of such a center can easily occur at 80 K, this is not possible at 4 K, and, furthermore, the center is retained upon cooling from 80 to 4 K, in agreement with experiment.

C. *C* Center

There seems to be no difficulty with transforming an interstitial Mn^{+2} into Mn^0, in accord with Ikeya and Itoh's suggestion, but our calculations show that the formation of a *C* center from a *B* center (of either model) by thermal excitation, as suggested by these authors, is for energetic reasons essentially impossible.

D. *E* Centers

The suggestion that an *E* center is formed when a Mn^0 formed at an interstitial position drops into a Cl^- vacancy (which is created by bleaching *F* centers) seems very reasonable. It is, on the other hand, difficult to conceive a mechanism which would lead to such *E* centers from other substitutional configurations. Our calculations, which are based on a purely ionic model, do not indicate the presence of off-center positions for the Mn^0 and this result agrees with the observed EPR spectrum at higher temperatures. The presence of shallow (~0.055 eV) off-center minima which seem to be observable at lower temperatures would perhaps follow if a covalent Mn^0-Cl^- interaction and admixtures of higher states of the transition metal were added to our purely ionic model.

E. *D* Centers

The tetragonal nature of the *D* center is easily explained if one assumes that it is a Mn^0 atom in a linear trivacancy which is formed when a *B* center attracts either a Na^+ or a Cl^- vacancy. Theoretical results in Sec. II show that single vacancies are attracted to a *B* center by a small binding energy and that the Mn^0 atom is displaced away from a central position by about 0.3 of the interionic distance. This model explains thus both the formation of the *D* centers and their tetragonal EPR spectrum.

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Simultaneous Energy Transfer and Optical Absorption in Condensed Matter*

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A discussion is given of the probability of absorbing a photon while simultaneously transferring electronic excitation energy from an already excited impurity. Estimates are given for several types of systems. A comparison is made with the probability for two-photon absorption (which is much smaller) and cooperative transfer processes. Several possible experiments are suggested.

I. INTRODUCTION

In the past 12 years numerous higher-order optical processes have been studied in solids, the interpretation of which calls on the theory of energy transfer via exchange or Coulomb interactions (the latter commonly expressed in near-zone multipole expansions). Among the most important of these are (i) cooperative absorption, in which the energy of a single photon is shared in the process of exciting electronic states of two similar or dissimilar neighboring atoms[1,2] (ii) cooperative emission, in which two excited atoms produce a single photon of energy equal to the sum of two excitation energies,[3,4] (iii) cooperative excitation, in which two excited atoms simultaneously transfer their excitation energy to another atom,[5,6] (iv) sequential excitation, in which two (or three) excited atoms transfer their energy to another one in stages,[6-8] (v) the well-studied phenomenon in solid anthracene in which two triplet excitons combine to produce a singlet exciton (fusion),[9] and (vi) the inverse process in tetracene (fission).[10] The latter is closely related to the predicted[11] and observed[12] effect of (vii) an excited atom simultaneously transferring its excitation energy to two other atoms. Some of these processes are remarkably efficient.

When we speak of "higher-order" or "nonlinear" processes in this paper our emphasis is that they are nonlinear in atomic density, and not nonlinear in light intensity (although indeed some of the effects mentioned above are quadratic or even cubic in intensity). That is, the effects we speak of here would not be observable in a dilute gas, though they could be in a liquid or glass as well as a solid.

In a recent brief note,[13] the authors have proposed another process in which an excited atom A^* transfers its energy to another atom B simultaneously, with the absorption of a photon. At that time we noted that the inverse process should also be observable, that is, an excited B^* atom transfers part of its energy to A and emits a photon to make up the energy difference. We have become aware that indeed this latter process has been observed.[14,15] Likewise, the effect predicted may also have been observed, as discussed below.

In this paper we calculate matrix elements and transition probabilities for the proposed process in a variety of cases which might be encountered in practice. Where it is feasible, we compare these probabilities with those for other competing effects.

In Sec. II we describe the general approach and calculate the cross section for the process. In Sec. III we apply the results to several cases and compare them with competing cooperative processes. Finally, in Sec. IV we include some discussion and make specific suggestions for systems that may exhibit the effects described.

II. DESCRIPTION OF SYSTEM AND CALCULATION OF CROSS SECTION

It is convenient to work in the tight-binding approximation, as in Ref. 2, partly for the convenience of bookkeeping. Throughout most of this paper we shall stipulate the presence in the medium of an impurity atom A which has a set of eigenfunctions $|A_\alpha\rangle$ of energy ϵ_α measured from its ground state $|A_0\rangle$ of 0 energy. These functions are assumed to have been orthonormalized to those of its surroundings, whatever the surroundings may be. We stipulate also the presence of an atom B with states $|B_\beta\rangle$ and energies ϵ_β. Thus the ground state of the system is $|\ldots A_0, B_0\ldots\rangle$ of 0 energy in the lowest order of perturbation theory. (The effects of thermal vibration will be introduced as required.) In considering absorption, we are explicitly interested in transitions from a state of the system in which at time zero only A is excited and is in state $|A_a\rangle$; i.e., the zero-order initial state is $|\ldots A_a, B_0\ldots\rangle$. However, if A and B interact with an interaction Hamiltonian H_{int} a correlation will be induced which can be expressed as a configuration mixing in first-order perturbation theory:

$$\Psi_i^{(1)} = |A_a, B_0\rangle - \sum_{\alpha\neq a}\sum_{\beta\neq 0}\frac{\langle a0|H_{\text{int}}|\alpha\beta\rangle}{\epsilon_\beta-(\epsilon_a-\epsilon_\alpha)}|A_\alpha, B_\beta\rangle\ . \tag{1}$$

We are concerned with transitions to some final state, which in zero order is $|A_a, B_b\rangle$, under the perturbation of a radiation field of frequency ω_2 described by

$$H_R = e\vec{\mathcal{E}}_{\text{eff}}(\omega_2)\cdot(\vec{\mathrm{R}}_A+\vec{\mathrm{R}}_B)\ , \tag{2}$$

where $\vec{\mathrm{R}}_A$ ($\vec{\mathrm{R}}_B$) is the sum of electronic coordinates of atom A (B), and $\vec{\mathcal{E}}_{\text{eff}}(\omega_2)$ is the electric field which is effective in inducing the transition we wish to detect. We are concerned with processes in which A^* transfers some or all of its excitation energy, so that $\epsilon_a > \epsilon_{a'}$; if it transfers all of it, $a'=0$. Accordingly the final state, to first order, will be written

$$\Psi_f^{(1)} = |A_{a'}, B_b\rangle - \sum_{\alpha\neq a'}\sum_{\beta\neq b}\frac{\langle a'b|H_{\text{int}}|\alpha\beta\rangle}{\epsilon_\alpha-\epsilon_{a'}+\epsilon_\beta-\epsilon_b}|A_\alpha, B_\beta\rangle\ . \tag{3}$$

We now compute the matrix elements of H_R between initial and final states. Since H_R is a sum of one-electron operators its matrix elements between the leading terms of Eqs. (1) and (3) will vanish, but this is not the case with the cross terms, nor for their sum. We shall ignore terms involving the square $|\langle H_{\text{int}}\rangle|^2$, since there will always exist linear terms. Thus we obtain

$$-\langle i|H_R|f\rangle = \sum_{\alpha\neq a, a'}\frac{\langle a0|H_{\text{int}}|\alpha b\rangle}{\epsilon_\alpha-\epsilon_a+\epsilon_b}\langle\alpha|H_R(A)|a'\rangle + \sum_{\beta\neq b, 0}\frac{\langle a0|H_{\text{int}}|a'\beta\rangle}{\epsilon_\beta-(\epsilon_a-\epsilon_{a'})}\langle\beta|H_R(B)|b\rangle$$

$$+\sum_{\beta\neq b,0}\frac{\langle \alpha' b|H_{\text{int}}|\alpha\beta\rangle}{\epsilon_\beta-\epsilon_b+\epsilon_a-\epsilon_{a'}}\langle\beta|H_R(B)|0\rangle+\sum_{\alpha\neq a,a'}\frac{\langle a'b|H_{\text{int}}|\alpha 0\rangle}{\epsilon_\alpha-\epsilon_{a'}-\epsilon b}\langle\alpha|H_R(A)|a\rangle\ . \qquad (4)$$

This matrix element is very similar to that of Refs. 2 and 14; in all of these cases, the transition proceeds via a virtual intermediate state. In Ref. 2, a photon disappears and two other atoms are simultaneously excited; in Ref. 14, one excited atom transfers energy to another and a photon simultaneously appears; and in the present case, one excited atom transfers energy to another and a photon is simultaneously absorbed. This matrix element would also apply to the case wherein two excited atoms become deexcited (or less highly excited) and a photon appears [effect (ii) in the Introduction and Refs. 3 and 4]. In the present case, the first term comes from selecting out of the sum in Eq. (1) the term $\beta = b$, that is, the term which couples in all intermediate states $|A_\alpha, B_b\rangle$ and then makes a radiative transition on A from $|A_\alpha\rangle$ to $|A_{a'}\rangle$. The other terms have similarly simple interpretations. Figure 1 shows schematically the intermediate states involved. The lightly dashed diagonal lines indicate the radiative transitions, numbered according to the order of their appearance in Eq. (4).

The vanishing of energy denominators in Eq. (4) would imply that energy could be conserved in a simple transfer process without the necessity of the radiation field. Of course this does occur – it is a common phenomenon known as the "sensitization of luminescence"[16,17] – but it is not the effect we are studying; i.e., in the first term of Eq. (4), for example, if there were some state $|A_{a'}\rangle$ below $|A_a\rangle$ such that $\epsilon_b = \epsilon_a - \epsilon_{a'}$, and if the interaction matrix element $\langle a0|H_{\text{int}}|a'b\rangle$ were nonzero, energy could be transferred from A to B exciting the state $|B_b\rangle$ even in the absence of the radiation field. In any case, we shall not be concerned with vanishing energy denominators, except to note that the cooperative transfer plus absorption rate will be enhanced with small denominators for intermediate states that are coupled both by H_{int} and H_R in the AB system involved.

In this same connection we note that commonly the transition energies, such as $\epsilon_a - \epsilon_{a'}$, are broadened substantially through interaction with the surroundings. Accompanying this broadening there is normally a Stokes shift between absorption and emission energies. Normally, we shall replace energy differences in the denominator by their mean values, that is, the peak energy of the appropriate absorption or emission band, without serious error. However, it is important to note that it would be difficult to detect unambiguously photons of energy $\hbar\omega_2$ of the same order as the width of a transition $|a0\rangle \rightarrow |a'b\rangle$ which could approximately conserve energy without the presence of the radiation field. That is, energy-conserving photons $\hbar\omega_2$ can only be detected if the transition energies are well defined to a spread less than $\hbar\omega_2$.

Let us look at the matrix elements of the photon-induced transitions arising from $\langle H_R(A)\rangle$ and $\langle H_R(B)\rangle$ in Eq. (4). For any real state $|A_a\rangle$ or $|A_{a'}\rangle$ ($|B_0\rangle$ or $|B_b\rangle$) there will always exist *some* intermediate states $|\alpha\rangle$ ($|\beta\rangle$) that couple to it by an electric dipole transition. Accordingly, we can replace each matrix element $\langle H_R(A)\rangle$ or $\langle H_R(B)\rangle$ by a quantity of the order $e\,\mathcal{E}_{\text{eff}}a_0$, where a_0 is the Bohr radius $\hbar^2/me^2$. Of course, we may have to pay the price of having a rather large energy denominator and perhaps also a reduced matrix element $\langle H_{\text{int}}\rangle$ for those states, but that price is generally well worth paying. As has been emphasized,[2,17] the radiative matrix element is vastly reduced for many transitions which are forbidden by optical selection rules (e.g., by a factor ~ 10^3 for pure electric quadrupole transitions) but the interaction matrix element for near neighbors is reduced by only a factor of about 10 if one of the atoms makes a quadrupole

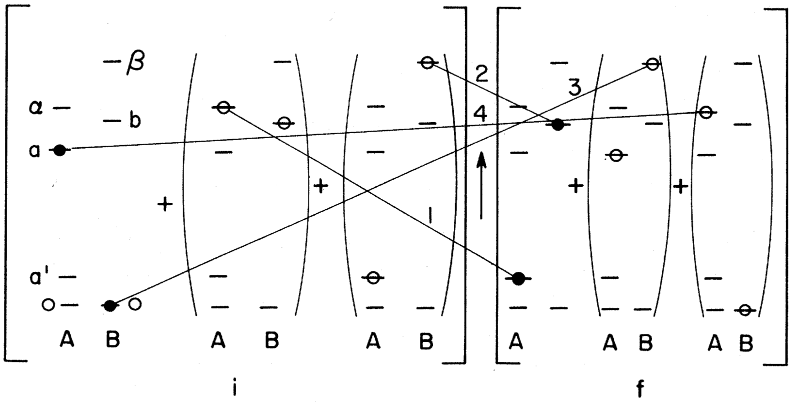

FIG. 1. Schematic representation of the initial and final states, *i* and *f*, namely, $|ao\rangle$ and $|a'b\rangle$ connected to first order in the interaction Hamiltonian by the small admixtures of the states in parentheses. Light diagonal lines labeled according to the order of their appearance in Eq. (4) connect the states coupled by the radiation field describing the absorbed photon $\hbar\omega_2$ as indicated by the vertical arrow in the center. Open circles describe virtually occupied states and solid circles the occupied real states.

transition. [That is, degree of forbiddenness of transition probability is expressed in powers of $(2\pi a_0/\lambda)^2$ for radiative transition matrix elements, but only by powers of $(a_0/\rho)^2$ in transfer via near-zone multipolar fields. Here λ is the wavelength of light and ρ is the atomic AB separation.] Of course in a solid an off-center equilibrium position or vibrational motion may make an apparently forbidden transition partially allowed, and a larger contribution may be made by some low-lying "forbidden" intermediate state than by a high-energy allowed one.

The next question relates to the magnitudes of $\langle |H_{\rm int}|\rangle$. Presumably the largest term $\gamma = \langle |H_{\rm int}|\rangle / \Delta E$ in Eq. (4) is much less than unity in order that perturbation theory be applicable. In the most favorable case of the expansion of $H_{\rm int}$ in a multipole expansion, there will be a nonzero dipole-dipole term, in which case we could expect the coupling strength to be of the order of or less than

$$\gamma_{dd} \sim e^2 a_0^2/\kappa\rho^3 W \ , \qquad (5)$$

where κ is a dielectric constant which will be hereafter assumed of order 1 and W is some characteristic energy denominator of order 1 eV. Some addition and cancellation will occur among the various terms in each sum and among the four summations in Eq. (4), but Eq. (5) represents a reasonable maximum value, which for near neighbors could be as large as 0.1.

Depending on the symmetries of A_a, $A_{a'}$, B_0, and B_b there may exist no intermediate states α, β such that the intermediate state can simultaneously be coupled by dipole transition elements to real states and contribute to a nonzero dipole-dipole term for $\langle H_{\rm int}\rangle$. In this case, Eq. (5) would be reduced by a factor of order a_0/ρ, to obtain for a dipole-quadrupole interaction a value, at most, of

$$\gamma_{dq} \sim e^2 a_0^3/\rho^4 W \qquad (6)$$

and for a quadrupole-quadrupole interaction,

$$\gamma_{qq} \sim e^2 a_0^4/\rho^5 W \ , \qquad (7)$$

and so forth. Contributions from exchange interactions cannot be written in as simple a form, since they depend on the details of the overlapping of the electronic charge distributions on A and B and not exclusively on the atomic symmetries. They are generally nonzero for all pairs of symmetries and may be significant for near neighbors in all cases. The concept of superexchange has been invoked in some cases where direct exchange interactions are expected to be small.[18]

We now express the absorption cross section for radiation of energy $E_2 = \hbar\omega_2$ in terms of the matrix elements, Eq. (4),

$$\sigma_{\rm PT}(E_2) = \frac{4\pi^2 e^2 E_2}{3\hbar c n(E_2)} \left(\frac{\mathcal{E}_{\rm eff}}{\mathcal{E}_0}\right)^2 |\langle i|\vec{\rm R}_A + \vec{\rm R}_B|f\rangle|^2 S_b(E_2) \qquad (8)$$

The subscript PT refers to photon plus transfer. In this expression $n(E_2)$ is the real index of refraction of the medium at energy E_2 and $\mathcal{E}_{\rm eff}/\mathcal{E}_0$ is the ratio of the field which is effective in inducing the transition to the average field in the medium. For most real centers this ratio is of order unity, as is n, and we shall ignore these factors in the following. $S_b(E_2)$ is the shape function of the absorption band normalized such that

$$\int S_b(E_2)\, dE_2 = 1 \ . \qquad (9)$$

It is clear that S_b depends on the properties of both A and B. Assuming that A and B are not coupled coherently by phonon interactions, we may express $S_b(E_2)$ as a convolution integral over the normalized emission line shape $s^{\rm em}_{a\to a'}$ of A and the normalized absorption line shape $s^{\rm abs}_{0\to b}$ of B,

$$S_b(E_2) = \int s^{\rm em}_{a\to a'}(E)\, s^{\rm abs}_{0\to b}(E_2 - E)\, dE \ . \qquad (10)$$

This expresses the conservation of energy in the total process of transfer plus absorption. For example, if the emission line on A were a δ function at energy $E_a - E_{a'}$, $S_b(E_2)$ would have the shape $s^{\rm abs}_{0\to b}$ but would be displaced to lower energy by an amount $E_a - E_{a'}$. If both individual shape functions are uncorrelated Gaussians, the shape function $S_b(E_2)$ is also a Gaussian with a width equal to the square root of the sum of the squares of those of the two separate shape functions.

Thus the absorption coefficient $\mu_{\rm PT}$ is given by the product of $\sigma_{\rm PT}$ and the number density N^* of pairs which can contribute to the absorption:

$$\mu_{\rm PT} = N^* \sigma_{\rm PT} \ . \qquad (11)$$

For some purposes, it will be convenient to refer to the integrated absorption coefficient

$$M_{\rm PT} = \int \mu_{\rm PT}(E_2)\, dE_2$$
$$= \frac{4\pi^2 e^2 \bar{E}_2}{3\hbar c} |\langle i|\vec{\rm R}_A + \vec{\rm R}_B|f\rangle|^2 N^* \ , \qquad (12)$$

where $\bar{E}_2$ is an average value, for example, the energy of the maximum of the absorption band near E_2. In general, N^* and hence $M_{\rm PT}$ will be functions of position in the sample, depending on the conditions of excitation.

The quantity N^* is not clearly defined by the above remark. All pairs A^* and B can contribute to the absorption up to a separation ρ at which $\langle H_{\rm int}\rangle$ vanishes, with decreasing efficacy as ρ increases. However, since $|\langle H_{\rm int}\rangle|^2$ generally will decrease rapidly with separation, exponentially or at least as rapidly as ρ^{-6}, no serious underestimate of the absorption cross section will be made if we express N^* as the product of the concentration of excited A atoms, N^*_A, and the probability that an unexcited B atom is in the nearest possible location.

Thus we write

$$N^* = N_A^* N_B n_c / N^+ \ , \tag{13}$$

where n_c is the appropriate coordination number (e.g., 12 for next-nearest neighbors in the rocksalt structure), N_B is the concentration of B atoms, and N^+ is the density of the appropriate lattice sites.

III. MAGNITUDE OF EFFECT AND COMPETING MECHANISMS

To proceed further it is necessary to specify the nature of the system and the method of excitation of the A atoms. We shall consider cases of radiative excitation for simplicity, that is, optical pumping, though obviously other means are available with charged particles. Even with radiative excitation a number of possibilities exist, depending on whether the initial state a is directly excited or the excitation to a results via some relaxation process. First, let us consider the simplest case, that in which we pump A directly from the ground state to a. We neglect any stimulated emission and nonradiative phonon relaxation to lower states of A and assume that the PT process is not a major one for deexciting the A subsystem. Admittedly these are a large number of assumptions, but they are all consistent, reasonable, and more or less applicable to a large number of systems. Accordingly, we imagine there to be incident on a homogeneous system in the x direction, a narrow beam of frequency ω_1 centered at the peak of the $0 \rightarrow a$ absorption band of A. With the surface of the sample the $x = 0$ plane, and N_A the concentration of A atoms, the intensity of the beam will decrease across the sample as $I_1(x) = I_1(0)\, e^{-\mu_1 x}$, where $\mu_1 = N_A \sigma_a(\hbar\omega_1)$ and $\sigma_a(\hbar\omega_1)$ is the atomic absorption cross section. In the steady state, the concentration of excited A atoms at depth x is

$$N_A^*(x) = N_A \frac{I_1(x)\sigma_a(\hbar\omega_1)}{2I_1(x)\sigma_a(\hbar\omega_1) + \hbar\omega_1/\tau_a} \ , \tag{14}$$

where τ_a is the lifetime of the excited state. The total number of excited A atoms (per unit *surface* of the beam) is then

$$\mathfrak{N}_A^* = \int_0^d N_A^*(x)\, dx$$

$$= \frac{N_A}{2\mu_1} \ln\left(\frac{2I_1(0)\sigma_a + \hbar\omega_1/\tau_a}{2I_1(0)\sigma_a e^{-\mu_1 d} + \hbar\omega_1/\tau_a}\right) \ , \tag{15}$$

where d is the sample thickness. Several limiting cases are possible, according to the experimental conditions. If $\hbar\omega_1/\tau_a \ll 2I_1(0)\sigma_a\, e^{-\mu_1 d}$, then we have saturation throughout the sample and

$$\mathfrak{N}_A^* \cong \tfrac{1}{2} N_A d, \quad N_A^* \cong \mathfrak{N}_A^*/d \ . \tag{16}$$

On the other hand, if $\hbar\omega_1/\tau_a \gg 2I_1(0)\sigma$, then

$$\mathfrak{N}_A^* \cong \frac{N_A}{\mu_1} \frac{I_1(0)\sigma_a\tau_a}{\hbar\omega_1} (1 - e^{-\mu_1 d}) , \tag{17}$$

$$N_A^* \cong \frac{\mathfrak{N}_A^* \mu_1 e^{-\mu_1 x}}{1 - e^{-\mu_1 d}} \tag{17$'$}$$

$$\rightarrow \mathfrak{N}_A^*/d \qquad \text{if } \mu_1 d \ll 1 \ . \tag{17$''$}$$

In the latter limit it is also of importance to consider the case in which only a pair of electronic states is involved and there are no significant lattice relaxation processes after excitation of A. Then the Einstein relation between σ_a and τ_a is applicable, and

$$\mathfrak{N}_A^* \cong \frac{N_A}{\mu_1} I_1(0) \frac{\pi^2 c^2}{\omega_1^3 \Delta_a} , \quad N_A^* = \frac{\mathfrak{N}_A^*}{d} \ , \tag{18}$$

where Δ_a is the absorption bandwidth of the $0 \rightarrow a$ transition. Note that N_A^* is independent of τ_a or σ_a in these cases.

Now let us consider some specific systems, in which we prescribe the nature of the electronic transitions in A and B.

Suppose that the transition $0 \rightarrow a$ on A is allowed, and suppose also that the transition $0 \rightarrow b$ on B is forbidden, e.g., an electric quadrupole transition as in an $S \rightarrow D$ transition (see Fig. 2). From the level structure of A and B we expect $|\langle i | R_A + R_B | f \rangle|^2 \sim 10^{-19}$ cm^2, making use of the second and third term in Eq. (4). When the experimental conditions are such that $N_A^*(x)$ [Eq. (14)] is essentially independent of x, as in the cases considered in Eqs. (16) and (17$''$), we can consider the integrated (over energy) absorption coefficient for the $\hbar\omega_2$ beam and find

$$M_{\mathrm{PT}} = \frac{4\pi^2 e^2}{3\hbar c} |\langle i | \vec{\mathrm{R}}_A + \vec{\mathrm{R}}_B | f \rangle|^2 \frac{N_A^* n_c}{N^+} N_B \bar{E}_2 \ ; \tag{19}$$

and therefore, if the $0 \rightarrow a$ dipole matrix element is of order ea_0,

$$M_{\mathrm{PT}} \cong (10^{-20}\ \mathrm{cm}^2)(N_A^* n_c/N^+) N_B \bar{E}_2 \ . \tag{20}$$

There is another mechanism by which the photon $\hbar\omega_2$ might be absorbed and the B system excited to

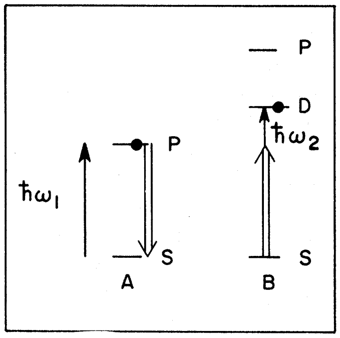

FIG. 2. A particular energy-level diagram indicating absorption of photons $\hbar\omega_1$ to a real state P, and energy transfer indicated by double arrows simultaneously with absorption of $\hbar\omega_2$. Here there is dipole-dipole coupling.

its state b, i.e., by two-photon absorption without any cooperation of subsystem A. We now want to compare Eq. (20) with the two-photon (PP) integrated absorption coefficient[19] of system B, which is expected to be of order

$$M_{\mathrm{PP}} \cong 10^{-37} I_1(N_B \bar{E}_2) \quad \text{(in cgs units).} \tag{21}$$

In order to carry out the comparison of the two processes, we must now express N_A^* in terms of N_A and $I_1(0)$. In the case where Eq. (18) is valid (no saturation) if $\Delta_a \sim 10^{-13}$ erg and $N_A n_c / N^+ \sim 10^{-2}$, we get $M_{\mathrm{PT}} \sim 10^5\, M_{\mathrm{PP}}$. On the other hand, if I_1 is so large as to induce saturation everywhere in the sample, then

$$N_A^* n_c / N^+ \sim N_A n_c / N^+ \sim 10^{-2}.$$

This occurs for an intensity larger than or about

$$\hbar\omega_1 / 2\sigma_a \tau_a = \omega_1^3 \Delta_a / 2\pi^2 c^2 \sim 10^{10}\ \mathrm{erg/(cm^2\,sec)} \tag{22}$$

(use was made of the Einstein relation). For $I_1 \sim 10^{10}$ erg/cm^{2}sec, we obtain

$$M_{\mathrm{PT}} \sim 10^4 M_{\mathrm{PP}}\,. \tag{23}$$

They would be equal for $I_1 = 10^4$ erg/cm^{2}sec. (One should remember that if the square of the dipole matrix element of the allowed $0 \to a$ transition is smaller than $e^2 a_0^2$, the calculated $M_{\mathrm{PT}}/M_{\mathrm{PP}}$ ratio is accordingly reduced by the same factor.)

In the intermediate cases, when $N_A^*(x)$ and $I_1(x)$ are varying appreciably across the sample, we can define the quantity

$$\mathfrak{M}_{\mathrm{PT}}(\bar{E}_2) = \int d(\hbar\omega_2) \ln\left(\frac{I_2(\omega_2, 0)}{I_2(\omega_2, d)}\right)$$
$$= \frac{4\pi^2 e^2}{3\hbar c} \left|\langle i | \vec{\mathrm{R}}_A + \vec{\mathrm{R}}_B | f \rangle\right|^2 \frac{\mathfrak{N}_A^* n_c}{N^+} (N_B \bar{E}_2), \tag{24}$$

which, in analogy with the integrated absorption coefficient, is the integral over the energy of the logarithm of the ratio of the incident intensity to the transmitted one; $\mathfrak{M}_{\mathrm{PT}}$ will not, in general, be proportional to d, but will have the more complicated dependence (15). The quantity $\mathfrak{M}_{\mathrm{PT}}$ is to be compared with $M_{\mathrm{PP}}d$, which is the attenuation of the $\hbar\omega_2$ beam due to the usual two-phonon process on the B-atom subsystem.

The most favorable experimental conditions for the PT process are obviously obtained by choosing the A concentration and the sample thickness that maximize $\mathfrak{N}_A^*$ [Eq. (15)]. Note that $\mathfrak{N}_A^*$ and therefore $\mathfrak{M}_{\mathrm{PT}}$ increase with increasing I_1 intensity; however, if one is interested in the comparison with the two-photon absorption on B, the relevant quantity is $\mathfrak{M}_{\mathrm{PT}}/M_{\mathrm{PP}}d$, and the experimental conditions which maximize this ratio do not coincide with saturation of A, because then $\mathfrak{M}_{\mathrm{PT}}$ is a slowly increasing function of I_1, whereas M_{PP} is still growing linearly.

There are other examples in which the PP process is not allowed, but for which the PT process has nearly the same probability as in the previous example, via the first and fourth term in Eq. (4). Consider the case in Fig. 3, in which the $S \to P$ transition on B by two-photon absorption is forbidden by parity in the dipole approximation, so that a reduction factor of $\sim 10^{-6}$ would have to be applied to the previous results for the PP process. It is important to remember that, in the limits of the Einstein relation, the steady-state population $N_A^*(x)$ is not strongly different for allowed or forbidden transitions.

For some cases it is necessary to invoke higher multipole terms for $\langle H_{\mathrm{int}} \rangle$, e.g., consider the system shown in Fig. 4. In this case the second and third term of Eq. (4) contribute to the matrix element, but the coupling parameter is an electric quadrupole in A, an electric dipole on B, and hence is of the magnitude of Eq. (6). Accordingly M_{PT} is reduced by a factor of 10^{-2} from the estimate of Eq. (23), or M_{PT} will be something like 10^2 greater than M_{PP} for this case.

For some particular energy-level structure of A and B, another competing process is possible, namely, cooperative transfer (TT) in which two excited A atoms simultaneously transfer their energy to the B subsystem. In order for this to happen, there must be a B level at the sum of populated energy levels in two A atoms (or an A atom and a C atom, or more complicated cases). In fulfilling this energy-matching condition one must take into account the nonzero linewidths of the A emission and the B absorption, that is, include the role of thermal assistance from the host lattice.

The probability for the TT process is given in Ref. 6, for the case of dipole-quadrupole coupling; this would apply to a level structure similar to that of Fig. 4 (with the energy of D_B about twice as large as that of D_A). From comparison of Eq. (3.13b) in Ref. 6 with our Eq. (4) we find a ratio for the

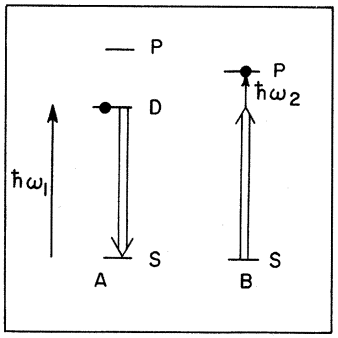

FIG. 3. Caption is the same as in Fig. 2, but for a different pair of ions again dipole-dipole coupled.

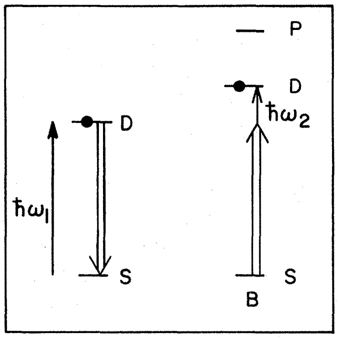

FIG. 4. Caption is the same as in Fig. 2, but for a pair of ions quadrupole-dipole coupled.

transition probabilities

$$\frac{W_{\mathrm{TT}}}{W_{\mathrm{PT}}}=\frac{N_A}{N^+}\,\frac{n_c(n_c-1)}{2}\,\frac{\pi c^3}{\omega_1^3\Delta_a}\left(\frac{Q_A}{R^8}\right)^2\frac{\rho_E^{\mathrm{TT}}}{\rho_E^{\mathrm{PT}}}\,.$$

Here Q_A is the quadrupole-moment matrix element for the $S \rightarrow D$ transition on A, whose value is, at most, of order ea_0^2, and ρ_E^{TT} and ρ_E^{PT} are the relevant density-of-states factors for the two processes. If we take $N_A/N_+ \sim 10^{-2}$, $n_c \sim 10$, $\omega_1 = 2 \times 10^{15}$ sec^{-1}, and $\Delta_a = 10^{-14}$ erg and assume the two densities of final states to be of the same order of magnitude, we find

$$W_{\mathrm{TT}}/W_{\mathrm{PT}} \sim 10^6 (Q_A/ea_0^2)^2;$$

i.e., in realistic cases the simultaneous transfer is more probable than the PT process. Remembering the results of our comparison with the PP process, it is possible to conclude that, other things being equal, processes including ion cooperation are more probable than those involving photon cooperation. Energy localized on A for a long time is more effective than that of a photon, which is available only for a transit time of the sample.

It is undoubtedly important in many cases to consider the population of state a by indirect means. A commonly observed phenomenon is the nonradiative relaxation between two closely spaced electronic levels by phonon emission, faster even than allowed radiative processes. Thus, for example, in Fig. 5 the A subsystem might be pumped into the state P indicated with high-absorption cross section, and fast radiationless transitions would populate the state D of long lifetime. It is important to remember that what matters is the population N_A^*, not how it is achieved, and in this case a population inversion is feasible, with an integrated absorption coefficient for the PT process of the order of that given by Eq. (20), for an intensity I_2 which may be smaller than the estimate of Eq. (22) by a factor dependent on the lifetime of the D state and relative transition probabilities from $P \rightarrow D$ and $P(A) \rightarrow S(A)$. A factor of 10^{-3} does not seem unduly small in real cases.

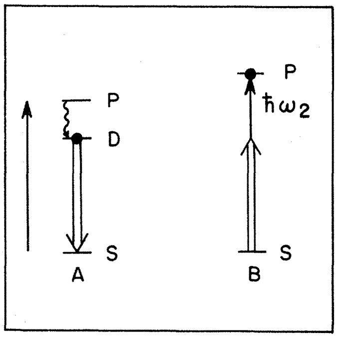

FIG. 5. Description is the same as in Fig. 3, except that the population of state S_1 on A is achieved by a radiationless transition from P_1, the state initially excited. From then on the description is the same as in Fig. 3.

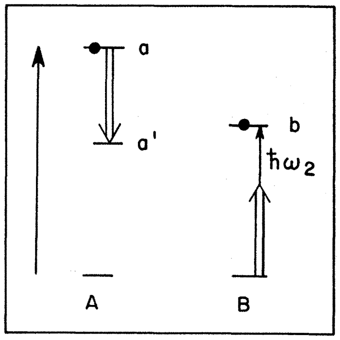

FIG. 6. Caption is the same as in Fig. 3, except that A does not transfer all its energy, but merely $\epsilon_a - \epsilon_{a'}$.

Of course this means of achieving a high population N_A^* is applicable generally, independently of the subsequent transfer to and nature of the subsystem B. That is, multiphonon transitions occur without regard to electromagnetic selection rules.

Diagrams such as Fig. 6 can also contribute in essentially the same way as for Figs. 2–4 under the various selection rules. Nothing essentially new is provided by transferring $\epsilon_a - \epsilon_a'$ rather than ϵ_a. As this diagram is drawn, of course, there is the additional possibility of transferring all of ϵ_a to B while emitting a photon of energy $\epsilon_a - \epsilon_b$, as observed in Refs. 14 and 15.

Finally, there is nothing that requires A and B to be dissimilar atoms. If one A atom transfers part of its energy to another A atom, the second can absorb photons of a lower energy than it normally could (see Fig. 7).

Furthermore, the same kind of phenomena can occur in an intrinsic material, the transition on A and B being replaced by excitonic or band-to-band transitions. There is little that is basically different for these cases except that the concentra-

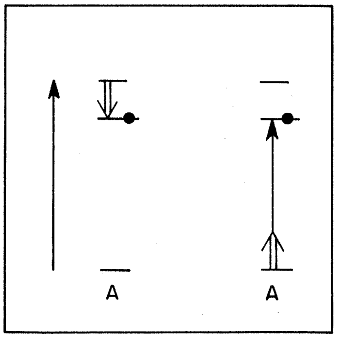

FIG. 7. Caption is same as in Fig. 6 for two identical atoms, showing the low-energy absorption that can occur on A.

tion N_B/N^+ in Eq. (13) is now unity. That this is so can be seen intuitively from the circumstance that we can always frame the problem with excitons or band-to-band transitions in terms of localized states either via tight-binding or Wannier functions.

There will of course be differences in detail. For example, the bandwidth of $s_{0\to b}^{\text{abs}}$ may be substantially increased over the case where B is an impurity, so that the width of S_2 is also increased. The integrated absorption coefficient, being proportional to N_B, is also increased for both PT and PP processes. Also the atomic selection rules we used in earlier discussion would represent an oversimplification. However, there seems to be no reason to change the order of magnitude estimates of M_{PT} or M_{PP} based on Eq. (18) and the following discussions, except for the B concentration.

In considering band-to-band transition, it is of interest to redraw Fig. 7 for pure material (no A atoms), and to imagine that we pump the system at an energy higher than the band gap (Fig. 8). For simplicity the valence band is shown with infinite mass. If the relaxation of electrons from ϵ_a to $\epsilon_{a'}$ is sufficiently slow (perhaps by application of an electric field), we might expect to see low-energy absorption at $\hbar\omega_2$ in the crystal. In fact, such low-energy absorption has recently been observed in CdS, where it is referred to as "electron-assisted transitions,"[20] analogous to "phonon-assisted" electronic transitions.

IV. DISCUSSION AND SUGGESTED EXPERIMENTS

A. Limitations of Model

Some of the assumptions made here have limited validity. Most serious is the assumption that perturbation theory is applicable for all separations of the interacting atoms. If the concentrations of both ions are low, then A-A, A-B, and B-B interactions should indeed be weak for *most* pairs, but *most* pairs will not contribute to the effect we are studying, just near neighbors. And even though the description may be valid for ground states, it may not be for excited states, as in excimer formation. The only real justification for the treatment would be that it works. This model *does* seem to work for rare-earth systems even at very high concentrations.

A related but less serious simplification is the neglect of lattice relaxation which accompanies Stokes shifts. The effect on the energy levels may be taken into account by inspection. That is, the energy available for transfer from atom A may not be $\hbar\omega_1$, the energy to excite it, but some lower amount(s) corresponding to the position(s) of its emission band(s). The effect on the wave functions themselves may be much more difficult to evaluate.[21]

In describing the line shape for absorption $\hbar\omega_2$ we have assumed incoherence between A and B in the phonons responsible for line broadening. One would expect this to be a satisfactory approximation for well-separated pairs, but it is not obviously valid at very small separations. There does not appear to be anything to do about this potential error in a general way, except to test it experimentally.

An oversimplification has resulted from labeling transitions as dipole allowed and assigning a value of ea_0 to the radiative dipole matrix element [leading to a dipole-dipole (d-d) coupling of $e^2a_0^2/R^3$]. It can be substantially smaller, varying roughly as the square root of the oscillator strength for the transition. Furthermore, we have neglected the angular variation of the dipole-dipole term. More serious is the labeling of a transition as a pure electric quadrupole, with a matrix element $ea_0^2/\lambda\!\!\!^{-}$ for radiative transitions, $(e^2a_0^2/R^3)(a_0/R)$ for the dipole-quadrupole (d-q) coupling, and $(e^2a_0^2/R^3)(a_0/R)^2$ for q-q coupling, exclusive of angular factors. There are two effects that must be considered. First, the radiative quadrupole matrix element, which is dimensionally of order $ea_0^2/\lambda\!\!\!^{-}$, may actually be much less than this in magnitude for a free

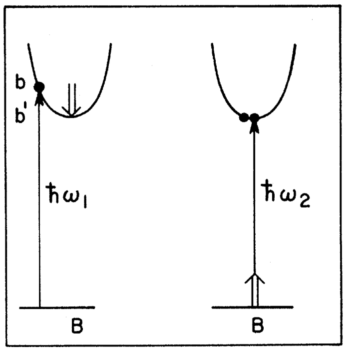

FIG. 8. Caption is the same as in Fig. 7, but drawn for band-band transitions.

ion, say less by a factor of $r < 1$. Then the spontaneous radiation probability would be of order of $10r^2$ sec^{-1} for the free ion. On the other hand, the crystal field will often admix an amount δ of states in either the ground or excited state or both for which the transition is dipole allowed. Thus the radiative transitions probability would become $10^8[(a_0 r/\bar{\lambda})^2 + \delta^2]$ sec^{-1}, and with $\delta > 10^{-3}$ it would be this admixture that would actually determine the decay time, e.g., 0.1 msec for $\delta = 10^{-2}$. The effect on H_{int} would be somewhat different. For example, the squared *d-q* matrix element would become

$$\left(\frac{e^2 a_0^3}{R^4}\right)^2 \left[r + \delta\left(\frac{R}{a_0}\right)\right]^2 .$$

At sufficiently large R the relatively small admixture of *d-d* coupling, i.e., the δR term, would dominate. For near neighbors, with $R/a_0 = 10$ and $\delta = 10^{-2}$, this term would dominate for $r < 10^{-1}$, but could be ignored for $r = 1$. It seems likely that in rare-earth systems the δ term will generally determine the decay time and often influence the interaction term, changing from *d-q* for nearest neighbors to *d-d* at larger separation.

B. Observability of Effect

Although the experimental results are not completely clear, there is evidence that the PT effect has been observed in CdS, as cited in Sec. III, and weaker evidence that the effect has been observed in a silicate glass containing Tb and Yb.[22] Here the $^5D_4$ state of Tb^{3+} (20 600 cm^{-1}) is excited by a neodymium pulse laser emitting at 9400 cm^{-1}. The interpretation of the authors is that a Yb^{3+} ion is excited by one 9400-cm^{-1} photon ($\hbar\omega_1$), and a second 9400-cm^{-1} photon ($\hbar\omega_2$) is simultaneously absorbed while energy is transferred from the excited Yb^{3+}. The authors rule out two-photon absorption because of an insufficiency of energy without thermal assistance on a Yb ion, and they rule out simultaneous transfer (TT) from two excited Yb ions because they observe no rapidly decaying emission from Tb (decay time 500 μsec), as would be expected from transfer from the short-lived (200 μsec) Yb ions—no such emission, at least, within 5 μsec (the resolution time of their detector). Hence they argue that the excitation of Tb^{3+} must occur during the laser pulse (2×10^{-8} sec).

The most favorable matrix element for the PT process comes from assuming that each Tb ion has an excited Yb ion as a nearest neighbor. Then under the conditions of pulsed excitation the transfer probability is 3.5×10^4 sec^{-1} [see Eq. (6)], or 2×10^{-4} Tb ions will be excited during the pulse. However, it is stated that about 10^{-2} Tb ions are excited, evidently leaving most of the transfer to occur later via cooperative transfer (TT). A substantial amount of cooperative transfer could indeed occur within the first 5 μsec after the pulse. Consider that in this system the decay time is 0.2 msec. This would correspond to $r \sim 2\times10^{-2}$. With nearest neighbors at $7.3a_0$,

$$W_{\text{TT}} = 7\times10^8(r + 7.3\delta)^4 \text{ sec}^{-1} \geqslant 3\times10^5 \text{ sec}^{-1},$$

for nearest neighbors regardless of r. Thus essentially all Tb ions having two excited Yb ions as nearest neighbors would become excited before the end of 5 μsec.

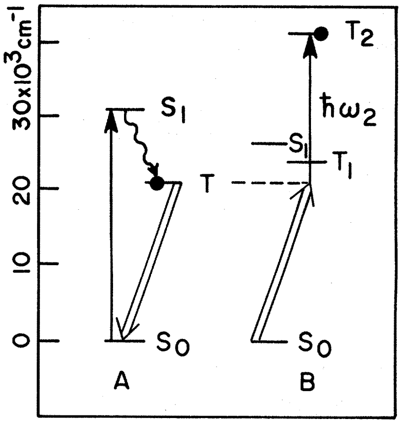

FIG. 9. Here each triplet manifold is shown to the right of the corresponding singlet manifold. The coupling of $|S_0(A)T_1(B)\rangle$ occurs by exchange while a photon $\hbar\omega_2$ excites the allowed transition $T_1 \rightarrow T_2$ on B.

The effects of Yb → Yb transfer and back transfer from excited Tb to Yb are difficult to estimate but they should be non-negligible. In any case it seems clear that the dominant means of exciting Tb is by the TT process. It is also clear that using a single beam, the Nd laser, both to excite Yb and to provide the photons necessary in the PT process, leaves ambiguities that could be avoided in other systems.

C. Specific Systems for Study

1. $\text{EuAlO}_3:\text{Cr}^{3+}$

Since this system has already been observed to transfer energy from Eu to Cr while emitting a photon,[14] it would be interesting to see if it could be made to operate in the other direction, that is, to excite Cr at 13 750 cm^{-1}, and by application of $\hbar\omega_2$=2350-cm^{-1} light to excite Eu luminescence at 16 000 cm^{-1} or elsewhere.

2. Naphthalene + Benzophenone

The energy-level scheme for this system is indicated in Fig. 9. Following excitation of S_1 in naphthalene (molecule A) one would expect a large fraction of the molecules to undergo a radiationless intersystem crossing transition to T of long lifetime. Hence one would expect N_A^* to be larger. By an exchange interaction one can virtually excite $|A(S_0)\,B(T_1)\rangle$ from which an allowed one-electron transition can be made to state $|A(S_0)\,B(T_2)\rangle$ as indicated. This will lead to a final radiative matrix element,

$$\langle i|\,\vec{\mathrm{R}}_A+\vec{\mathrm{R}}_B|f\,\rangle=\frac{\langle A(T)\,B(S_0)\,|e^2/r_{12}|A(S_0)B(T_1)\rangle}{E_B(T_1)-E_A(T)}\times\langle B(T_1)\,|\vec{\mathrm{R}}_B\,|\,B(T_2)\rangle .$$

Since exchange integrals of this sort are of order 10 cm^{-1},[23] we expect $\langle i\,|R_A+R_B|f\rangle\sim 10/(3\times10^3)a_0$ $\sim 3\times10^{-3}a_0$, substantially larger than that for an electric quadrupole transition. Accordingly, one might be able to measure the absorption of a beam centered around $\hbar\omega_2 = 20\,700\ \mathrm{cm}^{-1}$. It is also possible that one could detect the benzophenone $T_2 \rightarrow T_1$ emission at 17 600 cm^{-1} unless intersystem crossing to S is too probable on B.

3. $CaF_2 : Yb^{3+} + Eu^{3+}$

Here one would pump with $\hbar\omega_1 \sim 10\,000\ \mathrm{cm}^{-1}$ to excite the ${}^2F_{5/2}$ state of Yb^{3+}, and detect a beam of $\hbar\omega_2\sim 14\,000\ \mathrm{cm}^{-1}$ in exciting the ${}^5D_3$ level of Eu^{3+}. This level is particularly interesting since, owing to $5d$ admixture in the CaF_2 crystal field, it is dipole coupled to the $4f^7$ ground state, so that the radiative matrix element is unusually large for rare-earth ions, and the radiative lifetime is 6.8×10^{-7} sec.[24] The transition would be detectable by absorption of the $\hbar\omega_2$ beam or by emission from the ${}^5D$ manifold of Eu^{3+} from levels in the range of 22 000–17 000 cm^{-1}.

4. $CaF_2 : Yb^{3+} + Sm^{2+}$

The ion Sm^{2+} is isoelectronic to Eu^{3+}. Again one might pump into the Yb^{3+} state at $\hbar\omega_1\sim 10\,000\ \mathrm{cm}^{-1}$ and excite the ${}^5D$ manifold of Sm^{2+} with transfer plus absorption of $\hbar\omega_2\sim 4000\ \mathrm{cm}^{-1}$. This would be detectable by the very intense and sharp red Sm emission at 14 118 cm^{-1}, which is, in analogy with the previous example, due to $5d$ admixture in the wave function of the upper state.[25]

5. $NaI : Tl^+$

In NaI crystals containing Tl^+ impurities, excitation in the first fundamental band of NaI leads to host-sensitized luminescence of Tl at 31400 cm^{-1} at low temperatures, but at high T one observes pure NaI luminescence.[26] Here one might excite in the Tl^+ A band $\hbar\omega_1$ at He temperature and attempt to excite host luminescence by a beam $\hbar\omega_2$ $\sim 16\,800\ \mathrm{cm}^{-1}$.

6. Cu_2O

The $1s$ exciton in $\mathrm{Cu_2O}$ is reached only by a forbidden ($S\rightarrow D$) transition. It can be excited by two-photon absorption to satisfy the parity selection rule.[27] It could also be excited by the PT process if a suitable impurity can be incorporated. This would be an interesting system to study because of the expected long lifetime of the $1s$ exciton, and possibly a high concentration thereby.

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