_t/3$), and involves a weighted average over the scattering at all averages [10]. The change shows up in relating the transport mean free path, l_t to the effective mean free path, $l_{t,eff}$. The effective transport mean free path of the TiO_2 -Nb mixture, $l_{t,eff}D = vl_t/3$. is

$$l_{t,eff} = \frac{1}{n_{eff}\sigma_{m,eff}}, \quad (VII.4.2)$$

where

$$n_{eff}\sigma_{m,eff} = n_{Nb}\sigma_{m,Nb} + n_{TiO_2}\sigma_{m,TiO_2}. \quad (VII.4.3)$$

The $n_{TiO_2}\sigma_{m,TiO_2}$ was obtained from

$$n_{TiO_2}\sigma_{m,TiO_2} = \frac{1}{l_{t,TiO_2}}, \quad (VII.4.4)$$

where l_{t,TiO_2} was determined experimentally as explained in the previous paragraph. Therefore, substituting Eq. VII.4.4 into Eq. VII.4.3 and Eq. VII.4.3 into Eq. VII.4.2, l_{t,TiO_2} was calculated as

$$l_{t,eff} = \frac{1}{n_{Nb}\sigma_{m,Nb} + \frac{1}{l_{t,TiO_2}}}. \quad (VII.4.5)$$

The values of $l_{t,eff}$ for the mixture of TiO_2 and Nb particles, calculated in this way (using Eq. VII.4.5) is presented in Fig. VII.4.9 for different amounts of Nb in the mixture (2.5 – 66 %Nb). The number density of Nb, n_{Nb} , was known from measuring the weight of Nb and TiO_2 separately, during sample preparation (

presented in Fig. VII.4.1). In the above equation (Eq. VII.4.5) for $l_{t,eff}$ $\sigma_{m,Nb}$ was calculated according to expression [4]

$$\sigma_{m,Nb} = (1 - gw)\pi \left(\frac{d_{Nb}}{2} \right)^2 \quad (\text{VII.4.6})$$

where $g=0.10$ and $w=0.42$ [4] and l_{t,TiO_2} was taken to be 26μ (as determined from fitting Eq. VII.4.1 to the experimental data in case of scattering through pure TiO_2).

In Figs. VII.4.3 – VII.4.8 the fitting of Eq. VII.4.1 to the experimentally obtained data was performed in such a way that the calculated $l_{t,eff}$ (from Eq. VII.4.5) was used for l_t , so that the only free parameter was l_a . The l_a is then varied, until the best fit of the theoretically calculated temporal profile to the experimentally measured temporal profile is found. The values for l_a obtained in this way are shown in Fig. VII.4.10 for different amount of Nb in the mixture (in % by weight).

For 0%Nb to 5%Nb the fitting of the theoretical curves (based on diffusion theory) to the experimentally obtained data is very good. For 10%Nb to 66%Nb diffusion theory does not give good fits to the experimental data. The experimental results show that more light is transmitted at later times than predicted by diffusion theory.

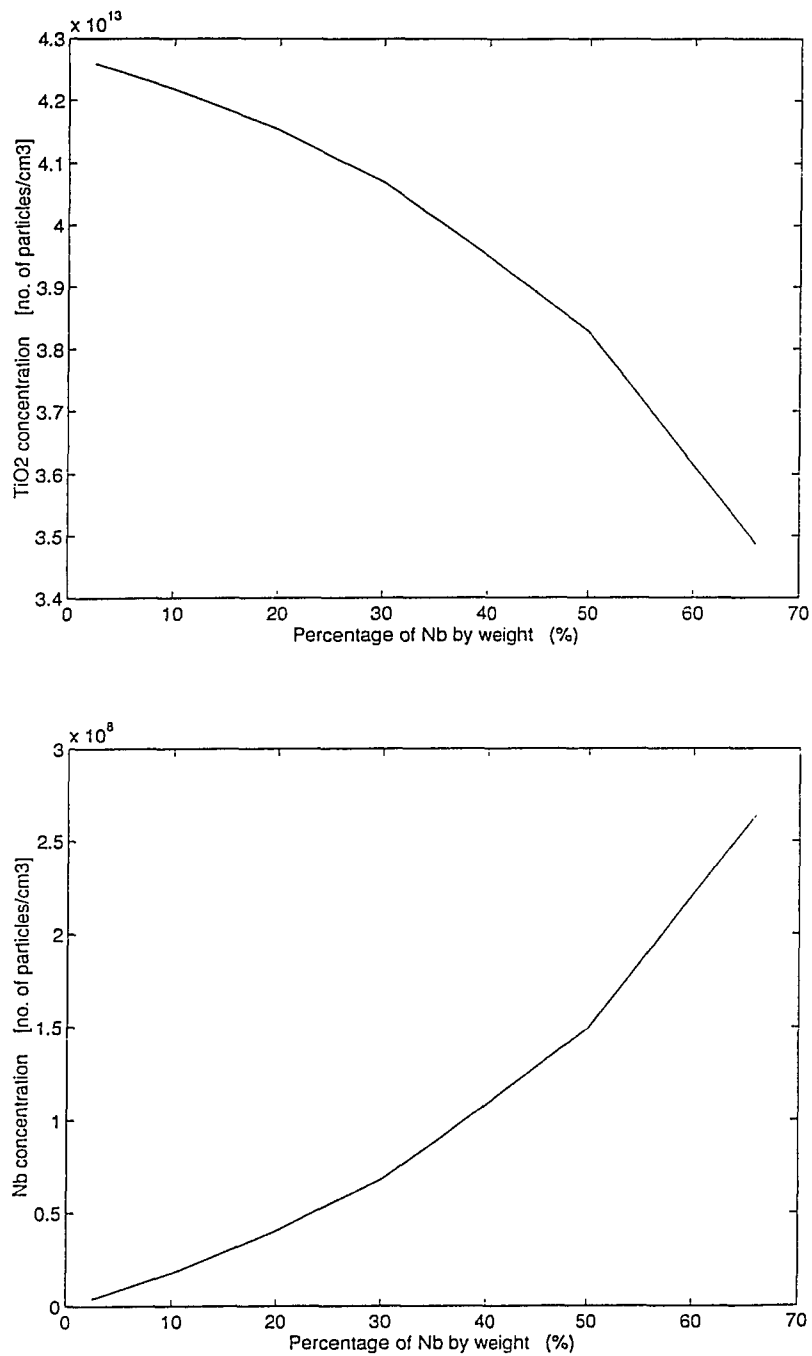


Figure VII.4.1 Number density of TiO_2 (top) and Nb particles (bottom) as a function of % (by weight) of Nb present.

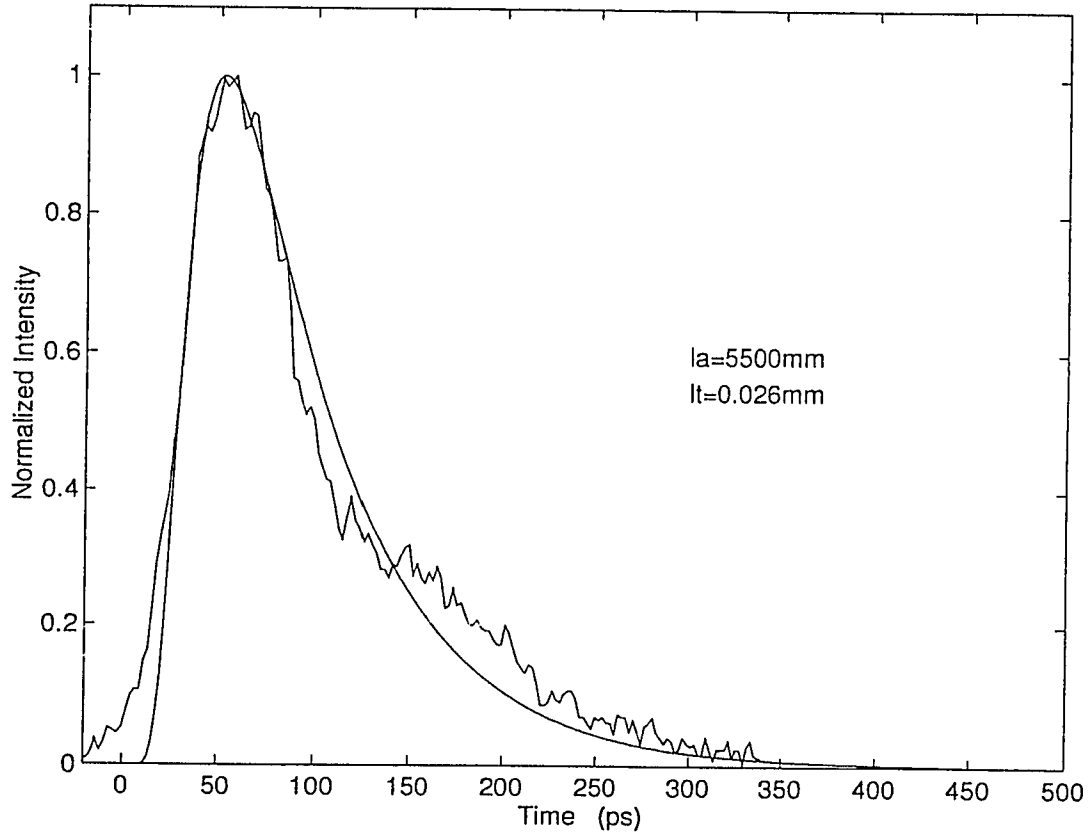


Figure VII.4.2 Case: 0%Nb. The measured temporal profile of the scattered pulse and the calculated temporal profile according to the diffusion model. Since TiO_2 is a nonabsorbing medium, l_a was taken to be very big so that l_t was the only fitting parameter in case of pure TiO_2 . The best fit was achieved for $l_{t,\text{TiO}_2} = 26\mu$.

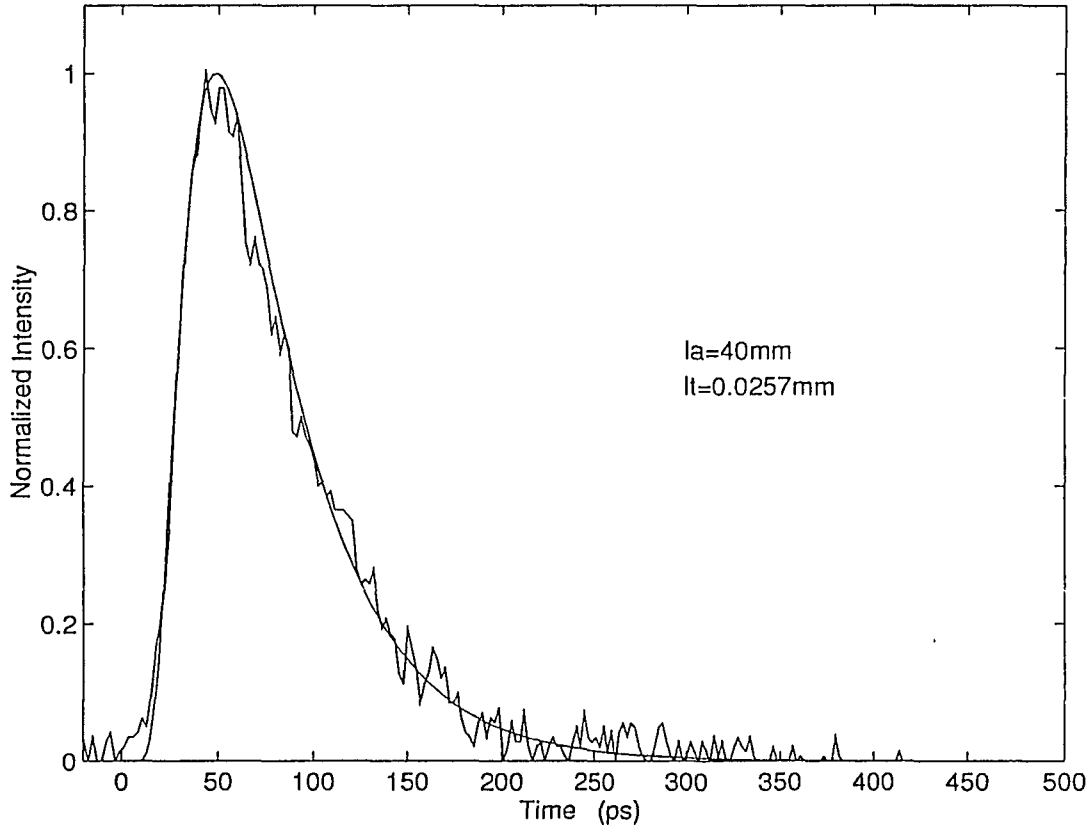


Figure VII.4.3 Case: 2.5%Nb. The measured temporal profile of the scattered pulse and the calculated temporal profile according to the diffusion model are presented above. l_t , ($l_t = l_{t,eff}$) is calculated from Eq. VII.4.5. l_a , which is used as a fitting parameter, has the value that gives the best fit of the diffusion model to the experimentally obtained temporal profile.

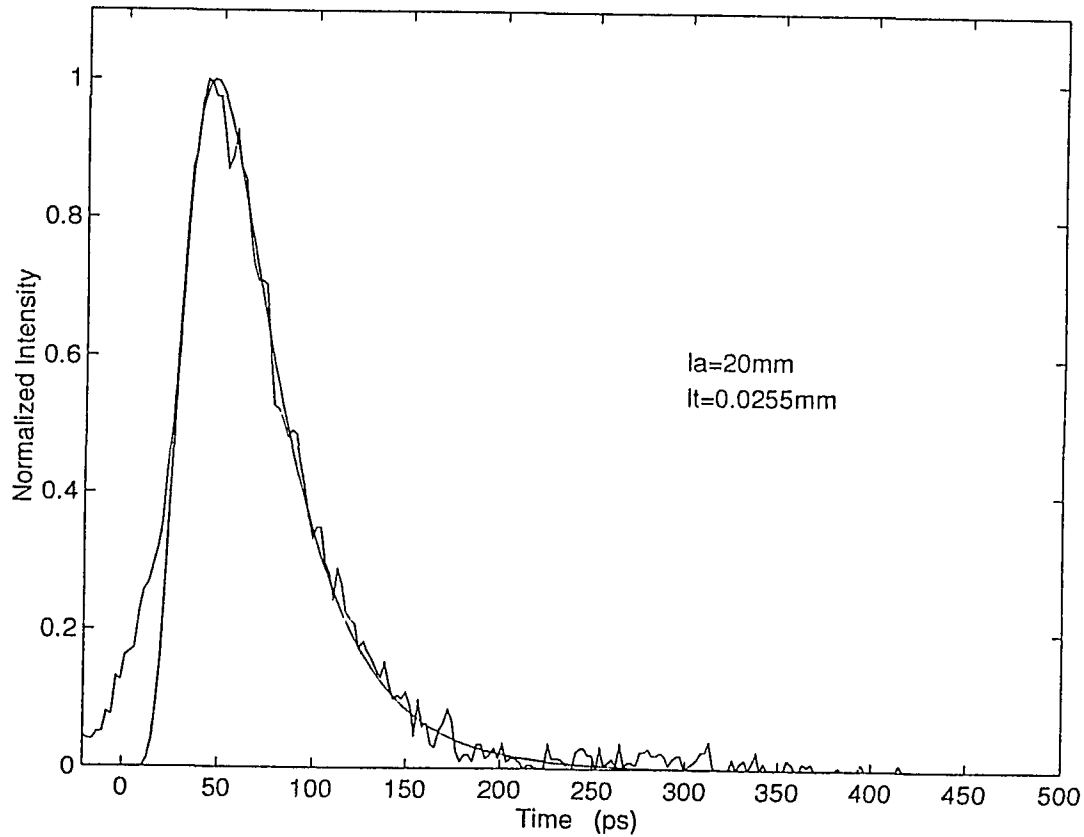


Figure VII.4.4 Case: 5%Nb. The measured temporal profile of the scattered pulse and the calculated temporal profile according to the diffusion model are presented above. l_t , ($l_t = l_{t,eff}$) is calculated from Eq. VII.4.5. l_a , which is used as a fitting parameter, has the value that gives the best fit of the diffusion model to the experimentally obtained temporal profile.

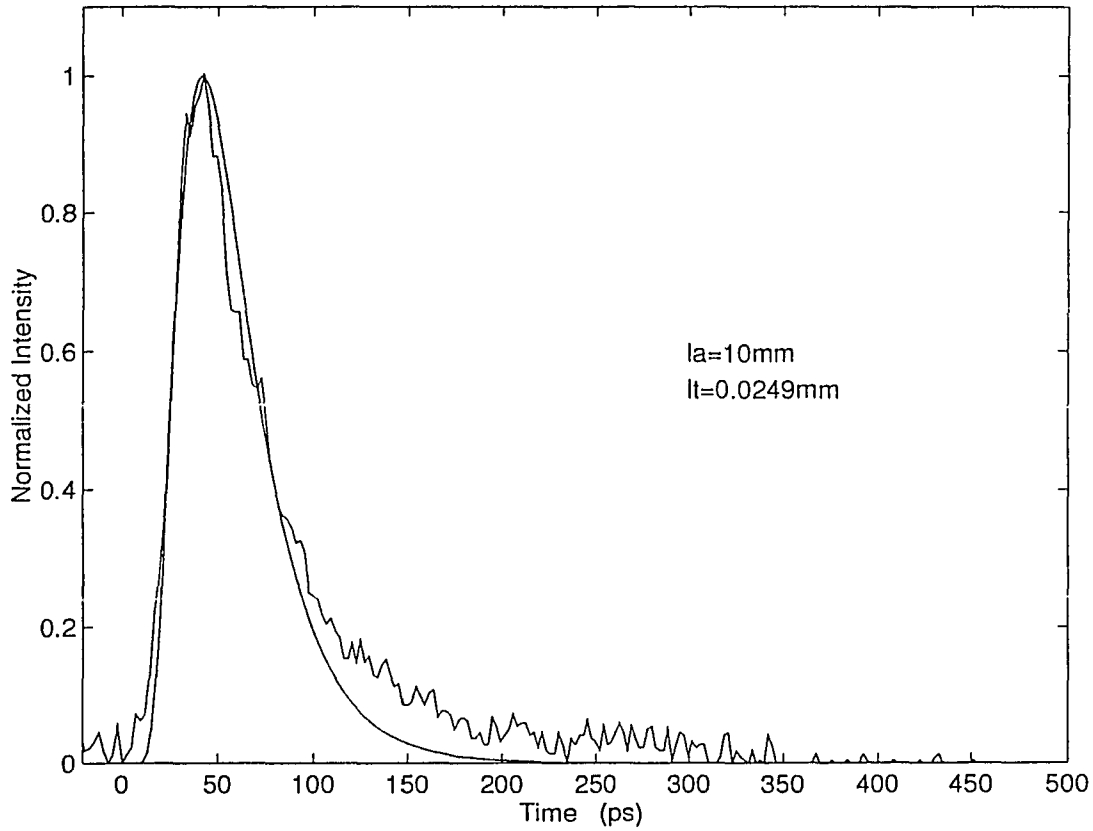


Figure VII.4.5 Case: 10%Nb. The measured temporal profile of the scattered pulse and the calculated temporal profile according to the diffusion model are presented above. l_t , ($l_t = l_{t,eff}$) is calculated from Eq. VII.4.5. l_a , which is used as a fitting parameter, has the value that gives the best fit of the diffusion model to the experimentally obtained temporal profile.

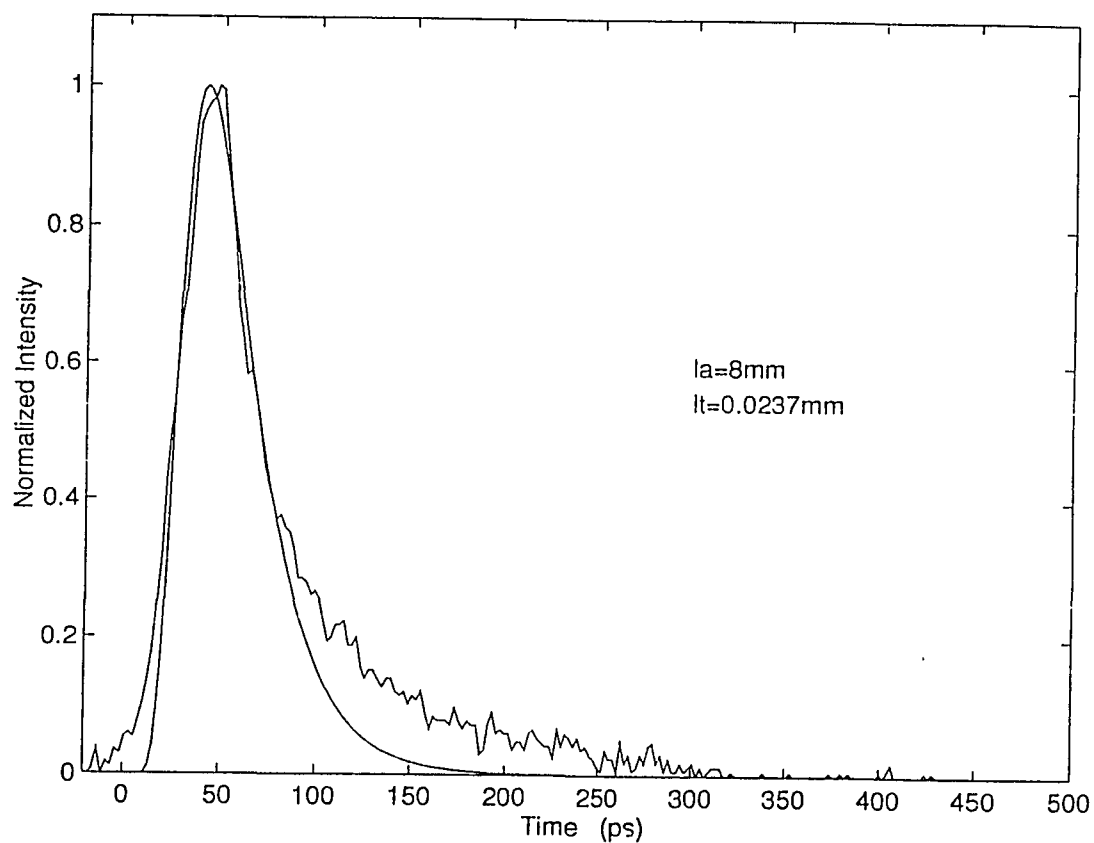


Figure VII.4.6 Case: 20%Nb. The measured temporal profile of the scattered pulse and the calculated temporal profile according to the diffusion model are presented above. l_t , ($l_t = l_{t,eff}$) is calculated from Eq. VII.4.5. l_a , which is used as a fitting parameter, has the value that gives the best fit of the diffusion model to the experimentally obtained temporal profile.

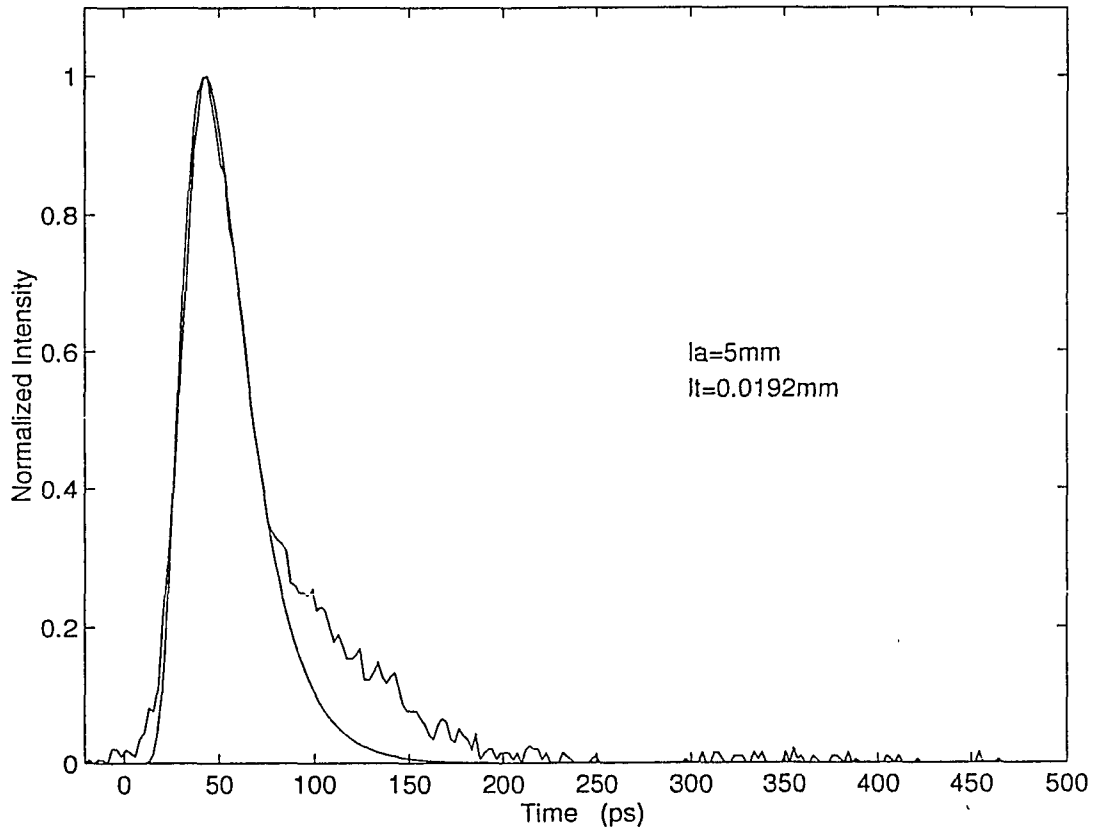


Figure VII.4.7 Case:50%Nb. The measured temporal profile of the scattered pulse and the calculated temporal profile according to the diffusion model are presented above. l_t , ($l_t = l_{t,eff}$) is calculated from Eq. VII.4.5. l_a , which is used as a fitting parameter, has the value that gives the best fit of the diffusion model to the experimentally obtained temporal profile.

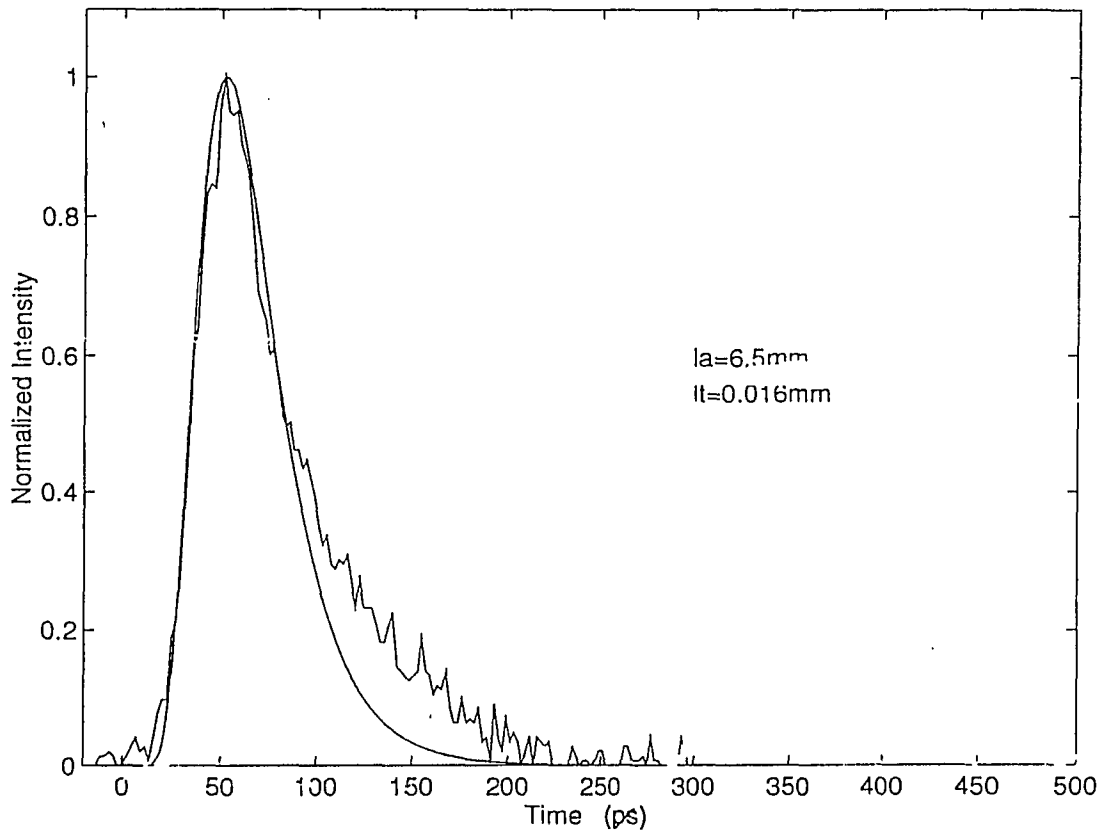


Figure VII.4.8 Case: 66%Nb. The measured temporal profile of the scattered pulse and the calculated temporal profile according to the diffusion model are presented above. l_t , ($l_t = l_{t,eff}$) is calculated from Eq. VII.4.5. l_a , which is used as a fitting parameter, has the value that gives the best fit of the diffusion model to the experimentally obtained temporal profile.

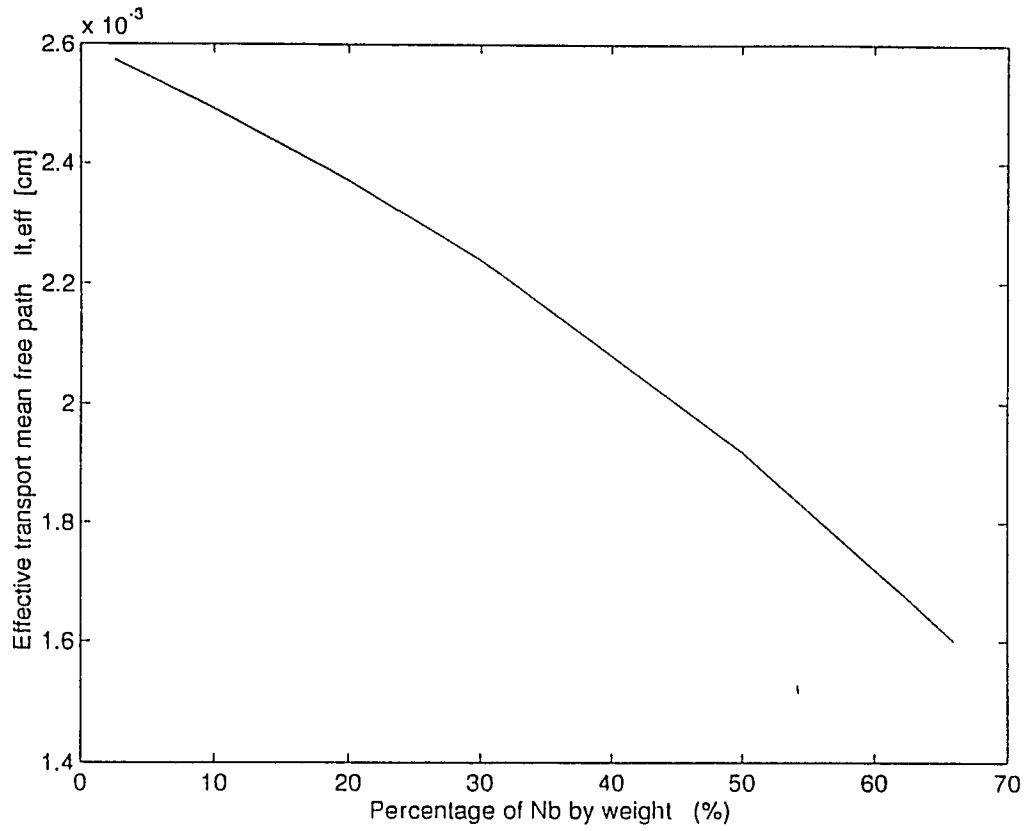


Figure VII.4.9 In this plot, the values of $l_{t,eff} = \frac{1}{n_{Nb}\sigma_{m,Nb} + \frac{1}{l_{t,TiO_2}}}$ calculated using Eq. VII.4.5 are presented for different amounts of Nb in the mixture (2.5 – 66 %Nb). $l_{t,eff}$ is based on theoretically calculated $n_{Nb}\sigma_{Nb}$ and experimentally determined l_{t,TiO_2} .

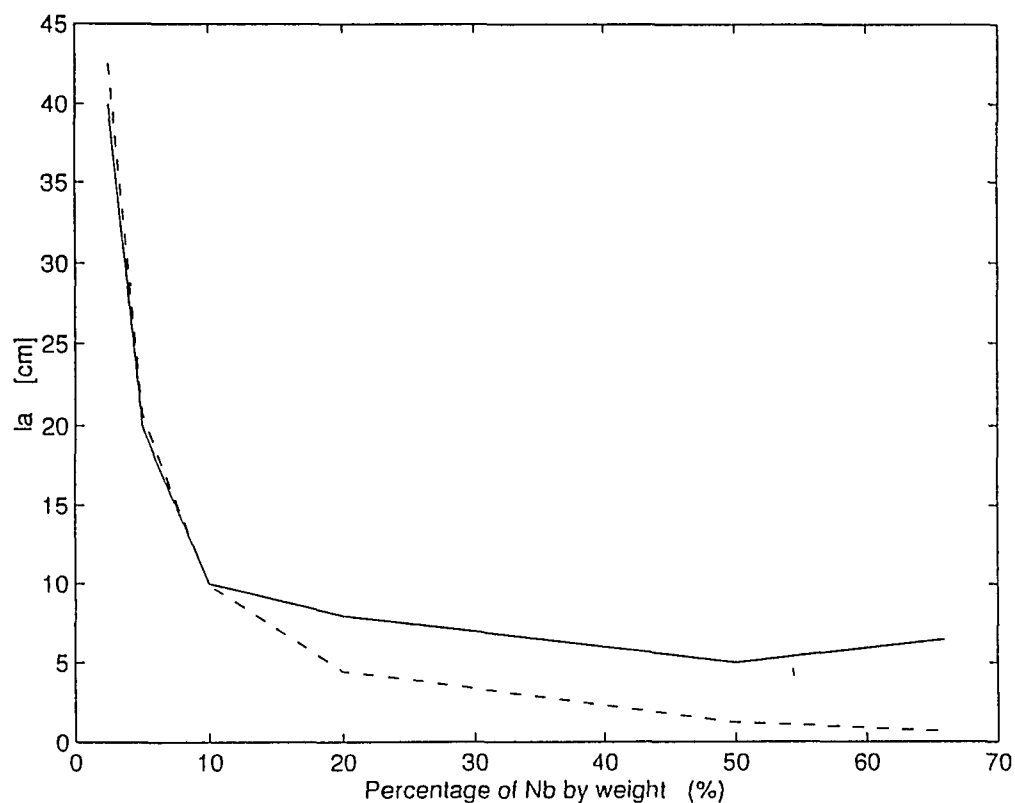


Figure VII.4.10 In this plot the solid line represents the values for l_a for 2.5 % Nb to 66 %Nb, obtained by fitting Eq. VII.2.10 to the experimental results in Figs. VII.4.3 – VII.4.8. Since Nb is the only source of absorption $l_a \propto 1/n_{Nb}$ is also plotted for comparison (dashed line).

VII.5. Discussion

The measured temporal profile of the scattered pulse through pure TiO_2 (Fig. VII.4.2) shows that a considerable amount of light arrives after a time delay of 100–300 ps. This result is characteristic of highly scattering medium, since scattered light arrives latest. When absorbing particles are added, it is the light which travels the longest path, that undergoes the strongest absorption. This result is illustrated in Fig. VII.4.3. The tail of the scattered pulse is reduced when the scattering medium contains only 2.5 %Nb.

The $l_{t,\text{TiO}}$ was found from the measured temporal profile with 0%Nb (Fig. VII.4.2). In that case, there is no absorption, and $l_{t,\text{TiO}}$ is completely determined. A value of 26μ is obtained for $l_{t,\text{TiO}}$ which agrees very well with values obtained by Saulnier et al. [5] for latex beads of similar size and concentration. Fig. VII.5.1 shows the transport mean free path for latex balls as measured and calculated by P. M. Saulnier. Departure from Mie theory (straight line) is shown for $n\lambda^3 > 1$. The x represents l_{t,TiO_2} as obtained in our experiment.

The tail of the measured temporal profile of the scattered light (in the 100–300 ps region) is due to the highly scattering TiO_2 particles. One can see in Figures VII.4.2, VII.4.3, VII.4.4, VII.4.5 that when Nb absorbing particles are added, it is the light in the 100–300 ps region, that undergoes the strongest absorption. As a consequence, duration of the scattered pulse decreases as the percentage of Nb particles in the mixture is increased. When the calculated values for $l_{t,\text{eff}}$ are used in Eq. VII.2.10 and l_a is changed to fit Eq. VII.2.10 to the experimental data, l_a halves as the Nb

concentration is doubled for all the measurements from 0%Nb to 10% Nb (Figures VII.4.2, VII.4.3, VII.4.4, VII.4.5) as presented in Fig. VII.4.10. This is as expected since Nb is the only source of absorption and $l_a \propto 1/n_{Nb}$.

Figs. VII.4.6, VII.4.7, VII.4.8 illustrate that as the Nb concentration is increased to 20% and above the absorption length does not decrease as $1/n_{Nb}$ any more and the fitting is poor. For concentrations 20% Nb – 66% Nb, as shown in Fig. VII.4.10, the effective absorption length decreases less rapidly (less than $1/n_{Nb}$) which means that classical theory for the Nb absorption does not hold any more. For 20% Nb and 50% Nb (Figs. VII.4.6, VII.4.7) the absorption length decreases from $l_a=10$ mm (for 10 % Nb) to $l_a=8$ mm (for 20 % Nb), and to $l_a=5$ mm (for 50 % Nb). More light seems to appear in later time region for concentration of 10%Nb –66%Nb. This effect may be an indication that correlation effects due to high density can arise at lower values of n' ($n'=n\lambda^3$, i. e. number of particles in λ^3) in case of larger ball diameters, as observed by Saulnier et al. [5]. This is especially true since it has been shown that spatial correlation affects extinction more strongly than transport [5], so l_a would be affected more than l_t . For these cases, where the percentage of Nb is higher, the fit of the diffusion model does not give very good agreement with the experimentally obtained temporal profile, since the $l_{t,Nb}$ can not be precisely determined due to correlation effects in Nb. The increase in the absorption length to $l_a=6.5$ mm for the case of 66% Nb (Fig. VII.4.8) supports the conclusion that there may be correlation effects among Nb particles which play a significant role in scattering to reduce absorption at higher Nb concentrations. More work is needed to explain this observation.

The 8-ps pulse, after being scattered through a 1-mm slab of pure TiO_2 , broadens and becomes 83 ps in duration. When niobium particles are added, this duration decreases down to 36 ps for 50% Nb in the mixture. As more Nb is added the

pulse starts to broaden, since the tail in the 100–300 ps region appears again due to correlation effects among Nb particles, when Nb density becomes high. This is shown in Fig. VII.5.2.

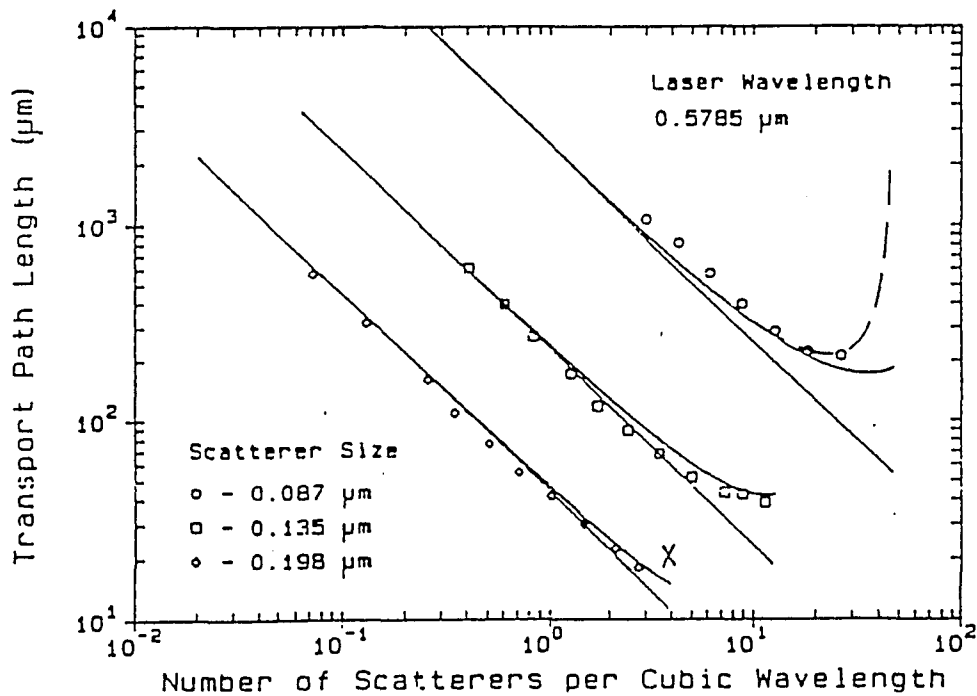


Figure VII.5.1 The transport mean free path for latex balls as measured and calculated by P. M. Saulnier [5]. Departure from Mie theory (straight line) is shown for $n\lambda^3 > 1$. The x represents l_{l,TiO_2} as obtained in our experiment.

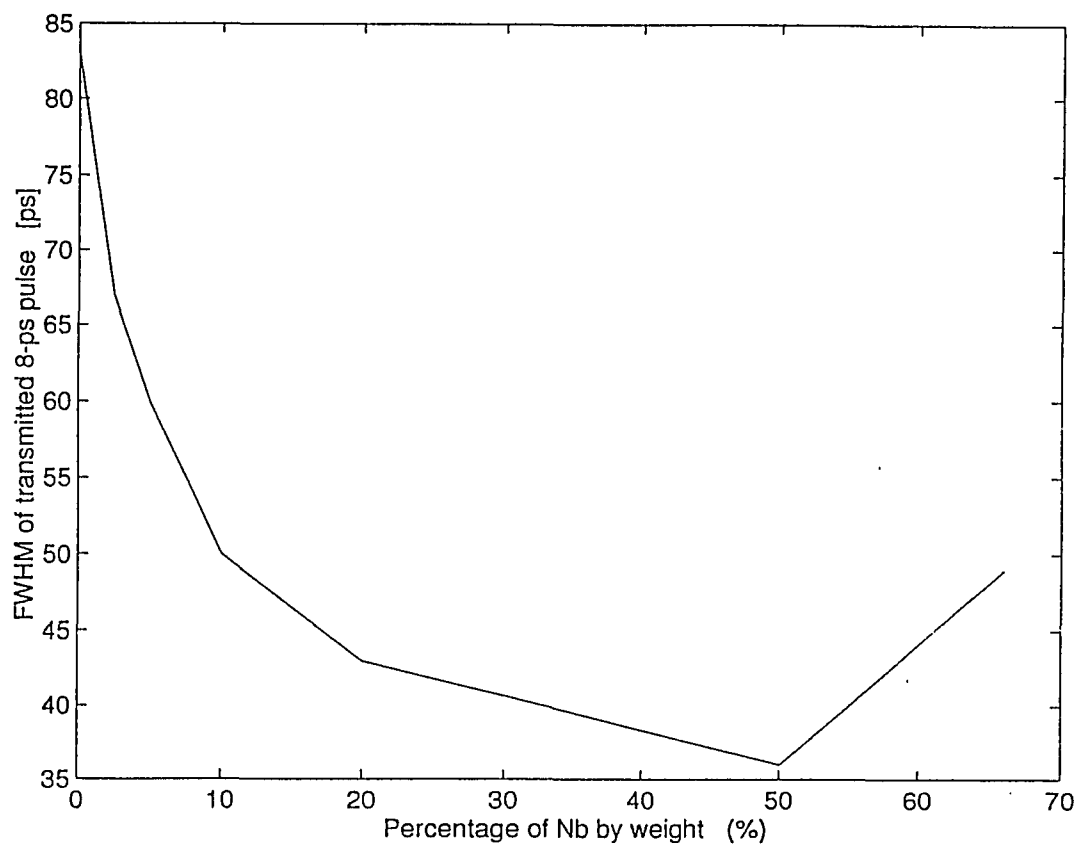


Figure VII.5.2 The 8-ps pulse, after being scattered through a 1-mm slab of pure TiO_2 , broadens and becomes 83 ps in duration. When niobium particles are added, this duration decreases down to 36 ps for 50% Nb in the mixture. As more Nb is added the pulse starts to broaden again due to correlation effects when Nb density becomes high.

VII.6. Conclusion

In this chapter, the temporal profile of a pulse scattered through dense medium with metallic particles has been measured and modeled using the diffusion theory. The 8-ps pulse, after being scattered through a 1-mm slab of pure TiO_2 , broadens and becomes 83 ps in duration. The scattering in TiO_2 clearly shows that correlation effects due to high particle density must be taken into consideration. If l_{t,TiO_2} were calculated classically, according to Mie theory (i.e. neglecting the correlation effects), a value of $l_{t,\text{TiO}_2} = 1.3 \mu$ is obtained, which is much less than the measured 26μ .

For all measurements, the increased presence of metallic particles decreases the duration of the pulse. The diffuse light that arrives last i.e. travels the longest distance is absorbed the most. When niobium particles are added, this duration decreases from 83 ps for pure TiO_2 down to 36 ps for 50% Nb in the mixture.

For measurements performed with 2.5–10% Nb the fits are reasonably good, and absorption length, which is due to metallic particles, decreases inversely with increasing Nb concentration. The diffuse light that arrives last is absorbed the most so that there is a less pronounced tail in the shape of the temporal profile, than in case of pure TiO_2 .

For measurements performed with 20% – 66% Nb, the Nb density is high enough so that the effect of pulse shortening due to the increasing presence of metallic particles is reduced because of correlation effects among niobium particles. This means that the absorption length l_a is longer than expected according to classical theory and the fits are poor. There may be some zone of waveguiding to trap the

light to arrive later with stronger intensity. Spatial correlation is observed to affect extinction more strongly than transport [5]. The angular dependence of the correlation effect is such that the effect is stronger at smaller angles and is more pronounced with increasing density. This angular dependence is considered similar to $(1-\cos\theta)$ already present in anisotropic scattering, i. e. the forward-scattering contribution to the overall cross section may be larger.

When niobium concentration is high, $l_{t,eff}$ can not be calculated according to Eq. VII.4.5. This deviation is especially pronounced in our measurements with the highest concentration of niobium (66% Nb). For higher concentration of niobium the scattered pulse starts to broaden with increasing Nb density, from 36 ps for 50% Nb to 49 ps for 66% Nb. This agrees with previous observations [5] that for $n' < 1$ correlation effects on transport length are relatively unimportant, but a significant correlation factor can arise for extinction length, even at lower values of n' . This effect of correlation on extinction length is especially true for larger ball diameters.

The increased anisotropic scattering due to a large presence of Nb particles (for $d_{Nb} \gg \lambda$ light scatters predominantly at smaller angles) also plays a considerable roll because of the already mentioned higher correlation effect at smaller angles.

Bibliography

- [1] M. Lax, V. Nayaramamurti, and R. C. Fulton, "Classical diffusive photon transport in a slab," in *Proceedings of the Symposium on Laser Optics of Condensed Matter* (J. L. Birman, H. Z. Cummins, and A. A. Kopyanskii, eds.), pp. 229–235, Plenum, New York, 1987.
- [2] K. M. Yoo. PhD thesis, Graduate Center of CUNY, 1990.
- [3] F. Liu. PhD thesis, Graduate Center of CUNY, 1993.
- [4] H. C. van de Hulst, *Light Scattering by Small Particles*. Dover Publications, London, 1981. p. 127, 225, 292.
- [5] P. M. Saulnier, M. P. Zinkin, and G. H. Watson *Phys. Rev. B* **42**, p. 2621, 1990.
- [6] A. Ishimaru, *Wave Propagation and Scattering in Random Media*, vol. 1. Academic Press, New York, 1978.
- [7] G. H. Watson, S. L. McCall, P. A. Fleury, and K. B. Lyons *Phys. Rev. B* **41**, p. 10947, 1990.
- [8] M. Lax, *Symmetry Principles in Solid State and Molecular Physics*. John Wiley, New York, 1974.
- [9] K. M. Yoo, F. Liu, and R. R. Alfano *Phys. Rev. Lett.* **64**, p. 2647, 1990.
- [10] M. Lax, "Private correspondence," 1994.

VIII Summary

In this thesis, I have applied ultrafast pulses in the investigation of the picosecond and subpicosecond processes in niobium metallic films in the normal and superconducting state using transient thermotransmittance spectroscopy. The transmitted laser pulse profile through a slab of random media with niobium metallic particles was also investigated using ps time resolution technique.

Experimental measurements of the electron-phonon relaxation time in niobium were performed to determine the temperature dependence of the electron-phonon relaxation process (electron-phonon relaxation time) under nonequilibrium conditions. These results were compared with theory for temperatures ranging from room temperature to superconducting temperatures. It was found that the electron-phonon relaxation time decreases from 370 fs at 292 K to 250 fs at 7 K. No special features were detected as the sample (initial) temperature was lowered from 10 K (above critical superconducting temperature, $\Theta_{c, Nb}=8.8$ K) to 7 K (superconducting temperature). A femtosecond set-up made of a colliding-pulse mode locked dye laser [1] [2] and amplifier that generates ultrafast (100 fs, 0.5 μ J) pulses was used in this project.

The time it takes for the electrons to thermalize with lattice, τ (i.e. the lattice temperature rise time) is governed by the electron-phonon coupling parameter g . Based on Allen's theory [3], that describes the energy exchange between the electrons and the phonons, we have derived the temperature dependence of the electron-phonon coupling parameter, g . We have shown that when temperatures are decreased below Θ_D , the electron-phonon coupling parameter, g , is not constant any more.

g becomes dependent on both electron temperature and phonon temperature and is found to decrease with decreasing temperature [4]. Since during the electron-phonon interaction, i.e. during the time it takes for the electrons to thermalize with phonons, both the electron and phonon temperature change in time rapidly, the value of the electron-phonon coupling parameter changes in time accordingly. Therefore in the two temperature model based, the electron phonon coupling parameter g becomes a dynamic variable.

To investigate the behavior of $g(t)$ we have calculated $g(t)$ for niobium film under laser pulse heating [5]. During the first 100 fs $g(\Theta_e, \Theta_l)$ increases with time as the electrons are heated by the 100-fs laser pulse, i.e. as Θ_e increases. Then, as the electrons cool down by transferring their energy to the phonons, $g(\Theta_e, \Theta_l)$ slightly decreases reaching a constant value in <500 fs, at temperatures when the electrons have thermalized with the lattice. One should note that $g(\Theta_e, \Theta_l)$ becomes time dependent only for temperatures below Debye temperature ($\Theta_D=275$ K for Nb).

The temperature dependence and time evolution of the electron-phonon coupling parameter $g(\Theta_e, \Theta_l)$ was included in the theoretical model to obtain the numerically calculated rise time of the lattice temperature. The rise time of the calculated time evolution of the lattice temperature (i.e. the electron-phonon relaxation time) was obtained as 10 % to 90 % of the total rise for a range of ambient (initial) temperatures from $\Theta_0=7$ K to $\Theta_0=292$ K. The time it takes for the electrons to thermalize with phonons, τ , decrease with decreasing temperature for all but the lowest ambient temperatures. At low temperatures, $\Theta_0 \leq 20$ K, τ starts slightly increasing with increasing temperature.

The experimentally obtained electron-phonon relaxation time for different ambient temperatures was compared to the calculated ones, obtained based on Allen's theory

[3], where the electron-phonon parameter $g(\Theta_e, \Theta_l)$ is a function of electron and phonon temperatures. The calculated electron-phonon relaxation time is in good agreement with the measured experimental values well below Debye temperature, down to 20 K. This confirms the validity of the theoretical model for $g(\Theta_e, \Theta_l)$ used for determining the time evolution of the electron-phonon coupling parameter. Experimental results show [6] [7] that the electrons thermalize with phonons faster at smaller ambient temperatures. No special features have been observed below superconducting temperature ($\Theta_{c,Nb}=8.8$ K) on this time scale.

For sample temperatures ≤ 20 K the experimental results show a continuous decrease in the electron-phonon relaxation time, while according to the theory the relaxation time starts increasing slightly with temperature for $\Theta < 30$ K. There is a strong indication that the theoretical model has to be improved for temperatures from 30 K to below Θ_c . The lower values and continuous decrease of the electron-phonon relaxation obtained by the experiment for $\Theta < \Theta_D/3$ are most likely due to a shake-off process taking place for $\Theta < \Theta_D/3$. The shake-off process [8] leads to a release of the lattice energy represented by λ and it is more pronounced at lower temperatures since λ increases with decreasing temperature. This explains the measured continuous decrease in electron-phonon relaxation time obtained in the experiment. The uncertainty in the experimentally obtained value of the electron-phonon mass enhancement parameter λ used in the calculations and the assumed temperature dependence [9] may also have contributed to the small discrepancy between theory and experiment seen at low temperatures.

Measurements of transient thermotransmittance decay in the ps time scale, for ambient temperatures from room temperatures to below superconducting temperature have been performed for niobium film using 100 fs laser pulses in a pump-probe

configuration [10]. The thermotransmittance signal has been related to the temperature change in the niobium film caused by cooling due to heat diffusion. For sample (initial) temperatures above superconducting temperature ($\Theta_0 > \Theta_c$), the measured thermotransmittance decay time, $\tau_{\Delta T} = 950$ ps, which remains the same during the 250-ps duration of our measurements, for $\Theta_0 = 10$ –292 K. The calculated temperature decay, $\Delta\Theta/\Delta t$, during the first 250 ps agrees with the experimentally obtained one and is the same for all initial temperatures $\Theta_0 > \Theta_c$. This is because the diffusivity is constant for temperatures > 100 K, and for all $\Theta_0 > \Theta_c$, the niobium film is heated and stays above 100 K in the first 250 ps of the diffusion process.

When the temperature is decreased below superconducting temperature ($\Theta_0 < \Theta_c$), a change in the transient thermotransmittance decay in the visible during the first 250 ps has been detected in Nb in the transition from normal to superconducting phase. When niobium in superconducting state is illuminated by a 2 eV, 100 fs laser pulse, it exhibits a faster decay of the transmissivity change ($\tau_{\Delta T} = 570$ ps for $\Theta_0 = 4.5$ K $< \Theta_c$), then when in the normal metal state. The measured faster decay of the thermotransmittance change, when illuminating a superconducting film at temperatures below superconducting temperature ($\Theta_0 < \Theta_c$), was related to increased diffusivity due to nonequilibrium processes in Nb in the transition from superconducting to normal state reflected in the formation of an intermediate state which consists of alternating regions of normal and superconducting phases.

An investigation of the temporal profile of a ps-laser pulse, after passing through a slab of dense random media, made of a mixture of dielectric particles and metallic particles has been performed. Diffusion theory was used to model the light after undergoing multiple random scattering. It is shown that the presence of metallic particles decreases the duration of the temporal profile and that correlation effects

in photon transport can not be ignored in this dense random system. The scattering in TiO_2 was successfully modeled using the diffusion theory and it shows phase correlation effects that decreases the effective cross section below that of an individual scatterer. In all measurements performed with Nb particles present, the increased presence of metallic particles decreases the duration of the pulse. The diffuse light that arrives last i.e travels the longest distance is absorbed the most. For measurements performed with 2.5–10% Nb, absorption length, which is due to metallic particles, increases inversely with increasing Nb concentration. The diffuse light that arrives last i.e travels the longest distance is absorbed the most. For measurements performed with 20% – 66% Nb, the effect of pulse shortening due to the increasing presence of metallic particles can not be explained with a simple model. For 20% – 66% Nb, the Nb density is high enough that the effect of pulse shortening due to the increasing presence metallic particles is affected by the correlation effects among niobium particles. For $n' < 1$ ($n' = \text{no. of particles} / \lambda^3$) correlation effects on transport length are relatively unimportant, but a significant correlation factor can arise for extinction length, even at lower values of n' . This is especially true for larger ball diameters.

Bibliography

- [1] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano *Opt. Lett.* **13**, p.987, 1988.
- [2] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano, *Ultrafast Phenomena VI*, vol. 48 of *Springer Series in Chemical Physics*. Springer-Verlag, Berlin, Heidelberg, 1988.
- [3] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.
- [4] M. Mihailidi and R. R. Alfano *Appl. Phys. Lett.* (accepted for publication), 1994.
- [5] M. Mihailidi and R. R. Alfano in *9th Interdisciplinary Laser Science Conference (ILS-IX)*, 1993.
- [6] M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [7] M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.
- [8] J. M. Ziman, *Electrons and Phonons*. Oxford University Press, London, 1960.
- [9] G. Grimvall, *The Electron-Phonon Interaction in Metals*. North-Holland, Amsterdam, 1981.
- [10] M. Mihailidi and R. R. Alfano *Phys. Rev. B (in review)*, 1994.

IX Future Research Directions

To obtain more information about the dynamics of the electron gas in metal films, one may perform femtosecond thermotransmittance measurements at ultra low temperatures (0.3 K to 5 K) with low intensity 100 fs laser pulses. The inelastic collision time τ_i at lower temperatures ($\Theta \lesssim 2$ K), is governed by inelastic electron-electron scattering. As the electron gas is heated to a temperature Θ_e above the low phonon temperature Θ_{ph} , Θ_e is established on a time scale of the order τ_i . The energy relaxation, τ_e , is slower, because it requires collisions between the electrons and phonons to cool the electron gas. At low temperatures, the electron-phonon collision time increases with decreasing temperature so that the higher Θ_e is maintained for a longer time. One can determine the relation between the energy relaxation time τ_e and the inelastic collision time, τ_i , by measuring the electron temperature, for example in Au, with the femtosecond thermotransmittance technique at ultra low temperatures and compare the results with the ones already known from magnetoresistance measurements in Au [1].

By exposing superconductors to photons, nonequilibrium superconductivity can be achieved. A nonequilibrium resistive state, where superconducting and nonsuperconducting regions coexist, was first observed in low temperature superconducting film [2]. With the discovery of high T_c superconductors, this intermediate state has been investigated with ultrafast laser pulses and the onset of the resistive state has been detected with ns time resolution [3]. However the dynamics of the onset of the resistive state, which is in the ps time domain, has not been measured neither in thin metal films nor in high T_c films. By using a high speed oscilloscope

with 5 ps resolution to measure the voltage across a microbridge prepared on a superconducting film, and 100 fs pulses to illuminate the superconducting film, one should be able to investigate the dynamics of the intermediate state and quantitatively verify Elesin's theory of nonequilibrium superconductivity [4].

Since the electrical transport properties can be inferred from the thermal transport measurements [5] one may use the transient thermotransmittance technique used for metal films, to investigate thermal transport in new high T_c materials. Its advantage over other techniques is its noncontacting, nondestructive nature.

Bibliography

- [1] S. I. Dorozhkin, F. Lell, and W. Schoepe *Solid State Commun.* **60**, p. 245, 1986.
- [2] G. A. Sai-Halasz, C. C. Chi, A. Denestein, and D. Langenberg *Phys. Rev. Lett.* **33**, p. 215, 1974.
- [3] L. Shi, G. L. Huang, C. Lehane, D. H. Kim, and H. S. Kwok *Phys. Rev. Lett.* **62**, p. 2830, 1993.
- [4] F. Elesin and Y. V. Kopaev *Sov. Phys. Usp.* **24**, p. 116, 1981.
- [5] B. M. Clemens, G. L. Eesley, and C. A. Paddock *Phys. Rev. B* **37**, p. 1085, 1988.

Appendix

A.1. Programs for Electron-Phonon Relaxation

The coupled Eq.'s (V.3.10), (V.3.11) and (V.3.12) are simultaneously solved using the Runge-Kutta method in time while integrating for $g(\Theta_e(t), \Theta_l(t))$ in the phonon frequency domain for each step in time. The electron-phonon coupling parameter $g(\Theta_e(t), \Theta_l(t))$ for niobium is calculated as a function of $\Theta_e(t)$ and $\Theta_l(t)$ according to Eq. (V.3.10) using numerical integration.

```
function w=srad1(begpos,zeropos,stepspeed,s,temp0,V0,Vf)
% scriptfile srad.m
% loads the file whose name goes into s,
% filters the noise and plots a smooth curve
% fits results to diff. eq'n solution

% parameters:
%*****
% begpos-position of the stepping motor at the beginning of the measurement
% zeropos-zero time, when pump and probe overlap
% stepspeed-no. of microns per sec.
% temp0-Nb sample temperature
% s-data filename
% V0-min voltage
% Vf-max voltage

eval(['load ',s,'.dat']);
t=eval([s,'(:,1)']); % time
V=eval([s,'(:,2)']); % voltage
N=9; % filter order
B=0.06; % filter bandwidth
% first, the noise is filtered out of the data:
smooth1(begpos,zeropos,stepspeed,t,V,N,B,s,temp0,V0,Vf);

function z=smooth1(begpos,zeropos,stepspeed,x,y,N,B,s,temp0,V0,Vf)
%
% z=smooth(x,y,N,B)
%
% This function smooths y(x). N is the filter order, B is bandwidth.
% Typically, N~5 & B~0.01.
[b,a]=butter(N,B);
[A,w]=freqz(b,a,256);
%plot(w/pi,abs(A));
%stN= num2str(N);
%stB= num2str(B);
%st1=['N=',stN];
%st2=['B=',stB];
```

```

st0=s;
%text(0.75,0.5,st0,'sc');
%text(0.75,0.7,st1,'sc');
%text(0.75,0.6,st2,'sc');
%print;
z=filtfilt(b,a,y);
plot(x,y,x,z);
%text(0.15,0.6,st1,'sc');
%text(0.15,0.55,st2,'sc');
text(0.15,0.5,s,'sc');
%xlabel(' time ');
%ylabel(' Voltage ');
%print;
tttran1(begpos,zeropos,stepspeed,x,z,s,temp0,V0,Vf);
function y=tttran1(begpos,zeropos,stepspeed,tt,VV,s,temp0,V0,Vf)
% translates timescale into delay and prints fit
% and data on scale -.4 to 1.2 ps, y-axis normalized.
sttemp=num2str(temp0);
st1=['T=',sttemp,'K'];
zerot=abs(begpos-zeropos)./stepspeed;
[yt,it]=max(tt);
%plot(tt,VV);
%%text(0.15,0.5,s,'sc');
%%text(0.15,0.55,st1,'sc');
%%print;
%fl=1
tt=tt-zerot;

    if VV(1)>VV(it)
        tt=-tt;
    end;

delay=tt*stepspeed*2*3.33567e-15;
%*****;
tt=delay;

%*****;
%fl=2
k=0;
for i=1:it
    if tt(i)>-.4e-13
        if tt(i)<1.2e-12
            k=k+1;
            newd(k)=tt(i);
            newV(k)=VV(i);
        end
    end
end
%*****;
%fl=3
VVn=(newV-V0)/(Vf-V0);
plot(newd,VVn);
text(0.15,0.5,s,'sc');
print;
t0=-.4e-12;
tf=1.2e-12;
x01=[temp0 temp0+0.1]';
%fl=4
%***** calculating theoretical curve %*****;

[t1,x1]=ode23('nbtemp',t0,tf,x01);
sz=size(x1);
xn=x1(sz(1,1),2);
l=xn-x01(2,1);
xml=(x1-x01(2,1))/d1;
dif1=t1;
dif2=xml(:,2);

```

```

fl=5
[maxdif1,maxdif1i]=max(dif1);
k=0;
for i=1:maxdif1i
    if dif1(i)>-4e-13
        if dif1(i)<12e-13
            k=k+1;
            newd1(k)=dif1(i);
            newd2(k)=dif2(i);
        end
    end
end
%%end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% calculating fit to data%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
gx01=[temp0 temp0+0.1]';
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%;
[gt1,gx1]=ode23('nbtemp292',t0,tf,x01);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%;
gsz=size(gx1);
gxn=gx1(gsz(1,1),2);
gd1=gxn-x01(2,1);
gxml=(gx1-x01(2,1))/gd1;
gdif1=gt1;
gdif2=gxml(:,2);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%;
%fl=6
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%;
gshift=0;
gdif1=gdif1-gshift*stepspeed*2*3.33567e-15;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%;
[maxgdif1,maxgdif1i]=max(gdif1);
k=0;
for i=1:maxgdif1i
    if gdif1(i)>-4e-13
        if gdif1(i)<12e-13
            k=k+1;
            gnewd1(k)=gdif1(i);
            gnewd2(k)=gdif2(i);
        end
    end
end
end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%;
fl=7
%axis([-0.4e-12,1.2e-12,-0.2,1.2]);
axis([-1.5e-12,3e-12,-0.2,1.2]);
plot(newd1,newd2,'-',gnewd1,gnewd2,'--',newd,VVn,'--');
text(0.15,0.5,s,'sc');
text(0.15,0.55,st1,'sc');
print;
plot(gnewd1,gnewd2,'-',newd,VVn,'--');
text(0.15,0.5,s,'sc');
text(0.15,0.55,st1,'sc');
print;
text(.19,.4,'theoretical','sc'),text(.43,.6,'fit to experiment','sc');
meta sincplot
plot(tt,VVn,t1,xml(:,2));
text(0.15,0.5,s,'sc');
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%;
st0=s;
text(0.15,0.5,st0,'sc');
sttemp=num2str(temp0);
%t1=['T=',sttemp,'K'];
text(0.15,0.55,st1,'sc');
xlabel(' time (s)');
ylabel('Normalized Transmissivity Modulation');
print;

```

```

function xdot=nbtemp(t,x)
%Nb dynamic diff. eq'ns for electron & lattice temperature
%Using Debye aprox.
%t=time; x=temperature
g=gAllen(x(1),x(2));
lam=0.82;
s=5.25e09;
if x(1)<100
    gama=720*(1+lam);
else
    gama=720;
end;
if x(2)>30
    cl=1.0.*clatt(x(2));
else
    cl=8.6.*x(2).^3;
end
fwhm=1e-13;
sigma=fwhm/(8*log(2))^0.5;
tshift=1.e-13;
absor=.05;
ttl=(sigma*(2*3.14)^0.5);
tt2=exp(-0.5.*((t-tshift)./sigma).^2);
xdot(1)=(1./(gama.*x(1))).*(-g.*(x(1)-x(2))+(absor*s/ttl).*tt2);
xdot(2)=g/cl.*(x(1)-x(2));

```

A.2. Programs for Heat Transfer by Diffusion

In order to calculate the change in Nb film temperature in the ps time scale, a heat flow model was applied based on standard heat diffusion equations

$$C_i \frac{\partial \Theta(x, t)}{\partial t} = k_i \frac{\partial^2 \Theta(x, t)}{\partial x^2} + Q_i, \quad i = 1, 2 \quad (\text{A.2.1})$$

where $i=1$ stands for the upper layer (Nb film) and $i=2$ stands for the underlayer (quartz substrate). The numerical approach was based on the unconditionally stable DuFort-Frankel explicit method [1]. This model was modified to account for temperature dependent C_i and k_i [2] [3]. The temperature dependent values for k_i and C_i are changed dynamically [2] [3] in the DuFort-Frankel mesh for each point in space as temperature changes with time.

```
% AAex5_9_10.m solving temperature diffusion with DuFort-Frankel difference met
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% setting physical parameters %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
T0=10
d=20e-9;
fwhm=1e-13;
I0=7.58e13;
alfa=5.8e7;
ro=5e-9
Nmemory=7000
TNb=[4 10 15 20 25 30 50 70 100 150 200 250 300 500];
cNb=[0.0036 0.0193 0.0463 0.0927 0.162 0.251 0.726 1.17 1.61 1.97 2.13 2.23 2.28
cNb=cNb*1e6;
kNb=[0.993 2.18 2.50 2.29 1.87 1.45 0.76 0.61 0.55 0.53 0.525 0.533 0.537 0.567]
kNb=kNb*1e2;
TQ=[4 10 20 60 100 200 250 300 400];
cQ=[0.00028 0.015 0.06 0.348 0.643 1.32 1.58 1.79 2.06];
cQ=cQ*9.2e6;
kQ=[1.0 1.2 1.5 3.5 5.5 11.6 13.9 16.0 20.0];
kQ=kQ*1e-3*1e2;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% setting time and space step %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
dz=5e-10;
Nz=200;
kd=d/dz;
%//// make sure dt chosen so that tbreak integer ////
dt=fwhm*0.3e-2;
mpoints=30;
Nt=12000;
tshift=2*fwhm;
```

```

%//// multiplying tbreak by 3 ////
tbreak=6*(tshift+2*fwhm)/dt;
%tbreak=(tshift+2*fwhm)/dt;
[junk,nNb]=size(TNb);
[jjunk,nQ]=size(TQ);

%%%%%%%%%% checking the no. of points limits %%%%%%%%%%%
coments=[': no. of time points too small! ':' no. of space points too small!']
if Nt<=tbreak
    ic=1
elseif Nz<=kd
    kd=Nz; ic=2
elseif rem(tbreak,1)~=0
    ic=4;
    rrem=rem(tbreak,1)
else
    ic=3
end;
coment=coments(ic,:);

%%%%%%%%%% calculating pulse energy absorbed %%%%%%%%%%%
sigma=fwhm/(8*log(2))^0.5;
stage=1
dt=dt
%%% in time %%%
Q1(1)=0;
for j=1:Nmemory
    Q1(j+1)=exp(-0.5*((j-1)*dt-tshift)/sigma^2);
end;

% Q1(1)=0;

% Q1(j+1)=exp(-0.5*((j-1)*dt-tshift)/sigma^2);
% end;
%-----increasing step-----
%dtex=dt;
%dt=1000*dt;
% for j=tbreak+1:Nt-1
%     Q1(j+1)=exp(-0.5*((tbreak-1)*dtex+(j-1-(tbreak-1))*dt-tshift)/sigma^2)
% end;
Q1=Q1';

%%% in space %%%
for k=1:Nz
    if k<=kd
        Q2(k)=exp(-alfa*(k-1)*dz);
    else
        Q2(k)=0;
    end
end

,

%%% in time and space %%%

Q=I0*alfa*Q1*Q2;

size(Q1)
size(Q2)
size(Q)
clear Q1;
clear Q2;

%%%%%%%%%% calculating the temperature using DuFort Frankel method %%%%%%%%%%%
%%%NOTE: gama & delta & D must be changed if variable grid is used
gama=dz/(dz+dz);
delta=(dz+dz)/2;

```

```

for k=1:Nz
    T(1,k)=T0;
    T(2,k)=T0;
    Tdownsh(k)=T0;
    Tupsh(k)=T0;
end;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%-----decreasing step-----
%dt=dt/1000;
jmin=2;
jmax=Nmemory;

t(1)=dt;
t(2)=2*dt;

stage=2
dt=dt

[t,T]=calTuseQ(jmin,jmax,dt,dz,Nz,kd,ro,TNb,cNb,kNb,nNb,TQ,cQ,kQ,nQ,T,Q);

jmax=Nmemory;
for j=1:jmax
    if j<=tbreak/6
        if rem(j,10)==0
            jj=j/10;
            for k=1:Nz
                TT(jj,k)=T(j,k);
            end
            tt(jj)=t(j);
        end;
        jjex=jj;
    elseif rem(round(j-tbreak/6),100)==0
        jj=(j-tbreak/6)/(100)+jjex;
        for k=1:Nz
            TT(jj,k)=T(j,k);
        end
        tt(jj)=t(j);
    end
    , jjex1=jj;
end

%----- end of saving reduced number of points for plotting -----

clear Q;

stage=3
dt=dt

Tnext(1,:)=T(Nmemory,:);
Tnext(2,:)=T(Nmemory+1,:);

size(T)
clear T;

size(TT)
size(tt)

fflag=0

T(1,:)=Tnext(1,:);
T(2,:)=Tnext(2,:);
clear Tnext

```

```

stage=4
dt=dt

calTmacro;

stage=5
dt=dt

fflag=1

%-----decreasing step-----
dt=dt*1e-3
for j=Nmemory+1:tbreak
    t(j)=j*dt;
end;

stage=6
dt=dt

%-----increasing step-----
dtex=t(j)
dt=100*dt
for j=(tbreak+1):Nt-1000
    t(j)=dtex+(j-tbreak)*dt;
end;
dtex=t(j)
dt=10*dt
for j=Nt-1000+1:Nt
    t(j)=dtex+(j-(Nt-1000))*dt;
end;

t=t';

stage=7
dt=dt

fflag=2

size(Tupsh)
size(Tdownsh)

clear Tupsh;
clear Tdownsh;

stage=8
dt=dt

%%%%%%%%%% calculating space coordinat for plotting %%%%%%%%%%%
for k=1:Nz
    z(k)=k*dz;
end;

%----- saving reduced number of points for plotting for j=Nmemory+1:Nt
jj=jjex1
for j=Nmemory+1:Nt
    if j<=tbreak,
        if rem(round(tbreak-j),100)==0
            jj=jj+1;
            for k=1:Nz
                TT(jj,k)=T(j-Nmemory+1,k);
            end;
        end;
    end;
end;

```

```

        end;
        tt(jj)=t(j);
    end;
    jjex2=jj;
else
    if rem(round(j-tbreak),10)==0
        jj=jj+1;
        for k=1:Nz
            TT(jj,k)=T(j-Nmemory+1,k);
        end;
        tt(jj)=t(j);
    end;
end;

end;

end;

I=jj;
stage=9
dt=dt

fflag=3

clear T;
%%%%%%%%%% selecting evry 2nd point in time %%%%%%%%%%%

ii=0;
for i=1:I
    if rem(round(i),2)==0
        ii=ii+1;
        TTT(ii,:)=TT(i,:);
        ttt(ii)=tt(i);
    end;
end;

I=ii;
ii=0;
for i=1:I
    if rem(round(i),2)==0
        ii=ii+1;
        TTTT(ii,:)=TTT(i,:);
        tttt(ii)=ttt(i);
    end;
end;

I=ii;
ii=0;
for i=1:I
    if rem(round(i),2)==0
        ii=ii+1;
        TTTTT(ii,:)=TTTT(i,:);
        ttttt(ii)=tttt(i);
    end;
end;

%%%%%%%%%% plotting temperature %%%%%%%%%%%

mesh(z,ttttt,TTTTT);
stdt=num2str(dt);
stNt=num2str(Nt);
st6=['dt=',stdt,'s  Nt=',stNt];
text(1e-8,0,220,st6);
stdz=num2str(dz);

```

```

stNz=num2str(Nz);
st7=['dz=',stdz,'m  Nz=',stNz];
text(1e-8,0,200,st7);
stro=num2str(ro);
st8=['ro=',stro,' m2K/W'];
text(1e-8,0,180,st8);
stT0=num2str(T0);
st9=['T0=',stT0,' K'];
text(1e-8,0,240,st9);

set(gca,'xlabel',text(0,0,'Distance (m)'));
set(gca,'ylabel',text(0,0,'Time (s)'));
set(gca,'zlabel',text(0,0,'Temperature (K)'));
print v3_5_9_10ex;
printpz;

mesh(z,ttttt,TTTTT);
view(30,30);
stdt=num2str(dt);
stNt=num2str(Nt);
st6=['dt=',stdt,'s  Nt=',stNt];
text(10e-8,0,200,st6);
stdz=num2str(dz);
stNz=num2str(Nz);
st7=['dz=',stdz,'m  Nz=',stNz];
text(10e-8,0,180,st7);
stro=num2str(ro);
st8=['ro=',stro,' m2K/W'];
text(10e-8,0,160,st8);
stT0=num2str(T0);
st9=['T0=',stT0,' K'];
text(10e-8,0,220,st9);
set(gca,'xlabel',text(0,0,'Distance (m)'));
set(gca,'ylabel',text(0,0,'Time (s)'));
set(gca,'zlabel',text(0,0,'Temperature (K)'));
print v3030_5_9_10ex;
printpz;

mesh(z,ttttt,TTTTT);
view(90,0);
stdt=num2str(dt);
stNt=num2str(Nt);
st6=['dt=',stdt,'s  Nt=',stNt];
text(1e-8,10e-11,190,st6);
stdz=num2str(dz);
stNz=num2str(Nz);
st7=['dz=',stdz,'m  Nz=',stNz];
text(1e-8,10e-11,170,st7);
stro=num2str(ro);
st8=['ro=',stro,' m2K/W'];
text(1e-8,10e-11,150,st8);
stT0=num2str(T0);
st9=['T0=',stT0,' K'];
text(1e-8,10e-11,210,st9);
set(gca,'xlabel',text(0,0,'Distance (m)'));
set(gca,'ylabel',text(0,0,'Time (s)'));
set(gca,'zlabel',text(0,0,'Temperature (K)'));
print v900_5_9_10ex;
printpz;

%%%%%%%%%% clearing all variables %%%%%%%%%%%
end;

```

```

%file: calTmacro.m
%calT(jmin,jmax,dt,dz,Nz,kd,ro,TNb,cNb,kNb,nNb,TQ,cQ,kQ,nQ,Nmemory,T)
%calculating temperature for a range of time from jmin*dt to jmax*dt

jmin=2;
jmax=tbreak-Nmemory;
[A1,B1]=coeffAB(dt,dz,cNb,kNb);
[C1]=coeffC(dt,dz,cNb,kNb);
[A2,B2]=coeffAB(dt,dz,cQ,kQ);
[C2]=coeffC(dt,dz,cQ,kQ);

for i=1:3

    for j=jmin:jmax
        for k=2:Nz-1
            Tdownsh(k)=T(j,k-1);
            Tupsh(k)=T(j,k+1);
        end;
        Tdownsh(1)=Tdownsh(2);
        Tdownsh(Nz)=Tdownsh(Nz-1);
        Tupsh(1)=Tupsh(2);
        Tupsh(Nz)=Tupsh(Nz-1);
        if kd<Nz,
            for k=1:kd-1
                for n=1:nNb-1
                    if TNb(n)<=T(j,k)<TNb(n+1)
                        T(j+1,k)=A1(n)*T(j-1,k)+B1(n)*Tupsh(k)+C1(n)*Tdownsh(k);
                    end
                end
            end;
            for k=kd+2:Nz
                for n=1:nQ-1
                    if TQ(n)<=T(j,k)<TQ(n+1)
                        T(j+1,k)=A2(n)*T(j-1,k)+B2(n)*Tupsh(k)+C2(n)*Tdownsh(k);
                    end
                end
            end;

            %/////at the interface/////
            for k=kd:kd+1
                for n=1:nQ-1
                    if TQ(n)<=T(j,k)<TQ(n+1)
                        kk2=kQ(n);
                    end
                end
                for n=1:nNb-1
                    if TNb(n)<=T(j,k)<TNb(n+1)
                        kk1=kNb;
                    end
                end
                din=kk1*kk2+dz*(kk1+kk2)/ro;
                if k==kd
                    T(j+1,kd)=(T(j+1,kd+2)*kk2*dz/ro+T(j+1,kd-1)*kk1*(kk2+dz/ro))/din;
                else
                    T(j+1,kd+1)=(T(j+1,kd+2)*kk2*(kk1+dz/ro)+T(j+1,kd-1)*kk1*dz/ro)/din;
                end
            end;
            %/////end of interface/////

```

```

else
    for k=1:kd
        for n=1:nNb-1
            if TNb(n) <= T(j,k) < TNb(n+1)
                T(j+1,k) = A1(n) * T(j-1,k) + B1(n) * Tupsh(k) + C1(n) * Tdownsh(k);
            end
        end
    end;
end;
end;
if i==1
    dt=100*dt
    [A1,B1]=coeffAB(dt,dz,cNb,kNb);
    [C1]=coeffC(dt,dz,cNb,kNb);
    [A2,B2]=coeffAB(dt,dz,cQ,kQ);
    [C2]=coeffC(dt,dz,cQ,kQ);
    jmin=tbreak-Nmemory+1;
    jmax=Nt-1000-Nmemory;
elseif i==2
    dt=10*dt
    [A1,B1]=coeffAB(dt,dz,cNb,kNb);
    [C1]=coeffC(dt,dz,cNb,kNb);
    [A2,B2]=coeffAB(dt,dz,cQ,kQ);
    [C2]=coeffC(dt,dz,cQ,kQ);
    jmin=Nt-1000-Nmemory+1;
    jmax=Nt-Nmemory;
end;
end;

```

```

function [t,T]=calTuseQ(jmin,jmax,dt,dz,Nz,kd,ro,TNb,cNb,kNb,nNb,TQ,cQ,kQ,nQ,T,Q
%calculating temperature for a range of time from jmin*dt to jmax*dt

[A1,B1]=coeffAB(dt,dz,cNb,kNb);
[C1]=coeffC(dt,dz,cNb,kNb);
[D1]=coeffD(dt,dz,cNb,kNb);
[A2,B2]=coeffAB(dt,dz,cQ,kQ);
[C2]=coeffC(dt,dz,cQ,kQ);

for j=jmin:jmax
    t(j+1)=(j+1)*dt;
    for k=2:Nz-1
        Tdownsh(k)=T(j,k-1);
        Tupsh(k)=T(j,k+1);
    end;
    Tdownsh(1)=Tdownsh(2);
    Tdownsh(Nz)=Tdownsh(Nz-1);
    Tupsh(1)=Tupsh(2);
    Tupsh(Nz)=Tupsh(Nz-1);
    if kd<Nz,
        for k=1:kd-1
            for n=1:nNb-1
                if TNb(n)<=T(j,k)<TNb(n+1)
                    T(j+1,k)=A1(n)*T(j-1,k)+B1(n)*Tupsh(k)+C1(n)*Tdownsh(k)+D1(n)*Q(j+1,k);
                end
            end
        end;
        for k=kd+2:Nz
            for n=1:nQ-1
                if TQ(n)<=T(j,k)<TQ(n+1)
                    T(j+1,k)=A2(n)*T(j-1,k)+B2(n)*Tupsh(k)+C2(n)*Tdownsh(k);
                end
            end
        end;
        %/////at the interface/////
        for k=kd:kd+1
            for n=1:nQ-1
                if TQ(n)<=T(j,k)<TQ(n+1)
                    kk2=kQ(n);
                end
            end
            for n=1:nNb-1
                if TNb(n)<=T(j,k)<TNb(n+1)
                    kk1=kNb;
                end
            end
            din=kk1*kk2+dz*(kk1+kk2)/ro;
            if k==kd
                T(j+1,kd)=(T(j+1,kd+2)*kk2*dz/ro+T(j+1,kd-1)*kk1*(kk2+dz/ro))/din;
            else
                T(j+1,kd+1)=(T(j+1,kd+2)*kk2*(kk1+dz/ro)+T(j+1,kd-1)*kk1*dz/ro)/din;
            end
        end;
        %/////end of interface/////
    else
        for k=1:kd
            for n=1:nNb-1

```

```

        if TNb(n) <= T(j,k) < TNb(n+1)
            T(j+1,k) = A1(n)*T(j-1,k) + B1(n)*Tupsh(k) + C1(n)*Tdownsh(k) + D1(n)*Q(j+1,k);
        end
    end
end;
end;
end;

```

```

function [A,B] = coeffAB(dt,dz,c,kk)
%calculating the coefficients for DuFort-Frankel method
%
%
gama=dz/(dz+dz);
delta=(dz+dz)/2;
omeg=kk*dt./(2*c*gama*(1-gama)*delta^2);
A=(1-omeg)./(1+omeg);
B=2*omeg./(1+omeg)*gama;

```

```

function [C] = coeff(dt,dz,c,kk)
%calculating the coefficient for DuFort-Frankel method
%
%
gama=dz/(dz+dz);
delta=(dz+dz)/2;
omeg=kk*dt./(2*c*gama*(1-gama)*delta^2);
C=2*omeg./(1+omeg)*(1-gama);

```

```

function [D] = coeffD(dt,dz,c,kk)
%calculating the coefficient next to source for DuFort-Frankel method for absorb
%
%
gama=dz/(dz+dz);
delta=(dz+dz)/2;
omeg=kk*dt./(2*c*gama*(1-gama)*delta^2);
D=2*dt./(c+2*kk*dt/(dz*dz));

```

A.3. Simplified Heat Diffusion Model

For the sake of better physical insight, we attempt to make a simple mathematical model of the following process that takes place in the metal film. Part of the laser pulse energy is absorbed by the thin metal film. This energy rises the temperature of the metal film and is subsequently transferred to the substrate. The transport of heat through this layer can be described by Eq. A.3.1, which is a standard heat diffusion equation, and Eq. A.3.2 that describes conservation of thermal flux at the interface. The temperature as a function of time and depth is given by

$$C_i \frac{\partial \Theta(x, t)}{\partial t} = k_i \frac{\partial^2 \Theta(x, t)}{\partial x^2} + \alpha_i I_0 \exp(-\alpha_i x) \exp\left(-\frac{1}{2} \left(\frac{t - t_0}{\sigma}\right)^2\right), \quad i = 1, 2 \quad (\text{A.3.1})$$

where $i=1$ stands for the upper layer (Nb film) and $i=2$ stands for the lower layer (quartz substrate). Here Θ denotes the change in temperature as a function of depth, x , and time, t . k_i is heat conductivity, C_i is heat capacity, α_i is the absorption coefficient and I_0 is the amplitude of the input laser intensity (assumed Gaussian). The heat conductivity, k_i , and the heat capacity, C_i , are temperature dependent. The boundary condition at the interface, representing the conservation of thermal flux, is

$$-\kappa_1 \frac{\partial \Theta(d^-, t)}{\partial x} = \frac{\Theta(d^-, t) - \Theta(d^+, t)}{\rho} = -\kappa_2 \frac{\partial \Theta(d^+, t)}{\partial x} \quad (\text{A.3.2})$$

where ρ is the interfacial thermal impedance. There are two additional boundary conditions; for the surface and sufficiently deep in the underlayer. They represent the assumption that the heat flow is negligible both out of the surface and deep in the underlayer;

$$\frac{\partial \Theta(x, t)}{\partial x} \Big|_{x=0} = 0 \quad (\text{A.3.3})$$

and

$$\frac{\partial \Theta(x, t)}{\partial x} \Big|_{x=x_{max}} = 0. \quad (\text{A.3.4})$$

The boundary conditions A.3.3 at the surface holds because the sample is in vacuum. For boundary condition A.3.4, sufficiently deep in the underlayer means that for the duration of our measurements (250 ps) some points, sufficiently deep in the underlayer, have not been heated yet. For quartz, $x=0.2 \mu\text{m}$ is sufficiently deep.

Lets consider a simplified model by introducing the following approximations;

(i) the parameters k_i and C_i are assumed temperature independent, thus making the diffusivity, D_i constant.

(ii) The source term (Gaussian heating pulse, 100 fs duration) may be neglected since the diffusion process. which takes -1 ns. Instead, initial and boundary conditions should be adjusted to reflect the situation after the heating pulse has been absorbed.

(iii) The conservation of thermal flux at the interface (described by Eq. A.3.2) is assumed to result in boundary conditions at the interface being represented with some function $B_i(t)$.

Then, having in mind the boundary conditions at the front surface of Nb and at the back surface of quartz specified by Equations A.3.3 and A.3.4 the diffusion Equations is substituted by

$$C_i \frac{\partial \Theta_i(x, t)}{\partial t} = k_i \frac{\partial^2 \Theta_i(x, t)}{\partial x^2}, \quad i = 1, 2 \quad (\text{A.3.5})$$

where $i=1$ stands for the upper layer (Nb film) and $i=2$ stands for the lower layer (quartz substrate). Now, the temperature distributions $\Theta_1(x, t)$ for the Nb film and $\Theta_2(x, t)$ for the quartz substrate may be solved in a closed form. Fig. shows the one dimensional model for (a) niobium, and (b) quartz together with the assumed initial and boundary conditions.

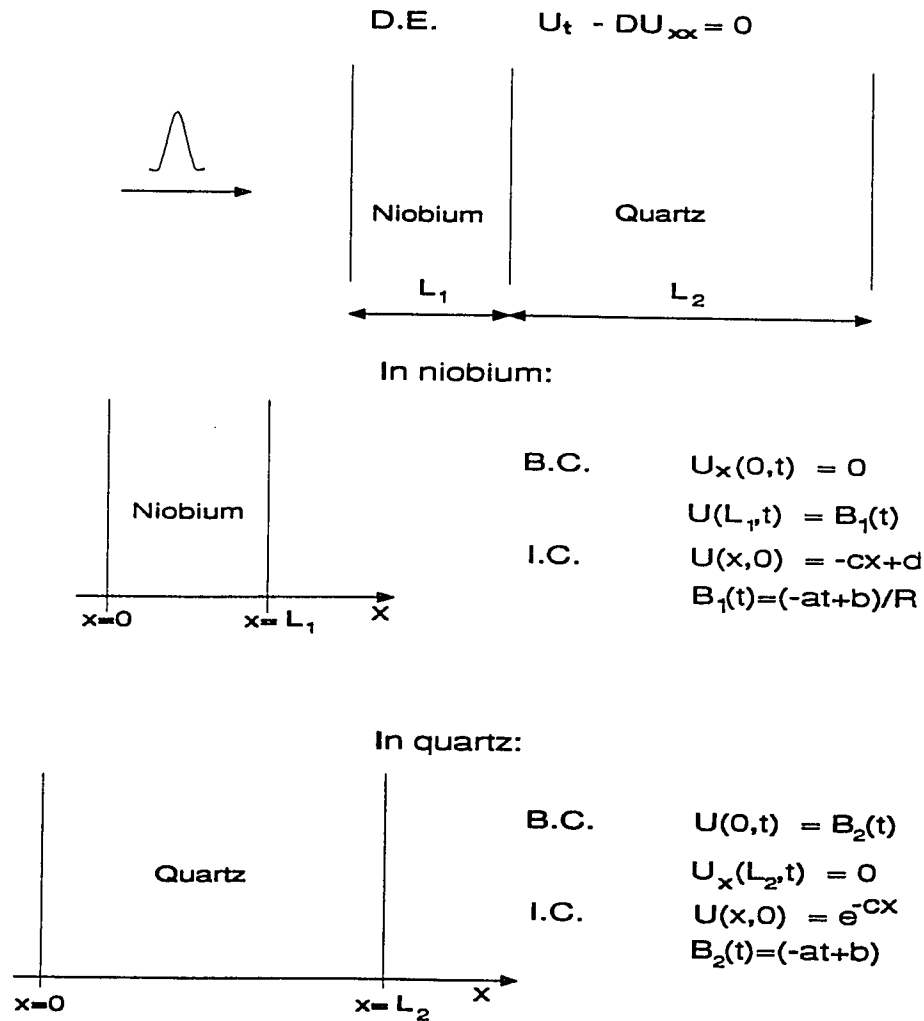


Figure A.3.1 The simplified diffusion model for the experiment describes in ch. VI; the one dimensional model for (a) niobium, and (b) quartz together with the assumed initial and boundary conditions.

A.3.1. Solution for Niobium

The differential equation and the initial and boundary conditions are:

$$\begin{aligned}
D.E. : \quad & \Theta_{1t}(x, t) - D_1 \Theta_{1xx}(x, t) = 0 \\
B.C.1 : \quad & \Theta_{1x}(0, t) = 0 \\
B.C.2 : \quad & \Theta_1(L_1, t) = B_1(t)
\end{aligned} \tag{A.3.6}$$

$$I.C. : \quad \Theta_1(x, 0) = -cx + d$$

where $D_1 = \frac{\kappa_1}{C_1}$ is the niobium diffusivity and L_1 is the niobium thickness. The above equation is solved by separation of variables. Before separating the variables, let's transform this equation into a diffusion equation with homogeneous boundary conditions by introducing the substitution

$$V(x, t) = \Theta(x, t) - K(x, t). \tag{A.3.7}$$

The problem that has to be solved now is

$$\begin{aligned}
D.E. : \quad & V_{1,t}(x, t) - D_1 V_{1xx}(x, t) = -K_{1t} - D_1 K_{1xx} = q_1(x) \\
B.C.1 : \quad & V_{1x}(0, t) = -K_{1x}(0, t) = 0 \\
B.C.2 : \quad & V_1(L_1, t) = B_1(t) - K_1(L_1, t) = 0 \\
I.C. : \quad & \Theta_1(x, 0) = -cx + d - K_1(x, 0) = f_1(x)
\end{aligned} \tag{A.3.8}$$

We assume $B_1(t) = -at + b$ and proceed to make the boundary conditions

$$\begin{aligned}
B.C.1 : \quad & K_1(x, t) = c_1(t) \\
B.C.2 : \quad & K_1(L_1, t) = B_1(t) = -at + b
\end{aligned} \tag{A.3.9}$$

homogeneous. Since

$$K_1(L_1, t) = c_1(t) \tag{A.3.10}$$

we have

$$K_1(x, t) = -at + b$$

$$K_{1t}(x, t) = -a \quad (\text{A.3.11})$$

$$K_{1xx}(x, t) = 0$$

and

$$q_1(x) = a \quad (\text{A.3.12})$$

$$f_1(x) = -cx + d - b.$$

Now we proceed with separation of variables. Assuming $V_1(x, t) = F(x)G(t)$ we solve the diffusion equation;

$$G_t F = D_1 G F_{xx} \quad (\text{A.3.13})$$

$$\frac{G_t}{D_1 G} = \frac{F_{xx}}{F} = -\lambda.$$

The solution for the space dependent part, $F(x)$ is

$$F = A \cos(\sqrt{\lambda}x) + \frac{B}{\sqrt{\lambda}} \sin(\sqrt{\lambda}x). \quad (\text{A.3.14})$$

From the boundary conditions, we have

$$F_x(0) = 0 \Rightarrow B = 0$$

$$F(L_1) = 0 \Rightarrow A \cos(\sqrt{\lambda}L_1) = 0 \Rightarrow \lambda_n = \left[\frac{(2n+1)\pi}{L_1} \right]^2 \quad n = 0, 1, \dots \quad (\text{A.3.15})$$

The solution for the space time part, $G(t)$ is

$$G_t + D_1 \lambda_n G_n = 0$$

$$G_n(t) = c_n e^{-D_1 \lambda_n t}$$

$$v_n(x, t) = F_n(x)G_n(t) = c_n A e^{-D_1 \lambda_n t} \cos(\sqrt{\lambda_n}x) \quad (\text{A.3.16})$$

$$V_1(x, t) = \sum_{n=0}^{\infty} v_n(x, t) = \sum_{n=0}^{\infty} C_{1n} e^{-D_1 \lambda_{1n} t} \cos(\sqrt{\lambda_{1n}}x)$$

where $C_{1n} = Ac_n$ and the index 1 stands for niobium. Applying initial conditions,

$$V(x, 0) = f(x) = \sum_{n=0}^{\infty} C_n \cos(\sqrt{\lambda_n} x) \quad (\text{A.3.17})$$

we get

$$C_n = \frac{2}{L_1} \int_0^{L_1} f(x) \cos(\sqrt{\lambda_n} x) dx$$

$$C_n = \frac{2}{L_1} \int_0^{L_1} (-cx + d - b) \cos\left(\frac{(2n+1)\pi}{L_1} x\right) dx. \quad (\text{A.3.18})$$

Now, having in mind the substitution A.3.7 we get for $\Theta_1(x, t)$

$$\Theta_1(x, t) = K_1(x, t) + V_1(x, t)$$

$$\Theta_1(x, t) = B(t) + \sum_{n=0}^{\infty} C_n e^{-D\lambda_n t} \cos(\sqrt{\lambda_n} x)$$

$$\Theta_1(x, t) = -at + b + \sum_{n=0}^{\infty} \left[\frac{2}{L_1} \int_0^{L_1} (-cx + d - b) \cos\left(\frac{(2n+1)\pi}{L_1} x\right) dx \right] e^{-D\left[\frac{(2n+1)\pi}{L_1}\right]^2 t} \cos\left(\frac{(2n+1)\pi}{L_1} x\right). \quad (\text{A.3.19})$$

A.3.2. Solution for Quartz

The differential equation and the initial and boundary conditions are:

$$D.E. : \quad \Theta_{2t}(x, t) - D_2 \Theta_{2xx}(x, t) = 0$$

$$B.C.1 : \quad \Theta_2(0, t) = B_2(t)$$

$$B.C.2 : \quad \Theta_{2x}(L_2, t) = 0$$

$$I.C. : \quad \Theta_2(x, 0) = e^{-cx} \quad (\text{A.3.20})$$

where $D_2 = \frac{\kappa_2}{C_2}$ is the quartz diffusivity and L_2 is the quartz thickness. The above equation is solved by separation of variables. Just like in case of the niobium film, before separating the variables, we have to transform this equation into a diffusion equation with homogeneous boundary conditions by introducing the substitution

$$V(x, t) = \Theta(x, t) - K(x, t). \quad (\text{A.3.21})$$

The problem that has to be solved now is

$$\begin{aligned} D.E. : \quad & V_{2,t}(x, t) - D_2 V_{2,xx}(x, t) = -K_{2,t} - D_2 K_{2,xx} = q_2(x) \\ B.C.1 : \quad & V_2(0, t) = B_2(t) - K_2(0, t) = 0 \\ B.C.2 : \quad & V_{2x}(L_2, t) = -K_{2x}(L_2, t) = 0 \end{aligned} \quad (\text{A.3.22})$$

$$I.C. : \quad \Theta_2(x, 0) = e^{-cx} - K_2(x, 0) = f_2(x)$$

We assume $B_2(t) = (-at + b)/R$, where R accounts for the interface resistance. Now, using the same approach as before for niobium film, we solve for the quartz substrate by making the boundary conditions homogeneous and then solving by the method of separation of variables. The obtained solution for the quartz substrate is

$$\begin{aligned} \Theta_2(x, t) &= B_2(t) + \sum_{n=0}^{\infty} C_{2n} e^{-D_2 \lambda_{2n}^2 t} \cos(\sqrt{\lambda_{2n}} x) \\ \Theta_2(x, t) &= (-at + b)/R + \sum_{n=0}^{\infty} \left[\frac{2}{L_2} \int_0^{L_2} (e^{-cx} - b/R) \sin\left(\frac{(2n+1)\pi}{L_2} x\right) dx \right] \\ &\quad e^{-D_2 \left[\frac{(2n+1)\pi}{L_2}\right]^2 t} \sin\left(\frac{(2n+1)\pi}{L_2} x\right). \end{aligned} \quad (\text{A.3.23})$$

where $\lambda_n = \left[\frac{(2n+1)\pi}{L_2}\right]^2$.

Bibliography

- [1] J. H. Ferziger, *Numerical Methods For Engineering Applications*. John Wiley & Sons, 1981.
- [2] R. C. Weast and D. R. Lide, *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida, 1989.
- [3] Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Matter*. IFI/Plenum, New York, 1970.

Thesis Bibliography

1. Bibliography-Ch. I

- [1] R. Yen, J. M. Liu, and N. Bloembergen *Opt. Commun.* **35**, p. 277, 1980.
- [2] M. B. Agranat, A. A. Benditskii, and G. M. Gandelman *Zh. Eksp. Theor. Fiz.* **79**, p. 55, 1980.
- [3] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen *Phys. Rev. Lett.* **53**, p. 1837, 1984.
- [4] S. I. Anisimov, V. A. Bendetskii, and G. Farkas *Sov. Phys. —Usp.* **20**, p. 467, 1977.
- [5] C. Chi, M. T. Loy, and D. Cronmeyer *Phys. Rev. B* **23**, p. 124, 1981.
- [6] S. D. Brorson, J. G. Fujimoto, and E. P. Ippen *Phys. Rev. Lett.* **59**, p. 1962, 1987.
- [7] G. L. Eesley, B. M. Clemens, and C. A. Paddock *Appl. Phys. Lett.* **50**, p. 717, 1987.
- [8] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus *Phys. Rev. Lett.* **64**, p. 2172, 1990.
- [9] K. E. Gray, *Superconductive Particle Detectors*. World Scientific, Singapore, 1988.
- [10] K. E. Gray *J. Phys. F* **1**, p. 290, 1971.
- [11] J. G. Fujimoto, S. D. Silversti, E. P. Ippen, R. Margolis, and A. Oseroff *Opt. Lett.* **11**, p. 150, 1986.
- [12] K. M. Yoo, F. Liu, and R. R. Alfano *Opt. Lett.* **16**, p. 1068, 1991.
- [13] B. M. Clemens, G. L. Eesley, and C. A. Paddock *Phys. Rev. B* **37**, p. 1085, 1988.
- [14] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano *Opt. Lett.* **13**, p. 987, 1988.
- [15] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.

2. Bibliography-Ch. II

- [1] G. Grimvall, *Thermophysical Properties of Materials*. North-Holland, Amsterdam, 1986.
- [2] G. Grimvall, *The Electron-Phonon Interaction in Metals*. North-Holland, Amsterdam, 1981.
- [3] W. L. McMillan *Phys. Rev.* **167**, p. 331, 1968.
- [4] C. Kittel, *Introduction To Solid State Physics*. John Wiley, New York, 1986.
- [5] H. Thirring *Phys. Zeitschrift* **14**, p. 867, 1913.
- [6] G. M. Éliashberg *Sov. Phys. — JETP* **16**, p. 780, 1963.
- [7] G. Grimvall *Phys. Stat. Sol.* **32**, p. 383, 1969.
- [8] G. Grimvall *Phys. Kondens. Materie* **9**, p. 283, 1969.
- [9] D. C. Wallace, *Thermodynamics of Crystals*. John Wiley, New York, 1972.

3. Bibliography-Ch. III

- [1] W. J. Scouler *Phys. Rev. Lett.* **18**, p. 455, 1967.
- [2] R. Rosei and D. W. Lynch *Phys. Rev. B* **5**, p. 3883, 1972.
- [3] N. E. Christensen and B. O. Seraphin *Phys. Rev. B* **4**, p. 3321, 1971.
- [4] G. P. Pella and M. Shiga *J. Phys. C* **2**, p. 1835, 1969.
- [5] S. D. Brorson, J. G. Fujimoto, and E. P. Ippen *Phys. Rev. Lett.* **59**, p. 1962, 1987.
- [6] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus *Phys. Rev. Lett.* **64**, p. 2172, 1990.
- [7] K. M. Yoo, X. M. Zhao, M. Siddique, R. R. Alfano, D. P. Osterman, M. Radparvan, and J. Cunniff *Appl. Phys. Lett.* **56**, p. 1908, 1990.
- [8] G. L. Eesley *Phys. Rev. B* **33**, p. 2144, 1986.
- [9] S. I. Anisimov, B. L. Kapelovich, and T. L. Perel'man *Zh. Eksp. Theor. Fiz.* **66**, p. 776, 1974.
- [10] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen *Phys. Rev. Lett.* **53**, p. 1837, 1984.
- [11] M. Cordona, *Modulation Spectroscopy*. Academic, New York, 1969.
- [12] C. Kittel, *Quantum Theory of Solids*. John Wiley, New York, 1963.
- [13] A. Miklós, Z. Bozókl, and A. Lörincz *J. Appl. Phys.* **66**, p. 2968, 1989.
- [14] C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc *Opt. Commun.* **60**, p. 55, 1986.
- [15] M. I. Kaganov, I. M. Lifshitz, and L. V. Tanatarov *Sov. Phys. JETP* **4**, p. 173, 1957.
- [16] G. L. Eesley, B. M. Clemens, and C. A. Paddock *Appl. Phys. Lett.* **50**, p. 717, 1987.
- [17] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.

- [18]H. E. Elsayed-Ali, T. B. Norris, M. A. Pessot, and G. A. Mourou *Phys. Rev. Lett.* **58**, p. 1212, 1987.
- [19]R. W. Schoenlein, W. Z. Lin, J. G. Fujimoto, and G. L. Eesley *Phys. Rev. Lett.* **58**, p. 1680, 1987.
- [20]M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [21]M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.
- [22]G. L. Eesley *Phys. Rev. Lett.* **51**, p. 2140, 1986.
- [23]G. M. Éliashberg *Sov. Phys. — JETP* **16**, p. 780, 1963.
- [24]J. H. Bechtel *J. Appl. Phys.* **46**, p. 1585, 1975.
- [25]C. A. Paddock and G. L. Eesley *J. Appl. Phys.* **60**, p. 285, 1986.
- [26]J. Opsal, A. Rosencwaig, and D. L. Willenborg *Appl. Opt.* **22**, p. 3169, 1983.
- [27]A. Rosencwaig, J. Opsal, W. L. Smith, and D. L. Willenborg *Appl. Phys. Lett.* **46**, p. 1013, 1985.
- [28]B. M. Clemens, G. L. Eesley, and C. A. Paddock *Phys. Rev. B* **37**, p. 1085, 1988.

4. Bibliography-Ch. IV

- [1] G. L. Eesley *Phys. Rev. B.* **33**, p. 2144, 1986.
- [2] S. D. Brorson, J. G. Fujimoto, and E. P. Ippen *Phys. Rev. Lett.* **59**, p. 1962, 1987.
- [3] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus *Phys. Rev. Lett.* **64**, p. 2172, 1990.
- [4] K. M. Yoo, X. M. Zhao, M. Siddique, R. R. Alfano, D. P. Osterman, M. Radparvan, and J. Cuniff *Appl. Phys. Lett.* **56**, p. 1908, 1990.
- [5] M. Mihailidi and R. R. Alfano *Appl. Phys. Lett.* (accepted for publication), 1994.
- [6] M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [7] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano *Opt. Lett.* **13**, p.987, 1988.
- [8] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano, *Ultrafast Phenomena VI*, vol. 48 of *Springer Series in Chemical Physics*. Springer-Verlag, Berlin, Heidelberg, 1988.
- [9] J. C. Diels, J. J. Fontaine, I. C. McMichael, B. Wilhelmi, W. Dietel, and D. Kuhlke *Sov. J. Quantum Electron.* **QE-13**, p. 12, 1983.
- [10] J. A. Valdmanis and R. L. F. nad J. P. Gordon *Opt. Lett.* **10**, p. 3, 1986.
- [11] P. B. Corkum, F. Brunel, and N. K. Sherman *Phys. Rev. Lett.* **61**, p. 2886, 1988.
- [12] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen *Phys. Rev. Lett.* **53**, p. 1837, 1984.

- [13]S. I. Asimov, B. L. Kopeliovich, and T. L. Perelman *Sov. Phys. JETP* **39**, p. 375, 1974.
- [14]R. H. M. Groeneveld, R. Sprik, and A. Lagendijk *Phys. Rev. B Rapid Comm.* **45**, p. 5079, 1992.
- [15]M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.

5. Bibliography-Ch. V

- [1] J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen *Phys. Rev. Lett.* **53**, p. 1837, 1984.
- [2] H. E. Elsayed-Ali, T. B. Norris, M. A. Pessot, and G. A. Mourou *Phys. Rev. Lett.* **58**, p. 1212, 1987.
- [3] R. W. Schoenlein, W. Z. Lin, J. G. Fujimoto, and G. L. Eesley *Phys. Rev. Lett.* **58**, p. 1680, 1987.
- [4] P. B. Allen, *Dynamic Processes in Solids*, Vol. 3, p. 95. North-Holland, Amsterdam, 1980.
- [5] W. L. McMillan *Phys. Rev.* **167**, p. 331, 1968.
- [6] G. D. Gaspari and B. L. Gyorffy *Phys. Rev. Lett.* **29**, p. 801, 1972.
- [7] F. S. Khan, P. B. Allen, W. H. Butler, and F. J. Pinski *Phys. Rev. B* **26**, p. 1538, 1982.
- [8] P. B. Allen *Phys. Rev. B* **36**, p. 2920, 1987.
- [9] R. H. M. Groeneveld, R. Sprik, and A. Lagendijk *Phys. Rev. B Rapid Comm.* **45**, p. 5079, 1992.
- [10] T. Juhasz, H. E. Elsayed-Ali, X. H. Hu, and W. E. Bron *Phys. Rev. B* **45**, p. 13819, 1992.
- [11] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.
- [12] G. L. Eesley, B. M. Clemens, and C. A. Paddock *Appl. Phys. Lett.* **50**, p. 717, 1987.
- [13] K. M. Yoo, X. M. Zhao, M. Siddique, R. R. Alfano, D. P. Osterman, M. Radparvan, and J. Cuniff *Appl. Phys. Lett.* **56**, p. 1908, 1990.

- [14]J. M. Ziman, *Electrons and Phonons*. Oxford University Press, London, 1960.
- [15]P. B. Allen *Phys. Rev. B* **6**, p. 2577, 1972.
- [16]W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor *Phys. Rev. Lett.* **68**, p. 2834, 1992.
- [17]G. B. Arnold, J. Zasadzinski, J. W. Osmun, and E. L. Wolf *J. Low Temp. Phys.* **40**, p. 225, 1980.
- [18]R. C. Weast and D. R. Lide, *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida, 1989.
- [19]M. Mihailidi and R. R. Alfano *Appl. Phys. Lett.* (accepted for publication), 1994.
- [20]M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [21]G. L. Eesley *Phys. Rev. Lett.* **51**, p. 2140, 1986.
- [22]G. Grimvall, *The Electron-Phonon Interaction in Metals*. North-Holland, Amsterdam, 1981.
- [23]M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.
- [24]M. Mihailidi and R. R. Alfano in *9th Interdisciplinary Laser Science Conference (ILS-IX)*, 1993.

6. Bibliography-Ch. VI

- [1] K. V. Mitsen, *Nonequilibrium Superconductivity*. Nova Science Publisher, 1986.
- [2] A. I. Golovashkin, K. V. Mitsen, and G. P. Motulevich in *The 18th All Union Conference in Low Temperature Physics* (Kiev, ed.), 1974.
- [3] A. I. Golovashkin, K. V. Mitsen, and G. P. Motulevich *ZhETF* **68**, p. 1408, 1975.
- [4] F. Elesin and Y. V. Kopaev *Sov. Phys. Usp.* **24**, p. 116, 1981.
- [5] F. Elesin *Sov. Phys. JETP* **46**, p. 185, 1977.
- [6] R. Janik, L. Morelli, and N. C. Cirillo *IEEE Trans. Magn.* **11**, p. 687, 1975.
- [7] G. L. Eesley *Phys. Rev. B.* **33**, p. 2144, 1986.
- [8] B. M. Clemens, G. L. Eesley, and C. A. Paddock *Phys. Rev. B* **37**, p. 1085, 1988.
- [9] C. A. Paddock and G. L. Eesley *J. Appl. Phys.* **60**, p. 285, 1986.
- [10] K. M. Yoo, X. M. Zhao, M. Siddique, R. R. Alfano, D. P. Osterman, M. Radparvan, and J. Cuniff *Appl. Phys. Lett.* **56**, p. 1908, 1990.
- [11] J. H. Ferziger, *Numerical Methods For Engineering Applications*. John Wiley & Sons, New York, 1981.
- [12] R. C. Weast and D. R. Lide, *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida, 1989.
- [13] Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Matter*. IFI/Plenum, New York, 1970.
- [14] S. B. Kaplan *Phys. Rev. B* **14**, p. 4854, 1976.
- [15] M. Tinkham and J. Clarke *Phys. Rev. Lett.* **28**, p. 1366, 1972.
- [16] L. R. Tesardi *Phys. Rev. B* **4**, p. 2159, 1971.

- [17]G. A. Sai-Halasz, C. C. Chi, A. Denestein, and D. Langenberg *Phys. Rev. Lett.* **33**, p. 215, 1974.
- [18]A. Rothwarf and B. N. Taylor *Phys. Rev. Lett.* **19**, p. 27, 1967.
- [19]M. Johnson *Phys. Rev. Lett.* **67**, p. 375, 1991.
- [20]M. Johnson *IEEE Trans. Magn.*, **27**, p. 1523, 1991.
- [21]W. H. Parker *Phys. Rev. B* **12**, p. 3667, 1975.
- [22]T. Gong, L. X. Zheng, X. Xiong, W. Kula, Y. Kostoulas, R. Sobolewski, and P. M. Fauchet *Phys. Rev. B* **47**, p. 14495, 1993.

7. Bibliography-Ch. VII

- [1] M. Lax, V. Nayaramamurti, and R. C. Fulton, "Classical diffusive photon transport in a slab," in *Proceedings of the Symposium on Laser Optics of Condensed Matter* (J. L. Birman, H. Z. Cummins, and A. A. Kopyanskii, eds.), pp. 229–235, Plenum, New York, 1987.
- [2] K. M. Yoo. PhD thesis, Graduate Center of CUNY, 1990.
- [3] F. Liu. PhD thesis, Graduate Center of CUNY, 1993.
- [4] H. C. van de Hulst, *Light Scattering by Small Particles*. Dover Publications, London, 1981. p. 127, 225, 292.
- [5] P. M. Saulnier, M. P. Zinkin, and G. H. Watson *Phys. Rev. B* **42**, p. 2621, 1990.
- [6] A. Ishimaru, *Wave Propagation and Scattering in Random Media*, vol. 1. Academic Press, New York, 1978.
- [7] G. H. Watson, S. L. McCall, P. A. Fleury, and K. B. Lyons *Phys. Rev. B* **41**, p. 10947, 1990.
- [8] M. Lax, *Symmetry Principles in Solid State and Molecular Physics*. John Wiley, New York, 1974.
- [9] K. M. Yoo, F. Liu, and R. R. Alfano *Phys. Rev. Lett.* **64**, p. 2647, 1990.
- [10] M. Lax, "Private correspondence," 1994.

8. Bibliography-Ch. VIII

- [1] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano *Opt. Lett.* **13**, p.987, 1988.
- [2] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano, *Ultrafast Phenomena VI*, vol. 48 of *Springer Series in Chemical Physics*. Springer-Verlag, Berlin, Heidelberg, 1988.
- [3] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.
- [4] M. Mihailidi and R. R. Alfano *Appl. Phys. Lett.* (accepted for publication), 1994.
- [5] M. Mihailidi and R. R. Alfano in *9th Interdisciplinary Laser Science Conference (ILS-IX)*, 1993.
- [6] M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [7] M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.
- [8] J. M. Ziman, *Electrons and Phonons*. Oxford University Press, London, 1960.
- [9] G. Grimvall, *The Electron-Phonon Interaction in Metals*. North-Holland, Amsterdam, 1981.
- [10] M. Mihailidi and R. R. Alfano *Phys. Rev. B (in review)*, 1994.

9. Bibliography-Ch. IX

- [1] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano *Opt. Lett.* **13**, p.987, 1988.
- [2] M. Mihailidi, Y. Budansky, X. M. Zhao, Y. Takiguchi, and R. R. Alfano, *Ultrafast Phenomena VI*, vol. 48 of *Springer Series in Chemical Physics*. Springer-Verlag, Berlin, Heidelberg, 1988.
- [3] P. B. Allen *Phys. Rev. Lett.* **59**, p. 1460, 1987.
- [4] M. Mihailidi and R. R. Alfano *Appl. Phys. Lett.* (accepted for publication), 1994.
- [5] M. Mihailidi and R. R. Alfano in *9th Interdisciplinary Laser Science Conference (ILS-IX)*, 1993.
- [6] M. Mihailidi and R. R. Alfano in *SPIE '92 Symposium on Advances in Semiconductors and Superconductors*, 1992.
- [7] M. Mihailidi, K. R. Xing, K. M. Yoo, and R. R. Alfano *Phys. Rev. B* **49**, 1994.
- [8] J. M. Ziman, *Electrons and Phonons*. Oxford University Press, London, 1960.
- [9] G. Grimvall, *The Electron-Phonon Interaction in Metals*. North-Holland, Amsterdam, 1981.
- [10] M. Mihailidi and R. R. Alfano *Phys. Rev. B (in review)*, 1994.

10. Bibliography-Appendix

- [1] J. H. Ferziger, *Numerical Methods For Engineering Applications*. John Wiley & Sons, New York, 1981.
- [2] R. C. Weast and D. R. Lide, *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida, 1989.
- [3] Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Matter*. IFI/Plenum, New York, 1970.