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Energy Transfer in Ruby

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The transfer of energy from single chromium ions to closely coupled pairs of chromium ions in ruby has been investigated. Ruby samples whose concentrations ranged from 0.003 to 1.0% Cr_2O_3 were prepared and in each crystal the intensity of single-ion fluorescence and of pair fluorescence was accurately measured. Radiative-decay measurements were also made in an attempt to unravel the dynamics of the transfer process. The transfer from single ions to pairs is shown to occur nonradiatively, and its efficiency is enhanced by a fast energy transfer between individual single ions. The possibility is explored that an electric quadrupole-quadrupole interaction is responsible for this transfer process.

INTRODUCTION

ENERGY transfer from one ion species to another in a solid is an interesting theoretical problem as well as of great importance in the search for efficient laser material. By this phenomenon one ion species with strong absorption characteristics can transfer its absorbed excitation to the second species, thereby greatly enhancing the latter's fluorescence output. Both ion species may be introduced as impurities into an optically inactive host, or in some cases one species may be an impurity and receive energy from optically active ions which are constituents of the host material. The energy transfer in each case comes about because of a sufficiently strong interaction between the ions concerned.

The simplest model used to describe the optical behavior of impurity paramagnetic ions introduced as a dilute impurity in a host is the single-ion crystal-field model. Each impurity ion is considered to be isolated from all other impurities and the effect of the neighboring diamagnetic host ions is described by an effective electric field. Although it is an approximation, such a model has built into it the correct symmetry properties of the system, and it has been successfully employed in the analysis of spectra. As the concentration of impurity ions is increased, additional effects are seen. One must now consider the possibility that two paramagnetic ions may be sufficiently close together to interact with each other. Additional lines found in the optical spectrum of concentrated ruby have been shown to originate on near-neighbor pairs of chromium ions,[1,2] where the ions forming the pair are strongly exchange-coupled. Similar effects due to exchange-coupled ions have been found in many other materials. An interaction between two impurity ions, one of which is in an optical excited state, may cause the excitation to move from one ion to the other. Such energy transfer may occur even when the two impurity ions are not of the same species.

The picture can be considerably complicated when the concentration of optically active ions approaches 100%. A very striking example of the effect of the interaction between optically active ions in concentrated crystals was pointed out by Varsanyi and Dieke,[3] who showed that the absorption spectrum of $PrCl_3$ contained lines whose energies corresponded to the sum of the energies in two individual Pr^{3+} transitions. This illustrates the fact that a pair of Pr ions, because of some interaction between them, can act as a unit and absorb a single photon which raises both Pr ions to excited levels. The importance of this pair interaction for energy-transfer considerations was also pointed out by these authors. In the case where there is 100% concentration of optically active ions and where the interaction between them is strong, the single-ion model completely loses validity. In this case one must look upon the excitation as residing not on any one ion but as being distributed about the crystal as a whole. This is the exciton picture.

Ruby (Cr^{3+} in Al_2O_3) is a material in which, by varying the chromium concentration, one can observe many of the phenomena outlined above. When the chromium doping is very dilute the spectrum is well described by the single-ion crystal-field model. At high concentrations one finds additional lines due to exchange-coupled pairs of chromium ions.[1,2] Furthermore, excitation is transferred from single ions to pairs of chromium ions. In the case where all the Al^{3+} ions are replaced by Cr^{3+} ions one has the antiferromagnetic material, Cr_2O_3, where the correct description of the absorption and fluorescence transitions is by means of the exciton picture.

We have examined the transfer of excitation from single chromium ions to exchange-coupled pairs of chromium ions in ruby. Ruby samples ranging in concentration from 0.003 to around 1.0% Cr_2O_3 were studied and in each crystal the relative intensity of single-ion fluorescence to pair fluorescence was measured. Radiative-decay measurements were also made and much interesting information about the transfer process can be extracted from these lifetime

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[1] A. L. Schawlow, D. L. Wood, and A. M. Clogston, Phys. Rev. Letters **3**, 271 (1959).

[2] N. A. Tolstoi, Liu Shun'-Fu, and M. E. Lapidus, Opt. i Spektroskopiya **13**, 242 (1962) [English transl.:—Opt. Spectry. (USSR) **13**, 133 (1962)]; N. A. Tolstoi and A. P. Abramov, Opt. i Spektroskopiya **14**, 691 (1963) [English transl.:—Opt. Spectry. (USSR) **14**, 365 (1963)].

[3] F. L. Varsanyi and G. H. Dieke, Phys. Rev. Letters **7**, 442 (1961).

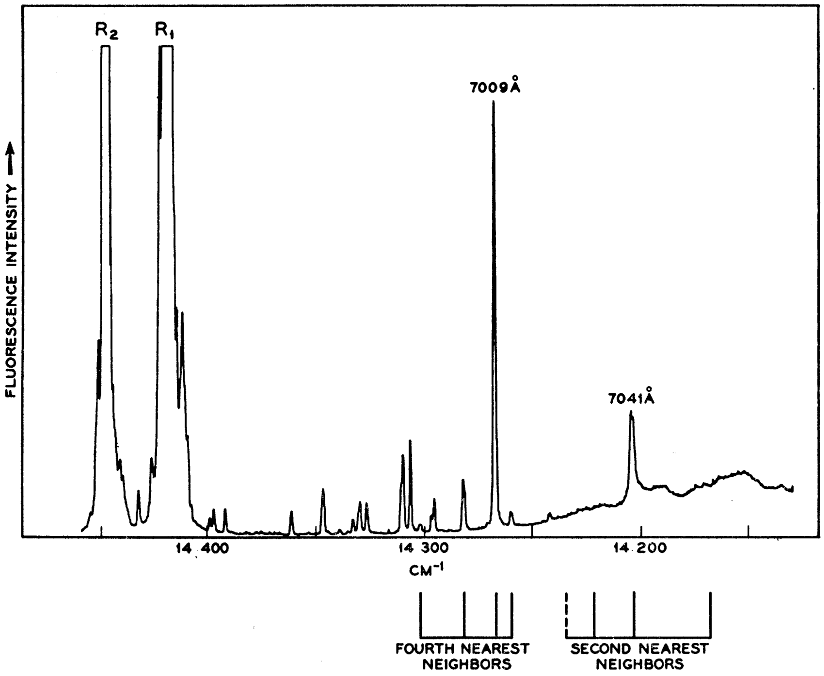

FIG. 1. Portion of the 77°K fluorescence spectrum of ruby (0.2% Cr_2O_3). The positions of the fluorescence lines from the lowest excited states of second and fourth neighbors is indicated (after Ref. 7). The broad-band fluorescence seen at long wavelengths is part of the vibrational sidebands of the R lines.

studies. The transfer from single ion to pair is shown to occur nonradiatively, and its efficiency is enhanced by a fast energy transfer between individual chromium ions.

Theoretical ideas underlying energy-transfer processes are considered following the treatment of Förster[4] and Dexter.[5] Exchange and magnetic dipole-dipole interactions are found to be too weak to explain the rapid energy transfer found experimentally. Similarly, an electric dipole-dipole interaction is found to be too weak. The possibility that a quadrupole-quadrupole interaction is responsible for the transfer is explored and an approximate estimate of this interaction indicates that it may be stronger than the other interactions considered, and consequently may be responsible for the transfer. The experimental results are in approximate agreement with the predictions of a quadrupole-quadrupole transfer mechanism.

RUBY FLUORESCENCE SPECTRUM

Part of the 77°K fluorescence spectrum of a medium-doped ruby (0.2% Cr_2O_3) is shown in Fig. 1. The two intense R lines can be seen as well as part of the vibrational sideband. This is the only fluorescence originating on isolated single chromium ions. A large number of weaker sharp lines can also be seen. These are called N lines and have been shown to originate on closely coupled pairs of chromium ions.[1,2] Since the probability that two chromium ions will come together to form a closely coupled pair increases as the square of the chromium concentration while the number of single ions increases linearly with concentration, one would expect that the relative intensity of pair fluorescence to single-ion fluorescence would increase linearly with concentration. However, Schawlow, Wood, and Clogston[1] found that the increase in relative fluorescence was faster than linear. They concluded that the pairs obtain some excitation by energy transfer from single ions.

Much work has been done in identifying the lines which come from the various types of pair.[6–9] Some lines which come from second- and fourth-nearest neighbors are indicated in Fig. 1. We are mainly concerned with the 7009-Å line (N_2), which comes from a fourth-nearest-neighbor pair, and the 7041-Å line (N_1) which comes from a second-nearest-neighbor pair.

The experimentally observed energy-level diagram for second- and fourth-nearest-neighbor pairs, as well as for single ions, is shown in Fig. 2. This figure has been drawn using the data of Kisliuk.[7] The splitting in the ground states of the pairs is satisfactorily explained by an isotropic exchange interaction ($J\mathbf{S}_1\cdot\mathbf{S}_2$), but the splitting in the excited states of the pairs is not amenable to a simple theoretical interpretation.[10] The chromium ions forming the second-nearest-neighbor

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[4] T. Förster, Ann. Physik **2**, 55 (1948).

[5] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[6] P. Kisliuk, A. L. Schawlow, and M. D. Sturge, *Advances in Quantum Electronics* (Columbia University Press, New York, 1964), Vol. II, p. 725.

[7] P. Kisliuk and W. F. Krupke, Internal Report, Aerospace Corp., El Segundo, Cal., 1964 (unpublished); J. Appl. Phys. **36**, 1025 (1965).

[8] A. A. Kaplyanskii and A. K. Przheruskii, Doklady Akad. Nauk, SSSR **142**, 313 (1962) [English transl.: Soviet Phys.—Doklady **7**, 37 (1962)].

[9] L. F. Mollenauer, Microwave Lab. Report No. 1325, Stanford University, 1965 (unpublished).

[10] A. M. Clogston (unpublished); quoted in Ref. 9.

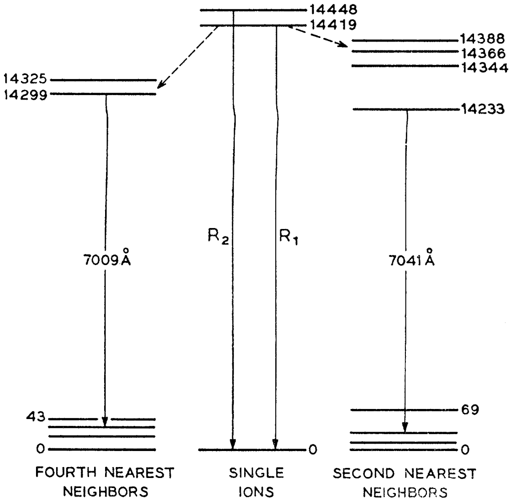

FIG. 2. Energy-level diagram for single chromium ions, second-nearest neighbors, and fourth-nearest neighbors. The data are taken from Ref. 7. Fine structure on the pair levels has not been shown and the values given are approximate.

pair are antiferromagnetically coupled in the ground state, while the fourth-nearest neighbors are ferromagnetically coupled in the ground state. As can be seen from this figure, no pair levels were found which were coincident with the excited single-ion levels.

One of the parameters which is of interest to us is the ratio of the strengths of the various N lines to the strength of the single-ion fluorescence. This measurement is complicated by the fact that there is strong radiative trapping in the R lines.[11] This has the effect of lengthening the observed decay time and reducing the intensity of the R lines; furthermore this effect is dependent on the size, shape, and concentration of the samples. Since the radiative quantum efficiency of single ions in ruby is approximately 80%,[12] the R-line fluorescence trapped by unexcited single ions has an 80% chance of being re-emitted as fluorescence, either as R-line fluorescence or as fluorescence in the sideband. Since no trapping occurs in the N_1 or N_2 lines, a meaningful measure of the relative intensity of pair fluorescence to single-ion fluorescence is given by the ratio of N_1 (or N_2) intensity summed over all polarizations, to total single-ion fluorescence (R lines plus sidebands) summed over all polarizations.

EXPERIMENTAL

The relative intensities of N_2 and N_1 line fluorescence to single-ion fluorescence are shown by the solid curves in Figs. 3 and 4. The measurements were made at 77°K. The intensities were measured photoelectrically using a Jarrell-Ash 1-m Ebert scanning spectrometer and an RCA 7102 photomultiplier as detector.

The radiative decay rates of the various lines (R_1, N_1, and N_2) were accurately measured at 77°K. A flash lamp capable of emitting a light pulse of 5-μsec duration and of being pulsed repetitively was used for the lifetime measurements. The photomultiplier output was fed into a multichannel analyzer, and by continuously averaging the signal over many decays, a good signal-to-noise ratio was achieved even for exceedingly weak lines.

At low concentrations ($\sim$0.02% Cr_2O_3) the N lines are about four orders of magnitude less intense than the R lines. Furthermore, the decay rates of the R lines and N lines are different. Figure 5 shows the observed decay patterns (plotted as number of photons per channel versus time) for R_1 line (8.8 msec) and 7009 Å line (1.10 msec). These measurements were made at 77°K. Even at the low concentration of 0.044% Cr_2O_3 in this sample, the trapping of R-line fluorescence has caused an increase in the observed R-line lifetime from its intrinsic value of 4.2 msec.[12] The decay times of some weaker N lines which are known to originate on the same fourth-nearest-neighbor pair also have the same

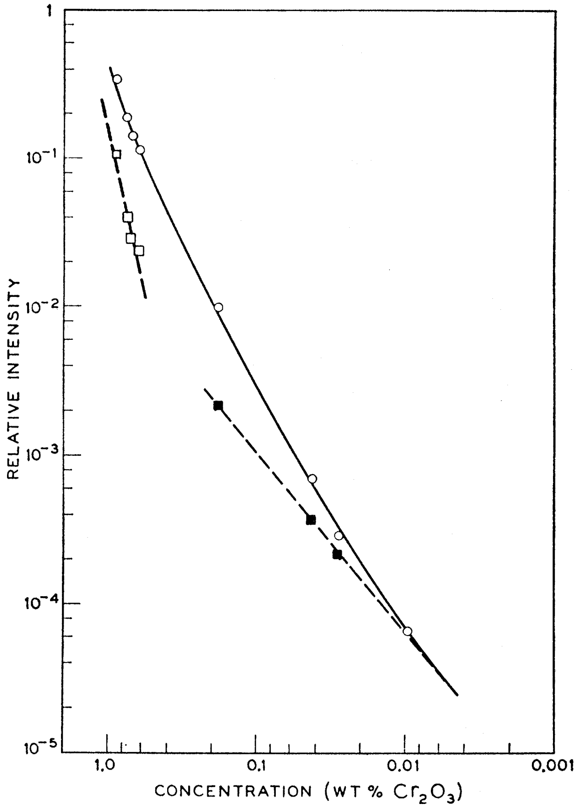

FIG. 3. The circles give experimental values of the relative intensity of 7009 Å fluorescence (averaged over all directions and polarizations) to total single-ion fluorescence measured at 77°K. ■ indicates the fractional amount of the total fluorescence which is contained in the rapidly decaying part of the 7009 Å fluorescence. □ indicates the experimental value of r/τ as discussed in the section on the concentration dependence of the different transfer processes.

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[11] F. L. Varsanyi, D. L. Wood, and A. L. Schawlow, Phys. Rev. Letters **3**, 544 (1959).

[12] D. F. Nelson and M. D. Sturge, Phys. Rev. **137**, A1117 (1965).

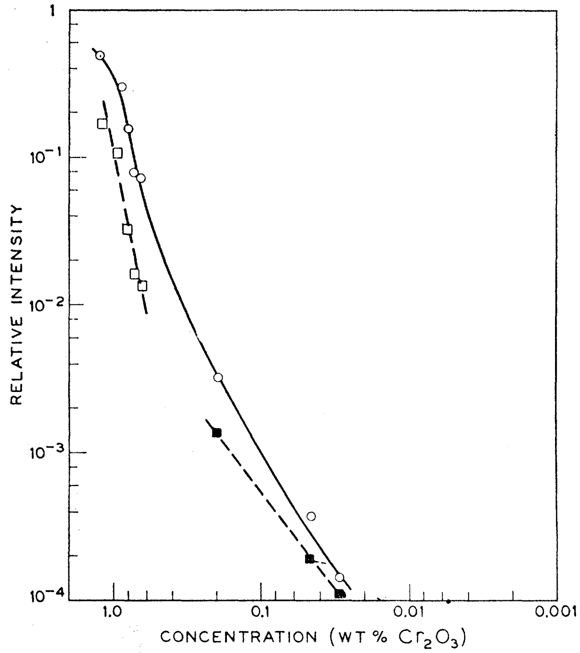

FIG. 4. The circles give experimental values of the relative intensity of 7041 Å fluorescence (averaged over all directions and polarizations) to total single-ion fluorescence measured at 77°K. ■ indicates the fractional amount of the total fluorescence which is contained in the rapidly decaying part of the 7041 Å fluorescence. □ indicates the experimental value of r/τ as discussed in the section on the concentration dependence of the different transfer processes.

value of decay time (~1.1 msec). In this same crystal the 7041 Å-line decay time is 1.3 msec. It would appear that at low concentrations the single ions and the different types of pairs are isolated from each other, that each is pumped by absorption into its own pump bands, and that at 77°K their intrinsic decays are 1.3 msec (second-nearest neighbors), 1.1 msec (fourth-nearest neighbors), and 4.2 msec (single ions).

At intermediate concentrations (~0.2% Cr_2O_3) the N lines have become more intense and they now exhibit a double decay time. This is seen in Fig. 6, which shows a semilog plot of intensity versus time for the R_1 line, 7009 Å line, and 7041 Å line. Trapping has increased the R-line decay to 10.0 msec. The N-line decay starts out at its intrinsic rate but each has a more slowly decaying tail with a decay rate which is just the decay rate of the R lines. This indicated that at these concentrations the pairs are receiving additional excitation from the metastable levels of the single ions. As the concentration is increased to around 1%, the N-line intensities become comparable to the R lines. The N-line decays now start out as an initial rise followed by a decrease which again has exactly the same decay rate as the R lines. This is just the behavior expected when energy transfer from single ions is the dominant pumping mechanism for the pairs.

To give mathematical expression to the double-decay mechanism in the N lines we adopt a very simple model. Let N_s^0 be the number of single ions initially populated by the lamp and which are capable of transferring excitation to the pairs. These ions have a decay rate f_s; $N_s(t)=N_s^0e^{-f_st}$. Let N_p^0 be the number of pairs of a certain type initially populated by intrinsic absorption and let f_p be the intrinsic decay rate of these pairs. We will assume $f_p>f_s$. The excitation transfer rate will be written in the simplest possible form, N_sf_x, where f_x includes information about the number of ion pairs and the average single-ion–ion-pair separation. We assume that we are at a sufficiently low temperature that transfer from pairs to single ions is negligible. Then the pair population is given by

$$N_p(t)=(N_p^0-N_p^1)e^{-f_pt}+N_p^1e^{-f_st}, \qquad (1)$$

where $N_p^1=N_s^0f_x(f_p-f_s)^{-1}$ is a measure of the population achieved by energy transfer. When $N_p^0>N_p^1$, which holds at low concentrations, the N-line decay will consist of an initial fast decay at f_p followed by a slower decay at f_s. At higher concentrations, where $N_p^1>N_p^0$, we expect an initial rise followed by a decay at f_s. Thus, the gross features of the experimentally observed N-line decay is explained by this simple mathematical model.

On this model the area under the $N_p^0e^{-f_pt}$ part of the decay is due to intrinsic pumping, and from the decay curve we can estimate what fraction of the total N-line fluorescence is caused by intrinsic absorption of pumping light by pair absorption bands. This intrinsic N-line fluorescence (divided by total single-ion fluorescence) is plotted for low concentrations in Figs. 3 and 4 where the experimental points are denoted by dark squares. As mentioned before, this quantity should increase linearly with concentration. Experimentally it is found to increase as concentration to the power of 1.2 (7009 Å line), and to the power of 1.3 (7041 Å line). There are two possible causes for this disagreement. The first is that the chromium ions do not enter the sapphire host

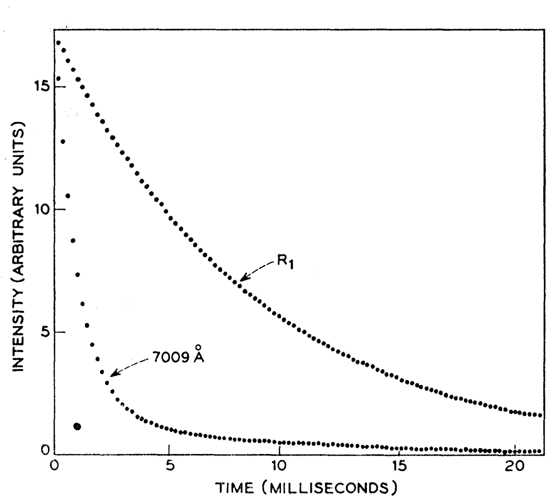

FIG. 5. Fluorescence decay signals from the R_1 and 7009-Å lines of a low-concentration ruby (0.044% Cr_2O_3) at 77°K.

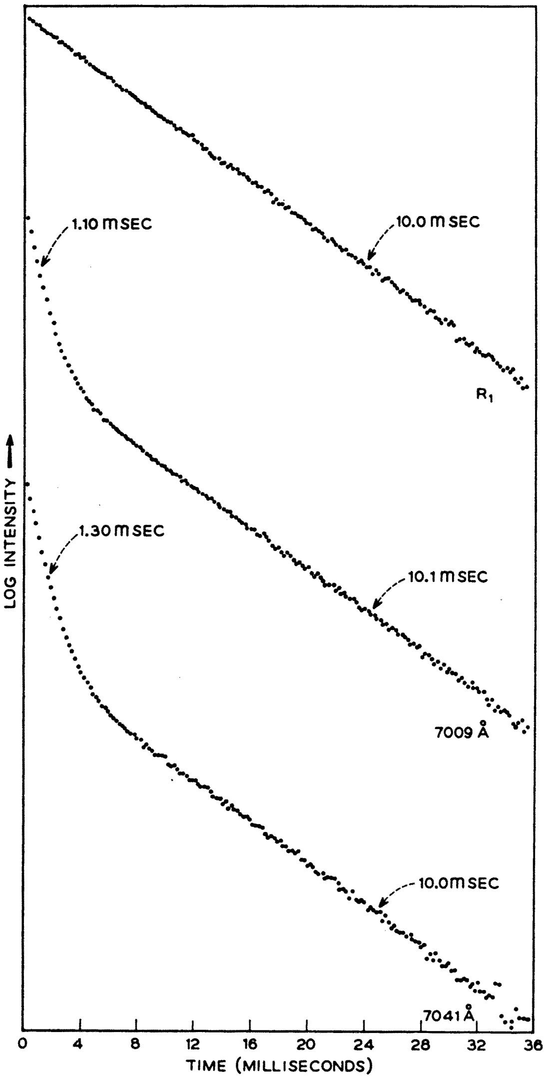

FIG. 6. Fluorescence decay signals from the R_1, 7009 and 7041 Å lines of a medium concentration ruby (0.2% Cr_2O_3) at 77°K.

randomly. (The assumption that the Cr ions enter the crystal randomly during growth is basic to the statistical reasoning which suggests that the density of pairs increases as the square of the concentration.) The second possible cause of the discrepancy, which is perhaps more real, is that the mathematical model adopted to explain the decay is too simple. It is likely that part of the fluorescence in the initial decay arises because of very rapid excitation transfer from nearby single ions.

NATURE OF THE SINGLE-ION-ION-PAIR TRANSFER

So far we have not considered the question whether the experimental behavior is best explained by a radiative or nonradiative energy transfer from single ions to pairs. Wieder and Sarles[13] have suggested that a likely mechanism for energy transfer is a radiative process, that is, single ions fluoresce emitting *R*-line radiation which is absorbed (or trapped) by pairs and re-emitted as *N*-line fluorescence. On the other hand, Tolstoi[14,2] and co-workers have considered that the transfer occurs nonradiatively. We first address ourselves to the problem of what is the nature of the transfer process—whether radiative or nonradiative.

The fact that the tail of the *N*-line decay is identical with the *R*-line decay fits the picture of a radiative transfer quite well, but other objections arise. In order for the transfer to be radiative there must exist a higher level of each pair system whose distance from the ground state corresponds to one of the *R* lines. Further, the absorption into this higher pair level must be very strong to compete successfully with the much more numerous single ions in the trapping of single-ion fluorescence. Indeed, one would need to postulate an unrealistically high absorption strength for this pair transition. As mentioned before, no such high pair levels were found by Kisliuk.[7] In case they exist and are difficult to observe because of overlapping *R* lines, we attempted to separate them out by applying a strong magnetic field on the assumption that their Zeeman splittings would differ from that of the *R* lines. Such a search in absorption did not reveal any additional lines. There are some extra lines very close to the *R* lines in ruby crystals of high concentration, but these are equally strong in absorption and emission at 77°K, and so cannot be attributed to transitions involving high levels of the second- or fourth-nearest-neighbor systems.

As a further check on the possibility of direct absorption of R_1 radiation by pairs, the fluorescence from a ruby crystal was studied when this crystal was pumped by R_1 laser light. The temperatures of the laser crystal and of the target crystal were identical to insure that the frequency of the laser radiation was the same as the resonant frequency of the target crystal. The relative intensity of pair fluorescence to single-ion fluorescence was the same, within experimental error, under laser pumping and under blue-light pumping. If the pairs could absorb laser light directly it was estimated that the ratio of *N*-line fluorescence to single-ion fluorescence should be much stronger under laser pumping than under blue-light pumping. This result would then seem to add to the other evidence that radiative transfer is not the major transfer mechanism. We conclude that a strong nonradiative transfer is the process which pumps the ion pairs. Other evidence to be cited later confirms this conclusion.

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[13] I. Wieder and L. R. Sarles, *Advances in Quantum Electronics* (Columbia University Press, New York, 1961), p. 214.

[14] N. A. Tolstoi and Liu Shun'-Fu, Opt. i Spectroskopiya **13**, 403 (1962) [English transl.—Opt. Spectry. (USSR) **13**, 224 (1962)].

The N_2-line decay curve of a fairly concentrated ruby (0.4% Cr_2O_3) under pulsed-blue exciting light and under laser pumping is shown in Fig. 7. The duration of the laser pulse was 0.2 msec. According to the simple mathematical model which describes the N-line decay, the intensity under the $e^{-f_p t}$ part of the decay arises because of pumping into the intrinsic absorption pair bands. Now, from statistical considerations about the number of pairs in the crystal, the intensity in the initial fast part of the decay under blue exciting light appears much too strong to be attributable only to intrinsic pair absorption. This discrepancy in interpretation is confirmed by studying the N-line decay under laser pumping. Since there is now no absorption into the broad bands of the pairs, the pairs are pumped only by energy transfer and, according to our mathematical model, we expect that the N-line decay should consist of an initial rise followed by a slow decay. Experimentally, it is seen that it is identical with the decay obtained under blue-light excitation. This indicates that our mathematical model is to simple. A correct model would allow not one, but many f_x values. Presumably at higher concentrations, the initial part of the N-line decay is caused mainly by fast transfer from very close single ions. The amount due to intrinsic pumping is presumably quite small. This is in keeping with the observation that at lower concentrations the intensity under the rapidly decaying part of the N lines increases more rapidly with concentration than our statistical reasoning predicts.

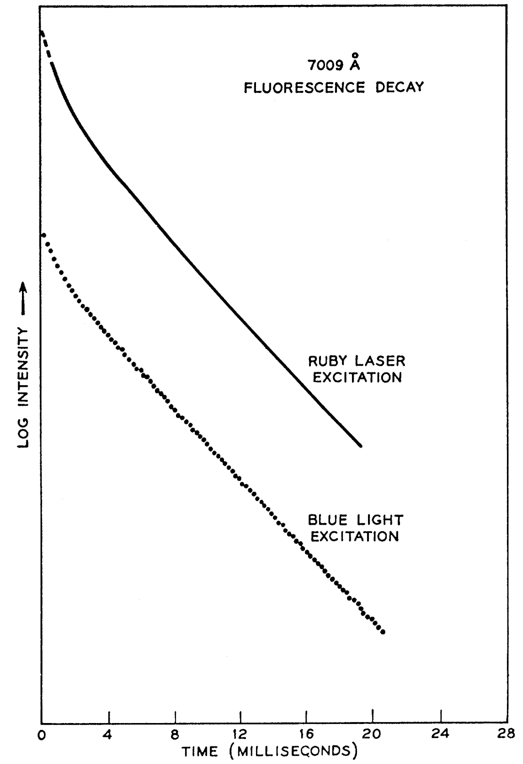
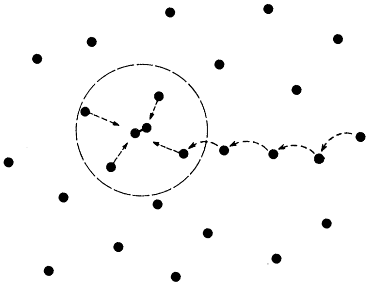


FIG. 7. The 7009 Å decay from ruby (0.4% Cr_2O_3) under laser pumping (upper) and under blue-light excitation (lower).

FIG. 8. Model to illustrate energy transfer to the pairs. Excitation can move rapidly along chains of single ions until it reaches the vicinity of a pair at which point it can be transferred to the pair.



The consequences of a nonradiative energy transfer from single ion to pairs will now be examined. The probability of nonradiative transfer falls off very rapidly with ionic separation, and so it is only those single ions close to pairs which can transfer excitation directly to pairs. These single ions then should have a more rapid decay rate than the main body of single ions since they can decay by radiative transition as well as by efficient energy transfer. This fast decay rate is just the decay time that we should see in the tail of the N-line decays. But as we saw, in each crystal the decay time in the tail is always equal to the decay time of the R line (which is the average decay time of the main body of single ions in the crystal, most of which do not have pairs nearby). Hence, we must adopt a model whereby the single ions which give up excitation directly to the pairs are being continually fed by energy transfer from the main body of single ions. Radiative trapping of R-line fluorescence by unexcited single ions is such a feeding mechanism, but it is not fast enough. We must invoke a nonradiative transfer of excitation along chains of single ions until it reaches the vicinity of a pair, at which point the excitation is transferred to the pair. This model is illustrated in Fig. 8. Since excitation can move rapidly around the crystal and possibly end up on a pair which has a fast intrinsic decay time of around

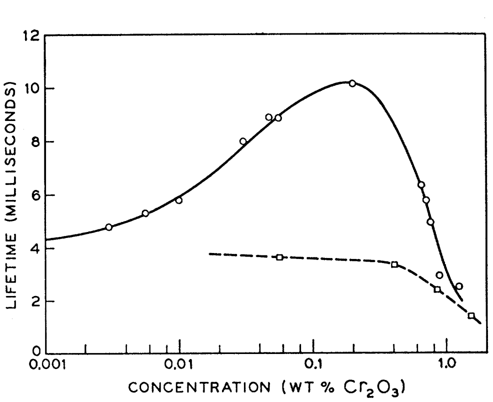


FIG. 9. Plot of R-line decay time measured at 77°K as a function of chromium concentration. The crystals were of approximately similar size (0.1 in.×0.1 in.×0.4 in.). The dashed curve is a plot of Tolstoi's (Ref. 14) lifetime data taken on very small samples where trapping was apparently negligible.

1 msec, this give a mechanism where the single-ion fluorescence can become quenched[15] and the lifetime become shortened. The measured R-line decay time plotted as a function of concentration is shown in Fig. 9. It rises initially because of trapping but at high concentrations, where there is efficient energy transfer to the more rapidly decaying pairs, the decay time falls below the intrinsic value of 4.2 msec. The dashed curve is a plot of Tolstoi's lifetime data[14] taken on very tiny samples where trapping is apparently negligible. The decrease in lifetime with increasing concentration can be understood on the basis of a fast nonradiative transfer from single ion to single ion until the excitation ends up on a rapidly decaying trap. It cannot be explained by a radiative energy transfer. At concentrations no greater than 1% Cr_2O_3 the pairs seem to constitute the only detectable traps. Above 1%, Tolstoi found additional centers which fluoresce farther out in the red with apparently very fast decay rates.[14] These may be triplets of chromium ions.

At this point, it is appropriate to give a specific number for the transfer times with which we are concerned. In order to explain the intensities and lifetime in a 1% ruby, we need to have approximately a 1-msec transfer time from a nearby single ion to a pair, and as we shall see, a much faster time (~1–10 μsec) for single-ion–to–single-ion transfer.

MECHANISMS OF NONRADIATIVE ENERGY TRANSFER

A theoretical treatment of nonradiative excitation transfer between ions in a crystal has been presented by Förster[4] and Dexter.[5] In this section we apply Dexter's treatment[5] to the ruby situation. We first state the basic problem of the transfer of excitation between two ions and write an expression for its probability.

Consider two ions 1 and 2, where ion 1 is in an excited state $|1^*\rangle$ and ion 2 in a state $|2\rangle$. The compound initial state is $|1^*,2\rangle$. We consider the probability that excitation can be transferred from ion 1 to ion 2 because of some static interaction V between them, in such a way that the final state is $|1,2^*\rangle$. The transfer of excitation can be looked upon as two individual transitions on the ions, $|1^*\rangle \to |1\rangle$ and $|2\rangle \to |2^*\rangle$, occurring simultaneously. The probability per unit time that this transfer occurs is given by

$$P=\frac{2\pi}{\hbar}|V_{fi}|^2\int g_1(E)g_2(E)dE. \qquad (2)$$

V_{fi} is the matrix element $\langle 1,2^*|V|1^*,2\rangle$, and $g_1(E)$ and $g_2(E)$ are the normalized line shapes for the individual transitions on ions 1 and 2, respectively. We will only consider nondegenerate levels. The integral in Eq. (2) expresses the condition that excitation can be transferred only if there is energy overlap between the transitions on ions 1 and 2.

The interactions V with which we shall be concerned are (i) exchange, (ii) magnetic interactions between ions, and (iii) the electrostatic interaction between ions which can be expressed as a multipole expansion and which contains electric dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, etc., terms.

We first consider the possibility that an exchange interaction can cause efficient transfer between single-chromium ion in ruby. We assume that the exchange interaction is of the form $J\mathbf{S}_1\cdot\mathbf{S}_2$. For an exchange coupling between two ground-state chromium ions an average distance apart (~15 Å) in a 1% ruby we adopt $J\approx 0.4$ cm^{-1}. Such a J value would lead to broadening of the R lines (due to unresolved ground-state exchange splitting) of around 2 cm^{-1}, which is approximately the width of the R lines in a 1% ruby. In the case where one of the ions in this exchange-coupled pair is in the excited ^2E state, we again write the coupling as $J\mathbf{S}_1\cdot\mathbf{S}_2$. Since the $^4A_2$ ground state and ^2E excited state involve the same orbital levels, we can expect that in this case J will have approximately the same value as when both ions are in the ground state. We adopt this value of J also in the case of nondiagonal matrix elements discussed here. The V_{fi} matrix element is

$$J\langle {}^4A_2,{}^2E|\mathbf{S}_1\cdot\mathbf{S}_2|{}^2E,{}^4A_2\rangle = J\langle {}^4A_2|\mathbf{S}_1|{}^2E\rangle\cdot\langle {}^2E|\mathbf{S}_2|{}^4A_2\rangle. \qquad (3)$$

Now there are no first-order matrix elements of $\mathbf{S}$ between ^2E and $^4A_2$. To obtain a nonvanishing matrix element we must mix $|{}^4T_2\rangle$ into *both* $|{}^2E\rangle$ and $|{}^4A_2\rangle$, and consequently the V_{fi} matrix element is of the order $J(\zeta^2/\Delta_1\Delta_2)^2$, where ζ is the spin-orbit coupling parameter (~250 cm^{-1}), Δ_1 is the energy separation between $^4T_2$ and ^2E (4000 cm^{-1}), and Δ_2 is the energy separation between $^4T_2$ and $^4A_2$ (18 000 cm^{-1}). This gives $|V_{fi}|\sim 4\times 10^{-7}$ cm^{-1}. The overlap integral in Eq. (2) is approximately the inverse of the linewidth, or 2.5×10^{15} erg^{-1}. One finds then that $P_{\text{ex}}\sim 0.1$ sec^{-1}. Allowing each chromium ion to have about four neighbors close enough to be loosely exchange-coupled (with $J\sim 0.4$ cm^{-1}) we see that the average time for excitation to travel from one single ion to another due to exchange is ~2.5 sec. This is very long compared with radiative decay (4.2 msec at 77°K) and cannot be the cause of the rapid transfer found in ruby.

In the calculation of the resonant transfer of excitation from single ion to single ion, the overlap integral depends on the homogeneous widths of the levels and on the energy separation between levels of the nearby chromium ions due to *local* strains. The integral can be written as the inverse of a linewidth. At 77°K, where our measurements were made, the homogeneous width due to phonon-induced broadening is around 0.1 cm^{-1}. It is difficult to determine the effects of local strains. Adopting the observed optical linewidth as the appropriate

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[15] D. L. Dexter and J. H. Schulman, J. Chem. Phys. 22, 1063 (1954).

linewidth to use in evaluating the overlap integral, which we have done above, is perhaps an extreme case, since this width depends on the *macroscopic* crystal strains. The other extreme is to neglect strains and consider only the homogeneous width, and this leads to a resonant transfer rate which is faster by a factor of around ten or so. However, the bottleneck in the energy transfer from the main body of single ions to the pairs is the final step, namely, the single ion-pair transfer, and there is no difficulty in the interpretation of the overlap integral in this case.

We next consider (iii) the electrostatic interaction between ions, and postpone the discussion of magnetic interaction until later. A Taylor expansion of the electrostatic interaction between two ions a distance R apart is given by Dexter,[5] and it contains dipole-dipole, dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole, etc., terms. If we consider only the dipole-dipole interaction, then the square of the interaction matrix element V is

$$|\langle V_{\mathrm{dd}}\rangle|^2=\frac{2e^4}{3n^4R^6}|\langle\mathbf{r}_1\rangle_{fi}|^2|\langle\mathbf{r}_2\rangle_{fi}|^2. \qquad (4)$$

n is the refractive index, and $\mathbf{r}_1$ and $\mathbf{r}_2$ refer to all the electrons on ions 1 and 2, respectively. Similarly, the square of the dipole-quadrupole interaction matrix element is

$$|\langle V_{\mathrm{dq}}\rangle_{fi}|^2=\frac{9e^4}{4n^4R^8}|\langle\mathbf{r}_1\rangle_{fi}|^2\Big[\sum_{j,k}|\langle x_jx_k\rangle_{fi}|^2\Big]. \qquad (5)$$

For the ${}^2E\rightarrow{}^4A_2$ transition in ruby we shall see that it is only the nondiagonal quadrupole matrix elements (x_jx_k, $j\neq k$) which are nonzero. Hence, the quadrupole term in Eq. (5) can be written as $\sum_{j,k,\,j\neq k}|\langle x_jx_k\rangle|^2$. Evaluation of the transfer probabilities under dipole-dipole and dipole-quadrupole interactions reduces to an evaluation of matrix elements of $\mathbf{r}$ and of x_jx_k for the transitions on the individual ions. Now these same matrix elements are also found in the expressions for electric dipole and quadrupole oscillator strengths, f_{ed} and f_{q} for these transitions. Consequently, the transfer probabilities can be expressed in terms of such observable quantities: f_{ed} and f_{q}. In order to see this we shall consider the interaction between the ion and the radiation field.

The probability that an ion interacting with the radiation field will undergo a transition from $|i\rangle$ to $|f\rangle$ and emit a photon, of wave vector $\mathbf{k}$ and polarization $\hat{\epsilon}$, into the solid angle $d\Omega$, is[16,17]

$$\frac{e^2\omega}{2\pi\hbar m^2v^3}|\langle(\mathbf{p}\cdot\hat{\epsilon}-i\mathbf{s}\cdot\mathbf{k}\times\hat{\epsilon})e^{-i\mathbf{k}\cdot\mathbf{r}}\rangle_{fi}|^2d\Omega. \qquad (6)$$

$\mathbf{p}$ is the linear momentum operator, $\mathbf{s}$ is the spin-angular momentum in units of $\hbar$, and v is the velocity of the optical wave in the medium. In the case where an electric-dipole transition is allowed one makes the dipole approximation whereby the matrix element is approximated by $\langle\mathbf{p}\cdot\hat{\epsilon}\rangle_{fi}$ or $-im\omega\langle\mathbf{r}\cdot\hat{\epsilon}\rangle_{fi}$. In the case where an electric-dipole transition is forbidden or only weakly allowed, we consider the $\mathbf{s}\cdot\mathbf{k}\times\hat{\epsilon}$ operator as well as the first two terms of the Taylor expansion of $\mathbf{p}\cdot\hat{\epsilon}e^{-i\mathbf{k}\cdot\mathbf{r}}$. If we further particularize to the case where a photon is emitted in the x direction with y polarization, then, neglecting interference terms, the emission probability can be written

$$\frac{e^2\omega^3}{2\pi\hbar v^3}\left[|\langle y\rangle_{fi}|^2+\left|\left\langle\frac{1}{2mv}(\mathbf{l}+2\mathbf{s})_z\right\rangle\right|^2+\left|\left\langle\frac{\pi xy}{\lambda}\right\rangle\right|^2\right]d\Omega. \qquad (7)$$

The three terms are the electric dipole, magnetic dipole, and electric quadrupole emission probabilities, respectively. Neglecting constant terms we see that the electric dipole oscillator strength f_{ed} depends on the square of $\langle y\rangle_{fi}$; the magnetic-dipole oscillator strength f_{md} depends on the square of $\langle\mu_z/e\rangle_{fi}$, where μ_z is the z component of the magnetic moment; and the electric quadrupole oscillator strength f_{q} depends on the square of $\langle\omega xy/\lambda\rangle_{fi}$, where this is closely related to the nondiagonal quadrupole moment $Q_{ij}=3x_ix_j(i\neq j)$. We note that the diagonal quadrupole moments Q_{ii} do not enter into the expression for the emission probability. Since the quadrupole operator in Eq. (7) can also be written as $\omega xy/2v$, we find that the ratio of electric quadrupole to magnetic dipole oscillator strengths is

$$|m\omega\langle xy\rangle|^2/|\langle l_z+2s_z\rangle|^2. \qquad (8)$$

The oscillator strength is generally assumed to refer to emission probability summed over all directions, and so we define the oscillator strengths in the more usual notation:

$$f_{\mathrm{ed}}=(2m\omega/3\hbar)|\langle\mathbf{r}\rangle_{fi}|^2,$$

$$f_{\mathrm{md}}=(2m\omega/3\hbar)\left|\left\langle\frac{\boldsymbol{\mu}}{e}\right\rangle_{fi}\right|^2,$$

$$f_{\mathrm{q}}=(2m\omega/6\hbar)\sum_{j,k;\;j\neq k}\left|\left\langle\frac{\pi}{\lambda}x_jx_k\right\rangle_{fi}\right|^2. \qquad (9)$$

Inserting this expression for f_{ed} into Eq. (4) and evaluating Eq. (2), we find the probability per second for energy transfer from ion 1 to ion 2, a distance R apart, by electric dipole-dipole interaction to be[18,19]

$$P_{\mathrm{dd}}=\frac{3\pi\hbar e^4}{n^4m^2\omega^2R^6}f_{\mathrm{ed}}^{(1)}f_{\mathrm{ed}}^{(2)}\int g_1(E)g_2(E)dE. \qquad (10)$$

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[16] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).

[17] A. Messiah, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1962).

[18] This expression is equivalent to Dexter's (Ref. 5) Eqs. (16) and (17), neglecting factors of statistical weight which cancel for the transitions involved here.

[19] J. D. Axe and P. F. Weller, J. Chem. Phys. **40**, 3066 (1964).

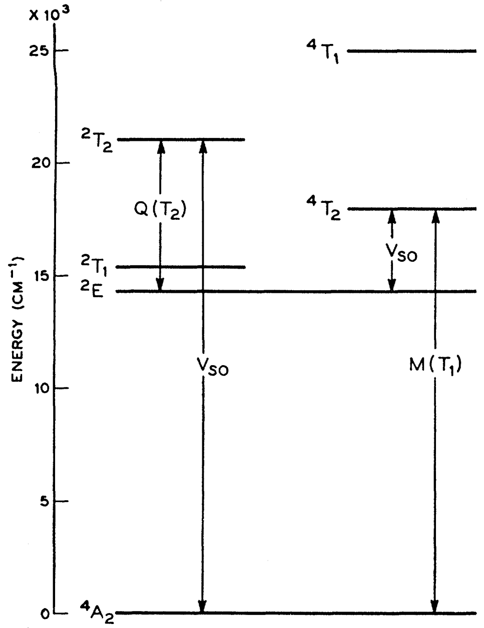

FIG. 10. Energy-level diagram for single Cr^{3+} ions in a cubic environment showing matrix elements used in the evaluation of magnetic dipole and electric quadrupole transitions.

Similarly, the probability for transfer between chromium ions under dipole-quadrupole interaction is

$$p_{\mathrm{dq}}=\frac{81\pi\hbar e^4}{4n^4m^2\omega^2R^8}f_{\mathrm{ed}}{}^{(1)}f_{\mathrm{q}}{}^{(2)}\left(\frac{\lambda}{\pi}\right)^2\int g_1(E)g_2(E)dE. \quad (11)$$

For a 1% ruby where $R\sim 15$ Å, $f_{\mathrm{ed}}=3\times 10^{-7}$,[20] $n=1.7$, $\omega=3\times 10^{15}$, and linewidth≈ 2 cm^{-1}, Eq. (10) gives $P_{\mathrm{dd}}\sim 200$ sec^{-1}. If there are four such neighbors around each single chromium ion we then get a transfer time of around 1.2 msec. On the average, excitation travels along a chain of around three to four single ions before radiation occurs. Now excitation transfer from single ion to ion pair with emission of the excess energy as a phonon is a much slower process. Its probability is given by Eq. (12).[21]

$$P_{\mathrm{dd}}{}^1=\frac{3\pi\hbar e^4}{n^4m^2\omega^2R^6}f_{\mathrm{ed}}{}^{(1)}f_{\mathrm{ed}}{}^{(2)}(E), \quad (12)$$

where $f_{\mathrm{ed}}{}^{(2)}(E)$ is the oscillator strength density in the absorption sideband associated with the $^4A_2\rightarrow{}^2E$ pair transition, and where this oscillator strength density is measured at the single-ion R-line frequency. Equation (12) is valid as long as the sideband transition is an electric-dipole process, whether vibronically induced or caused by the hemihedral field. Since the single-ion sidebands are reduced in peak intensity by a factor of 100–1000 from the peak intensity of a ruby no-phonon line 2 cm^{-1} in width, the same is presumably true for pair sidebands. Therefore, the estimated energy-transfer time from single ion to pair is a factor of 100–1000 longer than the single-ion–single-ion transfer time calculated by assuming that the width is 2 cm^{-1}; that is, the single ion-pair transfer time under electric dipole-dipole interaction is of the order of 100–1000 msec. Thus an electric dipole-dipole transfer process would appear to be much too weak to be responsible for the energy transfer found in ruby.

One of the consequences of Eq. (12) is that transfer is most efficient when the pure electronic transition on ion 1 corresponds to the peak of the absorption sideband on ion 2. The sideband strength is generally zero at the no-phonon line, increases as one moves away from this line, and has a first peak at a frequency corresponding to some acoustic cutoff or some effective Debye temperature. In ruby, the sideband intensity has an initial ω^3 dependence and rises to an initial peak at around 270 cm^{-1}. Thus it will be more favorable to have energy transfer with emission of a high-energy phonon (within the Debye limit) than with emission of a low-energy phonon, although the energy discrepancy is greater in the first case.

At this point we can consider the magnetic dipole-dipole interaction which we will assume enters as $\langle\mu^{(1)}\rangle_{fi}\langle\mu^{(2)}\rangle_{fi}/R^3$. We can write $|\langle\mu\rangle_{fi}|^2$ in terms of the magnetic dipole oscillator strength f_{md} by Eq. (9). From the analogy with the electric dipole case we see that the transfer probability under magnetic dipole-dipole interaction is given by Eq. (10) if we use f_{md} instead of f_{ed} and put $n^4=1$. However, in the present situation where f_{md} is an order of magnitude less than f_{ed}, the magnetic dipole-dipole interaction is less effective than the electric dipole-dipole interaction and need not be considered.

To consider a dipole-quadrupole transfer mechanism we need a value for f_{q}. Since quadrupole radiative processes are usually too weak to observe, we shall have to make an approximate calculation for f_{q} as follows. Both the electric quadrupole and magnetic dipole operators are of even parity, and the ratio of oscillator strengths is given by Eq. (8). We shall apply this ratio to the actual $^2E\rightarrow{}^4A_2$ ruby transition and estimate f_{q} in terms of f_{md}. Although f_{md} is not known for ruby, it is known for the $^2E\rightarrow{}^4A_2$ transition for Cr^{3+} in MgO and this should be very close to the ruby value. Using this value of f_{md} we can get an approximate value of f_{q}.

We shall work in the cubic approximation and neglect the effect of both the even trigonal and hemihedral crystal fields. In this approximation the transitions are isotropic and we will consider emission of a k_x,ϵ_y photon. The $^2E\rightarrow{}^4A_2$ ruby transition is first-order

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[20] M. D. Sturge, Phys. Rev. **130**, 639 (1963).

[21] Both sharp lines and sidebands are assumed to be electric dipole transitions. Because of the overlap integral in Eq. (2), the single-ion–to–pair transfer occurs only through the medium of that part of the ion-pair sideband absorption which corresponds to the sharp no-phonon line of the single chromium ion. If we define a sideband oscillator strength density $f(E)$ such that the integral $\int f(E)dE$ over the absorption sideband equals the total phonon-assisted absorption oscillator strength, then Eq. (10) easily reduces to Eq. (12).

spin-forbidden for both electric quadrupole and magnetic dipole transitions. We must invoke the spin-orbit interaction V_{so}. A study of the wave functions indicates that the lowest order nonzero matrix elements for electric quadrupole and magnetic dipole transitions are, respectively,

$$\langle {}^4A_2|V_{\mathrm{so}}|{}^2T_2\rangle\langle {}^2T_2|m\omega xy|{}^2E\rangle/\Delta_3$$

and

$$\langle {}^4A_2|1_z|{}^4T_2\rangle\langle {}^4T_2|V_{\mathrm{so}}|{}^2E\rangle/\Delta_4. \tag{13}$$

These matrix elements are indicated on the energy-level diagram (Fig. 10). Δ_3 is the energy separation between ${}^2T_2$ and ${}^4A_2$ (21 000 cm^{-1}), and Δ_4 is the energy separation between ${}^4T_2$ and ${}^2E$ (4,000 cm^{-1}). The nondiagonal quadrupole operator connecting the ${}^2E$ and ${}^2T_2$ states in Eq. (13) is of type T_2. Diagonal quadrupole operators (which are of type A_1 and E) connecting these states are forbidden by group theory. This is the basis for eliminating the $j=k$ matrix elements, which was discussed in connection with Eq. (5).

From Eq. (13) the ratio of electric quadrupole to magnetic dipole oscillator strengths is

$$\frac{f_{\mathrm{q}}}{f_{\mathrm{md}}}\approx\left|m\omega\langle xy\rangle\frac{\zeta}{\Delta_3}\right|^2\Big/\left|\langle 1_z\rangle\frac{\zeta}{\Delta_4}\right|^2$$

$$\approx|m\omega\langle xy\rangle\Delta_4/1_z\Delta_3|^2. \tag{14}$$

Taking $\langle xy\rangle\sim r_0^2$, where $r_0=0.5\times10^{-8}$ cm, and taking $1_z=\hbar$, this ratio is approximately 4×10^{-4}. We note that in ruby the quadrupole oscillator strength is more spin-forbidden by a factor of 25 or so than is the magnetic dipole or electric dipole oscillator strength. Now the ${}^2E\rightarrow{}^4A_2$ no-phonon line in MgO:Cr^{3+} is a magnetic dipole transition.[22] Further, the fluorescence quantum efficiency is believed close to 100%.[23] Consequently, we can estimate from the radiative lifetime that the magnetic dipole R-line oscillator strength is $\sim4\times10^{-8}$.[24] This gives $f_{\mathrm{q}}\sim1.5\times10^{-11}$, which we adopt as the ruby ${}^2E\rightarrow{}^4A_2$ electric quadrupole oscillator strength. It is to be compared with $f_{\mathrm{ed}}=3\times10^{-7}$.

Now it was pointed out by Dexter,[5] and emphasized by Axe,[19] and Brown,[25] that, even though the quadrupole oscillator strength is generally much less than the dipole oscillator strength, the probability for energy transfer under dipole-quadrupole interaction may not be negligible in comparison with a dipole-dipole transfer. To see this we can divide P_{dq} [Eq. (11)] by P_{dd} [Eq. (10)], and we find,

$$\frac{P_{\mathrm{dq}}}{P_{\mathrm{dd}}}=\frac{27}{4}\frac{f_{\mathrm{q}}}{f_{\mathrm{ed}}}\left(\frac{\lambda}{\pi R}\right)^2. \tag{15}$$

For a 1% ruby where $R\approx15$ Å, $\lambda=7000$ Å, $f_{\mathrm{ed}}=3\times10^{-7}$, and $f_{\mathrm{q}}\approx1.5\times10^{-11}$ we find $P_{\mathrm{dq}}/P_{\mathrm{dd}}\approx7.5$. Thus, it is not unreasonable to expect that in a 1% ruby a dipole-quadrupole energy transfer process is 7.5 times as efficient as a dipole-dipole process. If we extend these ideas to quadrupole-quadrupole interactions, we expect $P_{\mathrm{qq}}/P_{\mathrm{dd}}\approx(P_{\mathrm{dq}}/P_{\mathrm{dd}})^2\approx60$. It appears possible then that in a 1% ruby the time for excitation transfer from single ion to single ion by a quadrupole-quadrupole process is ~20 μsec. If we again assume that the transfer from single ion to pair is down by 100–1000, we get 2–20 msec for this quadrupole-quadrupole process. As previously indicated, a transfer time from single ion to pair of around 1 msec is necessary to explain the intensity and lifetime data found in a 1% ruby.

The observation that a quadrupole-quadrupole interaction may be stronger than a dipole-dipole interaction does not indicate that a multipole expansion of the electrostatic interaction is a diverging series. The even parity multipoles (quadrupoles, hexadecapoles, etc.) form a decreasing series in units of $(r/R)^2$, where r is an atomic dimension and R is the interionic distance, and the odd-parity multipoles (dipole, octopoles, etc.) likewise form a decreasing series. (The ratio of even-parity to odd-parity multipolar matrix elements depends on the system in question.) Because of the predominantly even-parity nature of the lowest lying ruby wave functions, the odd-parity multipolar matrix elements are only weakly allowed and the quadrupole terms in the multipolar expansion may be the largest.

To summarize: Our calculations show that exchange, magnetic dipole-dipole, and electric dipole-dipole interactions do not appear to be strong enough to explain the energy-transfer data. Although we can make only crude estimates of quadrupole effects, it does seem possible that an electric quadrupole-quadrupole transfer may be the most efficient of the processes considered and may be responsible for both the efficient single-ion–single-ion and for the single-ion–pair transfer.

EXPERIMENTAL CHECK ON THE ENERGY-TRANSFER MECHANISM

Since the different mechanisms depend on different powers of the ionic separation, it is possible in theory to make an experimental check on which mechanism is dominant. Because of our inability to vary the concentrations of single ions and pairs independently, we cannot use the normal tests. At the highest concentrations where the transfer is very efficient we will adopt a simple model and attempt to determine what the

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[22] S. Sugano, A. L. Schawlow, and F. L. Varsanyi, Phys. Rev. **120**, 2045 (1960).

[23] R. W. Weinert, J. H. Parker, Jr., J. G. Castle, Jr., and D. W. Feldman, Bull. Am. Phys. Soc. **9**, 405 (1964).

[24] The lifetime for the ${}^2E$ state of MgO:Cr^{3+} is 11.6 msec. However, in the ${}^2E\rightarrow{}^4A_2$ transition the vibrational sideband is 2.5 times as intense as the R line, so that the magnetic dipole R-line decay time is 40.6 msec. To estimate the oscillator strength f from the lifetime τ, the formula $f\tau=1.51\lambda_0^2/n^3$ was used. This gives $f\sim3.7\times10^{-8}$.

[25] M. R. Brown, J. S. S. Whiting, and W. A. Shand, J. Chem. Phys. **43**, 1 (1965).

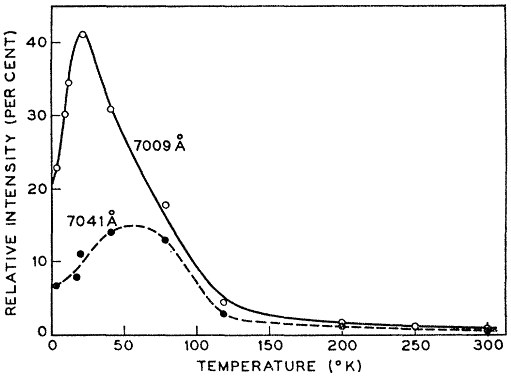

FIG. 11. Plots of relative intensity of both 7009 and 7041 Å lines as functions of temperature.

transfer mechanism may be. We assume that the transfer from single ion to pair is the bottleneck, and that the rapid transfer from single ion to single ion is such that we can consider that each single ion has the same probability of being excited. We will assume that all paramagnetic centers (single ions and pairs) are distributed about the crystal so that the distance of any center from one of its nearest neighbors is a constant, R. On this model each pair has a number of nearest single ions capable of transferring energy directly to the pair, and as the concentration is increased this number of nearest single ions will not change, but their separation from the pair will decrease. We will further assume that the ratio of the number of pairs (N_p) to the number of single ions (N_s) increases linearly with concentration. This last assumption restricts us to concentrations of no greater than 1% Cr_2O_3.

The initial excitation in the single ions can be written as $N_s\rho$, where ρ is the average probability that a single ion is initially excited. The energy which is transferred to the pairs and which appears as N-line fluorescence is proportional to the number of pairs (N_p), to the probability that the nearest single ions are excited (ρ), to the transfer rate between ions (P), and also to the length of time that the single-ion excitation resides in the crystal (the radiative lifetime τ). Thus, the relative intensity of pair fluorescence to total fluorescence, which we will denote by r, has the following proportionality relationship:

$$r \propto N_p \rho P \tau / N_s \rho \qquad (16)$$

or

$$r/\tau \propto (N_p/N_s)P. \qquad (17)$$

The assumption that the initial excitation is at all times available for energy transfer until it is emitted as fluorescence must be modified when a sizeable fraction of the excitation is emitted as pair fluorescence. We must allow for the fact that once excitation goes to a pair it is no longer available for transfer. Such an adjusted r/τ value is what is experimentally plotted and considered below.

Now for a dipole-dipole transfer mechanism, the rate P_{dd} which goes as R^{-6} varies as the square of the concentration, C^2. The dipole-quadrupole rate varies as $C^{2.6}$, and the quadrupole-quadrupole rate varies as $C^{3.3}$. Therefore, on this simple model, we expect that the relative intensity of pair fluorescence to total fluorescence divided by the radiative lifetime will vary as C^3 for a dipole-dipole mechanism, $C^{3.6}$ for dipole-quadrupole mechanism, and $C^{4.3}$ for quadrupole-quadrupole mechanism. If the transfer were radiative, this quantity would be expected to vary as the square of the concentration. Figures 3 and 4 show experimental values of the ratio of pair fluorescence to single-ion fluorescence as a function of concentration, for the 7009 Å line and the 7041 Å line (heavy curves). From these data and from the lifetime data of Fig. 9, values of r/τ are obtained and are shown in the upper dashed plots in Figs. 3 and 4. In both cases the experimental r/τ plot varies as $C^{4.3\pm0.5}$. It would appear then, on the basis of the model we have adopted, that a quadrupole-quadrupole process may be responsible for the energy transfer in ruby.

TEMPERATURE DEPENDENCE ON THE TRANSFER PROCESS

As the temperature is raised, the probability increases that excitation can be transferred back from pairs to single ions by phonon absorption. Increasing the temperature above 77°K does indeed lead to the expected decrease in the relative intensity of pair fluorescence, as can be seen from Fig. 11. A decrease in relative intensity is also found when the temperature is reduced below 50°K. This decrease in N-line intensity with decreasing temperature may be connected with the decrease in R_2-line intensity over the same temperature range. The single-ion $2\bar{A}$ level (from which the R_2-fluorescence line originates) is farther away from the metastable pair levels than is the $\bar{E}$ level (from which the R_1 line originates). Consequently, energy transfer from $2\bar{A}$, which occurs with emission of a higher energy phonon than is the case with transfer from $\bar{E}$, may be a more efficient process. Thus, decreasing the temperature depopulates $2\bar{A}$ and may result in less efficient transfer to the pairs.

One consequence of a rapid transfer between single ions may be noted here. In rubies of high concentration, the R lines have widths greater than 1 cm^{-1}. Let us assume that this broadening is caused mainly by randomly distributed strains. Ions in a region of high compressive strain will have their metastable energy levels reduced in energy (they will not split), while those in a region of expansive strain will have their levels shifted to slightly higher energy. The inhomogeneous broadening due to summing over all such regions causes the broad R-line profile. If we further assume that these regions of strain are of microscopic size and are randomly distributed, then because of the rapid transfer of energy from single ion to single ion, excitation may move to the more compressed regions and if the temperature is sufficiently low (~1°K) may become trapped there. This would show up as thermalization within the R_1 line. Experimentally, one finds that in going from 4.2 to 1°K the fluorescence intensity in the R_1 line shifts very slightly to longer wavelengths.

We must not discount the possibility that at high concentrations part of the wide R_1-line profile can be caused by the tendency of the chromium ions to form weakly coupled clusters. The R_1 lines from such a cluster would show a splitting which might be unresolved because of strains and appear only as an additional broadening, and by going to low temperatures we would then expect thermalization within the levels of the same ionic center (in this case the weakly coupled clusters). Indeed, some of the structure at the sides of the R_1 line at high concentration is attributable to just such centers. It is possible, however, that most of the observed thermalization is due to the rapid migration of excitation to regions of high compression in the crystal and is a thermalization involving all ions in a section of the crystal. Such thermalization within the normal emission line profile of the transition from the lowest spin-orbit component of the metastable $^3T_2$ state of Ni in $KMgF_3$ has been observed by Dietz.[26]

CONCLUSION

Many of the difficulties inherent in studies of energy transfer are apparent here. One must study a number of samples of widely differing concentrations and make certain hopeful assumptions about the random nature of the impurity doping. During the growth of highly concentrated samples, undetected impurities may be introduced or additional types of ionic centers may be formed, and these may act as highly efficient sinks of excitation, thereby introducing additional complications. The efficiency of transfer from the first ion system to the second is dependent upon whether or not there is transfer between like ions in the first ion system, and this possibility must enter into the analysis. Accurate intensity measurements, always difficult to make, may be further complicated by the existence of self-absorption effects. This is particularly true in the case of ruby. To these drawbacks one must add our inability to vary the concentrations of either of the two ionic species independently. This necessitated adopting a very simple model to describe the very complex distribution of single chromium ions and closely coupled pairs in ruby so as to be able to distinguish between the different transfer processes. Results based on this model must then be weighed against the inexact nature of our description of the actual system being considered.

Our experiments afford a strong indication that the transfer from single ions to pairs occurs nonradiatively, and that the efficiency of the feeding mechanism is enhanced by the rapid transfer of excitation from single ion to single-ion until it is close enough to be transferred to a pair. Such a transfer process has been found in a number of rare-earth systems. From our knowledge of the single-ion wave functions and optical transition probabilities it appears that exchange, magnetic dipole-dipole, and electric dipole-dipole interactions are not strong enough to explain the experimental results. The possibility that the transfer is caused by a quadrupole-quadrupole interaction is discussed, and although its strength can be only approximately estimated, a quadrupole-quadrupole transfer process may be the strongest of the processes considered. On the basis of a simple model, the experimental results seem to support the likelihood that the transfer is due to a quadrupole-quadrupole interaction. If the energy transfer in ruby is due to a quadrupole-quadrupole interaction, then it does not depend on the presence of the hemihedral field which causes the optical transitions to be electric dipole in nature. A similar rapid energy transfer could occur in systems where the ions are in centers of inversion symmetry. A search for such energy transfer in materials containing Cr^{3+} ions in sites of inversion symmetry would cast additional light on the question of the strength of the quadrupole-quadrupole transfer mechanism in ruby.

Finally, our experiments on ruby illustrate the importance of *both* intensity measurements and accurate lifetime measurements in the analysis of energy-transfer problems.

ACKNOWLEDGMENTS

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[26] R. E. Dietz, L. F. Johnson, and H. J. Guggenheim, *Physics of Quantum Electronics* (McGraw-Hill Book Company, New York, 1966), p. 361.