PHYSICAL REVIEW VOLUME 173, NUMBER 2 10 SEPTEMBER 1968

Energy Transfer between Chromium Ions in Nonequivalent Sites in $Li_2Ge_7O_{15}$

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(Received 10 April 1968)

The temperature dependences of the relative intensities and lifetimes of the R_1 lines of chromium ions in nonequivalent sites in lithium germanate are reported. Above ~100°K, the ratio of the fluorescent intensity of the R_1' line to that of the R_1 line is proportional to $\exp(-\Delta E/kT)$, where ΔE is the energy separation of the two lines. At lower temperatures, the intensity ratios deviate from this exponential temperature dependence. The fluorescent decay at the two lines is purely exponential with the same decay times above ~100°K; but below this temperature, their decay times differ, and the R_1 line exhibits a double exponential decay for a sample with 0.038% Cr^{3+} and initial rises in the fluorescence for samples with 0.12 and 0.18% Cr^{3+}. These results are interpreted in terms of energy transfer between chromium ions in nonequivalent sites, which is efficient enough at high temperatures to allow thermal equilibrium to be established between the two fluorescent systems, but which should permit pumping of the R system by the R' system at low temperatures. Analysis of the rate equations of the populations of two interacting fluorescent systems yields qualitative results consistent with experimental observations of both the relative intensity and the lifetime measurements. The nature of the energy transfer mechanism is also considered in terms of both the overlap of the two lines and a phonon-assisted process.

I. INTRODUCTION

THE optical absorption and emission spectra of a new luminescent material, $Li_2Ge_7O_{15}:Cr^{3+}$, have recently been reported.[1–4] The general features of these spectra are similar to those of trivalent chromium in other host lattices. The chromium ions occupy several nonequivalent sites in the lithium germanate lattice. This paper discusses some of the details of the thermal variation of the two most prominent optical fluorescent lines and the interaction between chromium ions in nonequivalent sites.

The four most prominent lines in the fluorescent spectrum of chromium-doped lithium germanate are two sets of R lines originating from Cr^{3+} ions in nonequivalent lattice sites. The energy transfer between these different fluorescent systems is investigated by studying the temperature dependences of the relative intensities and decay times of the emission at the R_1 lines of the systems. The integrated fluorescent intensities were obtained between temperatures of 24 and 200°K and the fluorescent lifetimes between 7 and 380°K for lithium germanate samples with 0.038, 0.12, and 0.18 wt% chromium as determined by neutron-activation analysis. The results are compared with those predicted from an analysis of the rate equations of the populations of the energy levels of two interacting fluorescent systems. Consideration is given to the nature of the energy transfer mechanism, using both a phonon-assisted model and a model involving the overlap integral of the two transitions.

II. EXPERIMENTAL

The lithium germanate samples used for this investigation were cut and polished with faces perpendicular to the a, b, and c axes of the crystal, and had approximate dimensions of 8×5×2 mm. They were mounted on the cold finger of a Janis model 8DT cryostat capable of continuous temperature variation from 4.2 up to 380°K.

For the fluorescent intensity measurements, the excitation was provided by an air-cooled General Electric BH6 1000-W high-pressure mercury lamp, filtered by 4 cm of saturated $CuSO_4$. The fluorescence, observed at 90° to the direction of excitation, was chopped and focused onto the entrance slit of a McPherson model 213 1-m scanning monochromator set to achieve a resolution of 0.6 cm^{-1}. The modulated signal, detected by an RCA 7102 photomultiplier tube cooled by liquid nitrogen and amplified by a P.A.R. JB-5 lock-in amplifier, was displayed on a strip chart recorder.

For pulsed fluorescence measurements, EG&G FX-12 and FX-33 flashtubes, and the same cryostat and monochromator described in the previous paragraph, were used. The monochromator was set for a resolution of 6 cm^{-1} and the decay of the fluorescence at 90° to the direction of the exciting light was photographed in a Tektronix 531 scope. The time resolution of the apparatus was ~50 μsec.

III. RESULTS

Figure 1 shows the fluorescence spectrum of lithium germanate with 0.18% chromium between 6500 and 8000 Å at temperatures of 27, 73, and 279°K. The spectrum consists of the sharp no-phonon lines labeled R_1, R_1', R_2, and R_2' and broad vibronic sidebands. At low temperatures, the positions of these four lines tend toward values of 14 359.6, 14 374.3, 14 422.4,

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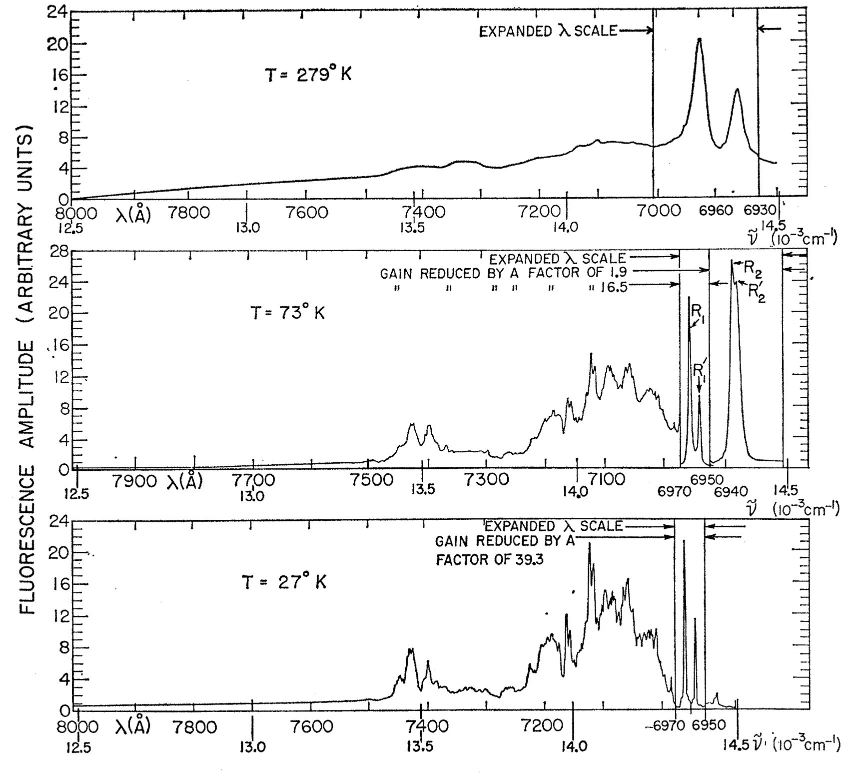

FIG. 1. Fluorescence spectrum of $Li_2Ge_7O_{15}$:Cr^{3+} with 0.18 wt%chromium at several temperatures. At very low temperatures, the positions of the R_1, R_1', R_2, and R_2' lines tend toward values of 14 359.6, 14 374.3, 14 422.4, and 14 429.6 cm^{-1}, respectively.

and 14 429.6 cm^{-1}, respectively. The energy difference between the R_1 and R_1' lines is about 15 cm^{-1}, while that between the R_2 and R_2' lines is about 7 cm^{-1}.

The integrated emission in the vibronic bands decreases as temperature is lowered, while the total emission in the no-phonon lines increases. The relative magnitudes of the various peaks in the low-energy vibronic sideband are significantly different for samples with different concentrations of chromium. Several of these peaks occur in pairs with separations equal to that between the R_1 and R_1' lines.

The spectra reported in Fig. 1 have not been corrected for photomultiplier response and grating efficiency. These corrections would cause the no-phonon lines to be slightly more intense than they appear with respect to the low-energy vibronic sideband.

Figure 2 shows the fluorescence spectrum in the vicinity of the R_1 lines at 40°K. Numerous satellite lines can be observed between, and on either side of, the R_1 and R_1' lines. Electron-spin resonance data has demonstrated the existence of at least four sites for chromium in the lithium germanate unit cell and a

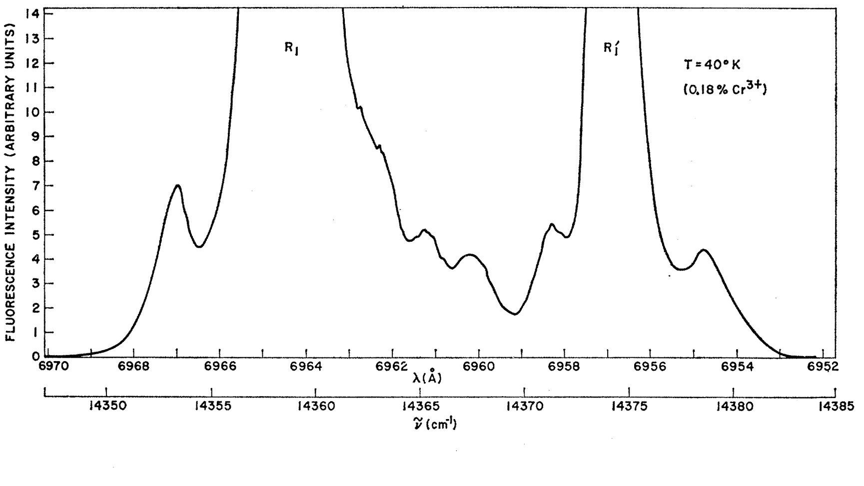

FIG. 2. Fluorescence spectrum in the region of the R_1 lines of $Li_2Ge_7O_{15}$:Cr^{3+} with 0.18 wt% chromium at 40°K.

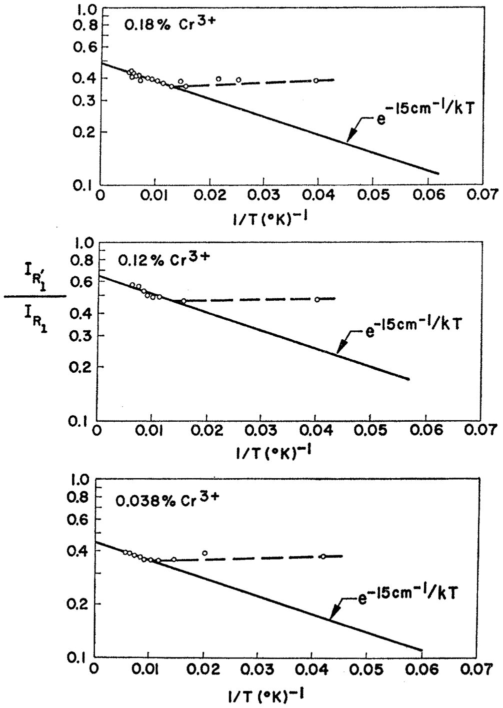

FIG. 3. Temperature dependence of the relative intensity of the R_1' line to the R_1 line in the fluorescence spectrum of lithium germanate with 0.038, 0.12, and 0.18 wt% chromium.

zero-field ground-state splitting of less than 1 cm^{-1}.[5] These EPR data and the fact that the energy difference between R_1 and R_1' is significantly greater than that between R_2 and R_2', eliminate an interpretation of the spectra in terms of a model with a large ground-state splitting. This information and the fact that both R_1 lines remain visible in the fluorescence spectrum at 4.2°K where the R_2 lines have both disappeared,[4] led to the conclusion that R_1, R_2, and R_1', R_2' are associated with chromium ions in nonequivalent sites. These smaller satellite lines are probably due to transitions from chromium ions in other less-populated nonequivalent sites.

The ratios of the integrated fluorescent intensities of the R_1' line to the R_1 line were obtained between 24 and 200°K for lithium germanate samples with 0.18, 0.12, and 0.038% chromium. Above 200°K, the lines are not resolved well enough to obtain accurate intensity data. These results are shown in Fig. 3. For all three samples, the relative intensities of these lines at high temperatures are proportional to an exponential Boltzmann factor $\exp(-\Delta E/kT)$ with an energy difference of 15 cm^{-1} which is equal to the separation of the two lines. At low temperatures, the relative intensities deviate from this type of temperature dependence. The deviation from an exponential temperature dependence occurs at 95°K for the 0.038% sample, 71°K for the 0.12% sample, and 75°K for the 0.18% sample.

The fluorescent lifetimes at the R_1 and R_1' lines of these same samples were measured at temperatures ranging from 7 to 380°K. The results are shown in Fig. 4. For all three samples, the decay times at the two lines coincide at high temperatures but differ at low temperatures. The values of the decay times increase continuously between 380°K, where they are approximately 0.2 msec, and about 110°K, where the two lines begin to show different decay times. The decay times at both lines tend toward constant values below 50°K. These values are ~5 msec for the R_1 line and between 6 and 7 msec for the R_1' line.

At temperatures where the lifetimes at the two lines coincide, the fluorescent decay is exponential. At lower temperatures, the fluorescent decay of the R_1' line remains exponential but that of the R_1 line does not. For both the 0.18% and the 0.12% samples, there is an initial rise in the fluorescence of the R_1 line preceding the exponential decay. The time $t_{\max}$ at which the maximum intensity of the fluorescence occurs is about 0.3 msec near 10°K for both samples and decreases as temperature is increased. For the 0.038% sample, the fluorescent decay of the R_1 line at low temperatures is a double exponential. The characteristic time of the faster initial decay is attributed to the intrinsic lifetime at the R_1 line; the subsequent fluorescence has the same decay times as the R_1' line.

Excitation spectra were also obtained for the R_1 and R_1' lines of these three samples and pumping was detected in the same bands seen in the unpolarized absorption spectra.[6] The R_1 line has a greater intensity of excitation than the R_1' line for all three samples. The relative excitation intensity of the R_1 line to the R_1' line is greatest for the 0.038% Cr^{3+} sample and least for the 0.12% sample.

IV. DISCUSSION OF RESULTS

The temperature dependence of the intensity of a fluorescence line is proportional to the change in the population of the excited state of the transition. The ratio of the populations of two levels with the same statistical weights in thermal equilibrium is a Boltzmann factor $\exp(-\Delta E/kT)$, where ΔE is the energy difference between the levels. Thus, the results shown in Fig. 3 of the temperature dependence of the relative fluorescence intensities of the R_1 and R_1' lines of chromium-doped lithium germanate, show that the populations of the excited levels of these transitions reach thermal equilibrium before fluorescence emission at high temperatures, but not at low temperatures. The deviation from thermalization at temperatures as high as 95°K

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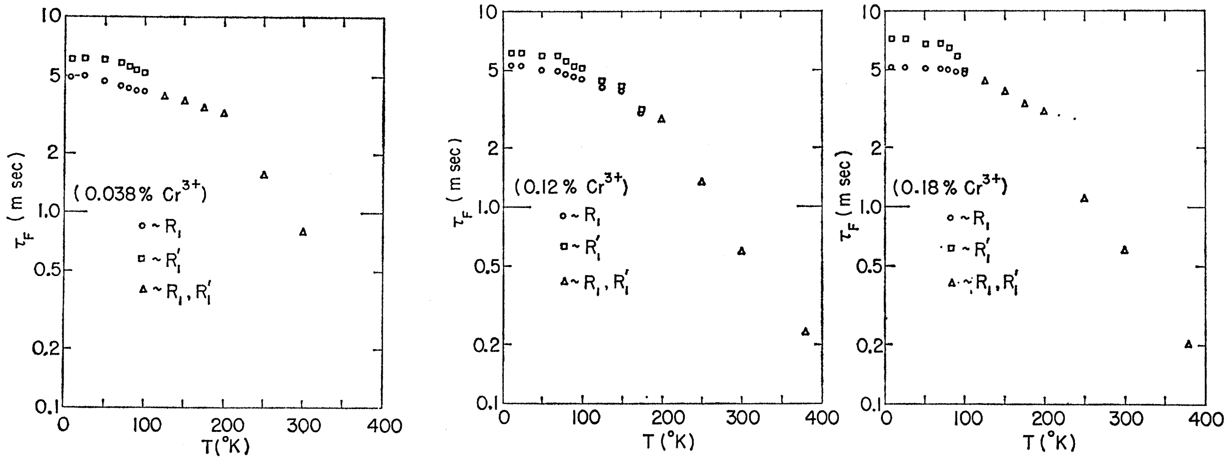

(a)

(b)

FIG. 4. Temperature dependence of the fluorescent lifetimes at the R_1 and R_2' lines in lithium germanate with 0.038, 0.12, and 0.18 wt% chromium.

gives further proof that the R_1 and R_1' lines come from different fluorescent systems and the observed thermalization above 100°K indicates that these systems interact strongly at high temperatures. The different temperatures, at which the intensity ratios for the three samples deviate from an exponential temperature dependence, may indicate that the strength of the interaction varies with chromium concentration. This is consistent with the results of excitation measurements, which indicate that the number of chromium ions in each of these two different nonequivalent sites also varies with chromium concentrations.[6]

Reabsorption within each system should have approximately equal effects on the R_1 and R_1' lines and these effects should vary with temperature in the same way for both systems. If cross-reabsorption between systems were significant at low temperatures, it would decrease the intensity of the R_1' line more than that of the R_1 line since the former could be reabsorbed by the R system, but the latter could not be reabsorbed by the R' system. This would cause the deviation from the exponential temperature dependence to be in the opposite direction from that observed experimentally. Thus, reabsorption cannot account for the observed results.

The temperature dependence of the values of the decay times of the R_1 lines of chromium-doped lithium germanate is similar to that of chromium ions in ruby. The decrease in the lifetime, as temperature is increased, is attributed to the increasing importance of vibronic emission processes. The constant lifetime observed at low temperatures should be close to the intrinsic value for the upper level of the transition. However, because of radiation trapping and energy transfer mechanisms, it is difficult to obtain exactly the intrinsic value. The values obtained here are somewhat larger than that found by Nelson and Sturge[7] of about 3.6 msec for the intrinsic lifetime of the R lines in ruby at low temperatures without reabsorption. Reabsorption in lightly doped ruby has been observed to lengthen the lifetime at 77°K by as much as a factor of four,[8] while in heavily doped ruby, the energy transfer between single ion and pair systems has been found to shorten the low-temperature lifetime of the R lines to less than 1 msec.[9]

Fluorescence lines originating from the same level, or from levels in thermal equilibrium, will have the same decay patterns and decay times. The fact that the decay times at the R_1 and R_1' lines at low temperatures are different is further indication that the two lines originate from different fluorescent systems which interact strongly at high temperatures. The decay patterns of the R_1 line at low temperatures indicate the pumping of the R system through the R' system. These results are consistent with the results of the relative intensity measurements.

V. ANALYSIS OF RATE EQUATIONS

These results can be interpreted in terms of energy transfer between chromium ions in nonequivalent sites, which is efficient enough in both directions at high temperatures to allow for thermal equilibrium to be established in the populations of the excited states before fluorescence emission, but which is not this efficient in both directions at low temperatures and, thus, the energy transfer is mainly from the high-energy system to the low-energy system. A qualitative

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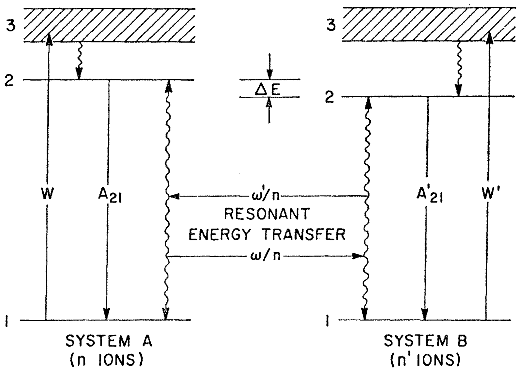

FIG. 5. Energy transfer between two fluorescent systems.

interpretation of the results can be obtained by examining the rate equations of the populations of two interacting fluorescent systems.[9]

Figure 5 shows a model for two fluorescent systems interacting through an energy transfer process. This is a nonradiative process in which a transition in one direction in one system is accompanied by a transition in the opposite direction in the other system and any energy difference ΔE between the two transitions is taken up by a phonon.

The rate equations for the populations of the energy levels of the two systems in Fig. 5 are

$$\begin{aligned}
\dot{n}_1 &= -Wn_1 + A_{21}n_2 + (\omega/n')n_2n_1' - (\omega'/n')n_1n_2', \\
\dot{n}_2 &= -\dot{n}_1, \\
\dot{n}_1' &= -W'n_1' + A_{21}'n_2' - (\omega/n')n_2n_1' + (\omega'/n')n_1n_2', \\
\dot{n}_2' &= -\dot{n}_1', \qquad (1)
\end{aligned}$$

where the energy transfer probabilities are normalized with the population of system B. It is assumed that the radiationless transitions between the absorption bands and the metastable states in both systems are extremely fast, that the pumping probabilities W and W' are approximately the same for both systems, and that the pumping strength is small enough so that most of the ions in both systems remain in the ground state.

If the metastable levels of the two systems are separated by an amount ΔE then the energy transfer in one direction will be accompanied by the emission of a phonon of energy ΔE, while the energy transfer in the opposite direction must be accompanied by the absorption of a phonon of the same energy. Thus, we would expect the ratio of the energy transfer probabilities in the two directions to be equal to the ratio of the probabilities of emission and absorption of phonons. That is,

$$\omega/\omega' = \exp(\Delta E/kT). \qquad (2)$$

In order to correlate these ideas with the results of the relative intensity measurements, Eq. 1 can be solved for equilibrium conditions to give

$$n_2 = \frac{Wn[A_{21}+\omega'(n/n')]+\omega'Wn}{(A_{21}+\omega)[A_{21}'+\omega'(n/n')]-\omega'\omega(n/n')},$$

$$n_2' = \frac{Wn'(A_{21}+\omega)+\omega Wn}{(A_{21}+\omega)[A_{21}+\omega'(n/n')]-\omega'\omega(n/n')}. \qquad (3)$$

The temperature dependence of the relative fluorescence intensity of the R_1' to R_1 line shown in Fig. 3 should be proportional to

$$\frac{n_2}{n_2'} = \frac{n}{n'}\left[\frac{A_{21}'+[(n/n')+1]\omega'}{A_{21}+[(n/n')+1]\omega}\right], \qquad (4)$$

where we relate system A of Fig. 5 to the R' system in chromium-doped lithium germanate and system B to the R system. At high temperatures, we would expect the radiationless transition probabilities to be much greater than the radiative transition probabilities and, thus, the second term in Eq. (4) should dominate the expression for n_2/n_2'. This is shown to be correct if Eq. (2) is substituted into Eq. (4) giving the exponential temperature dependence of the intensity ratios shown in Fig. 3.

According to Eq. (4), the ratio n_2/n_2' is also proportional to the ratio of the total number of ions in the two systems. Comparison with the relative intensity ratios in Fig. 3 indicates that the ratio of the total number of ions in the two systems, n_{R_1}'/n_{R_1}, is greatest for the lithium germanate sample with 0.12% chromium and least for the 0.038% sample. This is consistent with the results of excitation measurements.[6]

The radiationless transition probabilities will decrease with decreasing temperature and, when their values are such that the radiative transition probabilities can no longer be neglected, the relative intensity ratios should deviate from an exponential temperature dependence. The temperature at which the radiative transition probabilities can no longer be considered negligible with respect to the probabilities for radiationless transitions can be seen from Eq. (4) to depend on the ratio of the total populations of the two systems. The temperatures at which the fluorescence intensity ratios in Fig. 3 deviate from an exponential temperature dependence thus indicate that n_{R_1}'/n_{R_1} is greatest for the sample with 0.12% chromium and least for the 0.038% sample. This is consistent with the magnitude of these ratios described above and also with results of excitation measurements.

At low temperatures, where there are few phonons available for absorption, ω' is small so that A_{21}' dominates the numerator of Eq. (4). Both terms in the denominator may be important and the ratio n_2/n_2' is no longer proportional to an exponential Boltzmann factor. Since A_{21}' and A_{21} will be approximately constant at low temperatures, the slightly increasing slopes of the experimental lines shown in Fig. 3 indicate that energy transfer from the R' system to the R system is still active at low temperatures and that ω decreases as the temperature is lowered. There is no significant difference in the slopes of the lines at low temperatures, which indicates that the efficiency of the energy transfer is approximately the same for the three samples.

The results of the lifetime measurements can be explained using the same model shown in Fig. 5 with the same assumptions used to interpret the relative intensity measurements. Equations (1) and (2) still apply and the rate equations can be solved for the response of the systems to pulsed excitation. The time-dependent populations of the metastable states of both systems can be determined, assuming their statistical weights are equal.

At high temperatures, where the radiationless transition probabilities are greater than the radiative transition probabilities, we find that the populations of both levels decay exponentially with the same decay time:

$$n_2(t)=n_2(0)\ \exp(-t/\tau_F),$$

$$n_2'(t)=n_2'(0)\ \exp(-t/\tau_F), \tag{5}$$

where

$$\tau_F^{-1}=[n_2(0)+n_2'(0)]^{-1}\{[n_2(0)/\tau_A]+[n_2'(0)/\tau_B]\}. \tag{6}$$

This decay time is a weighted combination of the intrinsic decay times of the two levels and the weighting factors are the populations of the levels at the end of the exciting pulse. This qualitatively explains the experimental results shown in Fig. 4 above 110°K, where both the R_1 and R_1' lines have purely exponential decays with the same decay times.

At low temperatures, where the probability of absorption of a phonon is small, ω' will be small and the solutions to the rate equations are

$$n_2(t)=n_2(0)\ \exp(-p_3t),$$

$$n_2'(t)=\left[n_2'(0)+\frac{\omega}{p_3-A_{21}'}n_2(0)\right]$$

$$\times\exp(-A_{21}'t)-\frac{\omega}{p_3-A_{21}'}n_2(0)\ \exp(-p_3t), \tag{7}$$

where $p_3=A_{21}+\omega$; we have taken the time at the end of the excitation pulse to be $t=0$ and solved for $t>0$.

The expression for $n_2'(t)$ can be simplified for the specific cases if certain inequalities are satisfied for the transition probabilities and the populations at the end of the pulse. If the slope of $n_2'(t)$ is positive at $t=0$, an initial rise in the fluorescence will occur before the decay. The condition for an initial rise is

$$n_2(0)/n_2'(0)\geq A_{21}'/\omega. \tag{8}$$

The time at which the maximum in the fluorescence emission will occur is when the slope of $n_2'(t)$ is zero. This is

$$t_{\max}=(A_{21}'-p_3)^{-1}\ln\left[\frac{A_{21}'}{p_3}+\frac{A_{21}'(p_3-A_{21}')}{p_3\omega}\frac{n_2'(0)}{n_2(0)}\right]. \tag{9}$$

The decay following the initial rise will be exponential with a decay time which is the greater of $A_{21}'^{-1}$ and p_3^{-1}.

If the two conditions

$$n_2(0)/n_2'(0)<(A_{21}'-p_3)/\omega,\qquad A_{21}'>p_3 \tag{10}$$

are satisfied, then the expression for $n_2'(t)$ reduces to

$$n_2'(t)=A\ \exp(-A_{21}'t)+B\ \exp(-p_3t). \tag{11}$$

Thus, under these conditions, $n_2'(t)$ will exhibit a double exponential decay; the first having the decay time $(A_{21}')^{-1}$ and the second having the decay time p_3^{-1}.

Again, this model gives a correct qualitative explanation for the observed experimental results. The different decay times for the R_1 and R_1' lines and the decay patterns for the R_1 line at low temperatures indicate that the two systems are not in thermal equilibrium and that the R' system is pumping the R system. The first of Eqs. (7) predicts that the observed decay at the R_1' line will be exponential with a decay time which is a combination of the intrinsic decay time of the level and the characteristic time for energy transfer. The second of Eqs. (7) with the inequality of Eq. (8) explains the decay patterns observed for the R_1 line at low temperatures in the samples with 0.18% and 0.12% chromium. Equation (11) predicts the decay patterns observed for the R_1 line of the 0.038% Cr sample at low temperatures. The change in decay patterns from a double decay to an initial rise as concentration is increased has also been observed in heavily doped ruby.[9,10]

VI. ENERGY TRANSFER MECHANISMS

The observation that the R and R' fluorescent systems are in thermal equilibrium at high temperatures indicates that the energy transfer between these systems is a nonradiative process. The theory of energy transfer between optically active ions in solids has been developed by Dexter[11] based on the ideas of Förster.[12]

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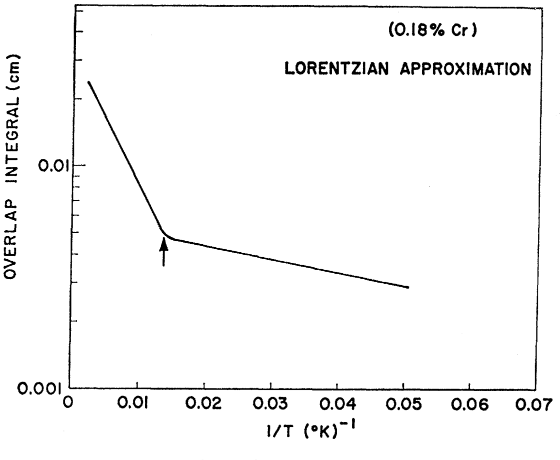

FIG. 6. Temperature dependence of the overlap integral of the R_1 and R_1' fluorescence lines for lithium germanate with 0.18 wt% chromium assuming Lorentzian line shapes. The arrow marks the temperature at which the relative intensities of the lines were observed to deviate from an exponential temperature dependence.

The probability per unit time for an emission transition in one system to be accompanied by an absorption transition in the other system is

$$P=(2\pi/\hbar^2)\mid\langle\psi_1,\psi_2^*\mid V\mid\psi_1^*,\psi_2\rangle\mid^2\int g_1(\omega)g_2(\omega)d\omega, \tag{12}$$

where V is the interaction between the two systems and the integral is over the normalized line shapes for the two transitions.

The temperature dependence of the energy transfer probability is contained in the overlap integral. If Lorentzian functions are assumed for the line shapes, the overlap integral becomes[13]

$$\int g_1(\omega)g_2(\omega)d\omega=\pi^{-1}\frac{\Delta\omega_S+\Delta\omega_A}{(\Delta\omega_S+\Delta\omega_A)^2+(\omega_S{}^0-\omega_A{}^0)^2}, \tag{13}$$

where $\Delta\omega_S$ and $\Delta\omega_A$ are the half-widths of the "sensitizer" and "activator" transitions, respectively, and $\omega_S{}^0$ and $\omega_A{}^0$ are their positions. Using the values for the widths and positions of the R_1 and R_1' fluorescence lines found experimentally for the lithium germanate sample with 0.18% chromium,[14] the overlap integral for these lines can be plotted as a function of temperature and is shown in Fig. 6. The actual line shapes are between Gaussian and Lorentzian functions, which means that the values of the overlap integral will be somewhat less than those shown in Fig. 6. However, as temperature is raised above 50°K, the lines tend to become more and more Lorentzian in shape.[14] The curve in Fig. 6 does indicate that the energy transfer probability will be greater at high temperatures than at low temperatures, as is observed experimentally. The temperature at which the relative intensities of the R_1' to the R_1 line were found to deviate from an exponential temperature dependence for this sample is shown by an arrow in Fig. 6.

It is difficult to determine the nature of the interaction mechanism between the two fluorescent systems because of the lack of crystallographic information about the host lattice. The lack of any obvious evidence of exchange effects in the optical and electron-spin resonance data indicates that exchange interaction is probably not strong enough to cause efficient energy transfer. In order to investigate the possibility of efficient energy transfer through electrostatic interaction, the interaction potential can be expressed as a multipole expansion. The first term is for dipole-dipole interaction and, substituting into Eq. (12), gives[11]

$$P_{\text{dd}}=\frac{1}{\epsilon^2}\left(\frac{3c}{8\pi^2}\right)\left(\frac{e^2}{mc^2}\right)\frac{f^Sf^A}{\omega^2R^6}\int g_1(\omega)g_2(\omega)d\omega, \tag{14}$$

where R is the separation between sensitizer and activator and f^S and f^A are the oscillator strengths of the transitions.

It is possible to calculate a very rough estimate of P_{dd} by assuming the values of the oscillator strengths to be that found for the R_1 line in ruby.[10,15] The value of R is critical in the calculation of the energy transfer probability. If the chromium ions are randomly distributed in these samples and if the nearest neighboring chromium ions are in nonequivalent sites, the values of R are approximately 23.3, 15.6, and 13.9 Å for the samples with 0.038% (1.87×10^{21} Cr ions per cm^3), 0.12% (5.88×10^{21} Cr ions per cm^3), and 0.18% (8.81×10^{21} Cr ions per cm^3), respectively. Even assuming as small a value as 10 Å for the ionic sepatation, using a value for the overlap integral of 0.01 cm gives a value of 24.6 sec^{-1} for P_{dd}. The characteristic time for the energy transfer would thus be an order of magnitude longer than the observed fluorescent lifetimes. If we assume that the values of the decay times measured at low temperatures are of the order of the values of the radiative lifetimes, then the dipole-dipole interaction cannot account for the observed energy transfer.

It is possible for higher-order multipoles to be more important than the dipole-dipole interaction.[11,16,17] This is true if the dipole-dipole interaction is parity forbidden in the zeroth order. Imbusch[10] has shown that the electric quadrupole-quadrupole interaction between single ions and pairs in heavily doped ruby may be more efficient than the electric dipole-dipole, magnetic dipole-dipole, and electric dipole-quadrupole interactions. Again, if we assume oscillator strengths

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similar to those of ruby, similar calculations can be made to give rough estimates for the energy transfer probabilities in chromium-doped lithium germanate. Assuming a separation of $R=10$ Å for the active ions, the dipole-quadrupole interaction will give an energy transfer time of the same order as the observed low-temperature lifetime and the quadrupole-quadrupole interaction will give an energy transfer time shorter than the measured low-temperature lifetime. Thus, for this value of R, the quadrupole-quadrupole interaction could cause the efficient energy transfer which is observed. However, any larger value of R, say 20 Å, will not lead to short enough energy transfer times.

Even assuming a quadrupole-quadrupole interaction with a very small value for R, Eq. (12) alone cannot give a correct qualitative explanation for the results shown in Fig. 3 consistent with Eqs. (2) and (4). Since the temperature dependence of the expression in Eq. (12) is contained in the overlap integral, and since the overlap integral is the same for energy transfer from sensitizer to activator as it is for transfer in the opposite direction, the ratio of energy transfer probabilities in the two directions should be independent of temperature. We would expect instead (and it is necessary to explain the experimental results) that this ratio should have an exponential temperature dependence.

Kröger[18] and Botden[19,20] developed a theory of energy transfer based on a model of Mott[21] and Seitz[22] using a configurational coordinate diagram. Although Dexter[11] criticized this theory on several points, he indicates specific modifications which could make it useful in certain cases. If these modifications are employed and if the vibrational oscillators can be considered in the classical approximation at temperatures as low as 100°K,[23,24] then it is possible for this theory to lead to the observed exponential temperature dependence.

Another possible explanation of the experimental results is in terms of phonon-assisted energy transfer. The probability for this type of energy transfer increases with increasing separation between the two lines involved because of the simultaneous increase in phonon density of states. Although the lines in this case are closely spaced, this still might be an important mechanism. The probability for phonon-assisted energy transfer can be written as[13]

$$P^{\text{phonon-assisted}}=(2\pi/\hbar^2)\,|\langle\psi_1,\psi_2^*|V|\psi_1^*,\psi_2\rangle|^2\left\{\frac{3\omega_p}{4\pi^2v^5\hbar\rho}\,|[\langle\psi_2^*|V_1|\psi_2^*\rangle-\langle\psi_2|V_1|\psi_2\rangle-\langle\psi_1^*|V_1|\psi_1^*\rangle-\langle\psi_1|V_1|\psi_1\rangle]|^2\begin{pmatrix}n_p+1\\ n_p\end{pmatrix}\right\},\quad(15)$$

where V_1 is the electrostatic part of the orbit-lattice interaction, ω_p is the phonon frequency, and the term in parentheses accounts for the occupation of phonon states for emission (upper) and absorption (lower) of phonons. Thus, the ratio of phonon-assisted energy transfer probabilities in opposite directions between two systems is simply the ratio of the probabilities of absorption and emission of phonons. This gives the desired exponential temperature dependence.

Equation (15) is equivalent to Eq. (12) where the overlap integral has been replaced by the term in curly brackets. It is possible to obtain a rough estimate for $P^{\text{phonon-assisted}}$ by assuming the value of 5000 cm^{-1} for the term in square brackets used by Orbach[13] for ruby. The characteristic energy transfer time for a dipole-dipole phonon emission process with $R=10$ Å turns out to be an order of magnitude less than the observed low-temperature lifetime. The quadrupole-quadrupole interaction is significantly greater than the dipole-dipole interaction and gives a short enough energy transfer time to account for the observed results, using the estimated values of R for these samples.

VII. SUMMARY AND CONCLUSIONS

The results of measurements of the temperature dependences of the relative fluorescent intensities and lifetimes at the R_1 and R_1' lines in $Li_2Ge_7O_{15}$:Cr^{3+} give further proof of the existence of nonequivalent lattice sites for the chromium and indicate the presence of energy transfer between chromium ions in nonequivalent sites. The efficiency of this energy transfer is great enough in both directions at high temperatures to establish thermal equilibrium between the two fluorescent systems, but it is not so efficient in both directions at low temperatures. The R' system continues to pump the R system at low temperatures.

An analysis of the rate equations of the populations of the energy levels of the two fluorescent systems

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[19] P. J. Botden, Philips Res. Rept. **6**, 425 (1951).

[20] P. J. Botden, Philips Res. Rept. **7**, 197 (1952).

[21] N. F. Mott, Proc. Roy. Soc. (London) **A167**, 384 (1938).

[22] F. Seitz, Trans. Faraday Soc. **35**, 74 (1939).

[23] As pointed out by Dexter (Ref. 11) a correct quantum-mechanical treatment of the Kröger model for energy transfer requires the use of an effective temperature, $T^*=T_D\coth(T_D/T)$, instead of T. Here, T_D is the Debye temperature and this substitution accounts for the zero-point vibrations. However, at temperatures high enough for a classical approximation to be used, the exponential expression will reduce to a Boltzmann factor in T. It has been found, in some cases, that the classical approximation is valid at temperatures at least as low as 90°K (Ref. 24).

[24] F. E. Williams, Phys. Rev. **80**, 306 (1950); **82**, 281 (1951); **84**, 1181 (1951); **113**, 97 (1959).

connected by energy transfer leads to a qualitative interpretation of the experimental results. The correct temperature dependences of the intensity and lifetime measurements are predicted and the initial rise and double-exponential decay patterns of the R_1 line at low temperatures are explained. When the two systems are strongly coupled, the ratio of the energy transfer probabilities in the two directions is proportional to an exponential factor.

An examination of the mechanism for the energy transfer through the overlap of the transitions indicates from very rough calculations that quadrupole-quadrupole interactions can be responsible for the energy transfer over ionic separations of 10 Å. This theory must be modified to obtain the correct temperature dependence for the ratio of the transition probabilities in the two directions. Phonon-assisted energy transfer leads to the experimentally observed temperature dependence and is efficient enough for quadrupole-quadrupole interaction to account for the efficiency of the observed energy transfer over the estimated chromium ion separations for these samples.

ACKNOWLEDGMENTS

The author would like to thank C. O. Dugger for the crystals used in this investigation and J. R. Weiner for determining their impurity content by neutron-activation analysis. He also would like to acknowledge O. M. Clark and T. J. Reichenbach for their assistance with the experiments.

PHYSICAL REVIEW VOLUME 173, NUMBER 2 10 SEPTEMBER 1968

Nuclear-Spin-Diffusion Relaxation to a Finite Density of Paramagnetic Impurity Ions[*][†]

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(Received 1 April 1968)

The effect of a finite concentration of paramagnetic impurity ions on nuclear-spin-diffusion relaxation is studied theoretically and experimentally. It is found that in the spin-diffusion limited case, which is the one of greatest interest here, the equation for the relaxation rate can be modified in such a way as to permit a moderately simple description of the relaxation for all normal ion densities. The modification consists in the replacement of certain exponents in the usual relaxation-rate expression for small ion densities by other exponents which are determined numerically when a single parameter has been specified. This parameter is $x=N^{1/3}(C/D)^{1/4}$, where N is the concentration of the ions, C/r^6 is the transition probability of the nuclei due to the dipole-dipole interaction between an ion and a nucleus, and D is the spin-diffusion coefficient. It is shown also that the amount of nonexponential behavior in the relaxation recovery depends on this same parameter, and that the effects of finite ion density on the way in which T_1 depends on ion concentration, frequency, and temperature can be studied at the same time as the nonexponential behavior. Applications are made both to results of pulse NMR experiments which are reported here for the first time and to the results of experiments that have been reported by other workers.

I. INTRODUCTION

IN spite of extensive studies of spin-diffusion relaxation by nuclear-magnetic-resonance (NMR) methods which have been in progress for a period of nearly 20 years since the concept was first introduced by Bloembergen[1] in 1949, it has not yet been possible experimentally clearly to distinguish the various limiting cases predicted by the theory nor to make wholly satisfactory determinations of various parameters on which the magnitude of the relaxation depends. Reasons for this are to be found partly in the difficulty of making independent determinations of such quantities as the paramagnetic ion density and the electron relaxation time, and partly in the inadequacy of the theory with respect to such considerations as the dependence of relaxation on ion density, on the magnitude of the diffusion-barrier radius, and on other factors.

Thus it is not surprising that much of the experimental work has been devoted to the study of the one case which appears most often, namely, the so-called diffusion-limited case, and to have been restricted, even within the range of validity of this case, to the mere determination of sets of numerical values for the parameters which are mutually consistent and are physically reasonable. In most cases even the electron relaxation time τ was permitted to be determined, along with all other quantities, from the measurements of nuclear spin-lattice relaxation

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[*] This research was supported by the National Science Foundation.

[†] This work was based on a part of a thesis submitted by Eiichi Fukushima in partial fulfillment of the requirements for a Ph.D degree at the University of Washington.

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[1] N. Bloembergen, Physica **15**, 386 (1949).