

the signal height is roughly proportional to the length of vortex line present in the container. Therefore, we conclude that for  $\omega \leq 9.23 \times 10^{-2} \text{ sec}^{-1}$  there is no vortex. For  $\omega \geq 9.90 \times 10^{-2} \text{ sec}^{-1}$  there is a vortex in the cylinder, and we can say that the experimental critical velocity  $\Omega_c$  is between the above velocities, or  $\Omega = (9.56 \pm 0.33) \times 10^{-2} \text{ sec}^{-1}$ . The error bars in the figure represent the amount of peak-to-peak noise observed in the signal over a period of  $\sim 30$  min. The larger variations in signal heights between different points are probably due to variations in the gain of the low-temperature proportional counter used to detect the trapped charge.

Using the above procedures to determine  $\Omega_c$  for a number of cylinders, we can make comparisons with the theoretically predicted critical velocities  $\Omega_t$ . Such comparisons are made in Table I. Although the theoretical formulas are exact with no adjustable parameters, the formulas do depend on the lateral dimensions of the cylinders. Because of imperfections in the machining and coating of the cylinder walls, there are uncertainties in the lateral dimensions, and these produce the indicated uncertainties in  $\Omega_t$ .

As shown in the table,  $\Omega_c$  and  $\Omega_t$  agree within the uncertainties, roughly 10%. We conclude from our observations that the method of sample preparation described above probably produces the equilibrium state, and that the calculations based on free-energy arguments predicts the cor-

rect equilibrium state.

Further refinements and more data are necessary before a more precise comparison between theory and experiment can be made.

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## Localization and Migration of Energy among $\text{Sm}^{3+}$ Ions in $\text{CaWO}_4$ Crystals

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We investigate energy transfer between  $\text{Sm}^{3+}$  ions in different crystal-field sites in  $\text{CaWO}_4$  crystals by use of laser time-resolved spectroscopy techniques. The dependence of the results on time and temperature show the interaction to be electric quadrupole-quadrupole and the interaction strength to be much less than the inhomogeneous linewidth of the transition. This leads to the localization of the energy at low temperatures, confirming the predictions of Anderson.

It has been theoretically predicted by Anderson<sup>1</sup> that for a system exhibiting inhomogeneously broadened transitions, spatial localization of excitations can occur under certain conditions. Such localization occurs below a critical concentration of active sites when the interaction causing transfer falls off faster than the inverse third power of the distance between these sites. Lyo<sup>2</sup>

found theoretically that the chromium-ion excitation energy in ruby crystals should be localized for concentrations less than about 0.3 at.% but it has been difficult to prove this experimentally.<sup>3</sup> Recently Orbach<sup>4</sup> has suggested time-resolved spectroscopy measurements of the energy migration among rare-earth ions as a method for observing the Anderson localization phenomenon.

However, systems investigated thus far by this technique have involved the dipole-dipole interaction which does not fall off fast enough with ion-ion separation to meet the localization criteria.

We report here results of a laser-excited time-resolved spectroscopy investigation of energy transfer between trivalent samarium ions in calcium tungstate crystals. The transfer mechanism is shown to be an electric quadrupole-quadrupole interaction. Energy localization is observed at low temperatures but diffusion occurs at high temperatures when homogeneous broadening of the transitions is present.

The crystals were excited by a nitrogen-laser-pumped tunable dye laser having a linewidth of  $\leq 4 \text{ \AA}$  and a pulse duration of about 5 nsec. A boxcar integrator was used to monitor the fluorescence at fixed delays after the laser pulse.

The samples were excited near  $4050 \text{ \AA}$  where the maximum absorption transition for  $\text{Sm}^{3+}$  occurs in  $\text{CaWO}_4$ .<sup>5</sup> The fluorescence spectrum consists of a series of lines originating from the lowest metastable level (the lowest crystal-field state from the  $^4G_{5/2}$  multiplet) and terminating at the various crystal-field levels of the multiplets of the  $^6H$  ground state. As the laser excitation is scanned from  $4050$  to  $4020 \text{ \AA}$ , different

sets of lines appear in the fluorescence spectrum which can be identified with samarium ions at different, nonequivalent types of crystal-field sites. The data described here concern lines assigned to transitions terminating on the lowest Stark level of the  $^6H_{5/2}$  ground-state multiplet for ions at these different sites. The two dominant lines in the spectrum occur at  $5614$  and  $5631 \text{ \AA}$  and are probably due to two types of local charge compensation, vacancies and sodium ions. There are smaller lines near to each of these which may be associated with sites having more distant charge compensation. Energy transfer between ions in these different sites is accompanied by phonon absorption or emission to conserve energy.

The most pertinent experimental results are shown in Figs. 1-3 for a sample containing 2 at.% samarium. Figure 1 shows the ratio of the relative integrated intensity of the  $5631\text{-\AA}$  line to that of its closest high-energy satellite line as a function of time after the laser pulse at  $10^\circ\text{K}$ . Theoretically this ratio should vary as<sup>6</sup>

$$\ln[I_a/I_s + 1] = \gamma t^{3/p} + \ln(W_a/W_s + 1), \quad (1)$$

where  $W_a$  and  $W_s$  are the activator and sensitizer pumping efficiencies and  $p = 3, 6, 8,$  and  $10$  corresponds to diffusion, electric dipole-dipole, di-

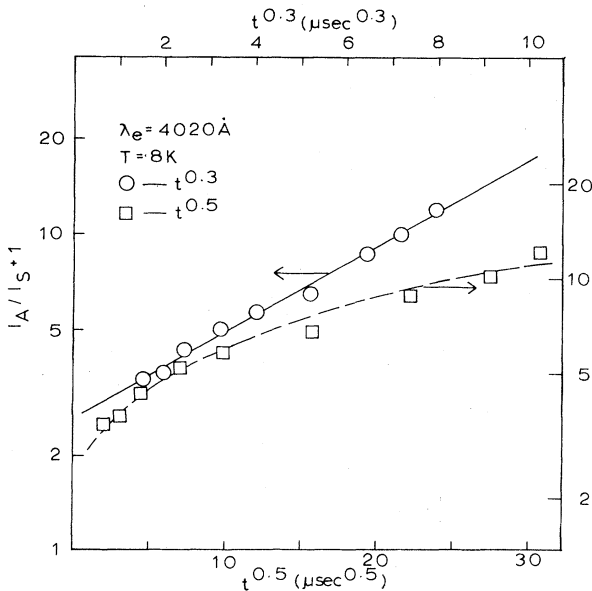


FIG. 1. Time dependence of the ratio of the integrated fluorescence intensity of the  $5631\text{-\AA}$  to that of the  $5627\text{-\AA}$  line at  $10^\circ\text{K}$  for a calcium tungstate crystal containing 2 at.% samarium.

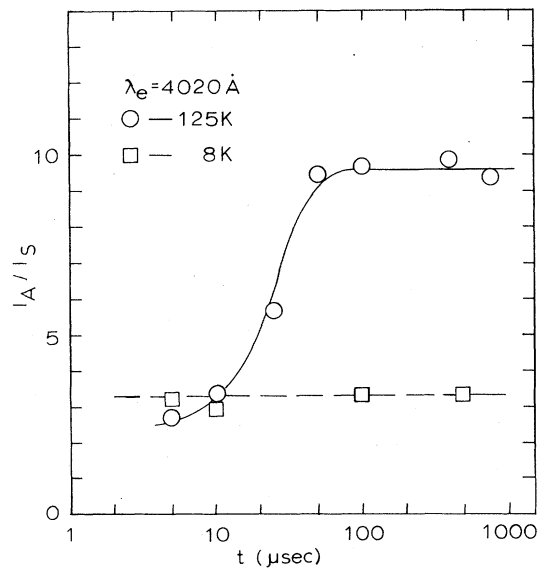


FIG. 2. Time dependence of the ratio of the integrated fluorescence intensity of the  $5631\text{-\AA}$  to that of the  $5614\text{-\AA}$  line at  $10^\circ\text{K}$  and  $125^\circ\text{K}$  for a calcium tungstate crystal containing 2 at.% samarium.

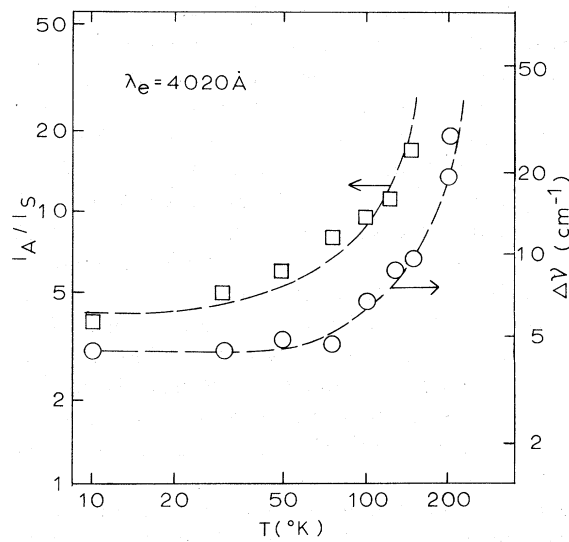


FIG. 3. Temperature dependence of the ratio of the integrated fluorescence intensity of the 5631-Å to that of the 5614-Å line at 250  $\mu$ sec after the laser pulse for a calcium tungstate crystal containing 2 at.% samarium. Also shown is the temperature dependence of the width of the 5614-Å line for this sample.

pole-quadrupole, and quadrupole-quadrupole energy transfer. Here  $\gamma = \pi D R C_a$  for diffusion (with  $D$  the diffusion coefficient and  $R$  the trapping radius) and

$$\gamma = \Gamma(1 - 3/p)(C_a/C_0)(\tau_s^0)^{-3/p}$$

for multipolar interaction, with  $C_0$  being a "critical concentration" and  $\tau_s^0$  the sensitizer decay time. The expression for  $I_s$  is derived in Ref. 6 under the assumption of no diffusion among sensitizers and no back transfer from activator to sensitizer. Both of these conditions should hold for our case at low temperatures, and a similar procedure can be used to obtain an expression for  $I_a$  under the same conditions. The ratio of these intensities results in Eq. (1) if it is assumed that the sensitizer and activator transitions have approximately the same fluorescence decay times and radiative lifetimes, which is verified experimentally. The second term on the right-hand side of the equation represents the ratio of the number of activator to sensitizer ions excited directly by the laser pulse at  $t=0$ . The interaction Hamiltonian causing transfer falls off as  $1/R_{sa}^{p/2}$ . Thus with a definition of the high-energy samarium site as the sensitizer and the low-energy site as the activator, a plot of  $I_a/I_s + 1$  versus  $t^{3/p}$  on a semilog graph should yield a

straight line for the physically correct value of  $p$ . Figure 1 shows the data to have an excellent straight-line fit for  $p=10$  and to exhibit significant curvature for  $p=6$ . This demonstrates that the interaction mechanism causing energy transfer between samarium ions at different crystal-field sites in calcium tungstate is higher order than electric dipole-dipole and probably is electric quadrupole-quadrupole in nature. Thus spatial localization due to inhomogeneous broadening may occur in this system.

At low temperature no energy transfer occurs between ions in the two dominant kinds of sites as shown by the lack of time dependence of their intensity ratio plotted in Fig. 2. This low-temperature value simply reflects the number of directly excited ions in the two types of sites. However, at high temperatures the intensity ratio of these lines exhibits an increase at short times and approaches a constant value at long times demonstrating the existence of energy transfer between ions in these two types of sites. The constant value at long times indicates that an equilibrium distribution has been reached between the populations of the two types of sites thus implying the existence of back transfer.

The increase of the intensity ratio of the two major lines with temperature is shown in Fig. 3. This indicates an increase in the energy transfer rate with temperature which is opposite to the predictions of a single-step, phonon-assisted process.<sup>7,8</sup> This is not surprising since there is no measurable spectral overlap between these two transitions. Also the increase in energy transfer cannot be attributed to increased population of higher-lying Stark components of the ground-state manifold since transitions between these levels and the lowest metastable state have lower oscillator strengths than the transition involving the lowest Stark level.<sup>5</sup> The most reasonable explanation of the observed temperature dependence of the energy transfer is that the excitation energy on the high-energy sites migrates by a multi-step diffusion process until it becomes trapped at a low-energy site where either emission or back transfer can occur.

Thus the excitation energy in the high-energy samarium sites is localized at low temperatures but delocalized at high temperatures. Since the Anderson model for localization should be related to the inhomogeneous contribution to the linewidth, the temperature dependence of the width of the high-energy line is plotted in Fig. 3. Below about 60°K the line has a Gaussian shape

with a constant width. This inhomogeneous broadening is due to small differences in the crystal fields at each samarium ion. At higher temperatures the linewidth increases significantly and the shape becomes more Lorentzian as a result of phonon-broadening processes. There is good correlation between the temperature-dependent increase of the energy transfer and the homogeneous line broadening. We conclude that differences in local crystal fields cause neighboring high-energy samarium sites to be out of resonance thus inhibiting energy migration at low temperatures. As phonon broadening increases the widths of the energy levels at each samarium site, neighboring samarium sites become partially in resonance allowing for energy transfer.

The qualitative dependence of the results on time and temperature described above demonstrate the existence of energy localization and migration for excited  $\text{Sm}^{3+}$  ions in  $\text{CaWO}_4$  crystals. The occurrence of spectral diffusion of excitation at high temperatures but not at low temperatures has been observed previously but transfer mechanisms were not determined.<sup>9,10</sup> Quantitatively the slope of the line in Fig. 1 gives a rough estimate of the interaction strength for Sm-Sm energy transfer. With the assumption of a quadrupole-quadrupole interaction, an upper limit on the magnitude of the nearest-neighbor interaction strength can be obtained by assuming perfect overlap of the sensitizer and activator lines with Lorentzian line shapes having half-widths on the order of a gigahertz. (Our measured linewidths are limited by the width of the laser line. The value used here is on the order of that found from experiments using lasers with much narrower linewidths.<sup>11</sup>) Expressed in wave numbers this is on the order of  $10^{-6} \text{ cm}^{-1}$ , which is very much less than the low-temperature inhomogeneous linewidth of  $4.4 \text{ cm}^{-1}$ . Even for more ideal overlap conditions which may exist for neighboring ions in high-energy sites, and with allowance for experimental broadening due to the width of the laser line, the interaction

strength will still be much less than the inhomogeneous broadening which is another criterion for Anderson localization to occur.<sup>1,2</sup> Finally, the solid line in Fig. 2 represents the best theoretical fit to the data assuming energy transfer by diffusion. This yields a value for the diffusion coefficient at high temperatures on the order of  $10^{-10} \text{ cm}^2 \text{ sec}^{-1}$  which is similar to values obtained from other investigations of energy migration among rare-earth ions in crystals and glasses.<sup>12</sup> The quantitative interpretation of these results will be discussed further in a more detailed description of this work.<sup>13</sup>

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