

Determination of upper limits for spatial energy diffusion in ruby

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Direct measurements of the diffusion distance of $\bar{E}({}^2E)$ state excitation by time-resolved degenerate four-wave mixing in ruby are reported. Measurements are made on crystals with Cr^{3+} concentrations varying between 0.05 and 1.55 at. % at 10°K. In all cases an upper limit of 30 nm is determined for the diffusion distance within the fluorescence lifetime.

Energy transfer in ruby (Cr^{3+} -doped Al_2O_3) has been the subject of many investigations. It has long been known that optically excited Cr^{3+} ions can nonradiatively transfer energy to Cr^{3+} ion-pair sites,^{1,2} and more recently a series of fluorescence line-narrowing experiments have beautifully demonstrated phonon-assisted spectral energy transfer between nonresonant single Cr^{3+} ions.³ Because both of these nonresonant energy transfers require phonon assistance, resonant nonradiative transfer between single Cr^{3+} ions having the same transition frequencies has been thought to occur much more quickly so that energy could rapidly migrate from single ion to single ion; i.e., such single-ion excitations would behave as delocalized excitons on the time scale of radiative decay.²⁻⁶ The concepts of Anderson localization^{7,8} have therefore been applied to the ruby system and it has been calculated⁵ that a critical concentration for single-ion to single-ion energy transfer should exist at about 0.3-at. % Cr^{3+} . Below this concentration the states would be localized, whereas above the critical concentration rapid energy migration would occur. A recent experiment⁶ has found some evidence for the existence of a mobility edge which would separate the delocalized or excitonic states from localized states within the R_1 line. In this paper we present the results of an attempt to make a direct measurement of the energy migration distance in ruby.⁹ The experimental results indicate that the Cr^{3+} $\bar{E}({}^2E)$ energy does not diffuse more than 30 nm in the fluorescence lifetime (~ 3 msec) for all concentrations between 0.05 and 1.55 at. % and that rapid energy diffusion over larger distances does not occur.

The technique which we utilized was time-resolved degenerate four-wave mixing.^{10,11} This technique can be viewed as the creation of a transient population grating in the ruby crystal. Transient gratings have been used to study energy transport and thermal diffusion by many groups¹²⁻¹⁵

and these techniques provide a convenient and direct method for measurement of diffusion processes. We shall briefly discuss the technique and some of the difficulties associated with its implementation in ruby. One problem has been the appearance of a complicating effect—the creation of high electric fields $\sim 10^6$ V/cm in the ruby crystals by optical illumination. A detailed report of this optically produced electric field will be published separately.¹⁶ We have been able to eliminate these fields so that our diffusion measurements were not disturbed by them.

The experimental arrangement differed slightly from that which we have used in earlier¹¹ measurements of degenerate four-wave mixing in ruby in order to facilitate diffusion measurements. Three beams from a vertically polarized argon-ion laser operating at 476.5 nm struck a thin (typically 0.01 cm thick) ruby sample. Two beams were exactly counterpropagating, while the third was at an angle $\theta = 3^\circ$ to the other two beams. The nonlinear mixing process in the crystal produced a fourth beam (backward wave) which propagated exactly counter to this third beam. This mixing process can be viewed as the production and subsequent reading out of a thick holographic phase and absorption grating whose spatial period is $\lambda/[2 \sin(\theta/2)]$, where λ is the wavelength in the medium. In the case of ruby, the generation is primarily due to a phase grating.¹¹ The application of gratings to the measurement of diffusion has been discussed by several authors^{12,14,15} and recently reviewed by Eichler.¹² In these measurements, the existence of diffusion caused the grating to relax at an increased rate with an increase which was dependent on grating periodicity. In our experiments, the grating was produced when the third beam interfered with one of the two counterpropagating pump beams, hence resulting in a spatial modulation of the $\bar{E}({}^2E)$ excited state population. To assure that only one well-defined grat-

ing was produced, mechanical choppers were used so that only one of the two counterpropagating beams was present during the grating writing time period. The path lengths of these two writing beams from the laser to the crystal were adjusted to be equal, hence assuring they would produce good interference fringes. The other counterpropagating beam was used to produce the backward wave by reading out the grating and was present only during the readout period. The relaxation of the $\bar{E}^{(2)E}$ population grating was monitored by measurement of the intensity of this backward wave. The use of the choppers also had the advantage that the amount of scattered light from the sample was minimized during the readout period, since at that time the sample was only illuminated by the readout beam. The backward wave was collected with a lens and passed through a pinhole to a photomultiplier. The pinhole eliminated nearly all of the scattered light in the experiment. The photomultiplier output was then averaged with a transient signal averager (PAR 4202).

The three laser beams were each loosely focused on the ruby crystal to a spot size of approximately 0.02 cm. The total laser intensity on the crystal was limited to approximately 25 W/cm². This low intensity was used to assure that the laser did not heat the crystal and to avoid possible complications due to high intensity, such as the creation of thermal gradients. Experiments were performed at temperatures ranging from 10 to 77 °K. The temperature was determined by monitoring the ratio of intensities of the R_1 and R_2 lines.

If the excitation transfers from one Cr³⁺ ion to another in a random way so that excitation energy migration can be considered diffusive, the population grating will smear out, causing a reduction in backward wave intensity. The time dependence of the intensity is given^{1,2} by

$$I_{BW} = I_0 \exp(-t/\tau), \quad (1)$$

where

$$\frac{1}{\tau} = \frac{2}{\tau_0} + 2D \left(\frac{4\pi}{\lambda} \sin \frac{\theta}{2} \right)^2; \quad (2)$$

τ_0 is the fluorescence lifetime, λ is the excitation wavelength in the crystal, θ is the angle between the writing beams (either 3° or 177°), and D is the diffusion constant. By comparing the backward wave lifetime obtained with the two periodicities determined by $\theta = 3^\circ$ or $\theta = 177^\circ$, we can determine the diffusion constant D .

Figures 1–3 illustrate some typical measurements of the backward wave intensity following the termination of the writing beams by the chopper. Each represents the average taken by the transient signal averager of about 10 000 writing and then

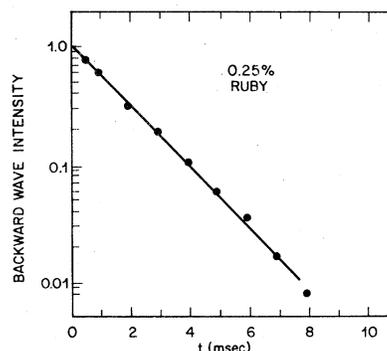


FIG. 1. Backward wave intensity vs time after writing beams are turned off. The angle between the writing beams was 177°; Cr³⁺ concentration was 0.25 at. %.

reading cycles. In Fig. 1 the decay is quite a good exponential, whereas the curves in Figs. 2 and 3 are decidedly nonexponential. We have determined that the nonexponential behavior is the result of interference effects between the desired backward wave signal and the scattered light which passes through the pinhole. Since this scattered light is relatively small, its effect appears only in the tail of the decay of the grating. In some cases the interference is constructive and leads to an apparent slowing of the relaxation as in Fig. 2, whereas in other cases the interference is destructive as in Fig. 3. We were unable to eliminate this interference effect. To reduce its influence on our measurements, we fitted them to only the initial slope of the backward wave relaxation curves when determining grating lifetimes; however, this effect was responsible for the error limits in our results.

The excitation wavelength of 476.5 nm was chosen

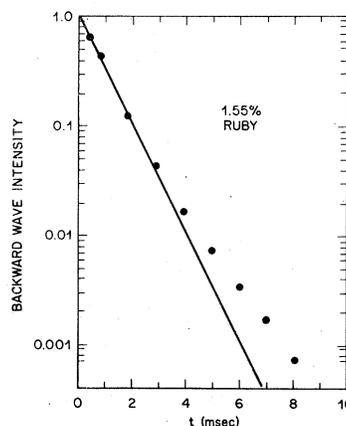


FIG. 2. Backward wave intensity vs time. The angle between the writing beams was 3°; Cr³⁺ concentration was 1.55 at. %.

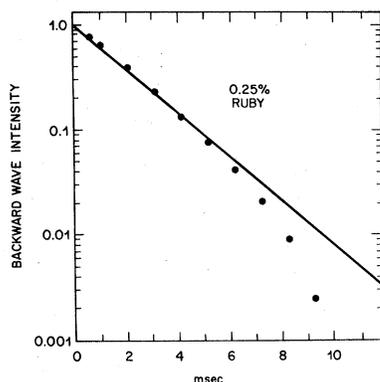


FIG. 3. Backward wave intensity vs time. The angle between the writing beams was 3° ; Cr^{3+} concentration was 0.25 at. %.

as a result of the discovery that illumination of the crystals with other lines of the argon laser quickly resulted in the production of large electric fields in the ruby crystal. For example, illumination with 514.5 nm radiation for a few minutes at 50 W/cm^2 produced a field of 10^6 V/cm in our 0.87-at. % sample. This field gives rise to a large Stark splitting¹⁷ and hence effectively broadens the linewidth. It makes the energy transfer process more unlikely since, for complete splitting of the lines, it essentially reduces by half the concentration of Cr^{3+} ions which are resonant with each other. We found it possible to eliminate this field by illumination at high intensity (greater than 3 kW/cm^2) due to large photoconductivity in the ruby samples. Hence all of our data were obtained by first (and periodically thereafter) illuminating the crystal with high-intensity 514.5 nm light and then performing the diffusion measurements at 476.5 nm.

In Table I we give values of measured backward wave lifetimes obtained at 10°K with the two gratings corresponding to $\theta = 3^\circ$ or $\theta = 177^\circ$. Several of these crystals (those with concentrations of 0.87 and 0.25-at. %) were also measured at room temperature and at 77°K with identical results. The lifetimes are clearly seen to decrease as the Cr^{3+} concentration is increased.¹⁸ While there appears to be a very small difference for the lifetimes of the two gratings, it is not significant with-

in the $\sim 5\text{-}10\%$ accuracy of our measurements. This lack of dependence on grating periodicity indicates the absence of rapid diffusion. The lifetime measurement¹⁹ on the 0.25-at. % sample of $\sim 1.85 \text{ msec}$ corresponds to a fluorescence lifetime of 3.7 msec in close agreement with the accepted value of 3.6 msec for dilute ruby crystals.

Measurements were also made on 0.05- and 0.1-at. % crystals with identical results. From these data we can estimate upper limits on the diffusion constant D and on the distance d for migration within the fluorescence lifetime of each sample. In all cases, the energy diffuses over distances less than 30 nm within this lifetime. Similar reports of extremely small diffusion constants in ruby have been made by Eichler¹³ and Hamilton *et al.*¹⁵ in room-temperature measurements.

The apparent absence of significant diffusion in the $\bar{E}^{(2E)}$ energy among the Cr^{3+} ions is quite surprising. Imbusch interpreted his fluorescent decay measurements² as implying an average single-ion to pair transfer rate of 10^3 sec^{-1} , from which Birgeneau estimated⁴ an average single-ion-single-ion transfer rate of 10^7 sec^{-1} for ruby of 1-at. % concentration. This rapid rate of transfer is consistent with Imbusch's model² of very rapid transfer of energy between isolated Cr^{3+} single ions such that they act as a bath which can continually feed energy to pair ions. Imbusch interpreted his observations of pair fluorescence relaxation in terms of this rapid single-ion transfer model. This model is still controversial, with some groups²⁰ favoring very slow single-ion energy transfer, although with rapid single-ion to pair transfer. However, the most recent measurements of Selzer *et al.*³ of single-ion to pair-ion transfer could only be explained if there exists rapid single-ion energy migration. Likewise the experiment of Koo *et al.*⁶ on Anderson localization was successfully analyzed, assuming rapid transfer. In particular, for a 0.25-at. % crystal, a transfer rate of $P > 10^6$ was required.

It is difficult to know exactly how to convert our upper limits for diffusion constants into limits for the excitation transfer rate. While the use of averages in a random system is always suspect, we

TABLE I. Diffusion parameters.

Concentration (at. %)	$\tau_{\theta=3^\circ}$ (msec)	$\tau_{\theta=177^\circ}$ (msec)	Upper limit for D (cm^2/sec)	Upper limit for d (nm)
0.25	1.85 ± 0.05	1.80 ± 0.03	3.4×10^{-10}	15
0.66	1.3 ± 0.08	1.3 ± 0.08	10^{-9}	23
0.87	1.3 ± 0.1	1.2 ± 0.1	1.5×10^{-9}	28
1.55	0.87 ± 0.05	0.8 ± 0.05	1.7×10^{-9}	25

will, for the moment, attempt to infer an average transfer rate from our data following one of the lines of reasoning used by others.²⁻⁴ One of these approaches assumes that spatial energy transfer occurs only between those homogeneous packets near resonance with each other. If the usual assumption of microscopic strain broadening is valid, then, in the inhomogeneously broadened R line, ions in resonance with each other should be considerably farther apart than the mean distance between all ions. The distance between resonant ions is calculated with the expression given by Lyo⁵ for average nearest-neighbor distance l within a homogeneous packet: $l^3 = 0.17/n_0$, where n_0 is the effective density of resonant Cr^{3+} ions and is determined by the sample concentration and the ratio of homogeneous to inhomogeneous linewidths. The ratio of the homogeneous linewidth to the inhomogeneous width is not known. However, if we take as an upper limit a homogeneous width of 50 MHz,²¹ then for an inhomogeneous width of $\sim 1 \text{ cm}^{-1}$ we obtain for the nearest-neighbor distance a value of 59 or 108 Å in the 1.55- or 0.25-at. % samples, respectively. From the relationship²² between diffusion constant and transfer rate $P = 6D/l^2$, we find that $P \leq 3 \times 10^4 \text{ sec}^{-1}$ in our 1.55-at. % sample. In a similar way we find $P \leq 1.7 \times 10^3 \text{ sec}^{-1}$ in the 0.25-at. % sample. Other estimates of the homogeneous linewidth would be smaller than 50 MHz; for example, if the width were determined only by Orbach relaxation²³ of the $\bar{E}(^2E)$ state, the width would be ~ 4 MHz at 10 °K,²⁴ which would imply $P \leq 5 \times 10^3 \text{ sec}^{-1}$ in the 1.55-at. % sample and $P \leq 3 \times 10^2 \text{ sec}^{-1}$ in the 0.25-at. % sample. One might also assume that the exchange interaction between Cr^{3+} ions is responsible for the homogeneous width; i.e., this width would be given by the transfer rate. With this assumption one finds that in order to be consistent with our upper limits for diffusion constants, $P \leq 10^{-2}$ (2×10^{-6}) sec^{-1} for the 1.55- (0.25-)at. % crystals. These values for transfer rates are all many orders of magnitude smaller than the estimate of Birgeneau⁴ and further appear to be inconsistent with the other experimental results which imply rapid transfer.^{2,3,6}

If, instead of microscopic strain broadening, we assume the R lines are broadened by macroscopic strains, then all Cr^{3+} ions in a given region of the crystal could be resonant. In this case the mean nearest-neighbor distance between Cr^{3+} ions is determined by the full concentration and one obtains values for the upper limits on the transfer rates of $P \leq 2 \times 10^6 \text{ sec}^{-1}$ and $1.2 \times 10^5 \text{ sec}^{-1}$ in the 1.55 and 0.25-at. % samples, respectively. While these limits are just a bit small, they are in closer agreement with the previous experiments. The

suggestion of macroscopic strain broadening has been made by several authors^{2,3,25,26} and the recent experiment of Selzer and Yen²⁶ tends to confirm this possibility. If the suggestion of macroscopic strain broadening is correct, our experiments imply that the experiments of Koo *et al.* in ruby⁶ must be interpreted in terms of finite-size domains inside of which delocalization or localization can take place. The macroscopic strains cause the excitation to always be localized to the extent of these domains, with our experimental results indicating a characteristic dimension of less than 30 nm for the domains.

One of the main deficiencies of the above attempts to correlate the seemingly slow diffusion (if any at all) of the Cr^{3+} excitation over distances comparable to the wavelength of light is the use of an average transfer rate. In our case, the anisotropic exchange $J(r_{ij})$, which is responsible for single-ion-single-ion energy transfer,⁴ varies exponentially with distance⁵ r_{ij} , thus converting a Poisson distribution of closest-neighbor single-ion distances into a very broad distribution of J 's extending over many decades. This, for example, is illustrated in a calculation of Walstedt on the distribution of exchange interactions between donors in a doped semiconductor.²⁷ A significant result of Walstedt's work is that in such a broad distribution of J 's, the magnetic percolation limit can lie several orders of magnitude below the median J . This result would tend to imply that diffusion over long distances is governed by the weak links of which there are a substantial number. Thus when diffusion does occur, it is conceivable that it may be very rapid in a small region of more tightly coupled centers, spending most of its time in such regions and making more infrequent jumps between these regions. Thus the effect of the broad distribution on diffusion is very similar to that of macroscopic strain broadening in that it may allow for rapid diffusion over relatively small distances but not over the larger distances measured in our experiments. We note that the previous experiments, such as Imbusch's original experiments on pair feeding,² the Koo *et al.* experiment on mobility edges,⁶ and parts of the Seltzer *et al.* experiments on spectral diffusion,³ probe single-ion diffusion over a region comparable to or less than the mean separation between pairs (~ 50 Å) and thus may indeed display rapid local diffusion unobserved over larger distances.

The use of averages in random systems to study diffusion can often even lead to qualitatively incorrect results as pointed out by Anderson in his study of localization.^{7,8} Our problem may be somewhat different from the original Anderson problem⁷ in which the disorder was diagonal and a single value

of transfer energy J was used between adjacent sites. In our case the off-diagonal disorder (spread in J_{ij}) may be as large or larger than the diagonal disorder. The problem of localization in this case has recently been treated²⁸ for a certain restricted class of distributions of J_{ij} . Lyo has calculated a critical concentration for the Anderson transition for the case of the broad distribution of transfer rates characteristic of exchange found in ruby; however, he did not derive a diffusion constant. It would be helpful to know what indeed is to be expected for diffusive behavior in such systems.

In summary, we have made direct measurements of energy migration in ruby which gives an upper limit of 30 nm for the diffusion distance within the fluorescence lifetime of ruby samples having concentrations between 0.05 and 1.55-at.%. The re-

sults support a model of slow single-ion to single-ion transfer if one assumes microscopic strain broadening and uses average transfer rates. However, because our experiments are sensitive to diffusion only over rather large distances, it is possible that rapid diffusion may still occur over small regions or domains. Macroscopic strain broadening or the effects of the broad distribution of exchange interaction energies may be the origin of such "domains."

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