Cooperative and Stepwise Excitation of Luminescence: Trivalent Rare-Earth Ions in Yb^{3+}-Sensitized Crystals*

TORU MIYAKAWA† AND D. L. DEXTER‡
University of Rochester, Rochester, New York 14627
(Received 7 August 1969)

The probability of cooperative energy transfer from two excited ions to a nearby ion is computed and compared with the probability of excitation by stepwise energy transfer. For Yb^{3+} sensitization of Er^{3+}, Ho^{3+}, and Tm^{3+} activated hosts, the cooperative transition rate from two excited Yb^{3+} ions is estimated to be in the range 10^7–10^9 sec^{-1}, depending on the degree of overlaps of absorption and emission bands. In the case of the $Er^{3+}+Yb^{3+}$ and $Ho^{3+}+Yb^{3+}$ systems, the dependence of output intensity on the exciting light intensity I_E and the concentration of Yb cannot discriminate between cooperative and serial transfer, but estimates of the transfer probabilities show that the stepwise process dominates. It is suggested that the $Tb^{3+}+Yb^{3+}$ system would be an excellent system in which to observe the cooperative effect unambiguously. In the $Tm^{3+}+Yb^{3+}$ system also, we expect stepwise transfer to dominate except for unfeasibly low I_E.

I. INTRODUCTION

NUMEROUS phenomena involving electronic energy transfer in condensed matter have recently been found. One of them is the so-called quantum-counter (QC) action[1] or visible from infrared by the summation of radiation (VISOR) action[2] reported in many rare-earth-doped crystals with or without additional rare-earth (RE) sensitizer ions.[3–9] The system $RE^{3+}+Yb^{3+}$, where RE^{3+} is a trivalent rare-earth ion such as Tm^{3+}, Er^{3+}, or Ho^{3+}, in various hosts is studied extensively because of the enhanced visible output in this system.[4–9] When these systems are excited with infrared light ($\lambda\sim0.9$–$1\ \mu$) they emit visible light with energy equal to approximately twice that of the incident photon.

Let us first describe qualitatively the nature of the effect using $BaF_2:Yb^{3+}+Tm^{3+}$ as a prototype: (1) The host crystal is transparent at photon energies of interest. (2) Yb^{3+} has an infrared absorption band at about $1\ \mu$ and no other absorption in the energy region of interest. (3) The crystal is irradiated with exciting light only in the Yb^{3+} absorption band. (4) Tm^{3+} does not absorb in this energy region. (5) Tm^{3+} emits light of approximately twice the energy of the exciting photons if and only if the Yb^{3+} is present. (6) This is not second harmonic generation (frequency multiplication) of the conventional sort, although it is definitely a nonlinear effect, nonlinear in both the exciting light intensity and the ionic concentration of Yb^{3+}.

In Auzel's[5] report on this phenomenon, he proposed a mechanism based on a "successive excitation transfer" model. On the other hand, Ovsyankin and Feofilov[6] proposed a model in which two excited Yb^{3+} ions transfer their electronic excitation energy simultaneously to a nearby Tm^{3+} ion, which subsequently emits a photon of the sum of these energies. They called this process a "cooperative sensitization of luminescence."

There are clear similarities between this latter mechanism and the annihilation of two triplet excitons in anthracene[10] to produce a singlet exciton (or the inverse in tetracene[11]), and the cooperative absorption[12,13] of one photon by two ions; it is the inverse of the predicted simultaneous excitation of two atoms by another excited atom.[14]

Tulub and Patzer[15] considered cooperative energy "transfer" from a point of view which does not really encompass transfer. That is, they treated coherent energy flow between two parts ($2Yb^{3+}$ and Tm^{3+}) of a precisely resonant system, as in the Perrin model of two coupled identical oscillators. If the system is coherent, energy flows periodically from one part to the other and back, with a period determined by the absolute value of the coupling matrix element, not its square. Actually phonon broadening would make this

* Research supported in part by a grant from the USAF Office of Scientific Research.

† On leave of absence from the Defense Academy of Japan. Present address: Department of Electrical Engineering, Defense Academy, Hashirimizu, Yokosuka, Japan.

‡ Address until June, 1970: Istituto di Fisica, University of Rome, Rome, Italy.

[1] N. Bloembergen, Phys. Rev. Letters **2**, 84 (1959).

[2] M. B. Brown and W. A. Shand, Phys. Rev. Letters **12**, 367 (1964); **8**, 19 (1964); **11**, 219 (1964).

[3] V. V. Ovsyankin and P. P. Feofilov, Opt. i Spektroskopiya **20**, 296 (1965) [English transl.: Opt. Spectry (USSR) **20**, 526 (1966)].

[4] V. L. Bakumenko, A. N. Vlasov, E. S. Kovarskaya, G. S. Kozina, and V. N. Favorin, Soviet Physics—JETP Letters **2**, 16 (1965).

[5] M. F. Auzel, Compt. Rend **262B**, 1016 (1966); **263B**, 819 (1966).

[6] V. V. Ovsyankin and P. P. Feofilov, Soviet Physics—JETP Letters **4**, 317 (1966); Appl. Opt. **6**, 1828 (1967).

[7] L. Esterowitz, J. Noonan, and J. Bahler, Appl. Phys. Letters **10**, 126 (1967).

[8] H. Rabin and J. Weller (private communications).

[9] R. A. Hewes and J. F. Sarver, Phys. Rev. (to be published).

[10] P. Avakian and R. E. Merrifield, Mol. Crystals **5**, 37 (1968).

[11] N. Geacitov, M. Pope, and F. Vogel, Phys. Rev. Letters **22**, 593 (1969); R. Merrifield, P. Avakian, and R. Groff, J. Chem. Phys. Letters (to be published).

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

[13] D. L. Dexter, Phys. Rev. **126**, 1962 (1962).

[14] D. L. Dexter, Phys. Rev. **108**, 630 (1959).

[15] A. V. Tulub and K. Patzer, Phys. Status Solidi **26**, 693 (1968).

TABLE I. Values of overlap integrals between two $4f$ functions of trivalent rare-earth ions, all times 10^5.

$R(a_0)$	7.3	7.7	8.3
Yb-Yb	2.992	1.332	0.306
Yb-Er	4.297		

an incoherent process,[16] even though it is possible that some reverse transfer might occur.

Recently, Hewes and Sarver[9] made a careful study of transfer phenomena in rare-earth trifluoride hosts. They report on the excitation spectra and the dependence of visible output intensity L on both the excitation light intensity I_E and the ionic concentration x of Yb^{3+} ions. They concluded that Auzel's stepwise mechanism seems to be operative in three cases in which the activator ion is Ho, Er, and Tm. Although their argument seems to be conclusive in the case of the $Yb^{3+}+Tm^{3+}$ system, it is less so in the cases of $Ho^{3+}+Yb^{3+}$ and $Er^{3+}+Yb^{3+}$ because the I_E and concentration dependences alone cannot discriminate between the two processes.

In this paper we discuss transfer processes, taking into account both cooperative and stepwise transfer mechanisms. It is shown that the cooperative transfer rate from two excited neighbors will be larger than the radiative decay rate of electronic excited states of interest but that stepwise transfer would mask cooperative effects in all cases considered. In $Yb^{+3}+Tm^{+3}$ systems cooperative transfer would dominate at low exciting intensities, but the resulting luminescence would be too weak to observe. The $Yb^{3+}+Tb^{3+}$ system is suggested as the most promising system in which to identify and study the cooperative transfer process unambiguously.

II. RATE EQUATIONS AND EMISSION INTENSITIES

In Fig. 1 we show the energy levels of Tb^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+} ions in the energy region of interest. This is a well-known diagram, taken from the classic work of Dieke.[17] The energy levels were measured in La and Y salts (see Table I), and differ only slightly from one host to another.

A. $Tm^{3+}+Yb^{3+}$ System

The central experimental fact is that excitation at $\sim 10^4$ cm^{-1} does produce characteristic Tm^{3+} emission at about 2×10^4 cm^{-1} when both Yb and Tm are present (in BaF_2, for example). One method by which energy can accumulate in the $^1G_4$ state of the Tm^{3+} ion is by the cooperative, simultaneous transfer of excitation energy from two excited neighboring Yb^{3+} ions, without

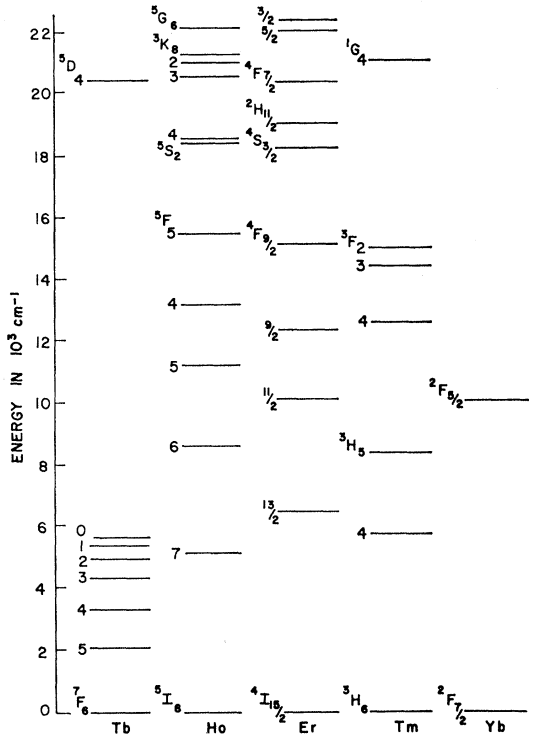

FIG. 1. Energy levels of Tb^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+} (after Dieke, Ref. 17).

going through a real intermediate state of Tm [Fig. 2(a)]. If we assume that energy transfer can occur between levels which appear not to overlap (such as $^2F_{5/2}$ of Yb^{3+} and $^3H_5$ of Tm^{3+}), a second possible mechanism is the stepwise triple transfer in which the excitation energy is first transferred from a Yb^{3+} ion to the $^3H_5$ level (level 2 of Fig. 3; see below) of the Tm^{3+} ion. After relaxation to the $^3H_4$ level (level 2′) the Tm ion is excited to the $^3F_2$ or $^3F_3$ level (level 3) by another transfer from some excited Yb^{3+} ion. Finally, the Tm ion will be excited to the $^1G_4$ level from the $^3F_4$ level (level 3′), to which it relaxes, by the third transfer from an Yb^{3+} ion [Fig. 2(b)]. By this process approximately one-third of the excitation energy is lost in the form of heat in exciting the Tm^{3+} ion.

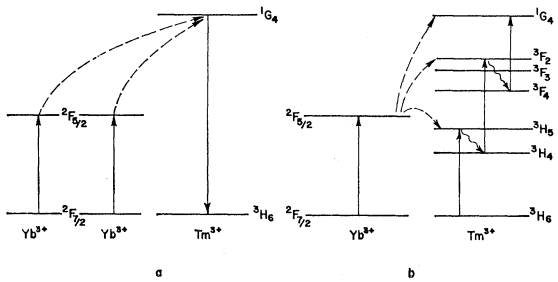

FIG. 2. Schematic illustration of two excitation processes of the Tm^{3+} ion to $^1G_4$ level. (a) Cooperative excitation. (b) Stepwise excitation.

[16] D. L. Dexter, Th. Forster, and R. S. Knox, Phys. Status Solidi 34, K159 (1969).

[17] G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Wiley-Interscience, Inc., New York, 1968).

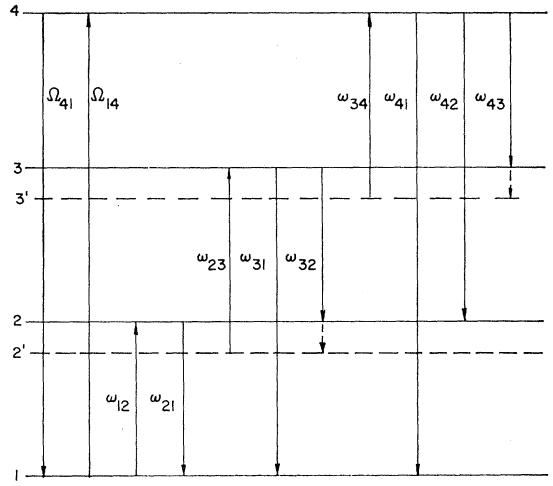

FIG. 3. Four-level model used in the analysis of the $Yb^{3+}+Tm^{3+}$ system.

To simplify the description of the Tm^{3+} ion we use a four-level model shown in Fig. 3. Here Ω_{14} is the cooperative excitation rate from level $1(^3H_6)$ to level $4(^1G_4)$ by the process of Fig. 2(a); ω_{12}, ω_{23}, and ω_{34} are the excitation rates (by transfer from excited Yb^{3+} ions) from levels 1, $2'(^3H_4)$ and $3'(^3F_4)$, respectively, to the next higher levels. In the following equations we are lumping together $^3H_5$ (level 2) and $^3H_4$ (level 2'), calling them level 2, and $^3F_2$ and $^3F_3$ (level 3) and $^3F_4$ (level 3') as level 3. Implicit in this simplification is the assumption that nonradiative relaxation from the higher of these levels to the lower ones, in each group, occurs rapidly on our time scale, say in less than 1 nsec. It should be noted that this phenomenon, the relaxation from $2\rightarrow 2'$ and $3\rightarrow 3'$, is related to the well-known Stokes's shift between absorption and emission bands which entails the rapid relaxation of the electron-lattice system to a state corresponding to a new equilibrium configuration of the lattice; here an explicit change in electronic states is also contained in our description.

In terms of the indicated transition rates, the rate equations for the occupation numbers N_i ($i=1$ to 4) of each of the four levels are[18]

$$\dot{N}_1=-N_1(\omega_{12}+\Omega_{14})+N_2\omega_{21}+N_3\omega_{31}+N_4\omega_{41}, \quad (2.1)$$

$$\dot{N}_2=N_1\omega_{12}-N_2(\omega_{21}+\omega_{23})+N_3\omega_{32}+N_4\omega_{42}, \quad (2.2)$$

$$\dot{N}_3=N_2\omega_{23}-N_3(\omega_{31}+\omega_{32}+\omega_{34})+N_4\omega_{43}, \quad (2.3)$$

$$\dot{N}_4=N_1\Omega_{14}+N_3\omega_{34}-N_4(\omega_{41}+\omega_{42}+\omega_{43}), \quad (2.4)$$

with $N=N_1+N_2+N_3+N_4$ being the total number of Tm^{3+} ions. The steady-state solutions of these equations are

$$N_4=[\omega_{12}\omega_{23}\omega_{34}+\Omega_{14}\{(\omega_{21}\omega_{31}+\omega_{32}+\omega_{34})+\omega_{23}(\omega_{31}+\omega_{34})\}]/\Delta, \quad (2.5)$$

$$N_3=[\omega_{12}\omega_{23}(\omega_{41}+\omega_{42}+\omega_{43})+\Omega_{14}(\omega_{21}\omega_{43}+\omega_{23}\omega_{41}+\omega_{23}\omega_{42})]/\Delta, \quad (2.6)$$

where Δ is given by

$$\begin{aligned}\Delta=&\omega_{12}\omega_{23}\omega_{34}+\omega_{12}\omega_{23}(\omega_{41}+\omega_{42}+\omega_{43})\\&+\omega_{12}\omega_{31}(\omega_{41}+\omega_{42}+\omega_{43})+\omega_{12}\omega_{32}(\omega_{41}+\omega_{42}+\omega_{43})\\&+\omega_{12}\omega_{34}(\omega_{41}+\omega_{42})+\omega_{23}\omega_{31}(\omega_{41}+\omega_{42}+\omega_{43})\\&+\omega_{23}\omega_{34}\omega_{41}+\omega_{21}\omega_{31}(\omega_{41}+\omega_{42}+\omega_{43})\\&+\omega_{21}\omega_{32}(\omega_{41}+\omega_{42}+\omega_{43})+\omega_{21}\omega_{34}(\omega_{41}+\omega_{42})\\&+\Omega_{14}[\omega_{12}\omega_{43}+\omega_{21}(\omega_{31}+\omega_{32}+\omega_{34}+\omega_{43})\\&+\omega_{23}(\omega_{31}+\omega_{34}+\omega_{42}+\omega_{43})\\&+\omega_{42}(\omega_{31}+\omega_{32}+\omega_{34})]. \quad (2.7)\end{aligned}$$

If we assume that the dominant decay modes of levels 4 and 3 are radiative decay (otherwise we have to multiply by a branching ratio), the intensities of emission $L_{41}(^1G_4\rightarrow{}^3H_6)$, $L_{42}(^1G_4\rightarrow{}^3F_4)$, and $L_{31}(^3F_4\rightarrow{}^3H_6)$ are given, respectively, by

$$L_{41}=N_4\omega_{41}, \quad L_{42}=N_4\omega_{42}, \quad L_{31}=N_3\omega_{31}. \quad (2.8)$$

From these equations and the conditions that in the absence of saturation effects the transition rates ω_{12}, ω_{23}, ω_{34} are all proportional to both I_E and x, the Yb concentration, one can easily see that if the cooperative mechanism is *not* operative, the intensities of emission must obey

$$L_{41}\propto I_E{}^3x^3, \quad L_{42}\propto I_E{}^3x^3, \quad L_{31}\propto I_E{}^2x^2. \quad (2.9a)$$

That is, exciting a Tm^{3+} ion to level 4 by a three-step excitation requires three excited Yb^{3+} ions, hence the cubic dependence, whereas the excitation of the Tm^{3+} level 3 requires just two steps. On the other hand, if the cooperative process is dominant ($\omega_{12}=\omega_{23}=\omega_{34}=0$),

$$L_{41}\propto L_{42}\propto L_{31}\propto I_E{}^2x^2 \quad (2.9b)$$

also neglecting saturation effects. These results have led Hewes and Sarver[9] to conclude that stepwise excitation is the dominant mode. In particular, the cubic dependence of L_{41} on both I_E and x at lower values of these parameters seems to show that cooperative excitation is negligible in this case. Moreover, they based their conclusion on the fact that the intensity of the $^3F_4\rightarrow{}^3H_6$ emission band (L_{31}) depends quadratically on I_E at low intensity. Although the saturation effect at higher intensity I_E seems to obscure the situation somewhat, this conclusion can be shown more clearly by plotting the ratio of intensities of the $L_{41}(^1G_4\rightarrow{}^3H_6)$ and $L_{31}(^3F_4\rightarrow{}^3H_6)$ emission bands. If the cooperative excitation were the only process, this ratio should be independent of both I_E and x. If on the other hand the stepwise process were the only mode, the ratio should be linear in both I_E and x. The dependence of this

[18] For the sake of simplicity we have lumped together the usual noncooperative decay rate $\omega_{41}{}^0$ and the cooperative back transfer rate Ω_{41}, in which a Tm^{3+} ion is deexcited to form two neighboring excited Yb^{3+} ions; i.e., $\omega_{41}=\omega_{41}{}^0+\Omega_{41}$. The effect of this cooperative back transfer can be included in our result when we multiply L_{41} in Eq. (2.8) in the following by a factor $\omega_{40}{}^0/\omega_{41}$.

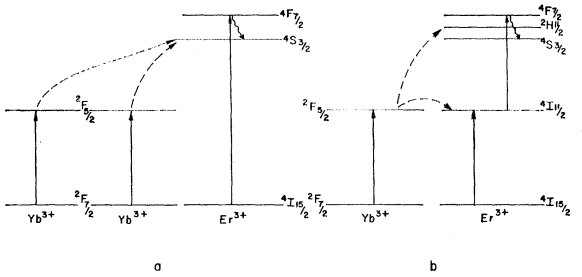

FIG. 4. Schematic illustration of two excitation processes of the Er^{3+} ion to the $^4S_{3/2}$ level. (a) Cooperative excitation. (b) Stepwise excitation.

ratio will be less sensitive to the effect of saturation. Replotting of Hewes and Sarver's data shows that this ratio is indeed linear in I_E for the whole range of I_E measured.

However, as the energy mismatch between the $^3H_5$ level of Tm^{3+} and $^2F_{5/2}$ level of Yb^{3+} is large ($\sim$1900 cm^{-1}), and the excitation energy of two excited Yb ions is within 300 cm^{-1} of the $^1G_4$ level of Tm^{3+}, one would like to understand why the stepwise transfer involving phonon emission is much more probable than the cooperative one.

B. $Ho^{3+}+Yb^{3+}$ and $Er^{3+}+Yb^{3+}$ Systems

In Fig. 4 we show schematically the cooperative and the stepwise processes in these systems. The corresponding three-level model is shown in Fig. 5. An analysis similar to that outlined for the four-level model in the preceding section gives expressions for the occupation numbers N_i $(i=2, 3)$[19];

$$N_3=(\omega_{12}\omega_{23}+\Omega_{13}\omega_{21})/\Delta', \tag{2.10}$$

$$N_2=(\omega_{12}\omega_{31}+\omega_{12}\omega_{32}+\omega_{32}\Omega_{13})/\Delta', \tag{2.11}$$

$$\Delta'=\omega_{12}\omega_{23}+(\omega_{12}+\omega_{21})(\omega_{31}+\omega_{32})+\Omega_{13}(\omega_{21}+\omega_{32}). \tag{2.12}$$

In contrast to the four-level model, one can easily show that the excitation to the level 3 requires two steps by either mechanism, which means that in both cases

$$L_{31}\propto I_E{}^2x^2. \tag{2.13}$$

Thus in this case the intensity (I_E) and concentration dependence of the main emission band intensity ($^4S_{3/2}\rightarrow{}^4I_{15/2}$ in Er^{3+}, $^5S_2\rightarrow{}^5I_8$ in Ho^{3+}) is insufficient to rule out the possibility of the cooperative mechanism. However, one may expect that the dependence on both I_E and x of the luminescence intensity L for $^4I_{11/2}\rightarrow{}^4I_{15/2}$ and $^5I_6\rightarrow{}^5I_8$ emissions in Er^{3+} and Ho^{3+} ions, respectively, will be determined by the excitation transfer rate ω_{12} unless it is strongly forbidden by symmetry, because Ω_{13} is a transition rate which is second order in both electromagnetic and electron-electron interactions while ω_{12} is a first-order rate. On the other hand, the cooperative mechanism may be responsible for the population of level 3 if Ω_{13} satisfies the following relation:

$$\Omega_{13}\gg\omega_{12}\omega_{23}/\omega_{21}. \tag{2.14}$$

This means that short lifetime of the intermediate state 2 (large ω_{21}) and small transfer rates from state 1 to state 2 followed by state 2 to state 3 are the favorable conditions to observe the cooperative transfer. Indeed, in a system such that there is no intermediate level 2 from which real excitation to level 3 can take place, one can see most clearly whether the cooperative excitation occurs or not. A candidate to test this possibility seems to be the system $Tb^{3+}+Yb^{3+}$ (see Fig. 1). Even if the state $^7F_0$ could be populated by transfer from excited Yb^{3+}, the $^5D_4$ state is at much too high an energy above the former to be excited by another transfer from an excited Yb ion.

III. EFFECTIVE INTERACTION AND TRANSFER PROBABILITIES

We now compute the transition probability per unit time between a specified pair of initial and final quasi-stationary states, on the usually valid assumption that real transfer occurs, i.e., that lattice vibration destroys phase memory. For the stepwise transfer we need consider only two interacting ions at a time, and obtain the usual result[20] for the transfer probability.

$$P_{\rm tr}=(2\pi/\hbar)|\langle f|H'|i\rangle|^2\rho_E,$$

where ρ_E is the density of states and $\langle f|H'|i\rangle$ is the matrix element of the perturbation Hamiltonian between initial and final states i and f.

For consideration of cooperative transfer, let us

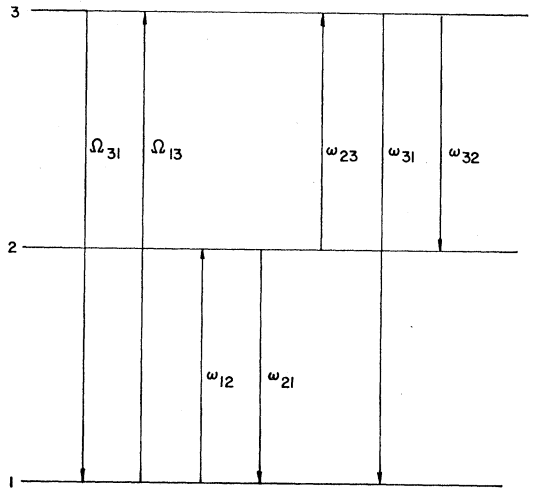

FIG. 5. Three-level model used in the analysis of the $Yb^{3+}+Er^{3+}$ or Ho^{3+} system.

[19] Here too we have lumped together the noncooperative decay rate $\omega_{31}{}^0$ and the cooperative back transfer rate Ω_{31} as $\omega_{31}=\omega_{31}{}^0+\Omega_{31}$. Thus one must multiply the output intensity L_{31} by an efficiency factor $\omega_{31}{}^0/\omega_{31}$.

[20] Th. Förster, Ann. Physik **2**, 55 (1948); D. L. Dexter, J. Chem. Phys. **21**, 836 (1953); D. L. Dexter and J. H. Schulman, *ibid.* **22**, 1063 (1954).

stipulate that at time $t=0$ atoms A and B are excited, in states A_a and B_b, and a neighboring atom C is in its ground state C_0. The atoms (or ions or molecules) are separated by R_{AB}, R_{BC}. Energy levels, or their mean values, are given by ϵ_α, ϵ_β, and ϵ_γ, in general, where α, β, and γ each stands for a set of electronic quantum numbers, with all energies measured from the ground states of the atoms, taken to be zero. We are interested in computing the transition probability per unit time P_{coop} to final state $A_{a'}$, $B_{b'}$, $C_{c'}$ that is, one in which both originally excited atoms change states and the other becomes excited. Conservation of energy will require that the excitation energy of C, ϵ_c, be approximately equal to $\epsilon_a-\epsilon_{a'}+\epsilon_b-\epsilon_{b'}$. (In the case of the $Yb^{3+}+Tm^{3+}$ system, both A and B are Yb^{3+} ions, C is a Tm^{3+} ion, and states $A_{a'}$ and $B_{b'}$ are ground states.)

Now, the important point in the interaction between three ions is that it vanishes unless either the effect of overlap-exchange[14] or that of second-order terms in the multipole-multipole interaction is taken into account. To do this, we may follow either of two approaches: (1) use from the outset time-dependent perturbation theory and keep terms up to second order in the interaction, or (2) first diagonalize the nondegenerate part of the interaction Hamiltonian to first order in the perturbation and then expand the time-dependent wave function into these nearly degenerate perturbed states to calculate the transition probability between them. Both these approaches give the same result to second order, but in the latter approach care must be exercised to avoid an excess factor of four which should not enter in the computation of the transition probability by the golden rule. Here we use the first approach and derive an expression for the probability of cooperative transfer.

For simplicity we assume that A and B (i.e., Yb^{+3}) have only one excited state in the energy region of interest. Ion C is assumed to have several excited states γ, in addition to and not necessarily close in energy to the excited state c to which transfer occurs.

As the concentration of sensitizer ions A, B is very high, the concentration of the charge-compensating lattice defects (presumably Ca^{2+} vacancies or substitutional O^{2-} ions) will be proportionately high. Thus their presence may have nonnegligible effects in CaF_2 type lattices. Possible effects of these defects or of the real host on the present problem are: (1) Negative ions (O^{2-} or even F^- ions of the host) might mediate the interaction between ions through overlap of the wave functions. This possibility has been pointed out in connection with the usual transfer mechanism.[21] However, as the effect appears only in higher order of perturbation theory and the excitation energy of these closed shell negative ions is large, we do not go into discussion of this point. (2) Lowering of the site symmetry around the rare-earth ions might cause relaxation of selection rules and shifts of energy levels. Rather extensive study of this effect is under way by the use of EPR spectra in conjunction with optical data,[22–24] and various absorption or emission peaks are assigned to transitions within rare-earth ions which occupy sites of particular symmetry. In fact, it is reported that the Yb^{3+} absorption peak position ranges from 10 185 to 10 995 cm^{-1} depending upon the method of crystal preparation (presumably resulting in different oxygen content), the absorption by ions at cubic sites being assigned to a weak peak at 10385 cm^{-1}. Unfortunately, EPR analysis cannot be carried through for concentrations above 1% because of the line broadening. The effects of charge-compensating defects are important in the analysis of absorption data which is used in the calculation of the overlap integral in BaF_2, but can be neglected in some other lattices such as LaF_3.

On the other hand, lattice vibrations have important effects on the transfer process. They give finite nonradiative lifetimes, as well as nonzero widths of the absorption and emission lines. Also phonon-assisted processes are important in the $2Yb^{3+}+Tm^{3+}$ system because the energy of the final state (Tm^{3+} excited, two Yb^{3+} ions in the ground state) is slightly larger than the energy of the initial state (Tm^{3+} in its ground state, two Yb^{3+} ions excited). Moreover, the interaction responsible for the relaxation of lattice vibrational states plays a decisive role in determining the irreversibility of the transfer process.[16,20,25] Accordingly, though both the width w (~ 10 cm^{-1} at 300°K [2,24]) and the temperature dependence (shift ~ 10 cm^{-1} between 4 and 300°K [26]) of the absorption and emission lines of Yb^{3+} ion are small, we must take the lattice vibrations into account.

The Hamiltonian of our total system can be written in the following form:

$$H_{\text{tot}}=H_e+H_L+H',$$
$$H_e=\sum_{I=1}^{3} H_{eI}, \tag{3.1}$$
$$H'=\sum_{I<J} H_{IJ}.$$

H_e is the effective Hamiltonian for the three sets of electrons localized on the ions A, B, and C including the static potential due to the other impurity ions; H' is the interaction Hamiltonian between electrons on these ions, and H_L is the lattice Hamiltonian. We make use of the adiabatic approximation in treating the lattice vibration and neglect the nonadiabatic part of the Hamiltonian,[27] so that H_L depends on the electronic states of the ions A, B, and C through frequencies

[21] C. G. Uitert, R. C. Linars, R. R. Soden, and A. A. Ballman, J. Chem. Phys. **36**, 702 (1962).

[22] J. Kirston and S. D. McLaughlan, Phys. Rev. **155**, 279 (1967).

[23] S. D. McLaughlan, P. A. Forester, and A. F. Fray, Phys. Rev. **146**, 344 (1966).

[24] M. R. Brown, H. Thomas, J. S. S. Whitting, and W. A. Shand, J. Chem. Phys. **50**, 881, 891 (1969).

[25] G. W. Robinson and R. P. Frosch, J. Chem. Phys. **37**, 1962 (1962); **38**, 1187 (1963).

[26] W. Low, J. Chem. Phys. **37**, 30 (1962); P. P. Feofilov, Opt. Spectry (USSR) **5**, 216 (1958).

[27] J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).

$\omega_s(\alpha\beta\gamma)$ and the equilibrium positions $a_s(\alpha\beta\gamma)$ of the lattice normal mode coordinates (or of the interaction mode).[28]

We assume that each electron is localized about one of the ions and that the wave functions $\varphi_\alpha(r)$ and energy levels ϵ_α of the (perturbed) ions are known. The wave function of the total system at time $t=0$, Ψ_i, can be given, in our approximation, as a product of the Slater determinants of the configuration specified by A_a, B_b, C_0 and a vibrational wave function $X(m_{ab0})$, where m_{ab0} represent a set of vibrational quantum numbers,

$$\Psi_i=\Psi(A_a,B_b,C_0)X(m_{ab0}). \tag{3.2}$$

The time development of the system wave function up to time $t=T$ is given in this approximation by

$$e^{(-iH_{tot}T/\hbar)}\Psi_i, \tag{3.3}$$

so that the transition amplitude to the final state specified by an electronic configuration $A_0B_0C_c$ and a set of vibrational quantum numbers m_{00c},

$$\Psi_f=\Psi(A_0,B_0,C_c)X(m_{00c}), \tag{3.4}$$

is given by

$$\langle\Psi_f e^{(-iH_{tot}T/\hbar)}\Psi^i\rangle. \tag{3.5}$$

Now, in order to assess the importance of the first-order overlap and exchange terms and the second-order multipole-multipole terms we retain the overlap term in the first-order term but neglect it in the second order. The first-order term is given by

$$\begin{aligned}-\frac{i}{\hbar}\Big\langle\Psi_f e^{-i(H+H_L)T/\hbar}&\times\int_0^T dt e^{i(H+H_L)T/\hbar}H'e^{-i(H+H_L)t/\hbar}\Psi_i\Big\rangle\\ &=-\exp[(iT/\hbar)(\epsilon_c+\sum_s\omega_s(00c)m_{00c}{}^s)]\langle\Psi_f|H'|\Psi_i\rangle\\ &\quad\times(e^{i\Delta\epsilon T/\hbar}-1)/\Delta\epsilon, \qquad (3.6)\\ \Delta\epsilon&=\epsilon_c-(\epsilon_a+\epsilon_b)\\ &\quad+\hbar\sum_s(\omega_s(00c)m_{00c}{}^s-\omega_s(ab0)m_{ab0}{}^s).\end{aligned}$$

In the adiabatic approximation for the lattice vibrations the matrix element $\langle\Psi_f|H'|\Psi_i\rangle$ consists of two factors, i.e., the electronic part and the vibrational part F, called the Franck-Condon factor

$$\langle\Psi_f|H'|\Psi_i\rangle=\langle 00c|H'|ab0\rangle F(m_{00c};m_{ab0}). \tag{3.7}$$

The electronic part of the matrix element can be evaluated by the method of Löwdin.[29] In the approximation[30] of neglecting quantities of the order of the square and higher powers of the overlap integral it is given by the following expressions, to be summed over triplets of electrons centered on A, B, and C,

$$\begin{aligned}\langle 00c|H'|ab0\rangle=&-S_{00}(A_aB_b|V|C_cB_0)\\ &-\delta_{00}(B_bA_a|V|C_cA_0)-S_{ca}(B_bC_0|V|B_0A_0)\\ &-\delta_{cb}(A_aC_0|V|A_0B_0)+\Delta_{a0}(B_bC_0|V|A_0C_c)\\ &+\Delta_{b0}(A_aC_0|V|B_0C_c), \qquad (3.8)\end{aligned}$$

where

$$S_{\alpha\gamma}\equiv\int\varphi_{A\alpha}{}^*(r_1)\varphi_{C\gamma}(r_1)dv_1,$$

$$\delta_{\beta\gamma}\equiv\int\varphi_{B\beta}{}^*(r_1)\varphi_{C\gamma}(r_1)dv_1,$$

$$\Delta_{\alpha\beta}\equiv\int\varphi_{A\alpha}{}^*(r_1)\varphi_{B\beta}(r_1)dv_1,$$

and

$$\begin{aligned}&(A_aB_b|V|C_cB_0)\\ &\quad=\int\varphi_{Aa}{}^*(r_1)\varphi_{Bb}{}^*(r_2)(e^2/r_{12})\varphi_{C_c}(r_1)\varphi_{B0}(r_2)dv_1dv_2.\end{aligned}$$

In the evaluation of the second-order terms we neglect the effect of overlap and exchange. Introducing the notation

$$\begin{aligned}d_{AC}(a0;0\gamma)\equiv&\int\varphi_{Aa}{}^*(r_1)\varphi_{C0}{}^*(r_2)\\ &\times(e^2/r_{12})\varphi_{A0}(r_1)\varphi_{C\gamma}(r_2)dv_1dv_2 \qquad (3.9)\end{aligned}$$

and denoting the virtual (intermediate) excited states of the ion C by a letter j we write the matrix element

$$\langle ab0|H'|0bj\rangle=d_{AC}(a0;0j)F(m_{ab0};m_{0bj}). \tag{3.10}$$

Also we denote the set of vibrational quantum numbers and the frequency of the sth normal mode in the configuration with the C ion in the (unrelaxed) virtual excited state by $m_{\alpha\beta j}{}^s$ and $\omega_s(\alpha\beta j)$. With this notation the second-order term can be written in the following form, when we neglect small energy nonconserving terms,

$$\begin{aligned}-\frac{1}{\hbar^2}\Big\langle\Psi_f e^{-i(H_e+H_L)T/\hbar}\int_0^T dt\int_0^t dt' e^{i(H_e+H_L)t/\hbar}H'e^{-i(H_e+H_L)t/\hbar}e^{i(H_e+H_L)t'/\hbar}H'e^{-i(H_e+H_L)t'/\hbar}\Psi_i\Big\rangle&\\ =\exp[-iT/\hbar(\epsilon_c+\hbar\sum_s\omega_s(00c)m_{00c}{}^s)](e^{i\Delta\epsilon T/\hbar}-1)/\Delta\epsilon\sum_{j,m'}\Big[\frac{d_{AC}(0a;cj)d_{BC}(0b;i0)F(m_{00c};m_{a0j'})F(m_{a0j'};m_{ab0})}{\epsilon_j-\epsilon_b+\hbar\sum_s(\omega_s(a^{\cap}i)m_{a0j}{}^s-\omega_s(ab0)m_{ab0}{}^s)}&\\ +\frac{d_{BC}(0b;cj)d_{AC}(0a_a;j0)F(m_{00c};m_{0bj'})F(m_{0bj'};m_{ab0})}{\epsilon_j-\epsilon_a+\hbar\sum_s(\omega_s(obj)m_{0bj}{}^s-\omega_s(ab0)m_{ab0}{}^s)}\Big]. \qquad (3.11)&\end{aligned}$$

[28] M. D. Sturge, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1968), Vol. 20.
[29] P. O. Löwdin, Phys. Rev. **97**, 1747 (1955).
[30] The nonorthogonality of $\Psi(00c)$ and $\Psi(ab0)$ can be neglected in this approximation.

For the case we are treating now, the intermediate state j of C does not fall at an energy within the emission band of either A or B. In this case we may properly neglect the vibrational part of the energy in the denominator of (3.11). Then making use of the completeness relation for the vibrational wave functions, we find that the second-order matrix element reduces to the form

$$\exp[-i(\epsilon_c+h\sum_s \omega_s(00c)m_{00c}{}^s)T/\hbar](e^{i\Delta\epsilon T/\hbar}-1)/\Delta\epsilon \times\sum_j \frac{d_{AC}(0a;cj)d_{BC}(0b;j0)+d_{BC}(0b;cj)d_{AC}(0a;j0)}{\epsilon_j-\epsilon_a}F(m_{00c};m_{ab0}). \quad (3.12)$$

Using the analytic Hartree-Fock wave functions of Freeman and Watson[31] we have computed the magnitude of some overlap integrals between two $4f$ functions of rare-earth ions for interionic distances which correspond to the nearest like neighbor separation in CaF_2, BaF_2, and SrF_2. (See columns 1, 2, 3, respectively, in Table I.) These values are very small, and we may safely conclude that the overlap-exchange mechanism is not operative in these cases. As any exchange terms in the matrix elements d would include the two center integrals they may also be neglected compared with the multipole-multipole terms.

Thus we are left with the lowest-order terms

$$\langle 00c|H'|ab0\rangle=\sum_j [d_{AC}(0a;cj)d_{BC}(0b;j0)+d_{BC}(0b;cj)d_{AC}(0a;j0)](\epsilon_j-\epsilon_a)^{-1}. \quad (3.13a)$$

If we assume, for simplicity, that both of the ions A and B are at the nearest-neighbor site of the ion C, and ignore the angular dependence of the matrix elements d, we get the result

$$\langle 00c|H'|ab0\rangle=2\sum_j \frac{d_{AC}(0a;cj)d_{BC}(0b;j0)}{(\epsilon_j-\epsilon_a)}. \quad (3.13b)$$

The summation on the right-hand side of this expression can be divided into intraconfigurational, or $4f$-$4f$ excitation terms, and interconfigurational, or $4f$-$5d$ terms. While the excitation energy in the latter part, ΔE_{4f-5d}, is about an order of magnitude larger than that for the former part of the summation, ΔE_{4f-4f}, the interconfigurational excitation is dipole allowed and hence will give an important contribution to the matrix element.

One can make a crude estimate of these terms by the use of a multipole expansion for the d's. For a $4f$-$5d$ transition of ion C the dipole allowed transition matrix element will be of the order of ea_0 where a_0 is the Bohr radius, while for $4f$-$4f$ transitions the mean value of the quadrupole matrix element will be of the order of $ea_0{}^2$.[32,33] We assume that A, and B (e.g., Yb) make a quadrupole transition. Thus we obtain,

$$\langle 00c|H'|ab0\rangle_{\text{inter}}\sim 2\left(\frac{e^2}{a_0}\right)^2(a_0/R)^8/\Delta E_{4f5d} \sim 0.4\times10^{-4}\text{ eV}=0.3\text{ cm}^{-1}, \quad (3.14)$$

where we have taken $\Delta E_{4f,5d}$ to be about 5 eV [34] and $R=7.3a_0$.

The ratio of the intraconfigurational matrix element to the interconfigurational one is given by

$$\langle 00c|H'|ab0\rangle_{\text{intra}}/\langle 00c|H'|ab0\rangle_{\text{inter}} \sim (a_0/R)^2\Delta E_{4f5d}/\Delta E_{4f4f}\sim\tfrac{1}{5}, \quad (3.15)$$

where we have assumed $\Delta E_{4f,4f}\sim 0.5$ eV.

From this result we may conclude that both interconfigurational and intraconfigurational contributions to the matrix element are of the same order of magnitude. Some cancellation will occur from the low-lying states in the intraconfigurational contribution.

The probability for the cooperative transfer in time T is given by

$$P_{\text{coop}}=(2\pi/\hbar)\sum_{m_{00c}}\langle|\langle\Psi_f e^{-iH_{\text{tot}}T/\hbar}\Psi_i\rangle|^2\rangle_{m_{ab0}}/T, \quad (3.16)$$

where $\sum_{m_{00c}}$ means to sum over all final phonon states and $\langle\ \rangle_{m_{ab0}}$ means to take the average over all initial phonon states. If we introduce the notation

$$D_{ab0}{}^{00c}\equiv\sum_{j\neq c,0}[d_{AC}(0a;cj)d_{BC}(0b;j0)+d_{BC}(0b;cj)d_{AC}(0a;j0)](\epsilon_j-\epsilon_a)^{-1}, \quad (3.17)$$

and specialize to the case of $A=B$, i.e., $\epsilon_a=\epsilon_b$, the cooperative transfer probability per unit time reduces to

$$P_{\text{coop}}=(2\pi/\hbar)|D_{ab0}{}^{00c}|^2\times\sum_{m_{00c}}\langle|F(m_{00c};m_{ab0})|^2\delta(\Delta\epsilon)\rangle_{m_{ab0}} =(2\pi/\hbar)|D_{ab0}{}^{00c}|^2\rho_E{}^{\text{coop}}, \quad (3.18)$$

where again

$$\Delta\epsilon=\epsilon_c-\epsilon_a-\epsilon_b+h\sum_s(\omega_s(00c)m_{00c}{}^s-\omega_s(ab0)m_{ab0}{}^s).$$

[31] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[32] The values of $\langle r^2\rangle_{4f}$ for Yb^{3+} (Ref. 31) and Tm^{3+} (Ref. 33) are, respectively, 0.60 and 0.75 $a_0{}^2$.

[33] K. Rajnak, J. Chem. Phys. **37**, 2440 (1962).

[34] E. Loh, Phys. Rev. **175**, 533 (1968).

We assume that ions A, B, and C interact incoherently with various modes of lattice vibration which broaden their emission and absorption lines. Under this assumption the Franck-Condon factor $F(m_{00c};m_{ab0})$ can be split into three factors

$$F(m_{00c};m_{ab0})=F_A(m_a';m_a)F_B(m_b';m_b)\times F_C(m_c;m_c'), \quad (3.19)$$

where m_a, m_b, m_c, and m_a', m_b', m_c' are the sets of vibrational quantum numbers which interact with ions A, B, and C in their ground and excited states, respectively. Likewise, we may split the vibrational part of the energy $\Delta\epsilon$ into those parts which are related to modes interacting with each of the three ions

$$\Delta\epsilon=\epsilon_c-\epsilon_a-\epsilon_b+\hbar\sum_s(\omega_s^A(00c)m_a^s+\omega_s^B(00c)m_b^s+\omega_s^C(00c)m_c'^s)-\hbar\sum_s(\omega_s^A(ab0)m_a'^s+\omega_s^B(ab0)m_b'^s+\omega_s^C(ab0)m_c^s).$$

Then the sum over final vibrational states and the average over initial vibrational states can be carried out independently for those three factors, with the only restriction being that the total energy difference between initial and final state $\Delta\epsilon$ be zero. Therefore the phonon density-of-states factor ρ_E^{coop} can be written in this approximation in the form of an overlap integral of the absorption line shape $S_C(E)$ of ion C with a convolution $S_{AB}(E)$ of emission line shapes $S_A(E)$ and $S_B(E)$ of ions A and B, respectively.

$$\rho_E^{\text{coop}}=\int dz\, S_C(z+E)S_{AB}(z), \quad (3.20)$$

where S_A, S_B, S_C, and S_{AB} are defined by the following expressions:

$$S_A(E)=\sum_{m_a^s}\langle|F_A(m_a';m_a)|^2\delta(\epsilon_a+\hbar\omega_s^A(ab0)m_a'^s-\hbar\omega_s^A(00c)m_a^s-E)\rangle_{m_a'^s}, \quad (3.21)$$

$$S_B(E)=\sum_{m_b^s}\langle|F_B(m_b';m_b)|^2\delta(\epsilon_b+\hbar\omega_s^B(ab0)m_b'^s-\hbar\omega_s^B(00c)m_b^s-E)\rangle_{m_b'^s}, \quad (3.22)$$

$$S_C(E)=\sum_{m_c'^s}\langle|F_C(m_c;m_c')|^2\delta(\epsilon_c+\hbar\omega_s^C(00c)m_c'^s-\hbar\omega_s^C(ab0)m_C^s-E)\rangle_{m_c^s}, \quad (3.23)$$

$$S_{AB}(E)=\int S_A(E')S_B(E-E')dE'. \quad (3.24)$$

We now return to the probability for a single transfer P_{tr} briefly mentioned in the beginning of this section. In the same approximation as has been used above to estimate D_{ab0}^{00c}, we may estimate the interaction matrix element $D=\langle f|H'|i\rangle$ from the approximate expression for the quadrupole-quadrupole interaction

$$D\sim(e^2/a_0)(a_0/R)^5, \quad (3.25)$$

and the phonon density-of-states factor is given[20] as an overlap integral of the absorption line shape of ion C, $S_C(E)$ with the emission line shape of ion A, $S_A(E)$

$$\rho_E=\int S_C(E+z)S_A(z)dz, \quad (3.26)$$

where S_A and S_C are given, respectively, by expressions (3.21) and (3.23) with the only difference being that a different electronic excitation energy of C is used in the case of single transfer.

To calculate the phonon density of states for the transfer process we need the line shapes of the sensitizer emission line as well as the activator absorption line. These line shapes are seldom measured with sufficient accuracy to be of quantitative value, particularly in rare earths, and it will be necessary to use indirect information to estimate the value of ρ_E.

At this point it should be noted that the energy dependence of ρ_E will be different in the case of weak electron-phonon coupling from that in the strong coupling case. In the limit of strong coupling many phonons are coupled to the electron, and the intensity distribution function of phonon side bands can be given in a good approximation by a Gaussian function. Moreover, because of the strong coupling, one cannot resolve individual phonon side bands but only see the smeared out over-all line shape.

If we were to approximate the line shapes (3.21) to (3.23) by

$$S_A(E)=S_B(E)=\exp[-(E-E_a)^2/W^2]/(\pi W^2)^{1/2},$$
$$S_C(E)=\exp[-(E-E_C)^2/W''^2]/(\pi W''^2)^{1/2}, \quad (3.27)$$

the phonon density of states ρ_E^{coop} would reduce to the form,

$$\rho_E^{\text{coop}}=\exp[-(2E_a-E_c)^2/(W''^2+2W^2)]/\{\pi(W''^2+2W^2)\}^{1/2}. \quad (3.28)$$

In this same limit the overlap integral of absorption and emission line shapes for stepwise transfer, Eq. (3.26) can also be given by a Gaussian function of energy gap $\Delta E=E_c-E_a$, just as in Eq. (3.28) without the factors of 2.

In the other limit, i.e., in the weak coupling limit, the effect of broadening of individual phonon components is small, and phonon side bands can be resolved. Moreover, the intensity distribution of these phonon side bands can be given in good approximation by an exponential dependence on energy rather than by a Gaussian dependence. Thus the overlap integral will also have an exponential dependence on the energy gap ΔE when this gap is larger than the phonon cutoff frequency. The study of phonon side bands in both LaF_3 and CaF_2 type lattices shows that the cutoff frequencies in these lattices are 350–360 cm^{-1}.[35] There-

[35] G. D. Jones and R. A. Satten, Phys. Rev. **147**, 566 (1966); S. Yatsiv, S. Peled, S. Rosenwaks, and G. D. Jones, in *Optical Properties of Ions in Crystals*, edited by Crosswhite and Moos, (Wiley–Interscience, Inc., New York, 1966); W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. **136**, A271 (1964); I. Richman, *ibid.* **133**, A1364 (1964).

fore if the energy gap between the absorption peak of the activator ion and the emission peak of the sensitizer ion is much larger than this cutoff frequency, the energy gap dependence of the energy transfer probability should be exponential rather than Gaussian. As the relaxation rates between various excited levels of a rare-earth ion are also determined by the electron-lattice interaction we should expect a qualitatively similar dependence on energy separation between these levels, although not quite the same. Indeed, the study of these relaxation rates W_{relax} in the above-mentioned host crystals[36–38] deduced from measurements of quantum efficiencies and lifetimes of luminescence shows that they can be fitted to a phenomenological exponential dependence on the energy gap ΔE,

$$W_{\text{relax}}=A\exp(-\alpha\Delta E). \tag{3.29}$$

This relation holds quite well over a range of energy gap between 1000 and 3000 cm^{-1} without marked deviation in various ions (Ho, Er, Dy, etc.) of the rare-earth group,[37] thus implying that the parameters A and α depend upon the characteristics of the host lattice but are insensitive to the nature of the levels or of local modes around the ions involved.

From experimental data[37,38] we have

$$\alpha\sim 5\times 10^{-3}\text{ cm} \quad \text{for } LaF_3 \text{ lattice},$$
$$\alpha\sim 4.6\times 10^{-3}\text{ cm} \quad \text{for } SrF_2 \text{ lattice}.$$

It can be shown[39] that the phonon-assisted transfer probability behaves quite similarly to the multiphonon relaxation probability.[37] That is, the transfer probability depends exponentially on the energy gap δE between the initial and final states of the system

$$P_{\text{tr}}(\delta E)=P_{\text{tr}}(0)\exp(-\beta\delta E), \tag{3.30}$$

where $P_{\text{tr}}(0)$ is the energy transfer probability when the zero phonon lines overlap, and β is another constant determined by the characteristics of the host lattice and the electron-phonon interaction.

An important difference between the multiphonon relaxation and the energy transfer probabilities is that the latter can be enhanced by the circumstance that two ions can share the M phonons needed to make up the energy mismatch δE. This gives[39] an extra factor $(1+g_b/g_a)^M$ to the transfer probability compared to W_{relax}, where g_a and g_b are the electron-phonon coupling constants of ion A and B, respectively. Thus the parameter β is related to α by

$$\beta=\alpha-\gamma, \tag{3.31}$$

where

$$\gamma=(\hbar\omega)^{-1}\ln(1+g_b/g_a) \tag{3.32}$$

and ω is the phonon cutoff frequency. If we assume $g_b=g_a$ and $\hbar\omega=350$ cm^{-1}, γ amounts to $\sim 2\times 10^{-3}$ cm, so that β is of the order one-half of α.

As was mentioned above, a criterion for the applicability of Eq. (3.30) is that the energy gap δE be larger than the phonon cutoff frequency. From data compiled by Dieke,[17] we have estimated in Table II values for the energy gap δE for stepwise as well as cooperative transfer processes. We see that except for the case of Er^{3+} we have large energy gaps for stepwise transfers, wheras they are small for cooperative transfer processes. Although these values of energy gap may vary from host to host and may also depend on the concentration of both sensitizer and activator ions, the change in these values is not expected to exceed 100 cm^{-1}.

Therefore one has to apply Eq. (3.30) to estimate P_{tr} for the stepwise transfer processes for Ho and Tm, while for the remaining transfer processes the overlap integral of Gaussian form may be more appropriate.

A crude estimate can be made for the value of $P_{\text{tr}}(0)$ as follows: If we assume that the zero phonon absorption line of the activator ion and the zero phonon emission line of the sensitizer ion coincide, we have $\rho_E{}^{\text{tr}}\sim 63$ eV^{-1} for a half-width (at e^{-1} of maximum) of 50 cm^{-1} for each line. With the use of the rough estimate for D according to (3.25) with $R\sim 7a_0$, we have

$$P_{\text{tr}}(0)\simeq 1.3\times 10^{12}\text{ sec}^{-1}. \tag{3.33}$$

For the $Er^{3+}+Yb^{3+}$ system the first step of excitation will proceed with a probability $\sim\frac{1}{10}$ that of (3.31) because the $^4I_{11/2}$ level of Er^{3+} is close to resonance with the $^2F_{5/2}$ level of Yb^{3+}. The second step of excitation of this system can take place through either of the three steps; to $^4F_{7/2}$, to $^2H_{11/2}$ or directly to the $^4S_{3/2}$ level. As we expect the transfer process to take place with a probability having a rapid dependence on energy gap δE, excitation to a level with the smallest energy gap will determine the rate of the process. Thus if we take

TABLE II. Values of the energy gap δE.

Ion	Transition		Transition energy (cm^{-1})	Gap (cm^{-1})
Yb^{3+}	$^2F_{7/2}$	$^2F_{5/2}$	10 282–10 574[a]	···
	Stepwise transfer			
Er^{3+}	$^4I_{15/2}$	$^4I_{11/2}$	10 111	170
	$^4I_{11/2}$	$^4F_{7/2}$	10 297	15
Ho^{3+}	$^5I_8$	$^5I_6$	8 665	1600
	$^5I_6$	$^5S_2$	9 765	400
Tm^{3+}	$^3H_6$	$^3H_5$	8 380	1900
	$^3H_4$	$^3F_2$	9 286	1000
	$^3F_4$	$^1G_4$	8 498	1800
	Cooperative transfer			
Er^{3+}	$^4I_{15/2}$	$^4F_{7/2}$	20 373	190
Ho^{3+}	$^5I_8$	$^5F_3$	20 590	26
Tm^{3+}	$^3H_6$	$^1G_4$	20 882	318[b]

[a] Yb^{3+} data in $YCl_3 6H_2O$; Tm^{3+} data in YCl_3; other ion data are in $LaCl_3$ (Ref. 17).
[b] The energy gap in this case ranges from +318 to −265 cm^{-1}.

[36] L. A. Riseberg, W. B. Gandrud, and H. W. Moos, Phys. Rev. **159**, 262 (1967).
[37] L. A. Riseberg and H. W. Moos, Phys. Rev. **174**, 429 (1968).
[38] M. J. Weber, Phys. Rev. **156**, 231 (1967); **156**, 157 (1967); **156**, 262 (1967).
[39] T. Miyakawa and D. L. Dexter (unpublished).

the $^4F_{7/2}$ level as the most efficient transfer level, P_{tr} will be of the order of 10^{12} sec^{-1} because of the small energy gap.

For the $Ho^{3+}-Yb^{3+}$ system the first ($^5I_8 \rightarrow {}^5I_6$) and the second steps of excitation ($^5I_6 \rightarrow {}^5S_2$) will have gaps $\delta E \sim 1600$ cm^{-1} and ~ 400 cm^{-1}, respectively. Thus the P_{tr} for these two transfer processes will be

$$\begin{aligned} &P_{tr}(^5I_8 \rightarrow {}^5I_6) \sim 1 \times 10^{10} \text{ sec}^{-1}, \\ &P_{tr}(^5I_6 \rightarrow {}^5S_2) \sim 3.8 \times 10^{11} \text{ sec}^{-1}, \end{aligned} \tag{3.34}$$

using the value of β estimated in (3.31), (3.32).

In the case of the $Tm^{3+}+Yb^{3+}$ system the three-step excitation will proceed through the following levels with the energy gaps

$$\begin{aligned} &\delta E \sim 1900 \text{ cm}^{-1} \quad \text{for } {}^3H_6 \rightarrow {}^3H_5 \text{ excitation}, \\ &\delta E \sim 1000 \text{ cm}^{-1} \quad \text{for } {}^3H_4 \rightarrow {}^3F_2 \text{ excitation}, \\ &\delta E \sim 1800 \text{ cm}^{-1} \quad \text{for } {}^3F_4 \rightarrow {}^1G_4 \text{ excitation}, \end{aligned} \tag{3.35}$$

and the P_{tr}'s will be of the order of

$$\begin{aligned} &P_{tr}(^3H_6 \rightarrow {}^3H_5) \sim 3.8 \times 10^4 \text{ sec}^{-1}, \\ &P_{tr}(^3H_4 \rightarrow {}^3F_2) \sim 5 \times 10^{10} \text{ sec}^{-1}, \\ &P_{tr}(^3F_4 \rightarrow {}^1G_4) \sim 5.7 \times 10^9 \text{ sec}^{-1}. \end{aligned} \tag{3.36}$$

In the case of Yb^{3+} emission and Tm^{3+} absorption there is insufficient information even as to the peak energy and widths to make more than a crude estimate as to the value of $\rho_E{}^{coop}$. One trouble is that the widths of these lines seems to be rather sensitive to the concentration of the sensitizer ions. For example, the width of the excitation spectrum of $Yb^{3+}+Tm^{3+}$ emission in LaF_3: $(YbF_3)_{0.20}(TmF_3)_{0.005}$($\sim 340$ cm^{-1}) is much larger than the width of the emission line in CaF_2: $(YbF_3)_{0.01}$(~ 30 cm^{-1}), thus suggesting that the width increases with increasing concentration of Yb^{3+} ions. In this event there may be inhomogeneous broadening occurring at high concentrations, and the larger estimates of ρ_E become unreliable.

A reasonable but large range of values for ρ_E can be estimated as follows: The excitation spectrum of Hewes and Sarver in $LaF_3(YbF_3)_{0.20}(TmF_3)_{0.0015}$ has a main peak with a half-value width of several tens of cm^{-1} which is not much different from the width (~ 30 cm^{-1}) of the Yb^{3+} emission spectrum in $CaF_2(YbF_3)_{0.01}$.[40] On the other hand, the absorption spectrum of the Tm^{3+} ion in $BaF_2(YbF_3)_{0.01}(TmF_3)_{0.005}$ is ~ 70 cm^{-1} to 100 cm^{-1}.[40] If we estimate the value of ρ_E in the Gaussian approximation using values of the energy gap δE listed in Table II for cooperative transfer in various systems with linewidths of 50 cm^{-1} ~ 100 cm^{-1} we get $\rho_E{}^{coop}$ of 10^{-2} to 10 eV^{-1}. However in the case of small overlap, an exponential dependence such as (3.30) would apply. Using $\rho_0{}^{coop} = 60$ eV^{-1}, $\beta = 3 \times 10^{-3}$ cm, and with δE ranging from 30 to 300 cm^{-1}, we compute $\rho_E{}^{coop} = 55$ to 24 eV^{-1}. As this value is close to the upper limit of the estimate for the $\rho_E{}^{coop}$ in the Gaussian approximation, the larger value of $\rho_E{}^{coop}$ will be more reliable. With $\rho_E{}^{coop} = 10$ eV^{-1} and the matrix element (3.14), we estimate P_{coop} to be on the order 10^8 sec^{-1}. It should be noted that this estimate for P_{coop} is greater than the reciprocal decay time of the Yb^{3+} ion in the absence of other impurities. Thus 2 excited Yb^{3+} ions adjacent to a Tm^{3+} ion would be more likely to excite the Tm^{3+} ion cooperatively than to return to the ground state independently. This is not to say that the cooperative excitation probability is greater than that for excitation of an intermediate level of Tm by independent energy transfer from each of the excited Yb^{3+} ion. [See Eqs. (3.36).]

[40] J. Weller (private communication); the authors are grateful to J. Weller for making available the yet unpublished data on Tm^{3+} absorption band in BaF_2; 0.10 YbF_3; 0.005 TmF_3.

IV. COMPARISON OF STEPWISE AND COOPERATIVE TRANSFER PROBABILITIES

The transition rates for the three-level system ω_{ij} and Ω_{lj} which appear in the rate equations of Sec. II may be written as

$$\omega_{12} = n^* P_{tr}(12) z x, \tag{4.1}$$

$$\omega_{23} = n^* P_{tr}(23) z x, \tag{4.2}$$

$$\Omega_{13} = n^{*2} P_{coop}(13) z(z-1) x^2/2, \tag{4.3}$$

where x is the concentration of Yb^{3+} ions; n^* is the (stationary) fractional number of excited Yb^{3+} ions on a nearest like neighbor site; z is the number of nearest like neighbor sites; $P_{tr}(12)$ and $P_{tr}(23)$ are the rates of excitation from levels 1 and 2 to levels 2 and 3, respectively, by energy transfer from excited Yb^{3+} ions; $P_{coop}(13)$ is the transition rate of the ion from the 1 to 3 state by the simultaneous (cooperative) transfer of energy from two nearby excited Yb^{3+} ions.

Similarly, for the $Tm^{3+}+Yb^{3+}$ system, we may write

$$\begin{aligned} &\omega_{12} = n^* P_{tr}(12) z x, \\ &\omega_{23} = n^* P_{tr}(2'3) z x \eta_{relax}(22'), \end{aligned} \tag{4.4}$$

$$\begin{aligned} &\omega_{34} = n^* P_{tr}(3'4) z x \eta_{relax}(33'), \\ &\Omega_{14} = \tfrac{1}{2} n^{*2} P_{coop}(14) z(z-1) x^2. \end{aligned} \tag{4.5}$$

Here $\eta_{relax}(ii')$ is the branching ratio describing the relative probability of relaxation from level i to i'; we have already commented on our expectation that η_{relax} will be close to unity.

We now compare the probabilities for the stepwise and cooperative mechanisms. In the case of the two-step transfer process (for Ho or Er+Yb) the condition that stepwise transfer dominates is

$$\omega_{12}\omega_{23} \gg \Omega_{13}\omega_{21} \tag{4.6a}$$

or, rewriting with the aid of (4.1) and (4.3),

$$P_{tr}(23)/P_{coop} \gg \omega_{21}/2P_{tr}(12). \tag{4.6b}$$

The left-hand side of this inequality is much greater than unity [see Eqs. (3.34)], that is, single transfer in all these cases has a higher transition probability than that for cooperative transfer, and the right-hand side is much less than unity, that is, an excited Yb^{3+} adjacent to an unexcited Er^{3+} or Ho^{3+} will almost certainly transfer its excitation energy before luminescing or undergoing multiphonon decay. Hence the inequality is easily satisfied, and stepwise transfer will dominate. Another way of saying this is that if a Yb ion becomes excited, it will transfer energy promptly, hence will not be available to participate in cooperative transfer, and that even if another Yb ion becomes excited before the first has transferred, each of them prefers to transfer individually rather than participate in cooperative transfer.

For the four-level system, $Tm^{3+}+Yb^{3+}$, the condition that stepwise transfer dominate is given by

$$\omega_{12}\omega_{23}\omega_{34} \gg \Omega_{14}[\omega_{21}(\omega_{31}+\omega_{32}+\omega_{34})+\omega_{23}(\omega_{31}+\omega_{34})]. \quad (4.7a)$$

Under conditions (see below) that saturation effects are unimportant this may be simplified to read

$$P_{\text{coop}}(14) \ll \frac{P_{\text{tr}}(12)P_{\text{tr}}(2'3)P_{\text{tr}}(3'4)n^*zx}{\omega_{21}(\omega_{31}+\omega_{32})}. \quad (4.7b)$$

For cooperative transfer to occur two photons must be absorbed on Yb^{3+} ions adjacent to a Tm^{3+} ion within a time less than the single transfer time P_{tr}^{-1}. On the other hand, in order to make the stepwise transfer operative, three photons must be absorbed within the shortest of the normal relaxation times of the Tm^{3+} ion from states $2'$ or $3'$ (i.e., $^3H_4$ or $^3F_4$). Thus at sufficiently low exciting light intensity I_E the quadratic, cooperative mechanism must be dominant. However, our estimates show that this would be at such a low exciting photon flux (10^{-14} W/cm^2) that Tm luminescence would be impossible to observe. Hence one expects a cubic dependence of Tm^{3+} output emission on I_E, as observed by Hewes and Sarver.[9]

The conditions that saturation effects can be neglected are

$$n^* < \omega_{21}/P_{\text{tr}}(2'3)zx, \quad n^* < (\omega_{31}+\omega_{32})/P_{\text{tr}}(3'4)zx, \quad (4.8)$$

or that the exciting flux is less than about 1 mW per cm^2. At larger I_E saturation effects should act to reduce the dependence of L on I_E from cubic to quadratic. Saturation effects also have been seen by Hewes and Sarver,[9] although they did not indicate the absolute light intensity where saturation began.

V. DISCUSSION

The calculations outlined in the preceding sections are based on the incoherent picture of energy transfer. That is, we assume that the interaction between ions is sufficiently weak that within a short time interval compared to the emission life time of the final state the wave function of the system loses its phase memory completely, and the transfer of energy and the emission of light proceed quite independently. (It is also required that the interaction be weak so that the first-order calculation is adequate, that is, so that we need not be concerned with $ErYb_2$ molecular states, for example.) From the estimate of the interaction matrix element in Sec. III we see that the interaction is indeed weak enough to assure the applicability of the incoherent approach. The density-of-states factors in the transfer process have been estimated from empirical relations for nonradiative transition probabilities and from guesses as to the linewidths and positions where these are not known. The estimates accordingly are crude, but the qualitative conclusions seem reasonably certain.

The results of Sec. IV show that the dominant mechanism for the sensitization of luminescence in the Tm^{3+}, or Er^{3+}, or $Ho^{3+}+Yb^{3+}$ systems is the stepwise transfer of energy from the Yb^{3+} ion. However, in the $Tb^{3+}+Yb^{3+}$ system there are no energy levels which can contribute to the stepwise process at low temperature. Thus one may expect to observe cooperative excitation of $^5D_4$ luminescence by excitation in the Yb^{3+} absorption band. (Tb^{3+} ions are also interesting in view of the low lying ^7F multiplets, the highest level of which is almost in resonance with the $^3H_4$ level of Tm^{3+}. Thus a Tb^{3+} ion in the $Tb^{3+}+Tm^{3+}+Yb^{3+}$ system should act as a quencher for the stepwise process in Tm.) The intensity I_E required in the Tb+Yb system would be much greater than that for Er+Yb, e.g., because of the low efficiency of the cooperative process. An estimate[41] based on the lines of Sec. III shows that an exciting light intensity about 10^5 greater would be required to produce the same light output in systems of the same concentrations, so that $I_E \sim 1$ W/cm^2 should produce observable $^5D_4$ Tb^{3+} luminescence.

We have not explicitly considered back-transfer effects. In principle they surely exist, but the uncertainties in our calculated densities of states make it pointless to speculate on the amount of back transfer that occurs.

Finally, we comment on our assumption that only nearest neighbors need be considered. The R^{-10} dependence for P_{tr} (R^{-20} for P_{coop}) leads to a reduction in transfer probability by a factor of 10^{-3} (10^{-6}) on doubling the separation, and no qualitative change could arise from consideration of other than nearest neighbors.

ACKNOWLEDGMENTS

We thank J. Weller and H. Rabin for helpful conversations, and R. Hewes and J. Sarver for permission to quote their paper before its publication.

[41] The energy mismatch between the Tb^{3+} excitation energy ($^7F_6 \rightarrow {}^5D_4$) and twice the Yb^{3+} excitation energy is about 100 cm^{-1} giving $P_{\text{coop}}(E)$ of 6.6×10^8 sec^{-1}.