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Observation of Laser-Induced Fluorescence Line Narrowing in Glass:Nd

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Laser-induced fluorescence line narrowing has been observed for the first time in a nonresonantly excited rare-earth system. Excitation with the 4727-Å A^+ line into the $^4G_{11/2}$ level of Nd^{3+} in glass results in narrowing of transitions from the $^4F_{3/2}$ to both the $^4I_{9/2}$ ground manifold and the $^4I_{11/2}$ excited manifold. The concentration dependence of the line narrowing provides information regarding resonant ion-ion energy transfer within the inhomogeneously broadened system.

Recently, Szabo[1,2] has reported the observation of laser-induced fluorescence line narrowing in ruby. By exciting the $^2E \rightarrow {}^4A_2$ R-line emission with resonant ruby laser light, it is possible to select a narrow energy band within the inhomogeneous linewidth, and in the absence of spectral diffusion a narrowed fluorescence output is observed. The narrowing that can be observed is limited of course by the homogeneous linewidth.

We report here the first observation of laser-induced fluorescence line narrowing (FLN) for (a) a nonresonantly excited rare-earth system, and for (b) emission to an excited level as well as to the ground state. In glass:Nd, there are several argon laser lines which overlap with absorption lines for which the large inhomogeneous linewidth (generally 100 cm^{-1} or more) is the dominant line-broadening mechanism. For all such cases, excitation is restricted to a narrow energy range within the inhomogeneous linewidth, and to a certain extent the FLN phenomenon is observed. We shall deal here specifically with the 4727-Å A^+ laser line, for which excitation takes place into the lowest-energy component of the $^4G_{11/2}$ multiplet. Subsequently, the ion decays by (single-ion) multiphonon emission to the $^4F_{3/2}$. Such multiphonon processes have been studied in a large number of rare-earth systems[3,4]; and, based on these results and the size of the gaps involved, this nonradiative cascade should occur in less than 1 μsec. If, during this decay and during the 700-μsec lifetime of the $^4F_{3/2}$ no spectral diffusion takes place from within the narrow energy band into the remainder of the inhomogeneously broadened line, then the emission from the $^4F_{3/2}$ will be narrowed. For the 4727-Å excitation, concentration-dependent narrowing is observed for both the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition at 8800 Å and the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition at 1.06 μm.

Samples of soda-lime-silicate glass doped with varying amounts of Nd_2O_3 were obtained from the American Optical Company. Impurity levels were 0.5, 1, 2, 3, and 5% Nd_2O_3. Small samples were immersed in pumped liquid helium at 2 K, and the 4727-Å A^+ laser light was focused onto the sample. In order to prevent local heating, the laser power was purposely limited to several milliwatts. However, the results were not sensitive to either pump power, even at much higher levels, or to pumping geometry. The emission was detected with a Spex 0.75 M spectrometer fitted with an ITT FW-118 S-1 photomultiplier and photon-counting electronics. A 600-lines/mm 4-in. grating provided an actual maximum resolution of about 0.3 Å in first order.

The line-narrowed spectra in the 1.06-μm region under 4727-Å excitation are reproduced in Figs. 1(b)–1(f). Figure 1(a) shows for comparison the unnarrowed spectrum obtained with broad-

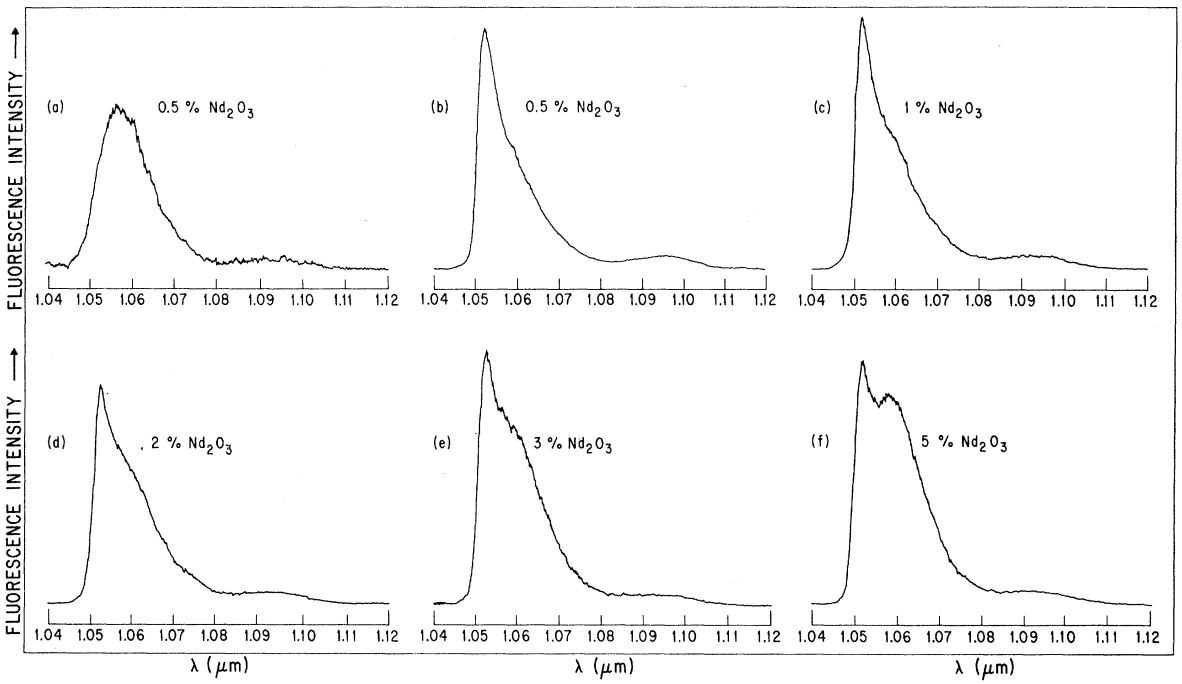

FIG. 1. (a) Emission spectrum at 2 K in the 1.06-μm region for glass:(0.5% Nd) under tungsten lamp excitation. (b)–(f) Emission spectra at 2 K in the 1.06-μm region for glass with 0.5, 1, 2, 3, and 5% Nd dopings under 4727-Å laser excitation.

band excitation for the 0.5% sample.

The FLN phenomenon is strikingly manifested in this set of spectra. It is seen that the 1.06-μm emission is composed of two contributions, one of which has the characteristic line shape of the unnarrowed inhomogeneously broadened line. The other contribution, appearing at the high-energy side of the line, consists of a component narrowed to 20–30 cm^{-1}. As the concentration of Nd_2O_3 is raised, this narrowed component decreases in intensity relative to the residual inhomogeneously broadened component, as a result of the onset of spectral diffusion due to resonant energy transfer. The line narrowing also decreases at elevated temperatures, and disappears by 175 K. The temperature dependence will be discussed elsewhere.[5]

The observed two-component line shape at 1.06 μm can be understood by reference to the absorption spectrum[6] in the region of the 4727-Å laser line, as shown in Fig. 2. The 4727-Å line has been superimposed on the absoprtion spectrum for comparison. It is seen that the laser line falls on the high-energy side of the lowest component of the $^4G_{11/2}$, and evidently excites in this way the line-narrowed component on the high-energy side of the 1.06-μm emission line. The 20–30-cm^{-1} width of the emission is consistent with the anticipated homogeneous linewidth for this level, in view of its 200-cm^{-1} separation measured at the peaks to the next lowest level, which is the highest-energy component of the $^2D_{3/2}$, and the expected lifetime broadening due to single-phonon relaxation over this energy gap.[7] It is also observed from Fig. 2 that for ions at certain sites, 4727-Å excitation takes place into the next highest level of the $^4G_{11/2}$, which is sepa-

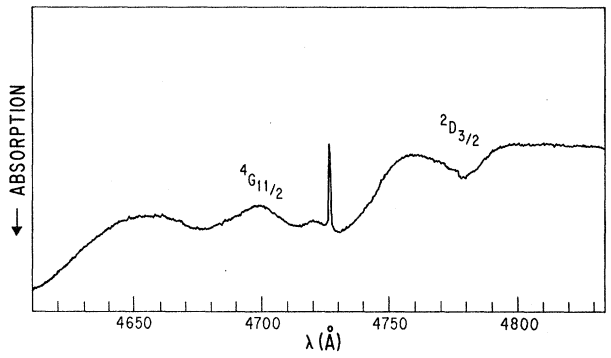

FIG. 2. Absorption spectrum at 2 K in the 4700-Å region for glass:Nd. The 4727-Å argon laser line is shown superimposed on the spectrum. Energy-level assignments are taken from Ref. 6.

rated from the $^2D_{3/2}$ by more than 300 cm^{-1}. For this energy gap, we would expect a substantially greater lifetime broadening as a result of the increased phonon density of states for the larger energy. If the lifetime broadening is at least comparable to the inhomogeneous width, then a narrow energy band will no longer be excited, and the emission will show fuller inhomogeneous broadening. Furthermore, any underlying absorption which is vibronically assisted is essentially homogeneously broadened (as a result of the breadth of the lattice vibration spectrum) and will result in the fully inhomogeneously broadened emission. These two effects, as well as any spectral diffusion from the line-narrowed region, would result in the observation of a portion of the emission with the full inhomogeneous breadth.

In order to gain insight into the concentration dependence of the spectral diffusion, we define the concentration-dependent line-narrowing fraction α,

$$\alpha(c) = \frac{\int \sigma_c(\nu)\, d\nu - \int \sigma_i(\nu)\, d\nu}{\int \sigma_c(\nu)\, d\nu},$$

where $\sigma_c(\nu)$ is the line-shape function for the 1.06-μm emission under 4727-Å laser excitation at the concentration c, and $\sigma_i(\nu)$ is the (concentration-independent) line-shape function at 1.06 μm under broad-band excitation. $\sigma_i(\nu)$ was normalized appropriately for each of the five concentrations, and $\alpha(c)$ was determined numerically. The result is plotted in Fig. 3.

There is a decrease in the diffusion rate at low concentrations, and a distinct knee at about the 1% concentration level. This behavior is strikingly analogous to that observed for resonant energy transfer in ruby[8] and discussed by Lyo in terms of a critical concentration for interactions which fall off quickly with distance.[9] For 1% Nd_2O_3 in this glass, the average interionic separation is approximately 11 Å. Dipolar interactions fall off too slowly to yield a critical-concentration behavior, so the interaction must be a higher-order multipole or exchange. At distances of the order of 10 Å, superexchange can be comparable to electric quadrupole-quadrupole coupling,[10] and by virtue of the orbital dependence of the exchange integral, the selection rules are much less stringent than in the case of multipolar interactions. Either mechanism could provide critical-concentration behavior.

Lyo points out, however, that in inhomogeneously broadened systems, one must consider

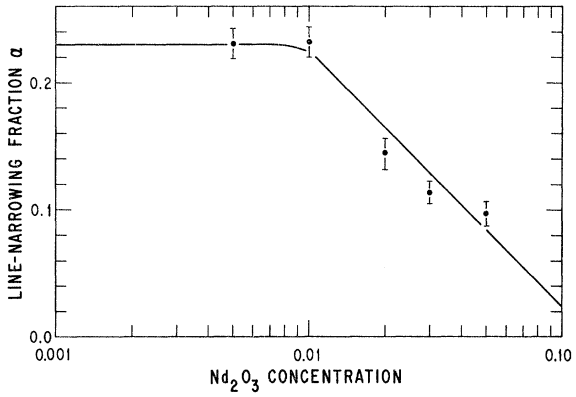

FIG. 3. Line-narrowing fraction α for the 1.06-μm emission in glass:Nd as a function of Nd_2O_3 concentration.

the question of whether or not a given excited ion is on "speaking terms" with a second ion within the interaction range. In fact, in the case of glass:Nd, in view of the small intrinsic (homogeneous) linewidth of the $^4F_{3/2}$ level compared with the inhomogeneous broadening, it is extremely unlikely that even within 20 Å, or twice the average distance at 1% concentration, there would be two ions with overlapping homogeneous lines. This conclusion, however, requires that the inhomogeneous crystal-field distribution be truly random on a microscopic scale, and that nonresonant diffusion processes are not important. One additional feature of our particular experiment is that during the multiphonon cascade the ion exists in levels with large amounts of phonon broadening for very short times ($10^{-10} - 10^{-11}$ sec), but it may be during this time that the diffusion occurs. In a recent study of diffusion in Cr-doped $Eu(PO_3)_3$ glass, the behavior was described well by a dipole-dipole interaction,[11] which has sufficient range to couple more distant ions which are compatible in energy. The dipolar interaction does not, however, introduce a critical-concentration behavior, such as we observe here; but it may be the source of the residual inhomogeneously broadened signal observed below 1% concentration, in addition to the sources discusses earlier. Experiments are being carried out at lower and higher concentrations, and these results as well as a detailed analysis of the energy-transfer behavior of this system, will be published elsewhere.[5]

In conclusion, Szabo's laser-induced fluorescence line-narrowing (FLN) technique has been extended to a nonresonantly excited rare-earth system with fluorescent transitions to excited

levels as well as to the ground state. The attractiveness in extending this technique to rare-earth crystalline systems is evident. In crystals, the lowest level of a multiplet generally relaxes by radiative decay or by multiphonon emission to the next lowest multiplet, and can have a homogeneous linewidth of less than 1 MHz. The limitation to the spectroscopic resolution is then the inhomogeneous width, which is generally of the order of 0.1 cm^{-1}. Since at low-enough concentrations the spectral diffusion is sufficiently arrested, a tunable coherent source, such as a dye laser or parametric oscillator, can be used to match the sharp rare-earth levels and thereby observe the FLN phenomenon. The possibility of using nonresonant excitation significantly extends the number of levels which can be studied by the FLN technique, with the additional experimental convenience that the emission is well separated in wavelength from the excitation. Application of Szabo's FLN technique to nonresonantly excited rare-earth systems should permit optical studies of a wide range of excited levels with resolutions of greater than 10^7.

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Very Low-Temperature Specific Heat of Submonolayer Helium Films*

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The specific heats of He^3 and He^4 films adsorbed on exfoliated graphite have been measured between 0.04 and 4.2 K, for fractional monolayer coverages between 0.25 and 0.63. He^3 films show anomalies around 0.1 K that are absent in the He^4 results. A possible explanation is given in terms of spin ordering of the He^3 atoms.

Recent experiments have[1,2] shown that submonolayer coverage He^3 and He^4 films adsorbed on exfoliated graphite (Grafoil[3]) have substantial lateral mobility, to the extent that they behave like ideal two-dimensional (2D) gases at temperatures around 4 K. In the range between $\frac{1}{4}$ and $\frac{2}{3}$ of a monolayer, published results can be summarized in the following way.

For fractional monolayer coverages x of about $\frac{1}{4}$ of a monolayer, He^4 heat-capacity measurements show a peak around 1.2 K while He^3 measurements show no peak; both tend to $C/Nk = 1$ at 4 K. The He^4 results have been interpreted[4] as quasi-2D Bose condensation produced by a weak inhomogeneity in the substrate adsorbing potential. The He^3 experimental curves were fitted by curves for a 2D ideal Fermi gas with high degeneracy temperatures (for example, $T_F{}^{2D} \simeq 3.4$ K for $x = 0.26$) provided that a small adjustment was made in the number of particles responsible for the signal.

At higher x large heat-capacity peaks appear for both isotopes at coverages that closely correspond to the helium atoms being in registry with the graphite lattice of the substrate, the most notable being the λ-type peak occuring for He^4 at $x = 0.6$, which is equivalent to $\frac{1}{3}$ of the hexagons of the graphite lattice being occupied by helium atoms.

Substantial mobility of helium atoms adsorbed on graphite is expected theoretically.[5] The ordering transition in registry with the substrate is receiving careful treatment[6] since it resembles a 2D lattice-gas order-disorder transition.