PHYSICAL REVIEW B VOLUME 34, NUMBER 12 15 DECEMBER 1986

Energy transfer among Yb^{3+} ions in a silicate glass

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(Received 2 June 1986)

We have used time-resolved fluorescence line narrowing to study energy transfer among Yb^{3+} ions in a silicate glass as a function of energy mismatch between donors and acceptors and temperature from 4.2 to 51 K. The observed spectra are consistent with a one-phonon-assisted multipolar interaction between Yb^{3+} ions with a variation with site separation of r^{-13}. These results are compared to that reported for other rare-earth-ion transitions in glasses and crystals.

I. INTRODUCTION

The phenomenon of energy transfer among optically active impurities in insulating glasses continues to be the subject of much speculation, despite a long history of experimental and theoretical investigation. Although the observation of energy transfer is not difficult, the extraction of quantitative information on the nature of the interactions responsible have been possible in few experimental studies. The lack of useful experimental data has not encouraged theoretical studies of this difficult problem.

We have used time-resolved fluorescence line narrowing (TRFLN) to study the migration of energy in the ${}^2F_{5/2}(1)$-${}^2F_{7/2}(1)$ transition of Yb^{3+} in a silicate glass. Although this transition has many properties which make it ideal for such studies, it has not been the subject of extensive investigation because of its location in an experimentally difficult region of the electromagnetic spectrum. We have developed a narrow-band pulsed color center laser that has allowed us to study this transition with a degree of sophistication impossible in previous studies. First let us review briefly the current understanding of energy transfer among optically active impurities in solids. We will then describe the experimental system we have applied to this problem and present the results of our studies. Finally, we will discuss these results in light of present models and draw what conclusions are possible.

II. REVIEW OF ENERGY TRANSFER IN SOLIDS

Energy transfer among different species of optically active impurities is easily observed, with reports of sensitized luminescence occurring as early as 1924.[1] Early studies investigated the concentration dependence of the transfer rate to extract the variation of the interaction between optically active centers with site separation.[2] The seminal works of Förster[3] and Dexter[4] identified the predominate interactions as exchange coupling and an induced multipolar interaction, the latter yielding a variation of transfer rate with site separation of A/r^s, where $s=6$, 8, and 10 for the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively.

These early theories required overlap between the emission and absorption spectra of the donors and acceptors in order to conserve energy, and were unable to account for the observation of transfer among rare-earth ions, which have well-separated, sharp optical transitions. Studies of such systems has led to the development of theories that include phonon-assisted interactions in order to conserve energy in the transfer process.[5,6] Transfer between different species of centers is generally accompanied by the emission of several phonons, due to the large energy differences involved,[7] typically 1000's of cm^{-1}. Transfer among a single population of ions in a crystal usually occurs via an inelastic scattering of two phonons,[8,9] the one-phonon direct process being ineffective due to the low density of states at the small energies characteristic of inhomogeneous linewidths of rare-earth ions in crystals, a few cm^{-1}, and interference effects when the phonon wavelength becomes comparable to the site separation between the donor and acceptors.[10] Transfer among a single population of rare-earth ions in a glass involves energy differences intermediate to that of crystals and different centers, with typical inhomogeneous widths being on the order of 100 cm^{-1}.

Studies of energy transfer among a homogeneous population of optical centers have been made possible only recently with the development of time-resolved laser spectroscopy.[11] In TRFLN, a pulsed narrow-band tunable laser is used to selectively excite a subset of ions from within the inhomogeneously broadened profile. Inokuti and Hirayama[12] modeled the decay of the donor fluorescence with time after the laser pulse as a function of the distance dependence of the transfer rate between centers. In the case of a multipolar interaction between donors and acceptors that both fluoresce, the ratio of the donor fluorescence to the total fluorescence intensity is given by[13]

$$R(t)=\frac{I_D(t)}{I_D(t)+I_A(t)}=\exp\left[\frac{-t}{\tau_{\mathrm{tr}}}\right]^{3/s}, \tag{1}$$

where $I_D(I_A)$ is the integrated intensity of the donor (acceptor) fluorescence and τ_{tr} is the mean transfer time, which is related to the critical concentration of the Förster-Dexter theory by

$$\tau_{\rm tr}=\tau_D\left[\Gamma(1-3/s)\frac{n_A}{c_0}\right]^{s/3}, \qquad (2)$$

where τ_D is the donor lifetime in the absence of transfer, $\Gamma(x)$ is the gamma function, n_A is the acceptor concentration, and c_0 is the critical concentration. There is no analytic expression for the decay of the luminescence intensity when exchange coupling dominates, and numerical methods must be used.[12]

The role of phonons in the transfer process is revealed by the energy mismatch and temperature dependence of the transfer rate. One-phonon processes lead to a vanishing transfer rate to centers with greater energy, as long as the population of the necessary phonon mode is $\ll 1$. Transfer occurs to centers with lower energy through the spontaneous emission of phonons. This process is also ineffective at small energies as discussed above. Two-phonon processes lead to equal transfer rates above and below the donor energy, and generally have a stronger temperature dependence than one-phonon processes.

TRFLN has been applied to the study of energy transfer in a number of rare-earth crystal systems.[14] One of the more-detailed studies investigated energy migration among Pr^{3+} ions in PrF_3.[8] Within the inhomogeneously broadened main line of the $^3P_0$-$^3H_4(1)$ transition, the transfer is observed to occur via a two-phonon process, due to the narrow inhomogeneous width, 2 cm^{-1}, while a one-phonon process is responsible for transfer between ions in this main line to ions in satellite lines, because of the much larger energy mismatch of 32 cm^{-1}. In this case, the distance dependence was consistent with a dipole-dipole coupling between ions. Optical transitions between the $4f$ levels of the rare earths occur via forced electric dipole transitions; however, it has been pointed out[15] that higher-order terms may dominate energy transfer processes due to the different interaction lengths involved. The emission of a visible photon involves a relatively long-wavelength perturbation, on the order of 1 μm, while the site separation between ions involved in energy transfer is typically much smaller. The strong distance dependence of the multipolar interactions can lead to higher-order processes dominating at small distances, especially as they can be allowed in first order, while the dipole moments of $4f$-$4f$ transitions vanish under the Laporte rule and require the crystal-field interaction to mix in the higher-lying $5d$ orbitals.

The application of TRFLN to rare-earth glass systems has been less successful, due to the large inhomogeneous broadening of the optical transitions. This leads to problems such as accidental degeneracy,[16] where the various components of the excited state overlap for different sites, resulting in nonselective excitation. This leads to broad backgrounds, making the separation of the spectra into donor and acceptor contributions ambiguous. For this reason, the most thoroughly studied rare-earth glass system has been the $^5D_0$-$^7F_0$ transition of Eu^{3+},[17–19] which is a singlet-to-singlet transition and does not suffer from this problem. However, the $(j=0)$-$(j=0)$ transition is highly forbidden and weak, and the results are not generally applicable to the majority of rare-earth-ion transitions.

The only other rare-earth transition that has been successfully used to study energy transfer in glasses is the $^2F_{5/2}(1)$-$^2F_{7/2}(1)$ of Yb^{3+}.[16,20,21] In this case the Stark splittings of the excited-state components are sufficient to overcome the inhomogeneous broadening due to the amorphous environment. As Yb^{3+} lacks only one electron to fill the $4f$ orbital, there are only two $4f^{13}$ configurations. This simple energy-level spectrum removes the possibility of cross relaxation between the initially excited state and some intermediate level,[22] which can compete with transfer processes that leave the excitation in the initially excited state. The separation of these two manifolds, $\sim 10\,000$ cm^{-1}, puts this transition in a difficult part of the spectrum at around 1 μm, where there are no stable laser dyes or sensitive detectors. Previous studies have used optical parametric oscillators,[16] broadband lamps filtered by monochromators,[20] or the fortuitous coincidence of a Kr-ion line with this transition[19] to provide excitation sources. These studies lacked either the resolution, sensitivity, or tunability to carry out a full determination of the transfer processes involved in the Yb^{+3} glass system. In the following section we will describe the experimental system we have developed to study this system in more detail.

III. EXPERIMENTAL CONSIDERATIONS AND RESULTS

The narrow-band pulsed color center laser used as the excitation source in our experiments has been described in detail elsewhere.[23] It provides a tunable source from 860 to 1000 nm with a peak pulse energy of 16 μJ in a $\sim$5-ns pulse with a bandwidth of 3.3 Ghz, allowing excitation throughout the $^2F_{5/2}$ manifold. The laser system was triggered by a chopper,[24] which blocked the observation path during the laser pulse to prevent saturation of the detection electronics by scattered light. A silicate glass sample(Lawrence Livermore National Laboratory Catalogue No. 8038) containing 2.12×10^{20} Yb^{3+} ions per cm^3 was placed in a gas-flow cryostat, along with calibrated germanium and platinum resistance thermometers. The fluorescence was dispersed by a 0.85M Ebert-Fastie spectrometer and measured with a Varian VPM-159 photomultiplier. This device has an InGaAsP photocathode, which has unparalleled sensitivity at these wavelengths, but which is unstable at room temperature. The phototube was kept in a thermoelectrically cooled housing at -50 °C at all times. Initial experiments were carried out using single-channel photon-counting techniques.[25] This method was adequate to measure the energy mismatch dependence of the transfer rate, but the time required for accurate characterization of the decay of the entire fluorescence spectrum with time was prohibitive. For these measurements a computer-controlled transient digitizer was used to measure the decay of the fluorescence as the computer stepped the spectrometer through the fluorescence spectrum. The transient digitizer consists of a two-channel 50-MHz analog-to-digital converter (ADC) connected to a microprocessor controlled display, analysis, and storage system, which is interfaced to a microcomputer via an IEEE-488 interface bus. This computer controlled the transient digitizer and an intelligent stepping motor connected to the spectrometer drive. The transient digitizer averaged the signal at a given wavelength for the desired amount of time, around 10 seconds, then this data was transferred to the microcomputer and the spectrometer stepped to the next wavelength. The laser power was monitored by a silicon photodiode connected to one channel of the ADC. An internal program was executed on the transient digitizer after each decay curve was acquired to calculate the average laser power during the measurement interval, which was stored in a data record in the transient digitizer. At the end of a spectral scan this data was transferred to the microcomputer for use in normalizing the fluorescence data. No correction was made for the spectral response of the detection system. A typical spectral scan consisted of 30 decay spectra taken at 5-Å intervals containing 40 points with a sampling period of 40 μs.

Examples of the data acquired using the single-channel counting system are shown in Fig. 1. Trace *A* shows the fluorescence observed 1.5 ms after the laser pulse for an excitation wavelength within the $^2F_{5/2}(1)$-$^2F_{7/2}(1)$ transition, while trace *B* shows the effect of nonresonant pumping when the laser is tuned to the higher-lying $^2F_{5/2}(2)$ state. This latter state relaxes rapidly to the $^2F_{5/2}(1)$ state, which then fluoresces. Due to accidental degeneracy and the homogeneous broadening of the $^2F_{5/2}(2)$ state, the fluorescence in this case reflects the entire inhomogeneous profile of the $^2F_{5/2}(1)$-$^2F_{7/2}(1)$ transition. On the other hand, when the laser is resonant with the lowest Stark component of the $^2F_{5/2}$ manifold, strong narrowing of the fluorescence is observed, along with the appearance of a broad background fluorescence that grows relative to the laser resonant fluorescence with increasing delay from the laser pulse. Comparison of the two fluorescence profiles reveals the energy mismatch dependence of the transfer process responsible for this background fluorescence, as shown by trace *C*. As can be seen, the transfer process is inhibited for ions closer than ~ 10 cm^{-1} in energy to the initially excited ions, then increases linearly with energy separation until it reaches a maximum at ~ 40 cm^{-1}, and then falls off with larger energy separation. This behavior is independent of where the laser is tuned within the high-energy side of the inhomogeneous profile. No transfer is observed to ions with higher energy than those initially excited. This is consistent with a one-phonon process relying on the spontaneous emission of phonons.

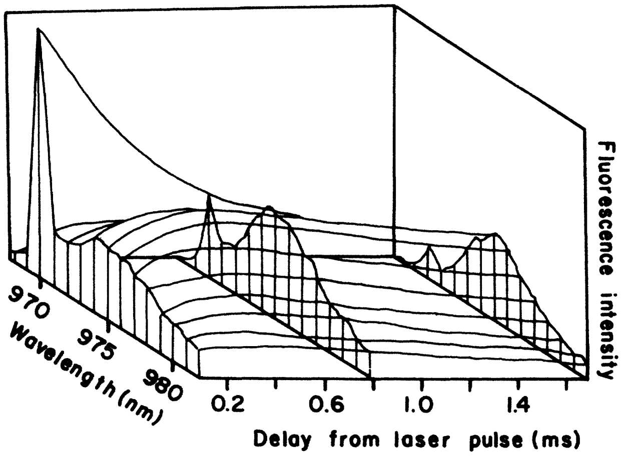

FIG. 2. Three-dimensional plot of fluorescence intensity versus delay from laser pulse and fluorescence wavelength of $^2F_{5/2}(1)$ state of Yb^{3+} in silicate glass at 51 K, $\lambda_{\text{excite}}=9700$ Å.

Figure 2 shows a representative scan of the fluorescence spectrum as acquired by the transient digitizer system. The general features discussed above are reproduced in this data, although the spectral resolution in this data is not as high as that obtained using the single-channel sys-

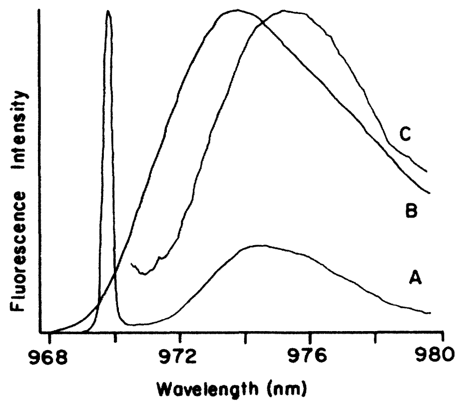

FIG. 1. Fluorescence spectrum of the $^2F_{5/2}(1)$ state of Yb^{3+} in silicate glass at 4.2 K, 1.5 ms after laser pulse, with $\lambda_{\text{excite}}=9697$ Å, within the $^2F_{5/2}(1)$ state (trace *A*), $\lambda_{\text{excite}}=9600$ Å, within the $^2F_{5/2}(2)$ state (trace *B*), and the normalized transfer rate as a function of wavelength, *B*/*A* (trace *C*).

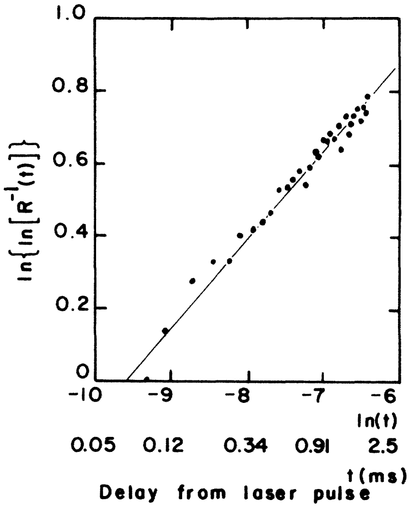

FIG. 3. Plot of $\ln\{\ln[R^{-1}(t)]\}$ versus $\ln(t)$ for the data shown in Fig. 2. The straight line is a linear regression fit to the data with a slope of 0.24 and a $\ln(t)=0$ intercept of 2.58.

TABLE I. Summary of results of $R(t)$ analysis.

T (K)	Slope	Intercept	s	τ_{tr} (μs)
16	0.233	2.48	12.9	23.8
24	0.227	2.23	13.2	54.1
29	0.261	2.57	11.5	52.9
41	0.239	2.58	12.6	20.5
51	0.239	2.75	12.6	10.1
mean			12.6±0.6	

tem. However, the important quantity in determining the multipolarity of the transfer interaction is the integrated intensity of the donor and acceptor fluorescence as a function of delay from the laser pulse, for which this data is clearly adequate and represents a factor of 40 increase in the information that can be collected in a single spectral scan over the single-channel system. The data was separated into donor and acceptor contributions and the value of $R(t)$ was calculated as a function of delay from the laser pulse, with a typical result shown in Fig. 3. The slope of the straight-line fit to the data is $3/s$, while the intercept at $\ln(t)=0$ is related to the transfer time τ_{tr} through Eq. (1). Table I summarizes the results obtained at five different temperatures for the slope and τ_{tr}. We shall discuss these results in the following section.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

The energy mismatch dependence illustrated in Fig. 1(c) is interesting in light of that reported by other workers,[16–21] who generally find the transfer rate is independent of energy mismatch and equal above and below the excitation wavelength, and thus ascribe the phonon interaction to a two-phonon process. However, many of these studies were carried out at higher temperatures than the work reported here, with excitation on the low-energy side of the inhomogeneous distribution. In such cases, the back transfer from the ions on the high-energy side of the distribution can distort the observed fluorescence spectrum, as can the Boltzmann distribution of phonons participating in the transfer process. In our experiments, the transfer occurs through the spontaneous emission of phonons, and the probability of back transfer is very small. This leads to a temperature-independent transfer rate, as confirmed by the values of τ_{tr} in Table I. These values are very sensitive to the value of s used in the extrapolation to $\ln(t)=0$, resulting in the large spread in the results. The fluorescence spectra reported here are very similar to that observed in the Kr lamp experiment,[20] which was also carried out at low temperature. No information as to the temporal development of the fluorescence spectrum was reported, and of course there was no possibility to study the variation of the spectra with excitation wavelength. Recent studies[19] of the ${}^5D_0$-${}^7F_0$ transition of Eu^{3+} showed transfer at low temperatures (100—10 K) was not uniform across the inhomogeneous profile, with the observed background showing several peaks. The typical concentrations of Eu^{3+} ions in these studies were nearly a factor of 10 higher than the Yb^{3+} concentration in the glass studied here. The peaks observed in the Eu^{3+} study may be indicative of clustering of the Eu^{3+} ions.

Comparison to the work of Alimov *et al.*[18] indicates the coupling between Yb^{3+} ions is much stronger than that between Eu^{3+} ions. Using a similar analysis, they found a mean transfer time of 6.6 msec at 77 K for a silicate glass containing 10^{21} Eu^{3+} ions per cm^3, assuming a quadrupole-quadrupole interaction between ions. The mean transfer time reported here is over 2 orders of magnitude smaller, while the ion concentration is a factor of 5 less. This difference is undoubtedly due to the forbidden nature of the ${}^5D_0$-${}^7F_0$ transition of Eu^{3+}.

The decay of $R(t)$ with time after the laser pulse is somewhat faster than would be expected for a simple quadrupole-quadrupole coupling of Yb^{3+} ions. Such a coupling is expected to dominate energy transfer in the case of Yb^{3+},[26] but a number of effects, such as the polarization of the ligands around the rare earth, may lead to a stronger distance dependence. Recent studies of cross relaxation among Pr^{3+} ions in LaF_3 have indicated that exchange coupling may dominate in this process.[27,28] The strong distance dependence observed here may be indicative of an exchange coupling between ions, but at present no model of such an interaction is available for comparison with the data.

Another possible explanation is that the Yb^{3+} ions have a fractal[29] distribution over the length scale of the transfer interaction. A fractal distribution would lead to the replacement of the 3 in the exponent of Eq. (1) with d, the fractal or Hausdorff dimension of the Yb^{3+} distribution.[30] The observed radial distance dependence of the transfer rate would then be consistent with a quadrupole-quadrupole interaction among Yb^{3+} ions distributed on a fractal of dimensionality 2.4. Considering the uncertainty of the distance dependence of such interactions, independent confirmation of such a distribution is called for.

V. CONCLUSIONS

We have presented the results of detailed experiments on energy transfer among Yb^{3+} ions in a silicate glass from 4.2 to 51 K. The observed spectra are consistent with a one-phonon-assisted quadrupole-quadrupole interaction between Yb^{3+} ions, with the distance dependence of the interaction being somewhat stronger than would be predicted by a simple model.

ACKNOWLEDGMENTS

We would like to thank M. J. Weber for providing the samples used in these experiments and his continued interest in this work, L. F. Mollenauer for the color centers used in the laser system, and D. L. Huber and G. P. Morgan for discussing these results with us. This work was supported by U.S. Department of Energy (DOE) Contract No. DE-AC02-83ER45023.

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