Laser-Induced Fluorescence-Line-Narrowing Spectroscopy of Glass : Nd

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Laser-induced fluorescence line narrowing has been studied in a series of samples of glass: Nd. The features of the nonresonant-excitation technique are described, and the results are discussed in terms of the known spectroscopic properties of the glass: Nd system. The concentration and temperature dependence of the line narrowing have been studied, and the spectral diffusion that is observed is analyzed in terms of resonant ion-ion energy transfer.

I. INTRODUCTION

The technique of laser-induced fluorescence line narrowing (FLN) in solids, first applied by Szabo in ruby,[1,2] permits the investigation of spectral transitions of impurities in solids with the removal of the accompanying inhomogeneous broadening which results from a site-to-site variation of the crystalline environment. If such a system is excited with a laser whose linewidth is narrow compared with the inhomogeneously broadened linewidth of the sample, a set of ions of narrow spectral definition is excited, and in the absence of spectral diffusion, only this set of ions will contribute to the fluorescence, which will then appear narrowed relative to *its* inhomogeneous linewidth. Of course, the extent of narrowing is limited by the homogeneous linewidths of both the absorption and the emission.

This technique is analogous to that of laser-induced FLN in a gaseous system, developed extensively by Feld and Javan,[3] in which a narrow velocity range within an inhomogeneously broadened Doppler profile is excited within the cavity of a laser. Here, in the absence of collisional cross relaxation within the Doppler line, a narrowed fluorescence is observed. Szabo has recently extended laser-induced FLN to the iodine system.[4]

Szabo's experiments involved resonance fluorescence of the ^2E-to-$^4A_2$ transition in ruby. Using a cooled single-frequency ruby laser with a 20-MHz bandwidth, Szabo was able to observe narrowing of the emission to approximately the self-convolution of the homogeneous linewidth. Szabo's technique, however, has more general applicability than the simple resonance case, and can be utilized in more complex spectroscopic systems involving nonresonant excitation, cascaded radiative and nonradiative transitions, and emission to excited levels as well as to the ground state. In such systems, the constraints on the homogeneous linewidths and absence of spectral diffusion remain applicable.

We have recently carried out a set of experiments examining laser-induced FLN in Nd: glass.[5-7] This work extended the generality of the FLN technique and demonstrated its wide applicability in rare-earth systems, with rather simple experimental techniques made possible by the spectroscopic characteristics of the rare-earth–glass system. In this paper we report the details of these experiments and discuss the experimental results.

In Sec. II the technique will be discussed in greater depth, while in Sec. III we describe the experimental details. In Sec. IV we present the experimental results and associated discussion, and Sec. V contains a summary and recommendations for further experiments.

II. DISCUSSION OF TECHNIQUE IN Nd: GLASS

The characteristic spectroscopic feature of rare-earth ions in glass is the substantial inhomogeneous broadening resulting from the distribution of the crystal fields at the variety of rare-earth-ion sites in the amorphous solid. Typical inhomogeneous linewidths of spectral transitions[8] for both absorption and emission are of the order of 50–100 cm^{-1}. It is therefore straightforward in glasses to find an overlap between a discrete laser line and an inhomogeneously broadened absorption line, and thereby excite only a class of ions in a narrow energy band within the inhomogeneous linewidth. If during the time between absorption and emission no spectral diffusion takes place, then only this class of ions will participate in the emission, and fluorescence line narrowing will be observed.

In the experiments on Nd: glass to be described, a useful overlap was noted between the 4727-Å line of the argon-ion laser and the lowest component of the $^4I_{9/2} \rightarrow {}^4G_{11/2}$ absorption of Nd: glass. In Fig. 1 we show the nature of this overlap. Here we see the absorption spectrum for Nd: glass in the 4700-Å region at 2 K. Superimposed on the spectrum is a small amount of scattered 4727-Å laser light to show the exact position to the over-
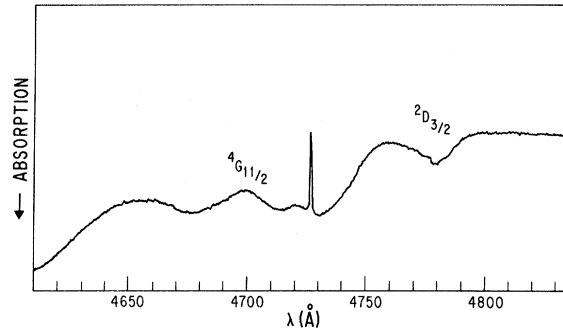
FIG. 1. Energy levels of Nd^{3+} in glass. Arrows indicate excitation and decay scheme for this experiment.

lap. It is seen that excitation takes place into the high-energy side of the lowest component of $^4G_{11/2}$. However, there are to a certain extent overlapping components which make the analysis somewhat more complex.

Figure 2 indicates the relevant relaxation processes involved in the experiment. After excitation into $^4G_{11/2}$ takes place, the ion quickly relaxes to the $^4F_{3/2}$ metastable level by means of a cascade of multiphonon relaxation processes across the small energy gaps separating the series of intervening levels. Studies of such multiphonon processes have been carried out and indicate the magnitude of the rates for these processes.[9,10] The time for the cascade from $^4G_{11/2}$ to $^4F_{3/2}$ can therefore be estimated to be of the order of 1 μsec or less. From the $^4F_{3/2}$, radiative emission takes place to the various levels of the ^4I term with a radiative lifetime of the order of 700 μsec. In this study we shall deal with the emission to the $^4I_{9/2}$ and $^4I_{11/2}$ multiplets in the 8800-Å and 1.06-μm regions, respectively. For each of these emission groups, there is a transition to the bottom level of the multiplet for which the inhomogeneous broadening is dominant, i.e., in this sense, a no-phonon line. It will be seen in the experimental section below that this is observed experimentally to be a necessary condition for observation of the FLN phenomenon. It is therefore useful at this stage to discuss the linewidth behavior for FLN observations under this type of nonresonant excitation.

Let us first consider the case where the inhomogeneous broadening is dominant both in absorption and fluorescence, i.e., $\Delta\nu_{ia} \gg \Delta\nu_{ha}$, $\Delta\nu_{if} \gg \Delta\nu_{hf}$, where $\Delta\nu_{ia}$ and $\Delta\nu_{ha}$ are the inhomogeneous and homogeneous linewidths of the absorption, respectively, and $\Delta\nu_{if}$ and $\Delta\nu_{hf}$ are the corresponding quantities for the fluorescence. The laser linewidth $\Delta\nu_l$ is assumed to be small compared with any of these linewidths. In general, the line shape of the FLN emission is given simply by the convolution of the homogeneous line-shape functions for
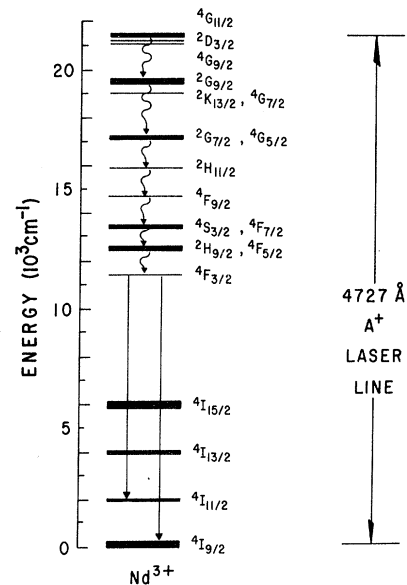

FIG. 2. Absorption spectrum of glass : Nd^{3+} in the 4700-Å region. The 4727-Å argon laser line is shown superimposed. Energy-level designations are taken from Ref. 8.

the absorption and the emission,

$$\sigma_{FLN}(\nu) = \int \sigma_{ha}(\nu_l - \nu')\sigma_{hf}(\nu' - \nu)d\nu' . \tag{1}$$

With this in mind, we specialize to the case here where the emitting level is metastable and the emission homogeneous linewidth is very small compared to the absorption homogeneous linewidth, since the absorption level undergoes fast relaxation by phonon decay across the initial gap.[11] The situation then is that indicated in Fig. 3, where we see that the emission reflects the homogeneous width of the absorption level. In physical terms, the narrow energy range that is excited has a width characteristic of the homogeneous broadening of the absorption level. The emission takes place from ions within this energy range and is therefore *inhomogeneously* broadened, but with a Lorentzian line shape that reflects the *homoge-*
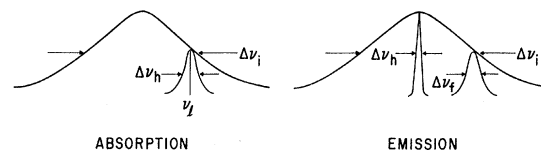

FIG. 3. Schematic diagram of linewidth behavior for laser excitation in the case of both absorption and emission having dominant inhomogeneous broadening. $\Delta\nu_h$ and $\Delta\nu_i$ indicate homogeneous and inhomogeneous linewidths, respectively, ν_l is the laser line, and $\Delta\nu_f$ is the linewidth of the emission. In this case, laser-induced fluorescence line narrowing is observed.
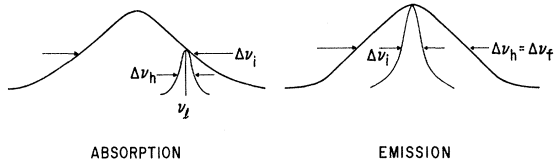
ABSORPTION   EMISSION

FIG. 4. Schematic diagram of linewidth behavior for laser excitation in the case of homogeneously broadened emission. No line narrowing is observed.

neous broadening of the absorption.

Now we consider a case of emission to a level where the homogeneous broadening dominates, such as occurs here for emission to the upper Stark levels of a multiplet, which have large homogeneous broadening as a consequence of their fast single-phonon relaxation to the Stark levels below. It is evident from Eq. (1) that this large $\Delta\nu_{hf}$ will be convolved with a narrow $\Delta\nu_{ha}$ into itself, and the emission shows the normal homogeneous width; i.e., the FLN phenomenon is not observed. This situation is indicated schematically in Fig. 4.

Finally, we consider the case where the absorbing level is, for example, an upper Stark level and has dominant homogeneous broadening because of the fast-phonon relaxation. The situation is shown schematically in Fig. 5. It is evident that for this case all ions within the inhomogeneous linewidth are excited proportionately; they all contribute to the fluorescence, and the FLN phenomenon is not observed.

Of course, these cases that have been discussed represent idealized situations. The actual FLN behavior in the Nd: glass is complicated by departure from the idealized models as well as by the overlap, both in emission and absorption, of components with different linewidth behavior.

III. EXPERIMENTAL DETAILS

A series of samples of laser glass with varying concentrations of Nd_2O_3 was obtained from the American Optical Co. The composition of the base glass specified by the manufacturer is as follows: 70.6% SiO_2, 7.6% Na_2O, 11.5% K_2O, 5.1% BaO, 1.6% Al_2O_3, 1.6% ZnO, 1.0% Sb_2O_3, 1.0% Li_2O. Small fluorescence samples, several millimeters on a side, were cut and ground for experimental study.

Samples were mounted for study in an immersion-type liquid-helium Dewar, which could be pumped on to reach a temperature of 2 K. For higher temperature, cold gas was passed over the sample, either nitrogen for temperatures above 77 K or helium for temperatures below 77 K. Temperature was monitored with a thermocouple and potentiometer.

Excitation was provided by a Coherent Radiation model 52 argon-ion laser. In the line-narrowing

studies, the laser power was maintained at several milliwatts, although there was no dependence of the observations on the power. Either back excitation or 90° edge excitation was employed and in most cases there was no depencence of the line-narrowing observations on the geometry of the excitation, although for the highest Nd_2O_3 concentrations there was resonance self-absorption which introduced a modification to the 8800-Å line shape. This feature will be discussed in greater detail below.

Detection was carried out with a Spex 0.75-m spectrometer fitted with an ITT FW-118 S-1 photomultiplier and photon-counting electronics. A 600-line/mm 4-in. grating provided an actual maximum resolution of about 0.3 Å in first order.

IV. RESULTS AND DISCUSSION

A. $^4F_{3/2} \rightarrow {}^4I_{11/2}$ Transition at 1.06 μm

Figure 6 shows the line-narrowed fluorescence spectra for the Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition in the 1.06-μm region under 4727-Å laser excitation. All spectra shown here are at 2 K. Figure 6(a) shows a comparison spectrum taken with broadband lamp excitation. Figures 6(b)−6(f) show the spectra for 0.5, 1, 2, 3, and 5% concentrations of Nd_2O_2 in the glass. In addition to these that we show here, line narrowing was also observed for the lower concentrations of 0.01 and 0.1% and for the higher concentration of 10%. These additional concentrations will be included below in our detailed discussion of the concentration dependence.

There are several observations to be made regarding the spectra of Fig. 6. First of all, in the peak near 1.06 μm, there are obviously two contributing components. One is the same spectrum seen under conventional broadband excitation exhibiting the full inhomogeneous linewidth. A second component, which is observed on the high-energy side of the line, shows narrowing down to a fraction of the full inhomogeneous width. By normalizing the inhomogeneous line-shape function and performing a point-by-point subtraction, it is possible to decompose the line-narrowed spectrum into these two components for further examination. The result of this decomposition is shown in Fig. 7.

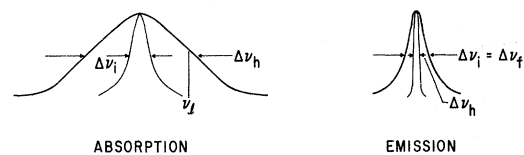The narrowed component in Fig. 7 has a rea-

ABSORPTION   EMISSION

FIG. 5. Schematic diagram of linewidth behavior for laser excitation in the case of homogeneously broadened absorption. No line narrowing is observed.
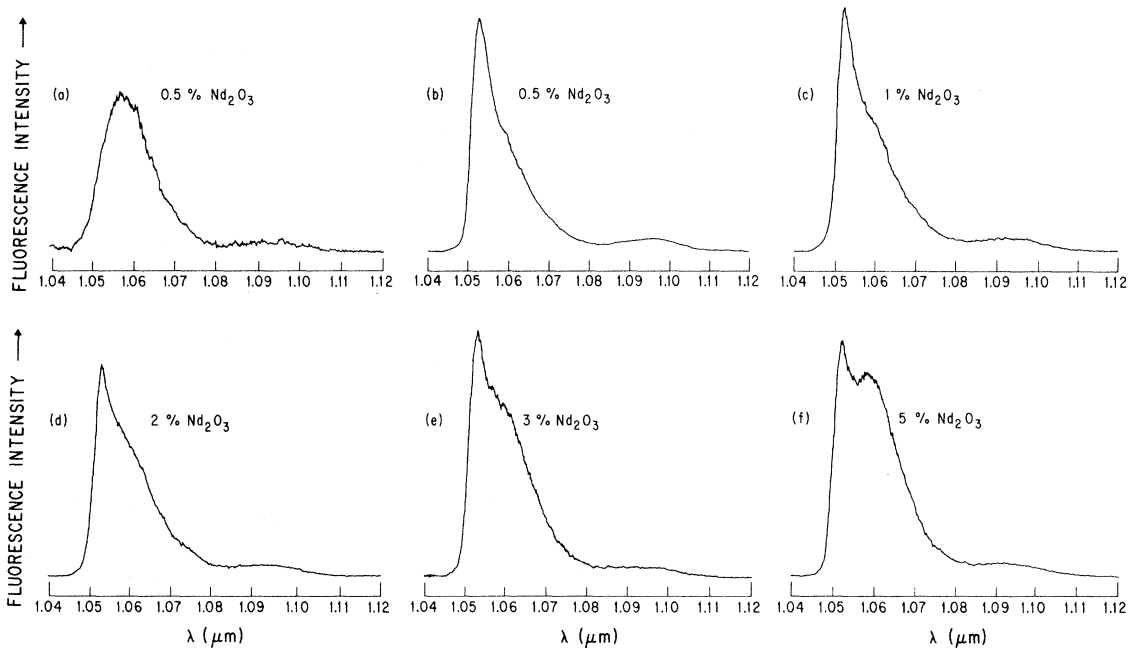
FIG. 6. Line-narrowing spectra in the 1.06-μm region for a series of concentrations of Nd_2O_3 in glass. For comparison, (a) shows the emission spectrum at 2 K in the 1.06-μm region for glass: (0.5% Nd^{3+}) under tungsten-lamp excitation; (b)−(f) are emission spectra at 2 K for glass with 0.5, 1, 2, 3, and 5% Nd dopings under 4727-Å laser excitation.

sonably good approximation to a Lorentzian line shape with a full width at half-maximum of 30 cm^{-1}. This is consistent with the excitation process discussed in Sec. II above. Referring back to Fig. 1, we see that the lowest component of $^4G_{11/2}$ (into which the 4727-Å excitation takes place) is separated by about 200 cm^{-1} from the next-lowest level, which is the uppermost component of $^2D_{3/2}$. For this kind of energy gap, single-phonon processes dominate and the relaxation rate is consistent with this amount of lifetime broadening. Thus, the 30-cm^{-1} width of the narrowed component reflects the homogeneous linewidth of this lowest component of $^4G_{11/2}$. The contribution due to the homogeneous linewidth of the fluorescence is expected to be small, since there are no fast relaxation processes associated with either the initial or terminal level of the radiation process.

Figure 7 also shows a large component of the emission with the full inhomogeneously broadened line shape. Such behavior would be expected for absorption by a level for which the homogeneous broadening is dominant (the situation indicated by Fig. 5). Again referring back to Fig. 1, we observe that in addition to excitation into the lowest component, there is excitation of the next-highest component of $^4G_{11/2}$ as a result of the overlap of these components. Since the separation in energy to $^2D_{3/2}$ is somewhat greater (~ 300 cm^{-1}), a larger homogeneous linewidth can be inferred. For a

sufficiently large homogeneous width (relative to the inhomogeneous width), line narrowing does not occur, and this may be assumed as a source of the residual component of the 1.06-μm emission which is not narrowed.

Referring again to Fig. 6, we observe that the line-narrowed component diminishes in intensity at high concentrations. This is a result of the onset of concentration-dependent spectral diffusion, and will be discussed in greater detail in Sec. IV C below.

A final point in Fig. 6 is the observation that line narrowing is not evident for transitions to the upper Stark components of $^4I_{11/2}$, as reflected particularly by the broadband emission peaking at 1.09 μm. Mann and de Shazer[8] have argued convincingly that such broadbands are composed of transitions to several superimposed Stark levels. (The 1.06-μm line is in fact partially composed of a transition to a second excited Stark level.) As a result of their single-phonon gaps to lower Stark levels, these levels have substantial homogeneous widths of their own. Figure 4 shows this situation, in which the homogeneous width of the emission washes out the line-narrowing behavior.

B. $^4F_{3/2} \rightarrow {}^4I_{9/2}$ Transition at 8800 Å

Figure 8 shows the line-narrowed fluorescence spectra for the Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{3/2}$ transition in the 8800-Å region wide 4727-Å laser excitation. The spectra are at 2 K. In this case it is the transi-
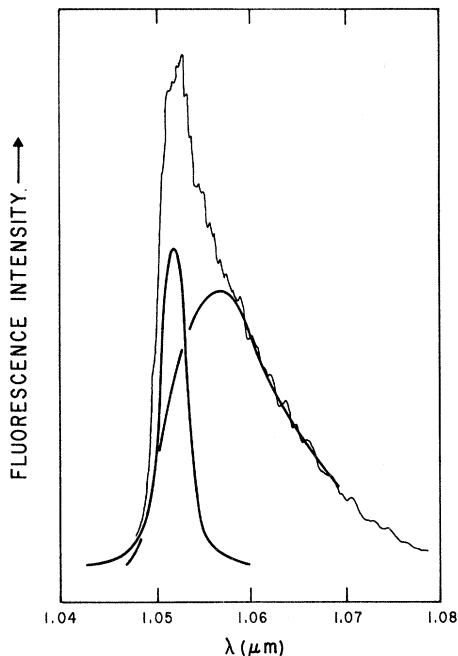
FIG. 7. Decomposition of line-narrowed emission at 1.06 μm into two components. The broad component shows the properly weighted conventional inhomogeneous line shape. The other component reflects laser-induced line narrowing and exhibits a half-width of 30 cm^{-1}.

tion to the ion ground state for which the inhomogeneous broadening is dominant and line-narrowing behavior is observed.

Figure 8(a) shows a comparison spectrum taken with broadband lamp excitation. Figures 8(b)–8(f) show the spectra for 0.5, 1, 2, 3, and 5% con-

centrations of Nd_2O_3 in the glass.

Generally speaking, the line-narrowed spectra for this transition reflect behavior similar to that of the spectra for the 1.06-μm group. Again in this case we observe line narrowing for the emission to the lowest component of the multiplet. This transition is to the lowest component of the $^4I_{9/2}$ multiplet, which is in fact the ground state of the ion. We also observe that the transitions to the upper components of $^4I_{9/2}$, which have substantial homogeneous broadening, do not exhibit line-narrowing behavior, as in the $^4I_{11/2}$ case.

The line-narrowed component again decreases as the concentration is increased, reflecting the onset of spectral diffusion. An additional concentration effect is observed here, however, in that there is a concentration dependence of the line shape, resulting from reabsorption of resonance emission. For this reason it is difficult to extract quantitative information on the line-narrowing behavior from this set of transitions. Consequently, in Sec. IV C below where the line-narrowing fraction is discussed, the 1.06-μm transition is used for quantitative information.

Finally, although only the transitions to $^4I_{9/2}$ and $^4I_{11/2}$ have been treated here, it is likely that the line-narrowing phenomenon would be equally manifest for transitions to the $^4I_{13/2}$ and $^4I_{15/2}$ multiplets, involving the lowest Stark levels in those cases as well, i.e., the emission lines without substantial homogeneous broadening.

C. Concentration Dependence

It has been pointed out that at higher concentrations the intensity of the line-narrowed component decreases as a result of the onset of spectral dif-
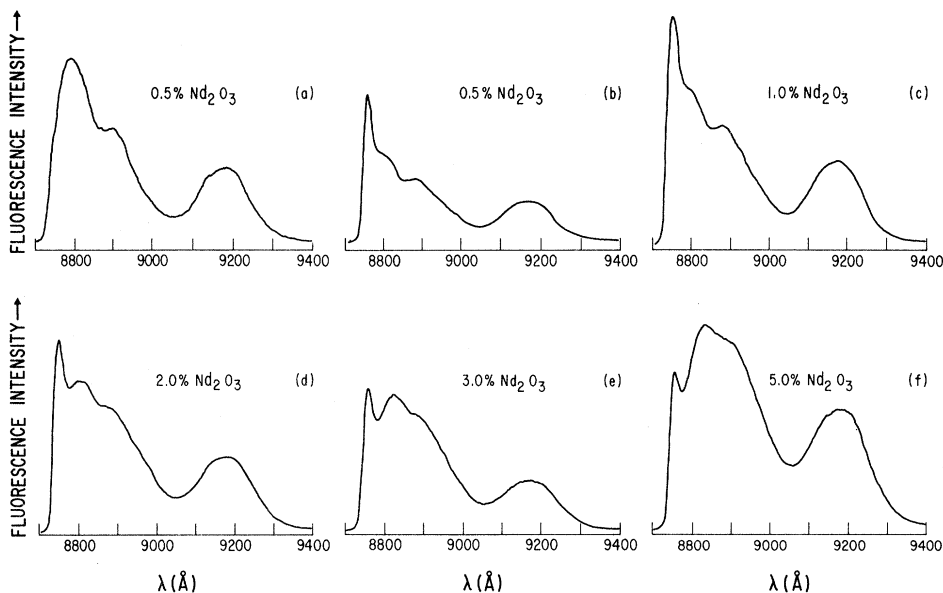

FIG. 8. Line-narrowing spectra in the 8800-Å region for a series of concentrations of Nd_2O_3 in glass. For comparison, (a) shows the emission spectrum at 2 K in the 8800-Å region for glass: (0.5% Nd^{3+}) under tungsten-lamp excitation; (b)—(f) are emission spectra at 2 K for glass with 0.5, 1, 2, 3, and 5% Nd dopings under 4727-Å laser excitation.

fusion. The source of this diffusion is the coupling between the Nd ions, by which the excitation is transferred to ions whose energies lie outside the line-narrowed portion of the spectrum.

In order to examine this behavior more closely it is necessary to quantify the diffusion process, and we therefore define the laser-induced line-narrowing fraction

$$\alpha(c, T) = \frac{\int \sigma_{c,T}(\nu)\,d\nu - \int \sigma_i(\nu)\,d\nu}{\int \sigma_{c,T}(\nu)\,d\nu} , \qquad (2)$$

where $\sigma_{c,T}(\nu)$ is the concentration- and temperature-dependent line-shape function under line-narrowing conditions, and $\sigma_i(\nu)$ is the conventional inhomogeneous line-shape function. The quantity α reflects the fraction of ions which show line-narrowing behavior, and can be understood in terms of Fig. 7 as the ratio of the two components of the 1.06-μm emission.

Numerical values of α were obtained for the 1.06-μm transition, over the concentration range 0.01–10%. These results are plotted in Fig. 9. It is evident that there is a sudden onset of spectral diffusion at approximately 1% Nd_2O_3 concentration. This critical-concentration behavior is similar to the critical-concentration behavior observed by Imbusch[12] for spatial diffusion in ruby. This behavior in ruby has been analyzed recently by Lyo[13] in terms of Anderson's model of diffusion in random lattices. For interactions which fall off sufficiently quickly with distance, it is found that there is a critical concentration, below which the excitation is localized and spatial diffusion does not occur.

The absence of spectral diffusion below 1% concentration in the glass does not necessarily preclude the occurrence of spatial diffusion: i.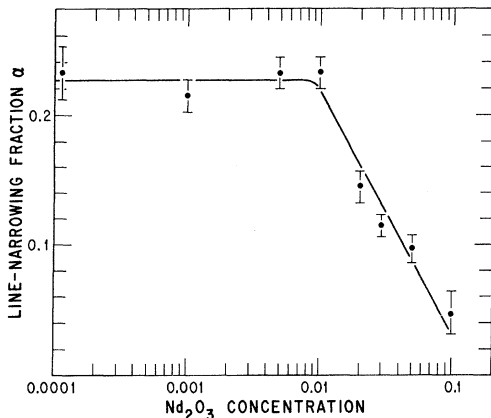e., the excitation could diffuse throughout the crystal, yet remain confined to a narrow energy range within the inhomogeneously broadened spectrum. However, for spectral diffusion to take place, it *is* necessary for spatial diffusion to be present. The critical concentration observed here for the onset of spectral diffusion may well reflect the critical concentration for spatial delocalization. The critical-concentration dependence of α suggests that the dominant ion-ion interaction yielding resonant energy transfer is short range in nature, i.e., either exchange or a higher-order electric multipole interaction. Exchange interactions in particular, by virtue of the orbital contribution to the exchange integral, have far less stringent selection rules than the low-order (long-range) electrostatic interactions.[14] Since in the energy transfer process a $^4F_{3/2} \to {}^4I_{9/2}$ transition is involved, this is a consistent interpretation. It is interesting to note that in several other recent studies[15-17] of energy migration in rare-earth crystals the effective interaction was identified to be electric dipole-dipole, and that in each case small changes in the quantum numbers were involved.

Lyo's treatment of energy transfer in an inhomogeneously broadened system involves consideration of the question of whether or not a given ion is on "speaking terms" with a second which is within the effective range of the interaction. In fact, for the case of glass there is such a large distribution in the crystal field (compared with the homogeneous linewidth) that one would not expect resonant transfer to occur at all for a random crystal field distribution. The observation of resonant transfer indicates that there is sufficient microcrystalline order for there to be a relatively slow site-to-site variation of the crystal field.

D. Temperature Dependence

In considering the temperature dependence of the line-narrowing behavior, we first consider the fundamental expression for resonant energy transfer,[18] in which the probability per unit time for the transfer of energy from ion 1 to ion 2 is given by

$$P_{12} = \frac{2\pi}{\hbar} |\langle 1\,2^* | V_{12} | 1^*\,2 \rangle|^2 \int \sigma_1(\nu)\sigma_2(\nu)\,d\nu , \qquad (3)$$

where $|i\rangle$ and $|i^*\rangle$ are the ground and excited states of ion i, in this case $^4I_{9/2}$ and $^4F_{3/2}$, respectively. V_{12} is the interaction, and $\sigma_i(\nu)$ is the homogeneous line-shape function for ion i.

The effect of the inhomogeneous broadening is to detune the σ_i with respect to one another. This reduces the value of the overlap integral in (3) and thus decreases the probability for resonant transfer. The effect of raising the temperature is to broaden[18] the σ_i and thereby increase the value of
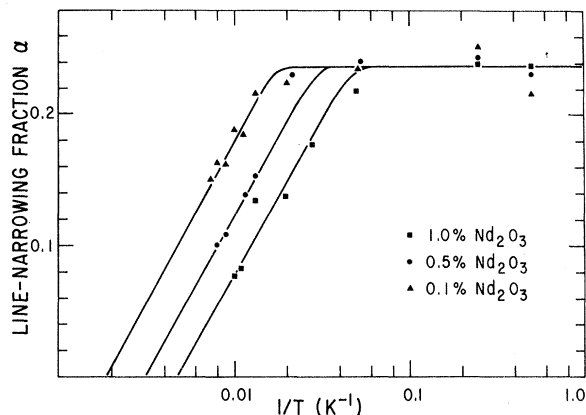

FIG. 9. Line-narrowing fraction α for the 1.06-μm emission in glass : Nd^{3+} as a function of Nd_2O_3 concentration.

FIG. 10. Line-narrowing fraction α for the 1.06-μm emission in glass : Nd^{3+} as a function of temperature for Nd dopings of 0.1, 0.5, and 1%.

the overlap integral, raising the energy transfer probability. Thus, any critical-concentration behavior has an intrinsic temperature dependence which is locked to the temperature dependence of the homogeneous linewidth.

The behavior of the line-narrowing fraction α as a function of temperature is shown in Fig. 10 for the concentrations 0.1, 0.5, and 1% Nd_2O_3 in glass, all of which are below the critical concentration at 2 K.

It is observed that at progressively higher temperatures for progressively lower concentrations, there is a sudden onset of spectral diffusion, with α continuing to decrease as the temperature is raised further. Since the critical concentration is temperature dependent, we interpret these temperatures to be those at which the critical concentration becomes equal to the concentration of the sample. As the temperature is raised further, the diffusion increases as a result of the continued increase in the overlap integral of Eq. (3).

V. CONCLUSIONS AND RECOMMENDATIONS

Laser-induced FLN has been studied for the first time in a nonresonantly excited rare-earth system. The behavior of the line narrowing as a function of concentration and temperature has yielded information regarding the spectral-diffusion properties of the system. It is observed that there is critical-concentration and temperature behavior, similar to the related phenomenon of spatial energy migration in these systems. It is not clear at this point, however, whether the spectral diffusion exhibits this behavior intrinsically or whether it is the spatial diffusion that shows critical behavior and the spectral diffusion merely reflects its dependence on the existence of spatial delocalization. Spatial effects can be studied straightforwardly through the dynamics of energy migration to impurities. It would be use-

ful to compare such a study with a line-narrowing study of the same system to elucidate this point.

The application of line-narrowing spectroscopy in rare-earth insulators has significant implications for the study of effects only observable at ultrahigh resolutions. In the case of rare-earth ions in glasses, the present study has been complicated by the presence of overlapping levels in both emission and absorption, as well as the relatively large homogeneous width of the absorption level. However, for other laser transitions and other rare-earth ions in glass with less complex energy levels, a much simpler experimental scheme should be possible.

However, in terms of analysis, the true value of this class of experiments should be manifested in the case of crystalline solids. In this case, though the inhomogeneous broadening still dominates for the no-phonon lines at low temperatures, it is far smaller, generally of the order of 0.1–1 cm^{-1}. Therefore, a tunable dye laser must be used to excite within the inhomogeneous width of these absorption levels. Such a source has been operated with a 7-MHz bandwidth, [19] and this currently imposes the limit on the resolvable homogeneous linewidth.

For such "no-phonon" transitions to the lowest level of a multiplet at low temperatures, the lifetime of the level will be determined by the multiphonon rate which can be of the order of 10^{-7} sec or longer. [9,10] (We assume that the radiative rate contribution is negligible.) At what point the homogeneous width becomes lifetime limited is not known, but it is likely that homogeneous widths of the order of 1–10 MHz should be observable in rare earths, thus implying a limiting resolution in excess of 10^7 (assuming equally small contributions to the line-narrowed width from the emission no-phonon line). Determination of the homogeneous width should in itself be a significant measurement, and complementary to the results of photon-echo experiments. [20] The achievement of such high resolution makes possible the study of effects previously inaccessible in the optical region (hyperfine interactions, Jahn–Teller effect, etc.). Thus, laser-induced FLN should become a significant new spectroscopic tool in studies of rare-earth insulators.

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Structure of the Adsorbed Helium Film near Monolayer Densities*

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A variational wave function is constructed for the ground state of He^3 and He^4 films adsorbed on graphite when the density is near that of a completed monolayer. By using this wave function, the density of the completed monolayer is calculated while the exchange effects and Debye temperatures are estimated. Comparisons with experiments are made. The pair-distribution function and the corresponding structure factor and Debye–Waller parameter are predicted.

I. INTRODUCTION

The general view of the adsorbed helium film is that near monolayer densities, the film exists as a compressed two-dimensional solid.[1] For instance, assuming two-dimensional close packing for He^4 adsorbed on graphite, the measured areal density of 0.115 $Å^{-2}$ for the monolayer[2] corresponds to a nearest-neighbor distance of 3.17 Å, much less than the 3.68-Å nearest-neighbor distance for the three-dimensional solid at 0 K and 25 atm. In fact, it is necessary to pressurize the solid at almost 500 atm to attain nearest-neighbor distances less than 3.2 Å. Debye-temperature measurements of the film[2] are consistent with this conception of the monolayer. Measured Debye temperatures of the film correspond to those of the solid pressurized from 300 to 500 atm. The cause of this compressional phenomena is the strong attractive interaction between the helium atoms and the graphite substrate. The energy it costs to compress the film by adding additional adatoms is compensated by the energy which is gained by having more adatoms in the deep potential well near the graphite surface. The monolayer density is then determined by a simple energy-balance criterion.[3]

Thermodynamic measurements cannot unambiguously determine the structure or phase of the monolayer. A definitive measurement could, however, be provided by a neutron scattering experiment. Such an experiment is now in the planning stages.[4] This type of experiment can measure the structure factor $S(Q)$ which is the Fourier transform of the pair-distribution function $g(r)$.[5] The calculation of $g(r)$, which is obtainable from the ground-state wave function, is the main motivation for this work.

The history of theoretical investigations of solid helium has demonstrated that short-range correlations, of the type incorporated into Jastrow wave functions, can be very important.[6] It would be expected then that these same correlations are also important in the adsorbed film. This expectation has, in fact, been demonstrated as correct at densities around 25 to 50% that of the monolayer, where there exists a liquid ground state.[7] However, recent theoretical investigations of quantum solids under very high pressure (greater than 10^3 bar) conclude that under these conditions two-particle correlations are not important and that quantum solids become harmonic solids.[8] Thus, it seems reasonable to expect the Gaussian–Hartree approximation[9] to be valid if applied to the ground