Nonradiative Spectral and Spatial Energy Transfer in Ruby*

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The first experimental evidence for distinct spectral and spatial energy transfer in ruby via nonradiative coupling is presented. Monochromatic laser excitation of the R_1 line results in a rise of the inhomogeneous background on a millisecond time scale, consistent with a one-phonon–assisted process and contrary to recent theory. However, time-resolved studies of trap fluorescence suggest a rapid, coherent, spatial transfer within the R_1 line which does not shift frequency.

Of all the optically active impurity-doped crystal systems, ruby ($Al_2O_3:Cr^{3+}$) has very likely been the most extensively studied. Its static properties are well understood, and over a decade of optical and ESR measurements has yielded values for a number of useful parameters.[1] While the presence of inter-ion dynamics has also been demonstrated,[2] a detailed understanding of these processes, particularly the mechanisms of energy transfer *within* the inhomogeneously (strain-)broadened R lines, is lacking and a number of conflicting models[2-4] have been proposed based on different types (and occasionally the same type) of indirect measurements.

In some recent experiments,[5,6] we have demonstrated the power of fluorescence line-narrowing[7] as a method for probing inhomogeneously broadened optical transitions in rare-earth–doped crystals and observing *directly* the spectral dynamics. Several new theoretical treatments of these dynamics[8-10] based on our earlier work but specifically directed toward ruby as a model have prompted an investigation of this latter system. In the course of our work, a number of hitherto unobserved phenomena have been studied. The results of nonradiative spectral and spatial transfer are presented herein, and comparison with the recent theory is made. Radiative transfer phenomena, also present in ruby, will be discussed in a subsequent publication.

When an inhomogeneous absorption is probed with a high-resolution laser pulse, only those ions in resonance with the laser (the donors) will emit immediately after the excitation. If an interaction mechanism exists which allows the excitation to transfer from ion to ion, then at later times emission from a different set of ions (the acceptors) is observed. If the acceptor energy level is exactly in resonance with that of the donor, no changes in the emission line shape occur in time. However, if the acceptors have slightly shifted energy levels because of strain broadening, then the emission line shape alters in time, and we speak of "spectral diffusion."

In ruby, two processes are responsible for energy transfer: a nonradiative coupling between ions in close proximity and a radiative transfer of photons between ions separated by as much as the dimensions of the crystal. These two processes should distinguish themselves in a number of ways: Since radiative transfer involves macroscopic dimensions, its magnitude depends on sample size or experimental geometry, whereas nonradiative transfer should be independent of these considerations. In addition, the spectral behavior and the dependence on laser pump frequency, dopant concentration, and temperature might be expected to differ for the two mechanisms.

The experimental arrangement is similar to that described previously[11] but with one significant improvement. Rather than using one etalon for fluorescence analysis, two tandem pressure-scanned etalons were employed, resulting in high resolution (~0.8–1.0-GHz passband) with a large effective free-spectral range (5 cm^{-1}). This configuration allowed observation of the entire inhomogeneously broadened emission profile (typically 1 cm^{-1}) without the complication of overlapping etalon orders. The pulsed dye laser (with a 0.8–1.2-GHz spectral width) directly pumped the R_1 absorption at 6934 Å, with a peak power of approximately 1 kW and a pulse length of 10 nsec. With this short pulse and relatively low power, we estimate the relative fraction of excited Cr ions within the excitation region to be less than 1%.[12] To minimize the problem of scattered laser light, the crystals were highly polished and the fluorescence was observed at right angles to the beam direction. This geometry also allowed the tightly focused beam to traverse the crystal at varying depths from the front surface and thereby

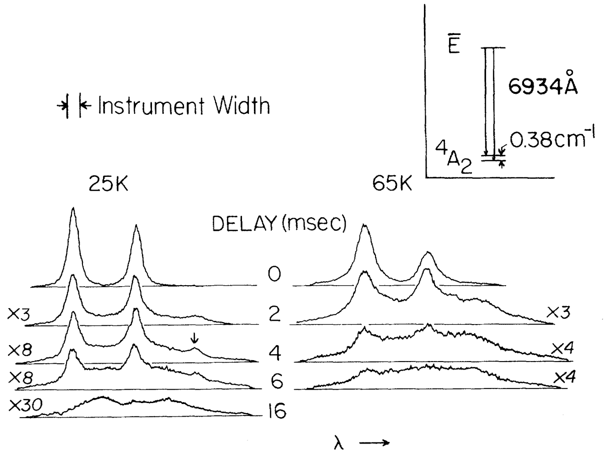

FIG. 1. Typical time-resolved studies for a 0.2-at.% ruby sample at two different temperatures, with the integrated intensities scaled to roughly the same value. Gain settings relative to the 0-delay traces are shown. Inset shows the R_1 fluorescence transitions involved. Below 40 K, the width of the narrowed components reflects the instrumental profile. The peak separation is 0.38 cm^{-1}, and the third peak indicated by an arrow is a radiative transfer effect, to be discussed in a subsequent article.

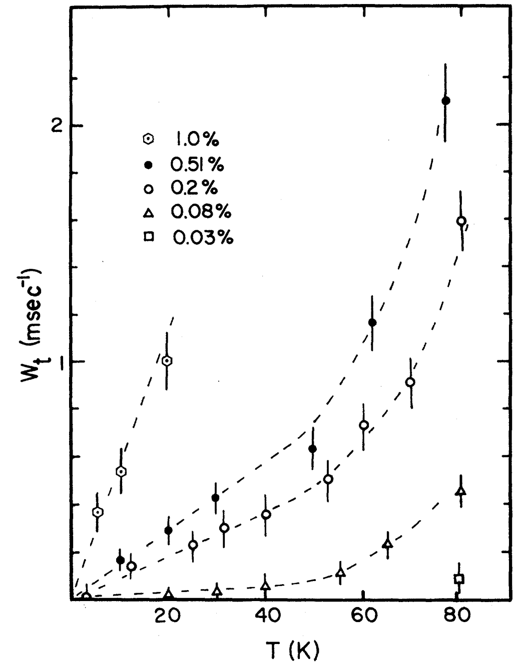

FIG. 2. Transfer rate plotted as a function of temperature for five different samples.

to alter the effective sample size.

All the data shown were taken with the laser excitation within 50 to 100 μm of the front surface to minimize the radiative contribution, and the nonradiative character of these results has been verified by lifetime measurement (showing a lack of trapping) and comparison with subsequent forced radiative transfer. Figure 1 presents typical time-resolved studies at two different temperatures for a 0.2-at.% sample, with the laser pumping slightly on the high-energy side of the absorption. Emission to both levels of the ground-state doublet (see figure inset) is always observed. As time progresses, the narrowed components of the line appear superimposed on a background of increasing magnitude. While a small amount of background might be present at zero delay from direct laser excitation, an absolute increase in background intensity is seen whenever the transfer rate is of the same order as or faster than the 3-msec broad-band lifetime. Comparison with absorption and excitation scans have indicated that this background has the shape, width, and location of the full inhomogeneous emission line. It is interesting to note that in all systems we have studied to date, from dilute glasses[13] to concentrated crystals,[14] the spectral evolution has been of a similar character—never has there been seen a gradual spreading of the narrowed component until it "fills" the inhomogeneous line shape.

In order to extract a transfer rate, the ratio of the integrated narrowed fluorescence intensity to the total emission intensity was plotted as a function of time. The $1/e$ point of this ratio is defined as the transfer time and the inverse as the characteristic rate.[15] In Fig. 2, this rate is shown as a function of temperature for five different samples. Particularly noteworthy is the linear dependence up to approximately 50 K. It has also been found that to within the roughly 20% accuracy of our analysis, the rate at which the background rises is independent of laser excitation frequency. A linear temperature dependence and an independence of the rate on $\Delta\omega$, the energy mismatch of the transfer, are consistent with "direct" one-phonon–assisted energy transfer,[16] although apparently a higher order process (most likely exhibiting Raman-like T^7 behavior) must contribute above 60 K.

Holstein, Lyo, and Orbach[8] have investigated the problem of phonon-assisted energy transfer in ruby, treating the single-ion to single-ion interaction in a third-order perturbation calculation. Using matrix elements derived from static strain measurements, they conclude that within the temperature range 5 to 30 K, the two-phonon "resonant" process, $W_{\rm res}$, should dominate all others by one or two orders of magnitude. Although the predicted spectral evolution of the line shape for this process could be deceptively similar to the one-phonon mechanism (i.e., all regions of the inhomogeneous line appearing simultaneously for a Gaussian line shape[9]) the former would depend exponentially on temperature below 40 K and would show a strong dependence on laser pump frequency, neither of which is observed. Other higher-order phonon processes with T^3 temperature dependence have in fact been shown to explain the spectral transfer in rare-earth systems with substantially larger energy shifts (5 to 10 $\rm cm^{-1}$).[5,6,14] It is surprising indeed that in ruby, a one-phonon process, generally ignored as vanishingly small for these energy shifts of typically $\lesssim 0.5\ \rm cm^{-1}$, should dominate.

In seeking an explanation for this unusual result, we also studied the emission from the well known 7009-Å pair line (N_2). Previous investigations have revealed complicated time evolution of this line after pulsed excitation of the R_1 line. This has been interpreted by some[2] as demonstrating the existence and by others,[3,4] the nonexistence, of rapid spatial transfer of energy between the isolated R_1-line ions until it is quenched by these N-line traps. A source of confusion has been the existence of an excited level of this pair which lies slightly below the R-line absorption.[17] Thus, "low-resolution" ($\gtrsim 1$ Å) excitation of the R line has resulted in a population of the N line both directly and indirectly via transfer.

With our high-resolution laser, we were able to populate the N line either directly or only through transfer from the R line. In the former case, a simple exponential decay with a lifetime of 0.72 msec is observed. When pumping is into the middle of the R_1 line and the N-line frequency is monitored, the time development consists of an exponential rise with a rate of approximately 0.5 msec followed by an exponential tail at the R_1 lifetime (varying from ~3.4 to 6 msec depending on concentration and the degree of trapping). A typical trace, with a decay of ~4 msec, is shown in Fig. 3. This behavior is independent of temperature between 4 and 40 K, of concentration for the 0.17-, 0.2-, and 0.51-at.% samples examined to date (although the *intensity* varies strongly with concentration and slightly with temperature), and of laser pump frequency within the R_1 line.

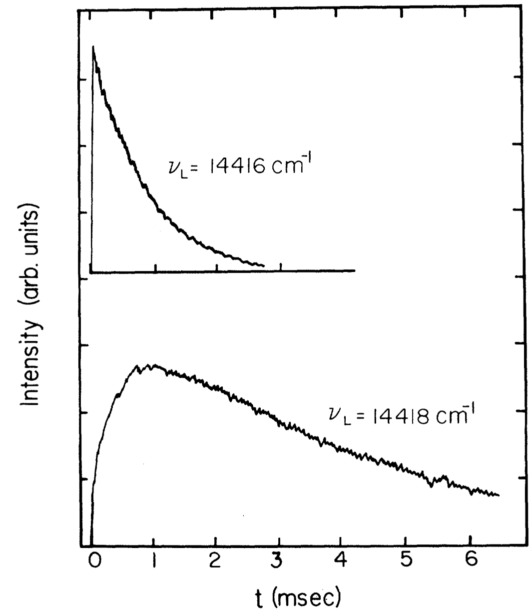

FIG. 3. Time-resolved studies for the 7009-Å N-line fluorescence in a 0.51-at.% sample at 5 K. Upper trace obtained when pumping directly into N-line absorption, lower trace when exciting center of R_1 absorption.

Careful measurements of the R_1 lifetime at 5 K have also been made, revealing strictly exponential behavior for over two decades, even in concentrations where the effective lifetime shortens below 3.8 msec. (Note that this is in contradiction with the results of Ref. 3.) Both these N-line and R-line lifetime measurements support a model of rapid transfer within the R line which continually feeds the N-line traps.[18] Since the phonon-assisted, incoherent process that transfers spectrally within the R line is likely to be too slow to account for this feeding, particularly at the lowest temperatures, we propose that a coherent transfer process is also occurring between resonant Cr ions—one which does not shift the frequency, within the limits of our resolution,[19] in several milliseconds. This is the first time to our knowledge that evidence for the existence of *distinct*, simultaneous spatial and spectral transfer in the same inhomogeneously broadened system has been presented.[20]

The simultaneous occurrence of a rapid spatial diffusion and a slow spectral diffusion is difficult to reconcile with microscopic strain broadening, since in this model of random energies and interion distances, ions in exact resonance will be considerably farther apart than nonresonant ions. Taking into account the ratio of the natural linewidth to the inhomogeneous width, we estimate that resonant ions should be separated by distances of greater than 100 Å,[21] at which point the interaction strength would be vanishingly small.

Coherent transfer, implying inter-ion transfer times on the same order as ion-phonon interaction times, is consistent with inter-ion coupling values on the order of $J \sim 10^{-2}$ cm^{-1},[22] and therefore transfer times ($\hbar/J$) in the low- to sub-nanosecond range. Hence, it might be more appropriate to speak of the optical excitation as an exciton and the spectral diffusion as exciton-phonon combined with exciton-exciton scattering. While the details of excitonlike behavior in an inhomogeneous medium are extremely complex, we believe that a model which incorporates the possibility of coherent transfer within appropriately chosen domains might have more success than the existing theory in predicting the observed spectral behavior.

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[1] For a number of articles detailing various experimental and theoretical results in ruby, see *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience, New York, 1967), pp. 171–254.

[2] G. F. Imbusch, Phys. Rev. 153, 326 (1966).

[3] Ya. Gerlovin, Fiz. Tverd. Tela, 16, 607 (1974) [Sov. Phys. Solid State 16, 397 (1974)].

[4] J. Heber, Phys. Status Solidi 42, 497 (1970).

[5] R. Flach, D. S. Hamilton, P. M. Selzer, and W. M. Yen, Phys. Rev. Lett. 35, 1034 (1975).

[6] P. M. Selzer, D. S. Hamilton, R. Flach, and W. M. Yen, J. Lumin. 12/13 737 (1976).

[7] A. Szabo, Phys. Rev. Lett. 25, 924 (1970), and Phys. Rev. Lett. 27, 323 (1971).

[8] T. Holstein, S. K. Lyo, and R. Orbach, Phys. Rev. Lett. 36, 891 (1976).

[9] T. Holstein, S. K. Lyo, and R. Orbach, Phys. Rev. B (to be published).

[10] T. Holstein, S. K. Lyo, and R. Orbach, Phys. Rev. B (to be published).

[11] P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen, and M. J. Weber, Phys. Rev. Lett. 36, 813 (1976).

[12] We have observed no nonlinear dependence of the fluorescence intensity on laser power even with tight focusing, indicating that the excited fraction of Cr ions is small and that interactions between excited ions can probably be neglected.

[13] M. J. Weber, J. A. Paisner, S. S. Sussman, W. M. Yen, L. A. Riseberg, and C. Brecher, J. Lumin. 12/13, 729 (1976).

[14] D. S. Hamilton, Ph.D. thesis, University of Wisconsin, 1976 (unpublished).

[15] If the feeding of the background were strictly exponential, the rate as thus defined would correspond to the decay rate of the exponential. However, the feeding rate appears to be slower than exponential; hence, the generalized definition.

[16] R. Orbach, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience, New York, 1967), p. 445.

[17] P. Kisliuk, N. C. Chang, P. L. Scott, and M. H. L. Pryce, Phys. Rev. 184, 367 (1969).

[18] See, e.g., R. Orbach, Phys. Lett. 48A, 417 (1974); also the theoretical section of Heber Ref. 4.

[19] Since the homogeneous linewidth contributes twice to the observed width, a change in the profile of 5 to 10% would indicate a $\Delta\nu$ of ~ 50 to 100 MHz.

[20] A coherent transfer process would be consistent with the concept of conduction above the critical concentration for "Anderson localization." However, our results show no evidence for a "mobility edge" as proposed by J. Koo, L. R. Walker, and S. Geschwind [Phys. Rev. Lett. 35, 1669 (1975)]. A detailed comparison of our results and theirs must await a subsequent article.

[21] As the appropriate value for ν_{natural} is not known, we may take as a worst case our experimental upper limit on this width of ~ 50 MHz. We then find that for an inhomogeneous width of ~ 1 cm^{-1}, ions with an energy separation of 50 MHz will be ~ 100 Å apart.

[22] R. J. Birgeneau, J. Chem. Phys. 50, 4282 (1969).