

Laser Spectroscopy of Solids II

Edited by W. M. Yen

With Contributions by

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With 144 Figures

Springer-Verlag Berlin Heidelberg New York
London Paris Tokyo

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ISBN 3-540-50154-1 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-50154-1 Springer-Verlag New York Berlin Heidelberg

Library of Congress Cataloging-in-Publication Data. – Laser spectroscopy of solids II. (Topics in applied physics; v. 65) Includes index. 1. Solids-Spectra. 2. Semiconductors-Spectra. 3. Laser spectroscopy. I. Yen, W. M. (William M.) II. Dlott, Dana Donald. III. Series. QC176.8.06L375 1989 530.4'1 88-24859

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Typesetting, printing and binding: Brühlsche Universitätsdruckerei, 6300 Giessen
2154/3150-543210 – Printed on acid-free paper

Preface

As we noted in the second edition of the first volume of *Laser Spectroscopy of Solids* (Topics in Applied Physics, Vol. 49), we were delighted by and grateful for the reception it received from the various spectroscopy communities. We believe that the acceptance of a review volume by a critical scientific audience is simply evidence that it fulfils a current need. This was fortunately the case with the first volume. It is, of course, the hope of the contributors to this sequel volume that it also appears at an appropriate time. All indications appear to be in our favor as the activity in laser spectroscopy applied to condensed phases continues to grow in an impressive fashion and to mature into an almost routine tool in the study of solid-state optical properties.

The first volume dealt principally with optically active ordered and disordered insulating systems; this was because many of the laser spectroscopic techniques transplanted from atomic studies were first applied in this type of solid. Inevitably, as tunable lasers of various types have become readily accessible, laser spectroscopic applications have expanded to include other types of condensed systems. For example, the advent of commercial picosecond laser systems has made it possible to study the dynamics occurring in semiconductors and in semiconductor structures, studies which would not have been possible a decade ago.

In this volume, we continue to contend that conceptually all optically active materials will, with an appropriate change in some gauge, behave in analogous ways and that differences which arise are to a large extent semantic. Thus, in the following contributions, we have endeavored to minimize specialized terminology and to emphasize the common thread and methodology that bind these studies. The chapters are sufficiently tutorial that they can serve as an introduction to those wishing to learn about the subject matter. However, they also possess the depth to serve as current reviews of the understanding that the use of laser spectroscopy has brought to the phenomena which affect optically excited states in condensed phases.

The authors of each chapter have played important roles in the advances which they review. Each of them therefore has the essential perspective necessary to survey the general advances in their respective fields in a fair and comprehensive manner. This is apparent in their contributions. I am personally most thankful to them for the effort and care they took in preparing their individual chapters, all of which I believe will withstand the test of time.

Finally, I wish to acknowledge the continued support and encouragement of Dr. H. K. V. Lotsch and the editorial staff at Springer-Verlag. Their patient guidance has considerably eased my task as the organizer of this effort. Support has also been provided by the National Science Foundation, the Department of Energy, and the University of Georgia.

Athens, GA, December 1988

William M. Yen

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1. Introduction:

Advances in the Laser Spectroscopy of Solids

William M. Yen

With 11 Figures

We are all aware of the central role spectroscopy has played in the evolution of our modern understanding of physical and chemical processes. The term spectroscopy, in its most general sense, embraces all those techniques in which an energy source is used to interact with and to probe some resonance in the atomic or material systems of interest. Advances in this area, more often than not, are intimately connected with the development of new energy sources, be they radiative or particulate, which allows greater finesse in our methodology and often leads to entirely new techniques and discoveries. The theme of this, as well as a prior volume [1.1], centers on the impact the advent of such a source, i.e., the tunable laser, has had on optical spectroscopies as they are applied to the properties of the condensed phases.

The introduction of stimulated optical devices has had a very noticeable and significant effect on spectroscopy; indeed, following a period of development, some of the techniques categorized under the heading of laser spectroscopy have become a part of the arsenal of tools used for the routine characterization of the optical properties of all types of materials. There exist many excellent and timely texts and reviews of conventional as well as laser spectroscopic methods and techniques [1.2]; consequently, it is not necessary to reiterate the contents of the existing literature. Instead, in this brief introductory overview (Chap. 1), we proceed under the assumption that the reader has been exposed to some of the basic literature, and review, briefly, the various experimental advantages which accrue from the use of laser spectroscopy. The other chapters contain material which supplements or updates subjects reviewed in [1.1]. Chapter 2 is a comprehensive and seminal review of two-photon processes in rare earth activated systems; the resurgent interest in these higher order processes is an important example of the contribution being made by laser spectroscopy. Recent advances achieved in understanding optical energy transfer in disordered systems are reviewed in Chap. 3. It should be apparent from that chapter that though some problems remain, we have made noticeable strides in obtaining a more fundamental and quantitative understanding of these processes as they occur in insulators. The discussion there centers on the application of the microscopic and macroscopic models of energy transfer which were developed in [1.1]. Chapter 4 presents a tutorial on the properties of optical color centers in insulators and reviews the experimental results obtained using spectroscopic methods based on the laser. Interest in these materials had waned until it was demonstrated that they could

be used as tunable solid-state lasers. The needs of technologies based on these relatively new devices have fueled an impressive revival in this area and this activity again bears testimony to the importance of the methods advocated in these volumes. Chapter 5 surveys yet another area in which new laser-based techniques have recently made an impact, that is, the study of relaxation and transfer processes which affect vibrational excitations in molecular crystals. The remaining two chapters deal with the optical properties of crystalline and amorphous semiconductors, respectively. These chapters go a considerable way towards rectifying the omission in the first volume of chapters dealing with this important class of materials. In the general spirit of these reviews, Chap. 6 contains a comprehensive tutorial on the optical properties of semiconductors, which serves as a useful introduction to the archival reviews of spectroscopic studies appearing later in that chapter and in Chap. 7. In both cases, the focus is on advances in which laser spectroscopic methods have played a significant role; these contributions are most obvious in the area of amorphous systems and in dealing with events occurring in the subnanosecond domain.

To return to this introductory chapter, in addition to reviewing the experimental advantages of laser spectroscopy, we also comment on recent developments in laser technology and advances in experimental methodology and correlate them to selective gains made in our understanding of the optical properties of solids in general. Some of these latter developments have been mentioned in the Addendum to the second edition of [1.1], while others are dealt with later in this volume. The field of laser spectroscopy of solids, however, is presently evolving so rapidly that we can present only a sampling of the most recent advances. This chapter concludes with some general remarks regarding the directions these studies may take in the near future.

1.1 Conventional Versus Laser Spectroscopy

Generally, in conducting spectroscopic studies, the precise methods to be used are determined simply by the available resources and their convenience or ease of application. The only requirement which is placed on the results obtained with a particular technique is that they be consistent with and complementary to those obtained by other means or techniques. Thus, for example, it is possible to conduct spectroscopic measurements on the same system in the frequency and time domains; the results are simply Fourier conjugates of each other in this instance.

Conventional optical spectroscopy embraces all those techniques which employ incoherent line or blackbody radiation sources in conjunction with some form of optical analyzer or spectrograph. These techniques have been, of course, crucial to the evolution of all of modern physics and chemistry, but because of the nature of the radiation sources used, they suffer from certain well-established limitations. All of these shortcomings have been remedied by the

use of lasers as the radiation source and it is now customary to identify spectroscopy which employs stimulated sources as laser spectroscopy.

Since the conception and first demonstration of the laser [1.3, 4], the intervening years have seen a rapid proliferation of stimulated devices covering an extremely broad range of frequency and temporal characteristics (Fig. 1.1). The advent of tunable lasers [1.5] is of particular importance, as is the development of pulsed laser devices which have unprecedented temporal resolutions [1.6]; these events have generalized the utility of lasers for spectroscopic applications. The virtues of laser radiation were recognized almost from the day of its discovery, so that lasers found immediate uses as alternatives to broad band, incoherent sources. More relevant to the theme of these volumes are the many other techniques which the laser made possible. A number of instances come to mind; the Raman effect in solids was first discovered in 1928 but did not become a practical analytic tool until continuous wave (cw) ion lasers became available [1.7]. Similarly, without the aid of the high power pulsed ruby laser, it would have been extremely difficult to have discovered the stimulated Raman process [1.8] and other nonlinear effects such as frequency doubling in solids [1.9]. Other early applications of the laser include the observation of two-photon absorptions in activated solids [1.10], the extension of the concept of spin echoes to the optical domain, where laser coherence plays a crucial role [1.11], and the demonstration of optically induced transparency in solids [1.12].

These early applications invariably utilized the monofrequency lasers which were then available; apart from Raman studies, this restricted the applicability of the laser-based technique to those systems in which some energy level fell in coincidence with the then accessible frequencies. For example, and as noted above, photon echoes were first observed and their properties studied in ruby; similarly, the technique of fluorescence line narrowing (FLN) in solids [1.13] was first demonstrated in the *R* lines of ruby. In both instances, the experiments employed temperature tuned ruby lasers [1.14]. The use of lasers for spectroscopic purposes remained limited until the introduction of the tunable dye laser [1.15], and this invention marks the origin of laser spectroscopy as we know it today.

We can also classify optical spectroscopy into two broad categories. The first, static spectroscopy, concerns itself with the structure of the spectra of the optically active solid. The features of such spectra are determined, of course, by the electronic levels of the optically active centers and by the effects of the environs on these levels. For these studies, high resolving powers in the frequency domain are often necessary.

In general, however, active centers in solids are not isolated and they may interact with each other as well as with a dynamic lattice environment. A different type of spectroscopy, i.e., dynamic spectroscopy, is required to probe into the effects of these interactions on the spectral properties. In these techniques, temporal measurements often play an important role with a concomitant requirement for high temporal resolution.

The spectra of all materials suffer from some degree of inhomogeneous broadening. This type of broadening has been discussed in detail in [1.1]. As pointed out there, the source of this broadening is to be found in some randomly fluctuating extrinsic perturbation to the atomic system. In crystals, for example, optical transitions are inhomogeneously broadened by unavoidable defects and imperfections of the lattice [1.16]. These external perturbations do not affect the intrinsic or homogeneous behavior of the optically active ion or center. However, in many cases the inhomogeneous broadening is sufficiently severe that it can obscure and conceal the intrinsic features which are of fundamental interest; this is the case, for instance, in optically activated glasses [1.17]. Laser spectroscopy has provided a convenient way by which inhomogeneous contributions are suppressed on behalf of the homogeneous features of interest; this is a central and important property of laser-based techniques. It is not that conventional spectroscopy is unable to yield the homogeneous spectra of materials [1.2], it is the experimental simplicity and ease of laser based techniques which have made them the obvious choice for such measurements.

1.2 Lasers as Spectroscopic Sources

The properties of laser radiation have been well established. The first of these to be exploited for optical experiments was the large power densities which are attainable with laser sources. In terms of spectroscopic measurements, the power simply translated into improvements in the signal-to-noise ratio, i.e., conducting spectroscopy with large effective apertures. In addition, as we have noted, the monochromatic power densities attained have allowed access to the whole spectrum of nonlinear optical properties.

The directionality and collimation of the laser beams make the steering and focusing of electromagnetic radiation a relatively simple experimental task, allowing experimentation in spatially confined areas and in small or irregular crystalline samples. In addition, the intrinsic coherent nature of laser radiation has allowed us to develop and pursue a host of techniques which find analogies in nuclear magnetic and electron spin resonance (NMR and ESR respectively) and which cannot be conducted with conventional sources. Coherent methods, such as transient or free induction decay (FID) and photon echoes, entailing time domain measurements are easiest to conduct whenever the relaxation rates encountered are long. This means the sharper a homogeneous line is in the frequency domain, the more readily accessible it is to coherent laser methodology. For solids, the slowest relaxation rate reported to data is found in the 7F_0 to 5D_0 transition of Eu^{3+} in Y_2O_3 where $T_2 = 420 \mu\text{s}$ at 2 K [1.18]. This is equivalent to a linewidth of 760 Hz, which is well beyond the resolution limit of all conventional optical analytic instruments.

Since the publication of [1.1], laser technology has continued to advance rapidly, thus expanding our experimental capabilities in all areas of laser-based

spectroscopies. For example, picosecond pulsed laser drivers were first commercialized in the late 1970s and have since become a fairly common source for spectroscopy. As an illustration, two of the reviews in this volume (Chaps. 4 and 5) present picosecond domain time-resolved studies applied to molecular vibrational dynamics and to semiconductor carrier properties, respectively. More recently, the development of colliding-pulse mode-locked (CPM) dye lasers and correlated technologies have succeeded in improving temporal measurements well into the femtosecond (fs) regime [1.19]. Here, the optical impulses entail a finite number of light oscillations, and thus fs pulses contain a broad range of Fourier frequency components centered at the laser frequency; in effect, pulses of this type can provide near white spectral coverage, a property which can be exploited experimentally [1.20].

Parallel laser developments have simultaneously enlarged the fraction of the electromagnetic spectrum over which tunable laser coverage can be obtained. Figure 1.1 summarizes schematically the regions over which laser devices can provide spectral coverage. The F-center tunable laser, which had just reached a developmental stage in the early 1980s, has expanded tunable laser sources well into the near IR [1.23]. These lasers were also instrumental in the development of soliton lasers employing optical fibers and the methodology for pulse compression. Various other solid-state systems, involving the 5d

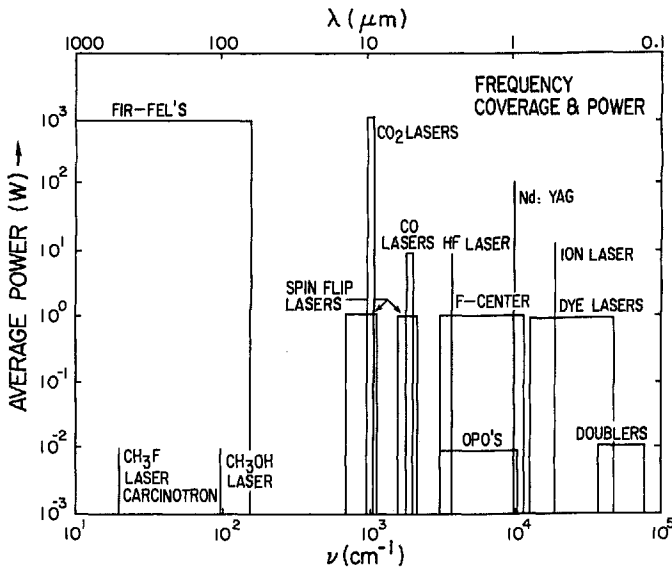


Fig. 1.1. Frequency coverage and average power outputs of a representative sampling of common monofrequency and tunable laser devices. In the FIR region, there are many molecular lines which have been used for lasing [1.21]; the Carcinotron is a traveling wave electronic device. Diode lasers operate in the general region in which F-center lasers operate; various free-electron lasers (FELs) are being attempted in the UV and VUV regions. (After [1.22])

bands of $4f$ ions [1.24] and phonon-assisted transitions of the transition metal ions [1.25], have also contributed to our arsenal of high power tunable sources predominantly in the visible and in the near IR. Semiconductor laser devices have become commercially available but they have not been fully exploited in the spectroscopic sense as yet [1.26].

The past decade has seen the successful demonstration of the principle of operation of a new class of lasers, the free-electron lasers or FELs [1.27]; these devices are unusual because they do not require a material medium for operation. As their name denotes, FELs rely on the radiation emitted by quasi-relativistic electrons as they traverse a region where they are accelerated by a periodically alternating magnetic field produced by an undulator. The principles of operation of FELs are closely related to that of traveling wave tubes and hence these devices are classical rather than quantum devices [1.28]. When the radiation emitted by the oscillating electrons is fed back, using mirrors in the case of FELs, it exerts a ponderomotive force on the electron beam, which results in beam bunching. The spatial periodicity of the electron bunches coincides with the central frequency of the radiation field. Omitting some kinematic factors, this frequency is given by

$$\omega = 1/\lambda_l \cong \gamma^2/\lambda_\mu, \quad (1.1)$$

where γ is the relativistic factor and λ_μ is the period of the magnetic field. Radiation from the electrons, subsequent to their bunching, interferes constructively, resulting in enhanced output in the forward direction. Though the principles governing the performance of FELs would seem to differ from that of conventional stimulated devices, the theory for both types of lasers may be brought into agreement [1.29] and the properties of the radiation obtained in either case are identical. Thus, FEL radiation can be utilized for spectroscopic purposes as that of any other laser.

The FEL possesses certain intrinsic advantages [1.30]. The one which has been principally exploited to date offers the prospect of generating extremely high power coherent radiation; this is based on the possibility of scaling up FEL devices, since in principle there is no active medium which might evince optical nonlinearities at higher powers. Additionally, if the electrons are recirculated in some manner, FELs can be operated with high wall-plug efficiencies, making them all the more attractive for certain high power applications [1.31].

For spectroscopic purposes, however, the most appealing feature of FELs is their potential as tunable sources spanning the whole electromagnetic range. As can be seen from (1.1), the output of the laser can be tuned by changing the energy of the electrons or the periodicity of the magnetic undulator. Present day undulators have a periodicity in the vicinity of 1–3 cm, thus with the electron accelerators available, FELs can operate well into the x-ray region [1.27].

The gain equations for FELs indicate that small signal gains are inversely proportional to the output frequency raised to the third power [1.30, 32]. Thus, the most advantageous region for FEL operation falls in the long wavelength

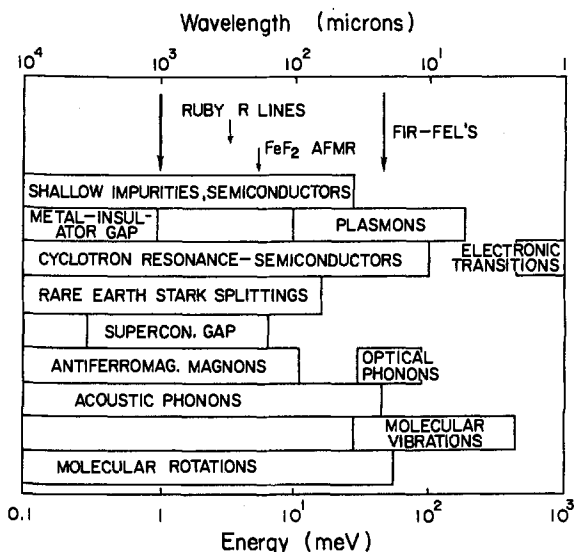


Fig. 1.2. Energies of a number of the elementary excitations in molecules and in condensed materials. The majority of the excitation which play important roles in determining the dynamical properties of optically excited states of interest to us are in the 1–100 meV (or 10–1000 cm^{-1}) region. The tuning region of the FEL [1.33] is shown by large vertical arrows which include this FIR region. (From [1.34])

portion of the spectrum, i.e., the far infrared (FIR). Though discrete frequency molecular lasers are available in the FIR [1.31], FELs offer potentially single source coverage for this whole region. Recently, a low voltage electrostatic (1–6 MeV) FEL has been demonstrated which has a tuning range from 10 to 80 cm^{-1} , outputting at several kilowatts peak power throughout the range [1.33]. The dearth of FIR sources has limited the extent to which spectroscopic investigation can be carried out in this region, yet many of the elementary excitations of solids which are of interest are to be found in this region [1.34], see Fig. 1.2. It follows that the development of FIR FELs signals the advent of laser spectroscopy in this traditionally difficult experimental region.

Visible and UV FELs have also been reported, however, invariably the range over which they can be tuned has been strictly limited by the fixed energy of the electron accelerators employed [1.30]. The optical properties of materials in the VUV and beyond still limit the development of high energy laser sources, with FELs being no exception.

More recently, efforts have been initiated to miniaturize FELs so that they can become laboratory rather than facility-sized instruments. This work centers partially in reducing the undulation period of the magnetic field. According to (1.1), a reduction in the period results in a square root reduction in the accelerator energy required for an equivalent laser frequency output. For one area of interest, i.e., the FIR, the development of appropriate micro-undulators would result in a considerable size contraction accompanied by beneficial cost reductions. Suitable micro-undulators have been constructed with periodicities of 3–4 mm, an order of magnitude reduction from undulators currently in use [1.35–37].

Insertion devices, such as the undulator, are also commonly employed with synchrotron sources to produce high intensity, high energy radiation [1.38]. The generation of radiation through the use of undulators and wigglers is the precursor to FEL operation. In the absence of broadly tunable lasers in the UV, synchrotron radiation (SR) has proven to be extremely useful as a spectroscopic source and has led to a number of SR-laser optical techniques which have helped in the elucidation of solid-state properties, especially those involving the atomic inner core of the constituents and those connected with boundary phenomena. Synchrotron radiation spectroscopies have also been reviewed in a number of places [1.39].

The performance of lasers, in general, has continued to improve in the past decade. The pulsed power of commercially available lasers, YAG:Nd, excimer, etc., driven tunable devices is now sufficient for most nonlinear optical experiments. These advances in peak as well as total power output have also made multi-laser beam spectroscopies practical. Improvements in other aspects of laser performance are also not to be ignored; for example, in cw lasers, stability of output frequencies of a few hertz have been achieved. This jitter produces an effective laser linewidth, thus, attainable laser frequency resolution is of the same order of magnitude [1.40].

The development of new laser sources allowing us access into new frequencies and into hitherto unheard of temporal resolutions, coupled with the general progress of the technical performance of all classes of laser sources, has simply resulted in a considerable increase in the experimental resources available to us and indicates the maturation of the techniques advocated in these volumes. Thus, the period since the publication of [1.1] is to be noted not so much for the pace of demonstrations of new laser-based experimental techniques as for the explosion of applications of these methods to various solid-state systems of interest.

1.3 Comments on Recent Advances of Laser Spectroscopy of Solids

The Addendum to [1.1] contains a brief update of the status of laser spectroscopic studies of solids, principally in insulating materials, up to 1985. For crystalline materials, for example, many of the conflicts surrounding optical energy transfer in the *R* lines of ruby [1.41] were resolved by the experiments of *Gibbs* et al. [1.42]. Similarly, the role of exchange in transfer and relaxation of rare earth systems [1.43] as well as the anomalous properties of the rare earth pentaphosphates [1.44] have largely been clarified. One of the gratifying results of the more recent experimental studies is that the theoretical framework for transfer and diffusion of energy developed in [1.1] has, in general, withstood the test of time [1.45]. A comprehensive update of experimental developments in transfer processes is presented in Chap. 3 of this volume and elsewhere [1.46].

Some of the other advances attained recently in our understanding of the optical properties of solids are detailed in this volume. It is notable, for example, that considerable progress has been achieved in unravelling multiphoton absorption processes in the transition metal [1.47, 48] and rare earth series [1.49, 50]. In rare earth systems, the presence of two-photon absorptions was established earlier [1.10] and explained soon thereafter in terms of the Judd-Ofelt [1.51] closure approximations by *Axe* and others [1.52]. The availability of high power tunable devices has allowed a comprehensive reexamination of these processes, resulting in a firmer understanding of this phenomenon and the resolution of a number of puzzles. The current status of this field is reviewed by one of the principal figures in these developments in Chap. 2.

In the past few years, laser spectroscopic methods have been applied to a widening assortment of materials. The fourth chapter deals with the properties of defect or color centers in various insulators; this class of optically active materials was studied extensively until the early 1970s and a basic framework for the understanding of the creation, stability and structure of the trapped electrons was established by then [1.53]. Renewed interest arose because of the development of the near IR tunable F-center lasers [1.23] and a more sophisticated foundation has evolved for these systems. As in the case of insulators, techniques such as site-selective spectroscopies used in conjunction with optically detected magnetic resonance (ODMR) have proved extremely valuable in these studies.

Similarly, both crystalline and amorphous semiconductors have also been investigated extensively with laser spectroscopy in the past decade. The application of site-selective methods has played an important role in characterizing various shallow and deep traps in ordered semiconductors and in establishing the nature of localized and delocalized states in disordered semiconductors [1.54]. Picosecond and subpicosecond laser sources have also proven to be powerful tools with which to investigate carrier dynamics in these systems and structures [1.55]. Bistable behavior of semiconductors under various optical pumping conditions has been investigated actively and has promising technical implications [1.56]. The last two chapters of this review volume detail advances in this field.

Another area in which laser-based optical methods have played a central role is in the study of elementary excitations of matter. Such excitations serve an important function in the relaxation and diffusion of optically excited states in solids and involve, more often than not, collective actions of the molecule, atomic complex or the solid lattice. Chapter 5 addresses one of these areas, i.e., vibronic relaxation processes in organic materials; as is to be noted there, the availability of short laser excitation pulses has been principally responsible for this development.

The topics selected for review in this volume are by necessity limited and, thus, no pretense is made that all significant advances in recent years are discussed. Indeed, one of the aims of this introductory overview is to provide a brief summary of happenings in the areas which are not covered or updated by

these reviews. With the understanding that the following may be tainted with personal preferences, we present a synopsis of significant developments in the application of laser-based spectroscopies to the study of solid-state optical properties.

1.3.1 Relaxation and Transfer in Glasses

The observation of anomalous behavior of the excited states of centers in disordered materials as manifested through their optical linewidths has aroused a great deal of interest and activity, which has resulted in a much clearer theoretical understanding of this problem [1.57]. Experimentally, linewidth studies have been extended to include disordered organic glasses, and FLN, hole burning, and coherent methods have all been implemented in these insulating systems. The relaxation had been shown to display a seemingly universal T^2 thermal dependence down to low temperatures in the bulk of systems studied. The relaxation rate at low temperatures were also found to be anomalously large compared to the crystalline values. The latter seemed to implicate the low temperature disordered modes postulated by *Anderson* and others [1.58] as consisting of two level excitations or TLSs. Various theoretical models involving TLSs were advanced to explain the increased relaxation at low temperatures; however, in each case, the theories failed to explain the totality of linewidth results. Figure 1.3 shows the experimental results obtained to date for rare earth activated inorganic and organic glasses [1.59].

A number of experiments conducted at extremely low temperatures, i.e., 1 K and below, successfully demonstrated deviation from the higher temperature T^2 dependence. For example, in measurements conducted by *Hegarty* et al. [1.60] using photon echoes in a Nd^{3+} -doped optical fiber, a linear T dependence of the linewidth was observed, obviously implying a behavioral crossover from earlier FLN results. Subsequently, the crossover was observed in a Yb^{3+} doped phosphate glass by *Brundage* and *Yen* [1.61]. See Fig. 1.3c. FLN studies of Cr^{3+} in glasses have also contributed to the probable resolution of the linewidth problem. In these studies *Bergin* et al. [1.62] have been able to resolve the phonon sidebands associated with so-called "high field" Cr ions within the inhomogeneous glass distribution. In the high field sites, the 2E state lies lowest and, hence, the FLN emission is mainly R -line like. Figure 1.4 illustrates the type of sideband obtained through these methods. As vibrational sideband shapes in solids can be correlated to the density of states, the figure implies that the vibrations coupling to the 2E state depart significantly from Debye-like acoustic phonons and other optical modes existing in crystals. There is, for example, a noticeable shift of the peaks in the density towards lower energies. Similar studies have been conducted in rare-earth-doped glasses [1.63]. However, the weaker ion to lattice coupling prevented the resolution of any structure in the sidebands observed.

Huber [1.64] has subsequently shown that an altered density of vibronic states, such as those discussed above, lends an explanation to the quasi-

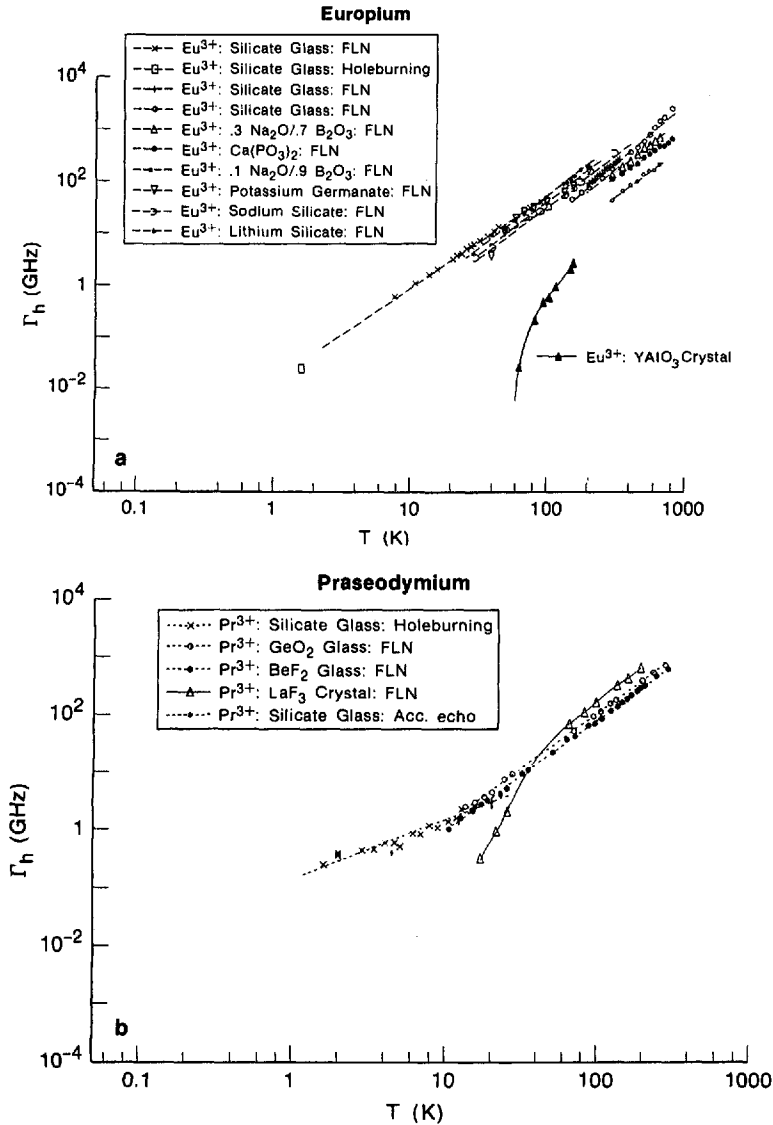


Fig. 1.3a-d. Summary of the extant experimentally measured homogeneous optical linewidths of transitions of trivalent rare earth ions and chromium doped into inorganic glasses of varying composition as a function of temperature. Data has been obtained using a number of laser spectroscopic techniques, as denoted in the inset. The plots illustrate the striking similarity of the linewidth behavior for all the activators, especially at higher temperatures where T^2 thermal broadening is observed. Of importance is the break from this thermal dependence observed in the 1D_2 state of Pr^{3+} , in Nd^{3+} and in Yb^{3+} . The 5D_0 to 7F_0 states of Eu^{3+} , the 3H_4 to 1D_2 and 3P_0 transition in Pr^{3+} , and $^4F_{3/2}$ to ground state $^4I_{9/2}$ transition in Nd^{3+} have been investigated. For Yb^{3+} the results are for the $^2F_{5/2} \leftrightarrow ^2F_{7/2}$ fluorescence and for Cr^{3+} the results are for the $^2E R$ lines. (From [1.59])