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**OPTICAL STUDIES OF DYNAMICAL PROCESSES IN DISORDERED
MATERIALS**

Progress Report

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PART I: SUMMARY OF ACTIVITIES UNDER THE PRESENT SPONSORSHIP AND PROPOSED CONTINUED PROGRAMS

A. Introduction:

In general terms, our research activities under the present Agency sponsorship continue to focus on processes and interactions which affect the dynamical behavior of excitations/excited states of optically activated amorphous or disordered solids. The framework of our understanding of these processes has been established with work performed over the past two decades. The advent of more refined spectroscopies, most of them laser based, has allowed a re-examination of these properties in a much more detailed and basic way [1]. A deeper understanding of the interactions which lead to relaxation, energy diffusion and nonlinearities in the disordered phases is important to the development of more efficient and better materials to service all of the technologies which employ optically activated materials.

In this document, we will present an abbreviated synopsis of the research we have conducted under the auspices of the present grant. We will then outline directions we wish to maintain and will render descriptions of new opportunities which have ensued from our current efforts and which we wish to exploit under renewed sponsorship.

We emphasize at the outset that the following description of our accomplishments during this period and our intentions for the next are by necessity limited by length requirements; it follows that we make no pretensions of being exhaustive in our treatment of the topics which we raise. Simply put, our hope is that we succeed in imparting a general impression of the very real progress we have attained as well as a flavor of our continuing thrust and directions in our research efforts.

A compendium summarizing our activities during the current support in terms of technical publications, presentations and thesis appears in the next section of this proposal.

Detailed descriptions of our progress in all the areas of our interest are to be found in the literature cited in that section.

We feel that we have been extremely productive during the past three years of DOE support; this is, of course, due to the continued encouragement granted by the Department, but is also due to the substantial support the University of Georgia has provided for our efforts. The latter has provided us with the means to maintain our currency in updated laser and recording equipment allowing us to remain competitive; UGA will continue to supplement this effort in the event continued agency support is approved (see attached).

B. Progress Attained During the Current Grant Period:

We have been concerned with two aspects of the problems of disordered or amorphous solids; our interest, of course, centers heavily on the micro- and macroscopic interactions which are responsible for the dynamics which occur in optical excited states of various glassine solids. However, in order to properly deal with the dynamical aspects, we first need to understand the nature of the static spectra of disordered systems of our interest. The optical spectra in amorphous materials is characterized by large inhomogeneous broadening induced by the randomness of the lattice or network which tends to obscure details and complicate their interpretation [2]; it is precisely in these systems that site selective, tunable laser spectroscopy has proven to be of such an important experimental tool as it allows the extraction of the intrinsic or homogeneous features of a transition [3]. When these spectroscopies are carried out in a time-resolved fashion (with pulsed lasers, for example) dynamical properties may be determined for individual sites [4].

During the period covered by this grant, notable progress has been made in developing theoretical frameworks for understanding various properties of disordered systems. For example, the relaxation processes which affect the excited states have been shown to implicate the so-called disordered modes at low temperatures and to result in a

distribution of relaxation rates [5,6]. Similarly, considerable progress has been made in reaching an understanding of processes which lead to the transfer and diffusion of optical energy in disordered systems [7]. We have made substantial contributions to some of these areas, details of which we discuss below.

i) – New Experimental Techniques: In the course of the present grant, we have been instrumental in developing and refining a number of novel spectroscopic techniques which have allowed us to address certain complicated spectral problems that we have encountered.

a) Saturation Resolved Fluorescence Spectroscopy (SRF): As noted above, various laser spectroscopic techniques, such as Fluorescence Line Narrowing (FLN), allow the isolation of designated subsets of ions within an inhomogeneously broadened distribution [2]. Overlapping or interaction coupled luminescences that cannot be resolved spectrally are often resolvable by relying on time-resolved methods which employ the time signature of the components of the spectra. In many cases, however, the components can be coupled very strongly and the underlying interaction between the centers causes spectral transfer in times comparable to the temporal width of the laser excitation pulse; time-resolved FLN or TRFLN can be rendered ineffectual in such instances. SRF was developed to address these cases. This technique is similar in spirit to the persistent spectral hole burning (PIRSH) developed by Ambrose and Sievers [8] in the infrared. In SRF, a laser is used to selectively saturate the donor ion spectra; this in effect also saturates all spectral features which are coupled to the donors through transfer interactions. Following the saturation, a second laser is tuned across absorptive features of the acceptor ions; any additional luminescence appearing under the combined excitation can only arise from the acceptor system alone. A schematic diagram of the experimental setup is shown in Fig. 1. The saturating and the secondary excitation beams are counter propagated collinearly close to the surface of the sample; steps are taken to insure that the secondary beam only induces emission from the saturated region. The luminescence is isolated by a mask to reduce background from

FIG. 1 Schematic diagram illustrating the SRF experimental configuration. The two laser beams are counter propagated through sample. Filters are used to control the relative intensity of the beams. The sample is masked to ensure that only luminescence from the region excited by both beams is collected.

FIG. 2 Emission spectra of Cr^{3+} :mullite ceramic at room temperature excited by (a) *R*-line saturation plus 532-nm (solid curve) or 660-nm (dashed curve) pump. (b) *R*-line saturation only. (c) SRF spectrum yielding the isolated *D*-acceptor emission for 532-nm (solid curve) or 660-nm (dashed curve) excitation. The resulting profile is typical of Cr^{3+} doped glasses. Spectra were obtained with a 10- μs gate and a 5- μs delay.

scattering and from long-range transfer processes. Representative spectra are shown in Fig. 2 for a Cr^{3+} activated sample of mullite glass ceramic where SRF was first demonstrated [9]. The utility of SRF appears not to be limited to deconvolution of strongly coupled spectra; the implication of our results is that dynamical processes such as energy transfer are in effect being driven nonlinearly in this case and it should be possible to expedite or stimulate transfer under certain conditions.

b) Fluorescence Line Narrowing in the Near Infrared: During the current period, we have been able to extend the frequency range over which FLN has been conducted well into the near infrared or NIR. We have obtain or developed laser sources which span the 1 to 2 μm range; these consist of F-center systems, Raman shifters and more recently a YAG:Nd^{3+} driven YAG:Cr^{4+} tunable laser. In order to investigate relatively weak isotropic luminescence signals, we have been able to devise an InGaAs detector coupled to a high gain amplifier capable of rise times in the submicrosecond region [10]. This speed is presently adequate to investigate luminescent and transfer processes in systems such as Cr^{4+} , Er^{3+} and Ho^{3+} in glasses which are of current technical interest [11]. FLN and TRFLN spectra of a Ni^{2+} compound are shown in Fig. 3; to our knowledge, these are the first FLN results reported for the NIR.

c) Far Infrared (FIR) Generation of Elementary Excitation of Solids: During the current grant period, we have also been able to develop on site a pulsed, high power, molecular laser which provides line tunable coverage of the FIR, roughly in the $5\text{--}100\text{ cm}^{-1}$ region [12]. This device has made it possible for us to conduct FIR spectroscopy of various excitations of solids; in view of this development, we no are no longer in need of external facilities such as the UCSB-FEL installation and we terminated our collaboration with this laboratory early during this grant period. In a series of publications [13–15], we have been able to demonstrate that we can generate high frequency, narrow band excitations such as phonons and magnons in crystals through FIR laser irradiation; the coupling mechanism between radiation and the lattice is defect induced as the latter breaks

FIG. 3 First instance of FLN in NIR in $\text{Ni}^{2+}:\text{MgF}_2$. (a) and (b) show nonresonant luminescence from $\text{B}_3(^3\text{T}_{2g})$ to the ground state after excitation into the $^1\text{T}_{2g}$ sideband. (c)-(f) show FLN resonant and nonresonant emission from the same transition observed after direct excitation at different positions within the $\text{B}_3(^3\text{T}_{2g})$ inhomogeneously broadened line. The position of the laser is indicated by the broken vertical line.

the translational symmetry. We have developed an optical analog to the boxcar in order to detect the behavior of these excitations in the frequency and in the time domains; the optical boxcar utilizes the anti-Stokes sideband of impurity electronic level introduced into the solid as was proposed by Orbach [16, 17]. This method is schematically illustrated in Fig. 4 with representative use obtained in exciting high frequency phonons in LaF_3 . Though these specific results were obtained under different sponsorship, these techniques are directly relevant to projects we wish to initiate in glass during a renewal period.

In general, we have been able to maintain the currency of our experimental equipment through the University and other forms of support, inclusive of the present grant; a modest amount of additional capital equipment monies is being requested in this renewal. Justification for the equipment is detailed in the appropriate section.

ii) - Materials Synthesis: During the current period, we have established a materials synthesis and growth capability which has added a great deal of flexibility to our research efforts by providing us with a unique supply of optical materials. With University support, a Laser Heated Pedestal Growth (LHPG) station which allows the growth of materials in fiber form was constructed in the earlier part of this grant [18, 19]; we have been able to synthesize and grow a great variety of materials which have been employed in work described here. (See Table I.) The LHPG method is a miniature variant of Czochralski growth which possesses a number of advantages; the method is schematically represented in Fig. 5. The capital costs and the growth stock materials required in LHPG are very modest. In addition, the melt is held together by surface tension and, hence, no crucibles are needed; the latter are generally known to be the principal source of unintentional contamination of samples, therefore, it follows that LHPG provides materials that can be of extremely high purity. One of the most attractive features of this technique is the rapidity in which fiber samples can be drawn for spectroscopic purposes; samples can be grown at a rate in the vicinity of 2-4 mm/min which allows materials to be synthesized for the first time with feedback within a reasonable time frame, i.e., hours instead of days

TABLE I

Single-Crystal Fibers Grown at UGA by the LHPG Method.

Al_2O_3	(sapphire, ruby)
MgAl_2O_4	(spinel)
Mg_2SiO_4	(forsterite)
Ga_2O_3	
LiGa_5O_8	
Y_2O_3 , YScO_3 , Sc_2O_3	
SrTiO_3 , BaTiO_3	
LaAlO_3	
YAlO_3	
$\text{Y}_3\text{Al}_5\text{O}_{12}$	(garnet)
CaWO_4	(scheelite)
$\text{NaLa}(\text{WO}_4)_2$, $\text{NaY}(\text{WO}_4)_2$	
PbMoO_4	
CaMoO_4	
LaGaGeO_7	
$\text{La}_3\text{Ga}_5\text{SiO}_{14}$	
CaF_2	(fluorite)
RbMnF_3	
LiF	(rock salt)

FIG. 4 (a) Schematic of phonon dispersion curve. FIR phonon generation via defect-induced one-phonon absorption is symbolized by the vertical arrow. (b) Energy level diagram for Pr^{3+} in LaF_3 . Phonons of energy Δ are detected via anti-Stokes absorption at the optical probe frequency ν_D , where $\Delta + \nu_D$ is the energy of the zero-phonon line. Phonon-induced absorption is monitored by observing the ν_{F1} fluorescence.

FIG. 5 Schematic of LHPG apparatus. The melt occurs at the focal point of the laser; growth and crystallization occur in the shadow cone.

or more. Finally, LHPG permits the growth of materials with high melting temperatures and the synthesis of incongruent crystalline structures. The last two properties are of direct relevance to the mission of this grant; the $Y_{2-x}Sc_xO_3$ crystals shown in Table I, for example, have a melting point near 2500C and hitherto have been grown only through scull techniques. This system, though crystalline, is structurally disordered and shows the inhomogeneous effects of interest to us (see Fig. 6). Incongruity is yet another type of disordered which can now also be explored; of interest to us at the moment are systems such as CaF_2 , Y_2O_3 activated with rare earths. These materials are presently being pulled and experimented with.

We have shown that the fiber configuration is ideal for optical characterization and spectroscopic studies [20]. We have measured, for example, the behavior of optical transitions under tensile and torsional stresses, measurements which are generally difficult to conduct in bulk samples [21]. We have also shown that the fiber samples are ideally suited for Raman scattering studies and that such studies are helpful in characterizing the crystal axis alignment of the fibers [22]; further, the wave guiding properties can also be exploited for spectroscopic purposes.

iii) - Transparent Activated Ceramics: We have concluded our studies of the optical properties of Cr^{3+} activated, transparent mullite ceramics. These materials had been considered to have potential as optoelectronic materials but in general they have shown disappointing low quantum efficiencies. The Cr^{3+} ions in these materials occupy a wide variety of sites falling into two categories: high field (HFS) and low crystal field (LFS) sites, i.e., those in which the 2E state of Cr^{3+} lies lowest and those in which the 4T_1 state is the principal emitting state, respectively [23]. Though the temporal signature, as well as the spectra, of these two groups of sites is different, they are strongly coupled through radiative transfer and the usual techniques of laser spectroscopy proved insufficient to decoupling their spectra. It is for this reason that SRF, discussed earlier, was developed and allowed us to resolve the individual components of the complex spectra from mullites;

FIG. 6 $^4I_{15/2} \rightarrow ^4S_{3/2}$ excitation spectra at 14 K of 1% Er^{3+} in (a) Y_2O_3 , (b) YScO_3 , and (c) Sc_2O_3 .

FIG. 7 Peak emission wavelength of LFS Cr^{3+} in mullite glass ceramic plotted as a function of excitation wavelength. The solid curve represents the peak positions of conventional time-resolved spectra taken with a 10- μs gate and 5- μs delay at room temperature. The dashed curve represents the peak positions of the directly excited LFS emission obtained by SRF spectroscopy.

the distributions of peak positions for the LFS are shown in Fig. 7. These results have allowed us to identify the locations of the Cr^{3+} ions within the mullite. The HFS Cr^{3+} ions clearly precipitate into the Al_2O_3 , while the LHS ions seem to congregate in the Al_2O_3 - SiO_2 transition boundaries rather than in the amorphous silicate volume as a whole; the proximity of the sets of sites is demanded by the strong radiative coupling observed in these materials. The enumeration of sites in accordance with their field strength has allowed us to fit the observed spectra of these systems. This work has resulted in a number of publications [9,24,25] and a doctoral thesis.

In terms of the mission of this grant, the above mentioned results are important since they have given us additional insights on the reasons why Cr^{3+} in disordered systems generally have suffered from low quantum efficiencies. We have been able to correlate, for example, the lifetime of the observed luminescences of various Cr^{3+} compounds to the spin orbit mixing between the ^2E and $^4\text{T}_2$ states [25]. Further, these studies have provided the first spectroscopic information on optical properties of ions in an order-disorder interface; these interesting results will be pursued in the course of the proposed renewal.

iv) – Relaxation in Disordered Systems: Under the present sponsorship, we were principals in the discovery of the anomalous behavior of the relaxation of excited states in disordered materials as measured by the temperature dependence of the linewidth. It is fair to say that this work was the stimulus for the considerable volume of activity in disordered organic and inorganic systems which has arisen in this area [26]. After a number of false starts, the work of Huber [5,6] has finally established a theoretical basis for the relaxation in terms of the elastic modulation produced by the so-called disorder modes or two-level systems (TLS) postulated by Varma and coworkers [27]. The proposed mechanisms for relaxation lead to relaxation times which show the appropriate temperature dependencies and which are in themselves time dependent, i.e., dependent on the time scale of the measurements; the different results obtained through different measurement techniques, i.e., FLN, echoes and hole burning, are now generally in

agreement because of this time dependence [28]. We are gratified that our results [29] have played a central role in the resolution of this important problem.

The precise nature of TLS, however, has not been clarified and they require additional consideration. For example, recent results indicate that the temperature dependence of the linewidth in disordered mixed crystal, such as $\text{Y}_{2-x}\text{Sc}_x\text{O}_3$ shown in Fig. 6, is also anomalous; similar results have been reported for $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ by a Japanese group [30]. We believe that these studies will provide additional clues as to the nature of these excitations.

v) - Localization of Single Centers in Glass Fibers: There is a continuing interest in the radiative properties of single atomic and ionic entities. The possibility of detecting single centers in a medium is of particular importance in organic sequencing, for example [31]. In our efforts in this area, we seek to obtain the spectra of a single rare earth ion situated in a disordered system. These results would allow the unique determination of the static electric fields present in that specific site, and hence allow the modeling of the disordered environment without the various "accidental coincidences" which occur in glasses [32]. In addition to providing a microscopic, site specific way of determining glass structure, studies of single ion properties also promise to yield fundamental information on the interaction of radiation with matter.

During the present sponsorship, we have developed a technique we have named Dilution Narrowing Laser Spectroscopy (DNLS) as a way to detect single ions or small clusters of ions. If the glass matrix contains a very dilute level of activators to begin with and the excitation laser is focused down so that it interacts with a smaller and smaller volumes of material, it is possible to reach conditions in which the total distribution of inhomogeneous sites is no longer sampled. This was initially demonstrated in crystalline solids [33]; the large inhomogeneous widths in frequency encountered in glasses give us an additional means of dilution within the sampling volume. Under these circumstances, the spectra observed will be a random sampling of the disorder distribution which would differ

from that observed in the bulk. Spectra obtained in this way is termed Dilution Narrowed as is illustrated in Fig. 8.

Activated single mode optical fibers provide us with an ideal configuration with which to conduct DNLS. The intentional doping of the core creates a minute excitation region, and the fiber naturally produces an efficient channel for the collection of the excited fluorescence of the centers. The experimental setup for our experiments is shown in Fig. 9, which allows cooling of the fiber samples and transmission of the light signals to the appropriate room temperature detectors and analyzers. Our initial experiments employed Nd^{3+} doped silicate single mode fibers obtained from AT&T Bell Labs which had been used in relaxation measurements [34] and obtained preliminary evidence of DNLS. The doping level of these fibers is at the ppm level, consequently, we expect structure only in the wings of the inhomogeneous distribution. Our results are shown in Fig. 10, where significant structure is seen at the wings. These traces were taken with a laser linewidth of 2 GHz which is far greater than the homogeneous linewidth of the transition. More resolved structure is expected with increased laser resolution. We have investigated a more diluted silicate fiber doped with Eu^{3+} and have searched for Pr^{3+} contamination in the Nd^{3+} fibers as a means of further dilution of dopants; in each case, results have been encouraging and we believe we are isolating ion clumps in the vicinity of 10 or less rare earth ions [35].

Single dye molecules have also been isolated in an amorphous matrix recently [36]; our experiments are more difficult because of the smaller oscillator strength of our rare earth atomic probes. In addition, we seek in these experiments to obtain the actual spectrum of these localized ions and are confronted with the problem of dispersing the fluorescences through analyzers. We have exerted a great deal of effort during this grant period in physically stabilizing the experimental setup as any extraneous vibrations or laser jitter adversely affect our observations; in addition, we have also concentrated in

FIG. 8 A simulated dilution narrowed spectrum within a Gaussian envelope. The broadening is eight times larger than the homogeneous linewidth.

(a)

(b)

FIG. 9 (a) Schematic of experimental setup for DNLS in fibers. (b) Details of fiber mount.

(a)

(b)

FIG. 10 (a) Excitation spectrum of Nd^{3+} in a glass fiber. (b) Excitation spectra of the low energy wing. The traces have been vertically offset for comparison. Structure is real and is evidence of DNLS.

developing ultra sensitive detection methods. This leaves us well poised to conclude these important experiments under the forthcoming sponsorship.

Summary: In the preceding, we have presented a brief summary of the results which we have obtained during the current grant period. We believe we have made significant progress in our attempts to obtain a more detailed understanding of the structure and dynamics of disordered systems. Progress has been achieved in several areas: a) in the development of new spectroscopic techniques, b) in the synthesis and growth of disordered materials, c) in the understanding of relaxation processes, and d) in the demonstration of DNLS to localize single ions in glass. These developments provide us with a good foundation from which to continue our experimentation.

C. Continuing and Proposed New Programs:

We now outline various areas in which we wish to continue our investigations into properties of the disordered state and for which we seek additional support from the Department. We have already alluded in Section B to a number of experiments which are currently under way and which we naturally wish to conclude. In addition, we propose a number of new initiatives which are based on our previous work and constitute logical extensions of our efforts. These projects can be classified into three broad categories, as follows:

i) - Studies of Relaxation and Transfer in the Excited State: As noted earlier, much progress has been achieved during the past few years in this area. The more detailed understanding we have gained of the dynamical processes affecting the optically excited state in amorphous system also provides us with new ways to consider these interactions.

a) Linewidth measurements: In the area of relaxation, we propose to continue our investigation of linewidth of optical transitions in disordered systems. More specifically, as much has been done in the case of rare earth activated glasses and the results are consistent with theoretical predictions [5,37], we now wish to conduct similar studies as a function of

the degree of disorder. These studies will, we believe, help us elucidate the nature of the elementary excitation of amorphous solids or TLS, especially at low temperatures. There are two ways in which we can control the disorder; the first entails the boundary between ordered and disordered systems such as those found in the case of transparent ceramics, the second can be produced in crystalline materials by introducing compositional disorder, in cases such as mixed or incongruently grown materials, for example.

For ceramics, we propose to investigate the temperature dependence of the linewidth of the R-like transitions of the HFS Cr^{3+} in mullite. As we have noted, our prior work has allowed the determination of the distribution of sites in this material. We believe that the crystal field in the HFS ions can be correlated to their proximity to the Al_2O_3 - SiO_2 boundary; that is, the lower their transition energy of the site, the more likely the site is being influenced by the SiO_2 disordered phase. Consequently, measurements of the linewidth behavior across the HFS site or frequency distribution are equivalent to measurements as a function of the degree of disorder. We have also noted that the Cr activated mullite spectra is strongly coupled and complex, consequently, FLN techniques employed in the linewidth measurement in glasses are not possible as other techniques are required. Two alternate methods will be employed, accumulated photon echoes and hole burning. In the first, a laser pulse train from an appropriate mode locked tunable source is made incident on the sample, creating a population or a phase gradient which reforms to produce an echo which is related to the dephasing time T_2 or linewidth [38,39]. We have conducted such experiments in Nd^{3+} doped glasses before so that we have these experimental capabilities in place. These studies will be carried out as a function of frequency and as a function of temperature. Any variations of the temperature dependences that appear across the inhomogeneous profile of HFS Cr^{3+} ions will be correlatable to the degree of disorder and its effects on dephasing and non-radiative relaxation. In the case of hole burning, the results in SRF which allowed the deconvolution of the HFS and LFS spectra, were made possible because the donor states or HFS in this

case could be saturated. That is, holes can easily be burned into the HFS distribution and the hole detected by a low intensity sweep of the absorption using a second laser. Hole burning results can generally be carried to higher temperatures; frequency and temperature dependences would be studied and compared with echo results. Comparison would provide additional insights on the time dependent relaxation process discussed earlier [5,6].

We are in the process of studying the temperature dependence of transitions of Er^{3+} in the mixed crystal $\text{Y}_{2-x}\text{Sc}_x\text{O}_3$ where x can be made to range from 0 to 2. Of course, this study is made possible by our access to samples through our LHPG facilities. The behavior of the Er^{3+} linewidths in the pure Y and Sc materials behave as expected for crystalline solids [40], certain deviations in the temperature dependence begin to appear in the vicinity of $x = 1$ which must have their origin in the compositional disorder. We propose to continue and conclude these studies and ascertain the nature of the anomaly. As noted previously, similar results are being reported by a Japanese group [30].

b). Photothermal measurements: The results above will also be relevant to the determination of non-radiative relaxation processes as Powell and his coworkers have shown recently [39]. We have recently applied photothermal laser spectroscopy to a number of Cr^{3+} doped crystals and glasses [40,41]. These techniques provide an accurate measure of the quantum efficiencies of materials; in addition, they can also be used to determine the nature of the ion phonon coupling at the ion site. Most recently, we have been able to determine the bulk expansion caused by the relaxation around an excited Cr^{3+} ion in glass [42]. In these experiments, the deflection of a probe laser beam is monitored following pulsed laser excitation and its time dependence is recorded; the time dependence is then analyzed in terms of thermal and elastic effects on the index of refraction of the material. Extremely small volumetric changes of the excited ion can be derived in this way; in the work on silicate glass, the expansion of the Cr^{3+} is found to be much smaller than that measured for crystals (GSGG) and is attributable to the difference in the local structure and provides us with a microscopic probe on the intrinsic coupling

FIG. 11 Change of the index of refraction of ED-2:Cr³⁺ following pulsed excitation into the ⁴T₂ absorption at 715 nm. The points are the experimental data and the solid line a fit according to theory. The lower line gives the purely thermal response.

From: Hommerich and Strauss.

between ion and excitations in glasses. Figure 11 illustrates the photothermal signal observed in Cr^{3+} activated ED-2 silicate glass.

The principal in this important development has been Dr. Eugen Strauss who joined the faculty at the University of Georgia at midpoint of this grant; unfortunately, Professor Strauss passed away earlier this year. Nevertheless, we propose to continue these studies by extending the photothermal deflection measurements to other Cr^{3+} systems such as in the mullite ceramics. In addition, a number of other ions suggest themselves: we are presently conducting studies in Ti^{3+} doped silicate glass; and the single d electron in Ti undergoes a Stoke's shift which exceeds that experience by the Cr^{3+} ion. It follows that a sizable effect is expected. Similar experiments would be conducted in Cr^{4+} activated glasses; both of these ions are of technical significance as tunable laser sources, yet little has been done to determine their efficiencies in glasses.

ii) – Studies of structure and nonlinear properties of silicate fibers: The advent of optical fiber technology has led to significant advances in the structuring of glasses and to the invention of various on line optoelectronic devices such as lasers, modulators and amplifiers. We have pointed out that the fiber configuration is ideal for spectroscopic studies and have demonstrated these advantages in DNS experiments, for example. We wish to propose a number of areas in which to study dynamic properties of the excited states of glasses utilizing the geometric properties of fibers [20].

a) Structure of modified silicate fibers: Through an external collaboration, we have been able to obtain a series of activated silicate fibers with various network modifiers; the introduction of these modifiers in amounts equivalent to the level of doping produces significant changes in the spectra of the activator. These changes include variations of branching ratio, energy and splitting of the Stark manifolds. A sampling of the nature of the changes observed are shown for three different modifier elements in Fig. 12. The implication of these results is that the spectra of a given rare earth can be tailored by the

[from K. Arai, et al., *J. Appl. Phys.* 59, 3430 (1986)]

FIG. 12 Branching ratio changes as a function of codoping of SiO_2 .

Courtesy: M. J. Weber.

appropriate choice of modifiers; though these properties have generally been known, no in-depth microscopic studies have been made.

We wish then to conduct an FLN study of these silicate fibers as a function of modifier ion. The aim of this study would be to determine as was done by Brecher and others [43], the nature of the crystal field affecting these centers in glass. These results will allow us to predict the general behavior of this class of materials—the aim being to tailor the spectra of glasses to specific technical needs inclusive of their relaxation and efficiency.

b) Nonlinear optical properties: A number of unexpected and unusual nonlinear optical properties have been reported recently in activated glasses. For example, persistent laser induced gratings have been reported in a number of glasses [44]; in addition, certain other glasses show efficient upconversion, the latter being enhanced in the long interaction lengths employed in fibers [45]. These properties have implications to a host of technologies [46]; we wish to concentrate our attention in processes which produce upconversion in rare earth glasses as they will invariably entail the coupling of two or more ions through energy transfer interactions. Upconversion in crystals, for example, can be a rather complex process which can involve a number of intermediate states with cross relaxation often playing an important role. In a way, the inhomogeneous broadening encountered in glasses is expected to play a simplifying role in producing upconversion by providing resonant pathways through spectral overlap. Further simplification can be obtained by observing the effects of saturating suspected intermediate states in the upconversion pathway in the spirit of SRF; in these cases, the acceptor rather than the donor state would be driven nonlinearly with a second laser while upconversion of the donor states would be monitored. We propose to consider as our first example Er^{3+} silicate fibers in which strong $^4\text{S}_{3/2}$ green upconverted fluorescence is observed when the NIR $^4\text{I}_{9/2,11/2}$ states are pumped with an appropriate source [47]. The strength of the upconverted signal would be monitored as a laser saturates the ^4I and the ^4F states of the Er ion; the second laser will either

enhance or inhibit upconversion, thus incriminating the intermediates. Tm^{3+} is also a promising candidate for these studies [48].

A second type of process entails cooperative transition between two ions of the rare earth series with Yb^{3+} generally acting as the donor ion. These processes can be traced to earlier work by Shionoya and Nakazawa in crystals and can lead to sum and difference luminescence [49]. We propose to study these cooperative transitions in glass with an aim of identifying the appropriate microscopic, interionic interactions and the intermediate states involved in the upconversion processes using the two beam techniques discussed above.

We note that these experiments are made possible simply because new and tunable laser sources in the NIR and FIR have become available to us, as have new detection techniques. An additional experiment we would like to attempt is the stimulation of energy transfer in glasses; it has been established that lattice vibrations play a mediating role in the diffusion of optical excitation in glasses. We have shown recently that FIR laser pumping of solids allows the direct tunable generation of lattice vibrations in cases where translational symmetries do not exist; this applies, of course, to glasses. The proposed experiments would entail monitoring the spectral dynamics of Yb^{3+} in glass [7] while phonons of different frequency are generated by FIR pumping; these results would allow us to pinpoint the type of excitations involved in these dynamical processes and would be a possible way to map out the density of states function of TLS [50].

iii) — Studies of Extremely Diluted and Single Ions in Glasses: Our progress in this area has been outlined in Section A; as noted there, we are at the verge of successfully obtaining the visible-NIR spectrum of a single rare earth ion in a glass fiber at low temperatures. These experiments have proven to be extremely difficult and challenging, but we feel that the results obtained in these studies will also be extremely rewarding as they will allow the microscopic mapping of fields in disordered structures. During the

first portion of the renewal, we propose to focus our resources on this experiment and bring our present measurement to a satisfactory conclusion as soon as it is feasible.

In our present experiments which have used silicate fibers containing Nd^{3+} , Er^{3+} or Eu^{3+} invariably contain background fluorescences originating from a yet-to-be-identified defect in the host [51]; this signal is bothersome because of the very low photon count produced by the isolated ions. We have reduced the stray signal somewhat by proper gating techniques but have not as yet totally suppressed it. The composition of the fibers is attractive because it is one of the simplest of glasses; it might be necessary to attempt our experiments in other fibers whence this bothersome defect is not present. It is also generally true that 4f ions invariably are contaminated with their neighbors in the periodic table [52]; thus, if tens of the principal doping ion are isolated in the field of view as our experiments presently indicate, the volume will contain even fewer ions of the neighbor species. We are presently searching for Pr signals in the Nd samples, for Sm in the Eu samples and for Tm in the Er samples. In the latter, further discrimination can be effected by looking for upconversion or multiphoton recycling.

In the event we fully succeed in isolating the spectrum of a single ion, we propose to conduct a full analysis of the crystal field parameters and to model the structure leading to this field. We can then proceed with a mapping of the disordered structures as a function of position within the inhomogeneous distribution. Various other questions related to the quantum statistics of radiation can then also be considered.

Summary: We have described a number of areas of research into the dynamic properties of disordered systems which we propose to continue pursuing. These areas are continuations of work currently underway or a logical extensions of research which has been carried out under the present grant's auspices. The proposal deals with three areas which we believe are of fundamental importance to our understanding of amorphous systems:

- 1). Relaxation and transfer studies as a function of disorder, i.e. across an order-disorder boundary or disorder induced by compositional changes.
- 2). Studies of nonlinear properties of activated glasses with an emphasis on upconversion processes.
- 3). Conclusion of the Dilution Narrowing Studies and the isolation of a single center in glass; this work would then lead to a mapping of disordered structures.

We note in closing that we continue to fulfill one of the most important mission of this grant and that is the training of students in materials sciences. We have produced one doctorate degree during the current period and a second student will conclude his thesis under the present grant sponsorship.

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PART II: TECHNICAL REPORTS APPEARING UNDER DE-FG090-87ER45291

A. Refereed Articles:

1. W. M. Yen, Optical Spectroscopy of Activated Crystal Fibers in "Excited States of Transition Elements," W. Strek et.al., eds. (World Scientific, Singapore, 1989), pp. 631-635.
2. W. M. Yen, Spectroscopy of Materials with Restricted Dimensions, SPIE 1033, 100 (1989).
3. Robert Knutson, H. Liu, W. M. Yen and T. V. Morgan, Spectroscopy of Disordered Low Field Sites in Cr^{3+} :Mullite Ceramic, Phys. Rev. B40, 4264 (1989).
4. W. Jia, H. Liu, K. Lim and W. M. Yen, Piezospectroscopy Study of Ti^{3+} -Doped Sapphire Fibers, J. Lumin. 43, 323 (1989).
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16. S. M. Jaffe and W. M. Yen, Detecting Dilution Narrowed Systems, *Proceedings of OE/LASE '91-Optical Methods for Ultrasensitive Detection*, SPIE, in press.

B. Reviews:

1. W. M. Yen, Spectroscopy of Inorganic Glasses in "Disordered Solids: Structure and Processes, B. DiBartolo, ed. (Plenum, New York, 1989) pp. 299–315.
2. W. M. Yen, Introduction and Overview in "Dynamical Processes in Disordered Solids", W. M. Yen, ed. (Trans. Tech., Aedermannsdorf, 1990) Ch. I.

C. Monographs:

1. C. W. Struck, B. DiBartolo and W. M. Yen, eds., *Proceedings of the Symposium on Luminescence Science and Technology-Chicago*. The Electrochemical Society: Proceedings Volume **88–24** (ECS, Pennington, 1989).
2. W. M. Yen, ed., "Dynamical Processes in Disordered Solids," (Trans. Tech. Publications, Aedermannsdorf, 1990).

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D. Theses:

Robert Andrew Knutson: Site Resolved Spectroscopy of Cr^{3+} :Mullite Glass-Ceramic, Ph.D., August 1989. Present Position: St. Olaf College, St. Paul.

Steven Merrill Jaffe: Dilution Narrowed Spectroscopy in Activated Glass Fibers, Ph.D., expected December 1991.

E. Presentations:

We have presented invited talks at the following meetings and conferences:

1. March meetings of the American Physical Society, Anaheim (1990) and Cincinnati (1991).
2. Vth International Conference on Tunable Lasers, Irkutsk, October 1989.
3. Conference on the Dynamical Properties of Excited State in Condensed Matter (DPC '89), Athens, August 1989.
4. Annual meetings of the Electrochemical Society, Hollywood (1989) and Seattle (1990).
5. US-Japan Binational Seminar on Dynamics in the Excited State, Honolulu, October 1989.
6. Optical Society of America, Annual Meeting, Boston, October 1990.
7. OE/LASE '91, Los Angeles, January 1991.

We have contributed papers to ASPS March meetings in 1989-91, also to the Solid State Laser Conference (Hilton Head, 1991), to ICL'90 (Lisbon, 1990) and to CLEO/IQEL (Baltimore, 1991).

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