Resonant Optical Energy Transfer in Ruby

P. E. Jessop and A. Szabo
Division of Electrical Engineering, National Research Council of Canada, Ottawa, Canada K1A 0R8

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Measurements are reported of resonant nonradiative energy transfer in the R_1 line of ruby at 5 K using a fast Stark shifting technique. The transfer rate for 0.8% ruby is found to be slow, ~ 1 msec^{-1}, contrary to the much more rapid rates proposed earlier by several workers but in fair agreement with the results of Heber. Implications of the results for the occurrence of an Anderson transition in ruby are discussed.

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Starting with the pioneering work of Imbusch[1] in 1967, mechanisms of optical energy transfer in ruby have received much theoretical[2,3] and experimental[4-6] attention. Recently, high-resolution (1.8 GHz) fluorescence line narrowing (FLN) techniques[7] have given[6,8] quantitative data on nonresonant phonon-assisted energy transfer between single ions. Also grating techniques[9] have given upper bounds[9-11] on the transfer rate, P, suggesting[11] that P may be less than 1.7 msec^{-1} for 0.25% ruby. Until now, no direct measurements of resonant transfer have been made and various estimates have been the subject of much controversy, with some groups (Refs. 1, 3, 5, 6, and 8) favoring fast transfer (10^2–10^4 msec^{-1}) and with other groups[4,12] concluding that the transfer is slow (< 4 msec^{-1}). As emphasized by Selzer *et al.*,[6] the main observation favoring fast transfer is the reduction of R_1 lifetime at Cr concentrations above about 0.4%. Other indirect evidence cited for fast transfer is the observation of strictly exponential decays[1,6] and the supralinear rise of N line intensity with increasing Cr concentration.[1] In this Letter, we describe a direct, high-resolution (40 MHz) measurement of nonradiative resonant transfer in concentrated ruby and find it to be slow.

The technique[13] used to measure resonant transfer relies on fast Stark shifting[14] of laser-excited ions in and out of resonance with unexcited ions. The operation time sequence is shown in the inset of Fig. 1. A cw single-frequency dye laser beam (1 MHz linewidth) which is resonant (within ± 100 MHz of line center) with the $^4A_2(\pm\frac{3}{2}) \rightarrow \bar{E}$ transition in ruby is switched on by an acousto-optic modulator for 0.8 msec and focused onto the sample. During this time, a voltage exists across the sample producing a pseudo Stark splitting of $2S = 1$ GHz. About 100 μsec after the laser pulse, the Stark voltage is reduced to zero for a contact time τ_c allowing frequency packets initially excited at the laser frequency ν_L and unexcited ones at $\nu_L \pm 2S$ to come to a common frequency at $\nu_L \pm S$. After τ_c, the Stark voltage is reinstated and transfer is observed by spectral analysis of the FLN signal. The presence of transfer is indicated by the appearance of FLN lines at $\nu_L \pm 2S$ centered about the directly excited line at ν_L as shown in Fig. 1. A boxcar was used to measure the ratio of the peaks vs τ_c and results for various Cr concentrations are shown in Fig. 2.

All measurements were done at sample temperatures of ~5 K and in zero magnetic field.

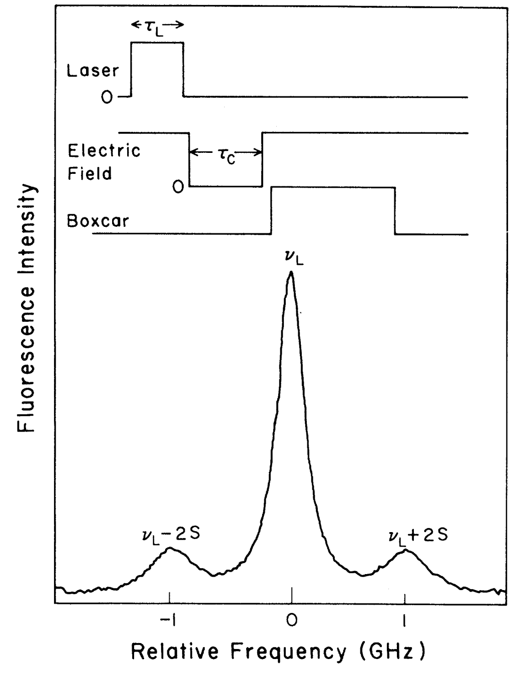

FIG. 1. Fluorescence line narrowing signal showing transfer lines at $\nu_L \pm 2S$ and directly excited line at the laser frequency ν_L in 0.37-wt.% Cr_2O_3 ruby at 5 K. Inset shows measurement time sequence where the laser pulse length is $\tau_L = 0.8$ msec, followed by a Stark pulse of length τ_c, and finally the boxcar gate of 2 msec length.

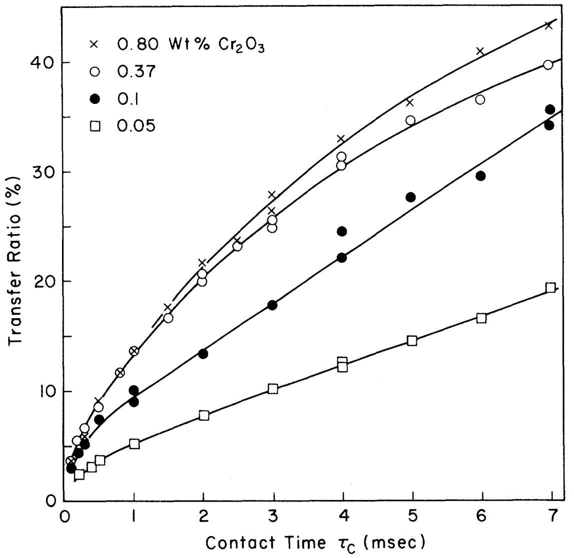

FIG. 2. Experimental variation of the transfer ratio (sum of the two transfer peaks divided by central peak) vs contact time for various Cr concentrations.

(At this temperature, the nonresonant phonon-assisted transfer rate[8] is <0.3 msec^{-1} for concentrations up to 1%.) The laser power incident on the crystal was 10 mW focused along the c_3 axis, close to the observation surface, to a diameter $2a = 0.1$ mm. The fluorescence was detected at right angles to the c_3 axis and analyzed by a plane Fabry-Perot interferometer (Burleigh Model RC110; free spectral range, 7.6 GHz; finesse, 200). A cooled RCA C31034 photomultiplier followed by a PAR Model 115 preamplifier and 162 boxcar was used for signal detection.

The data in Fig. 2 indicate that the resonant transfer occurs in two stages, in particular for the 0.05 and 0.1% samples. There is a fast transfer involving a few percent of the ions in the first few hundred microseconds followed by a slower transfer over several milliseconds. We interpret the former to be a nonradiative process and the latter a radiative process. With use of a simple model of radiative transfer described below, the radiative contribution was deconvoluted from the curves of Fig. 2 to give the nonradiative transfer data shown in Fig. 3.

To describe the radiative transfer, consider an infinitely long cylinder of radius $r=a$ containing a density $N_{De}{}^0$ of laser-excited donor ions at a time $t=0$ which are radiatively decaying at a rate γ_r. Integration over the cylinder shows that the photon intensity increases from $P_a(t=0) = \frac{1}{2}aN_{De}{}^0\gamma_r$ at $r=a$ to $P_0 = \sqrt{2}\,P_a$ at $r=0$. For simplicity, we assume a uniform photon intensity, inside the cylinder, of P_a. The time dependence of P_a is

$$P_a(t) = \tfrac{1}{2}aN_{De}{}^0\gamma_r \exp(-\gamma_l t)\,, \tag{1}$$

where γ_l is the inverse lifetime determined by nonradiative and radiative decay and energy transfer. For our excitation geometry, decay time measurements gave $\gamma_l = \gamma_r = (4 \text{ msec})^{-1} \equiv \gamma$ to within 20% for all samples. Assume that at $t=0$, a density N_A of ground-state acceptor ions is switched into resonance with the donor ions. The time dependence of N_{Ae} is given by

$$dN_{Ae}/dt \approx \sigma P_a(t) N_A - \gamma N_{Ae}\,, \tag{2}$$

where we assume that the number of excited ions $N_{Ae} \ll N_A$. Solving (1) and (2) gives for the time dependence of the ratio of acceptor to donor fluo-

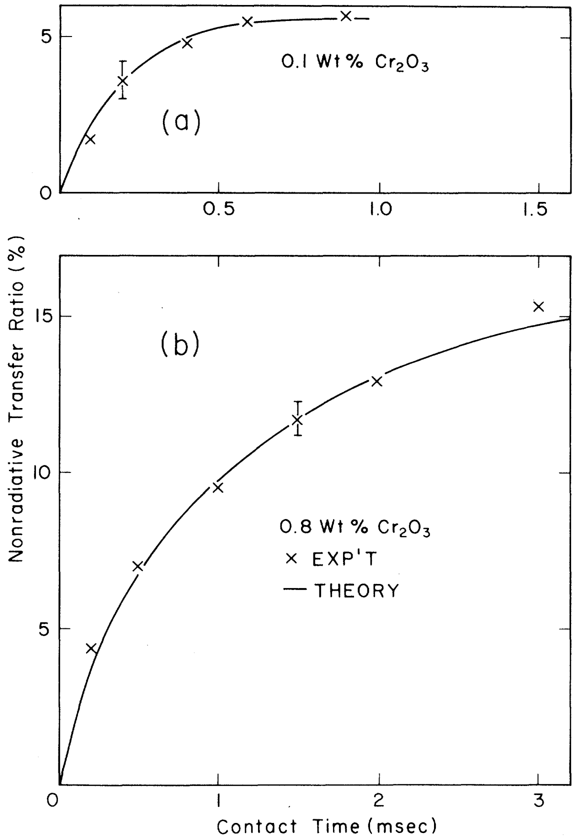

FIG. 3. Comparison of theoretical and experimental variation of the nonradiative transfer ratio (see text) vs contact time. (a) 0.1% ruby, theoretical parameters $A = 5.6\%$, $\beta = 5.5$ msec^{-1}; (b) 0.8% ruby, theoretical parameters $A_1 = 3.0\%$, $\beta_1 = 5.5$ msec^{-1}; $A_2 = 13.0\%$, $\beta_2 = 0.8$ msec^{-1}.

rescence,

$$R_{\rm rad} \equiv N_{Ae}/N_{De} = \alpha a \gamma t/4, \tag{3}$$

where $2\sigma N_A = \alpha$, the absorption coefficient. This analysis predicts a linear rise of $R_{\rm rad}$ with time with a slope proportional to the absorption coefficient. Just such a behavior is observed at long transfer time in Fig. 2 for the 0.05 and 0.1% samples. For the more concentrated samples, the two kinds of transfer are not as distinctly separated.

The peak absorption coefficient of the 0.8% sample is nearly equal to that of the 0.1% sample, 25 cm^{-1}. (The more concentrated sample has a greater inhomogeneous width.) Therefore, we take the radiative transfer to be the same in both cases. Subtracting the linear radiative contribution from the curves in Fig. 2 gives the nonradiative transfer data in Fig. 3.

The observed value of $R_{\rm rad}$ for the 0.1% sample is about 4 times larger than the calculated value using $\alpha = 25\ \text{cm}^{-1}$, $a = 0.005$ cm, and $\gamma = 250\ \text{sec}^{-1}$ in Eq. (3). However it should be noted that in the analysis, transfer outside radius a is neglected and thus $R_{\rm rad}$ is underestimated since the viewing volume, as determined by the lens preceding the Fabry-Perot, extends outside the excitation volume.

We describe the nonradiative transfer by a cross-relaxation equation

$$\frac{dN_{De}}{dt} = -\gamma N_{De} + \frac{\beta}{N_A + N_D}(N_{Ae}N_{Dg} - N_{Ag}N_{De}) \tag{4}$$

with a similar equation for N_{Ae} where β is an average single-ion–single-ion (S-S) transfer rate. A more refined model should incorporate a distribution of β's as recently discussed by Huber and Ching[15]; however, we found that the data could be reasonably fitted with one or two values of β. A solution of the equations for $N_{Ae} = 0$ at $t = 0$ gives for the ratio of acceptor to donor fluorescence

$$\frac{N_{Ae}}{N_{De}} = \frac{A(1 - e^{-\beta t})}{1 + Ae^{-\beta t}}, \tag{5}$$

where $A = N_A/N_D$. The curves in Fig. 3 are a fit of this equation to the data for various A and β parameters. The total A values are found to be in the range ~6 to 16% rather than $A = 100\%$ given by the simple model with the reasonable assumption that the inequivalent sites are equally occupied by impurity ions. The observed small A values indicate that the major fraction of ions are localized and do not resonantly transfer energy. The need to use two sets of A, β parameters in Fig. 3(b) suggests that two distinct kinds of spatial distributions of ion resonant frequencies exist in the crystal. This could arise, for example, if Cr ions tend to precipitate along dislocations or near other defects.

We now consider the interaction mechanisms responsible for the nonradiative transfer. The fastest observed transfer rate to one of four near neighbors[1] is $P = 5500/4\ \text{sec}^{-1}$ from which we calculate the interaction matrix element $\langle I \rangle$ from the transfer equation[1]

$$P = \hbar^{-2}\langle I \rangle^2 \int g_1(\nu) g_2(\nu)\, d\nu, \tag{6}$$

where the overlap integral is $1/\pi\Delta_h$ and Δ_h is the observed homogeneous linewidth of ~100 MHz for 0.8% ruby. This gives $\langle I \rangle = 3.5 \times 10^{-6}\ \text{cm}^{-1}$ compared to the value $\langle I \rangle_{\text{dip-dip}} = 4.4 \times 10^{-7}\ \text{cm}^{-1}$ calculated for a dipole-dipole interaction[1] for an ion spacing[11] $R = (0.17\Delta_i/\Delta_h N)^{1/3}$ (assuming there is microscopic broadening) where $\Delta_i \approx 10$ GHz is the inhomogeneous width and $N = \frac{1}{2} \times 2.6 \times 10^{20}\ \text{cm}^{-3}$ for 0.8% ruby. These matrix elements are considerably smaller than the exchange matrix element of $2.5 \times 10^{-3}\ \text{cm}^{-1}$ estimated by Birgeneau[3] for single-ion–pair (S-P) transfer. We conclude that his estimate of a 0.1-μsec S-S transfer time using the exchange matrix element is not appropriate for ruby at low temperatures because of inhomogeneous broadening and the increased distance between resonant ions. Thus it appears while S-P[3] and phonon-assisted nonresonant transfer[6] occur via an exchange interaction, resonant S-S transfer in ruby at liquid-helium temperatures occurs via an electric multipole interaction, possibly dipole-dipole.

In conclusion, studies in a magnetic field might allow a direct measurement of the radiative transfer since the nonradiative transfer would presumably be suppressed because of the large reduction of the homogeneous linewidth (~150× for 0.2% ruby)[16,17] when a field is applied along the c_3 axis. Another aspect which needs further study is the lineshape and width, Δ_t, of the transfer line which will affect the derived magnitude of the nonradiative transfer. For example, if the transfer were all radiative involving a single emission and absorption sequence, then we would expect a linewidth[7] $\Delta_{tr} = 2\Delta_l$ where Δ_l is the laser-excited fluorescence linewidth at ν_L. The nonradiative transfer width Δ_{tn} (for a single transfer) will be in the range $\Delta_l < \Delta_{tn} < 2\Delta_l$ depending on the spatial distribution of the ion resonant frequencies. Experimentally, we observe $\Delta_t = 1.3\Delta_l$ to $2\Delta_l$ depending on position of the crystal. Obviously, the two transfer processes can be intermingled in a complicated way.

Finally, our observed slow nonradiative transfer rate in concentrated ruby is consistent with the earlier results of Heber[4] and Gerlovin[12] as well as with other recent experiments.[11,13,18] Also, we see no evidence of any sudden increase in transfer rate as the Cr concentration is increased from 0.05 to 0.8% which, along with other recent work,[13,18,19] suggests that an earlier claim[5] for observation of an Anderson transition in ruby may be incorrect. If such a transition occurs in small domains,[11] then this must involve less than ~1% of the ions.

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Energy Transfer and Anderson Localization in Ruby

S. Chu, H. M. Gibbs, S. L. McCall, and A. Passner
Bell Laboratories, Murray Hill, New Jersey 07974

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Nonradiative resonant energy transfer has been directly observed in ruby. However, the transfer rate is much slower than previously thought. For example, at 0.25% Cr concentration, an excitation will transfer roughly once in the radiative lifetime. We conclude ruby is unsuitable for observing an Anderson transition.

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It is believed by many researchers that excited Cr^{3+} ions in pink and red ruby resonantly transfer their energy to neighboring ions rapidly. This conclusion[1,2] is based on theory and the absolute ratio of the single-ion fluorescence intensity at 6934 Å, and the trap fluorescence intensity at 7009 Å, and further supported by the similar decay lifetimes even though the trap lifetime is 4.6 times shorter than the single-ion lifetime. Energy transfer in ruby attracted widespread interest when the trap/single-ion fluorescence ratio was used to monitor the ion-ion energy transfer within the inhomogeneously boradened R_1 line. A sharp "break" in the ratio as a function of laser frequency was interpreted[3] as evidence for mobility edge[4] in an Anderson transition.[5] The experimental results were also in rough agreement with earlier calculations.[6]

We have directly observed resonant nonradiative energy transfer in ruby,[7] and find that the ion-ion transfer is much slower than previously believed. This fact eliminates the possibility of observing an Anderson transition in ruby as reported by Koo, Walker, and Geschwind.[3] The conflict