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It is tempting to represent the data on CD_3H and CH_3D by slightly different values of $r_0(\text{C}-\text{H})$ and $r_0(\text{C}-\text{D})$ (but neglecting the change in angle), as was attempted in the case of the methyl halides by Miller *et al.*¹⁷ However, here again a surprisingly large difference has to be assumed: one finds $r_0(\text{C}-\text{H}) = 1.0972_4\text{\AA}$, $r_0(\text{C}-\text{D}) = 1.0902_1\text{\AA}$. At the same time the moment of inertia of CH_4 would have to be 5.3719×10^{-40} , which

¹⁷ Miller, Aamodt, Dousmanis, Townes, and Kraitchman, *J. Chem. Phys.* **20**, 1112 (1952).

deviates widely from the observed value. Clearly the effect of zero-point vibration cannot be taken into account in such a simple way.

The author wishes to thank Dr. A. E. Douglas for suggesting the problem and for giving experimental and theoretical help. He is grateful to Dr. G. Herzberg for much helpful discussion. The cooperation of Dr. J. A. B. Nolin and Dr. L. C. Leitch in supplying the deuterated methyl halides and of Dr. F. P. Lossing in analyzing the gases by mass-spectroscopic methods is also greatly appreciated.

A Theory of Sensitized Luminescence in Solids

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The term "sensitized luminescence" in crystalline phosphors refers to the phenomenon whereby an impurity (activator, or emitter) is enabled to luminesce upon the absorption of light in a different type of center (sensitizer, or absorber) and upon the subsequent radiationless transfer of energy from the sensitizer to the activator. The resonance theory of Förster, which involves only allowed transitions, is extended to include transfer by means of forbidden transitions which, it is concluded, are responsible for the transfer in all inorganic systems yet investigated. The transfer mechanisms of importance are, in order of decreasing strength, the overlapping of the electric dipole fields of the sensitizer and the activator, the overlapping of the dipole field of the sensitizer with the quadrupole field of the activator, and exchange effects. These mechanisms will give rise to "sensitization" of about 10^2 – 10^4 , 10^2 , and 30 lattice sites surrounding each sensitizer in typical systems. The dependence of transfer efficiency upon sensitizer and activator concentrations and on temperature are discussed. Application is made of the theory to experimental results on inorganic phosphors, and further experiments are suggested.

I. INTRODUCTION

ONE of the important problems of solid state physics is that of a description of the processes which follow the absorption of visible or ultraviolet light by an insulating crystal. Of the several possible general processes, luminescence has received the most experimental attention, although unfortunately there seems to be no simple crystal yet investigated for which luminescence associated with the undistorted lattice has been unambiguously demonstrated.¹ Consequently most experimental work on luminescence has dealt with systems consisting of a host lattice and one or more types of impurity atoms.^{2,3} The theoretical work in this field has not kept up with experiment for two main reasons: (1) The development of the field of luminescence, because of its commercial significance, has been

guided largely by practical considerations, with a resulting reduction in the attention directed towards development and investigation of the simplest possible luminescent systems, which might be more easily interpreted. (2) The theoretical problems of luminescence are exceedingly difficult to treat even in their simplest form, not only because they involve the simultaneous interactions among radiation, matter and phonons, but also because the specific details of the wave functions are of first-order importance. The experimental results on luminophors consisting of electronically similar impurity atoms in the same host lattice and of the same impurity atom in similar host lattices demonstrate the strong influence of the details of the coupling between the impurity atom and its surroundings and thus emphasize the "many-body" nature of the problems to be solved.

A branch of luminescence investigated in recent years, namely, "sensitized luminescence,"^{4–13} appears at first,

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¹ The edge emission of CdS [F. A. Kröger, reference 31, C. C. Klick, *Phys. Rev.* **89**, 274 (1953)] may prove to be an example of true lattice emission. A number of more complicated inorganic crystals, CaMoO_4 and CaWO_4 , for example (see references 8 and 12), apparently luminesce even in the absence of imperfections, as do a number of organic crystals, e.g., anthracene and naphthalene.

² P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949).

³ H. W. Leverenz, *Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950).

⁴ S. Rothschild, *Physik. Z.* **35**, 557 (1934); **37**, 757 (1936).

⁵ Schulman, Evans, Ginther, and Murata, *J. Appl. Phys.* **18**, 732 (1947).

⁶ J. B. Merrill and J. H. Schulman, *J. Opt. Soc. Am.* **38**, 471 (1948).

⁷ H. C. Froelich, *J. Electrochem. Soc.* **93**, 101 (1948).

⁸ F. A. Kröger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., Houston, Texas, 1948).

perhaps, to be even more complicated than the more common forms. That this is not the case is, as we shall see, a result of the difference in the questions that we may ask regarding the various processes.

According to common usage, sensitized luminescence refers to the process whereby an impurity atom (activator) having no appreciable absorption band in a given region of the (visible or uv) spectrum is made to emit radiation upon excitation in this region as a result of absorption by and transfer from another impurity atom (sensitizer) or from the host lattice. We shall refer to these distinct processes as impurity-sensitized and host-sensitized luminescence, respectively.

We may now see the relatively simple nature of the problems to be investigated. If we accept the experimental facts regarding the positions and strengths of the absorption band of the activator and the emission band of the sensitizer, we may isolate the most fundamental problem peculiar to *sensitized* luminescence as follows: What is the mechanism of the process by which the excitation energy is transferred from sensitizer to activator, and what is its efficiency as a function of temperature and of activator and sensitizer concentrations? That is, we may in this case avoid all of the difficult problems of common luminescence and concentrate on those of sensitized luminescence alone.

The purpose of this paper is to examine the above questions regarding sensitized luminescence in insulating crystals on the basis of a resonance theory of energy transfer. Such a theory does not involve transitions to or from the conduction band and hence does not take account of photoconductivity. Other theoretical work on sensitized luminescence in solids includes Mott and Gurney's¹⁴ suggestion that electrons and holes which are freed by absorption of light at the sensitizer travel through the conduction and valence bands, eventually to recombine at the activator. Such processes, involving photoconductivity, are not included within the present theory.

A resonance theory of energy transfer is of course not new. Franck, Cario, and many others have demonstrated the mechanism in gases,¹⁵ and a quantum theory was given by Kallmann and F. London.¹⁶ Transfer has similarly been shown in solutions containing organic molecules,¹⁵ and both classical¹⁷ and quantum-mechanical^{18,19} theories have been formulated for transfer

processes involving allowed transitions. Investigations of the propagation of excitons in insulators have likewise been based on resonance theories,²⁰ as has a theory of the annihilation of *F* centers by excitons.²¹

Previous theoretical work has been concerned with resonance between two allowed (electric dipole) transitions. In the common organic systems the transitions involved are allowed, and the significance of Förster's work¹⁹ has been generally recognized by workers in the organic field. However, one of the principal reasons for the interest in sensitized luminescence in inorganic solids has been that resonant transfer can be obtained between an allowed transition in the sensitizer and a forbidden transition in the activator. That is, an activator with a suitable emission spectrum (for example, manganese with a forbidden transition) can be made to luminesce after energy transfer from an absorbing sensitizer, although the activator will not absorb the energy directly.²² Clearly a description of forbidden transitions is essential.

Several authors have suggested, on the basis of the above analogies in gases and liquids, that resonant transfer occurs in the systems they have investigated.⁴⁻¹³ Some of these writers state that the transfer probability is determined by the overlapping of the wave functions of the sensitizer and activator⁹⁻¹¹ and that only when activator and sensitizer occupy adjacent lattice sites may transfer occur.^{9,10} Inspection of the above-mentioned resonance theories shows that overlap integrals between activator and sensitizer occur only in the normalization of the wave functions and are of minor importance. Furthermore, in the case of impurity-sensitization exchange intervals (which depend partially on overlap) are unimportant when strong electric dipole transitions are allowed. Previous treatments of sensitized luminescence therefore have not included exchange effects and are concerned with the overlapping of the "near-zone" electric fields, and not the wave functions. It will be shown that exchange effects become important for magnetic dipole (and higher order) transitions.

Section II contains discussions of the physical model employed here and of the procedure for normalization of the wave functions. Sections III, IV, and V treat electric dipole-dipole, dipole-quadrupole, and exchange effects and electric dipole-magnetic dipole transitions, respectively. The above all refer to impurity-sensitization, whereas Sec. VI discusses host-sensitization.

organische Verbindungen (Vandenhoeck and Ruprecht, Göttingen, 1951); (c) *Z. Elektrochem.* **53**, 93 (1949).

²⁰ The latest paper on this subject, W. R. Heller and A. Marcus, *Phys. Rev.* **84**, 809 (1951), contains references to other previous work.

²¹ D. L. Dexter and W. R. Heller, *Phys. Rev.* **84**, 377 (1951).

²² A second practical benefit of sensitization comes from the double degradation of the absorbed energy, as a result of a Stokes' shift in both the sensitizing and activating center. For example, the Hg 2537 line can be used for excitation, and emission can be obtained in the visible, as in the ordinary fluorescent lamp. (In this example it is probable that internal transitions to lower excited states of the Mn ion are responsible for part of the shift.)

⁹ Th. P. J. Botden and F. A. Kröger, *Physica* **XIV**, 553 (1948).

¹⁰ F. A. Kröger, *Physica* **XV**, 801 (1949).

¹¹ Schulman, Ginther, and Klick, *J. Electrochem. Soc.* **97**, 123 (1950).

¹² Th. P. J. Botden, *Philips Research Repts.* **6**, 425 (1951).

¹³ J. Franck and R. Livingston, *Revs. Modern Phys.* **21**, 505 (1949). This paper contains references to work on organic systems.

¹⁴ N. F. Mott and R. W. Gurney, *Electronic Process in Ionic Crystals* (Oxford University Press, New York, 1940), p. 207.

¹⁵ For references to the original work see, for example, references 2 and 13.

¹⁶ H. Kallmann and F. London, *Z. Physik. Chem.* **B2**, 207 (1929).

¹⁷ J. Perrin, *Compt. rend. Paris*, **184**, 1097 (1927).

¹⁸ F. Perrin, *J. phys. et radium* **7**, 1 (1936).

¹⁹ Th. Förster, (a) *Ann. Physik* **2**, 55 (1948); (b) *Fluoreszenz*

The transfer probabilities are evaluated from optical data in Eqs. (16), (17), (25), (26), and (30). Section VII contains a discussion of the application of the theory to experiment.

II. NORMALIZATION PROCEDURE

For the next four sections we shall be concerned with impurity sensitization in an insulating crystal. The natural physical model is that of an atomic fraction x_s of sensitizing impurity atoms or ions arranged at random on the suitable lattice sites of the crystal, without appreciable mutual interaction, and a fraction x_a of activators similarly arranged. For the present we shall assume weak concentrations x_s and x_a , such that the transfer probability from one sensitizer to another is negligible, such that the probability of the formation of new crystalline phases is negligible, and such that effects depending on pairs or clusters of activators are unimportant. Interactions of the lattice vibrations with the sensitizer and with the activator will be accounted for experimentally. Interactions between impurities and the charged bodies of the lattice will be taken into account by means of a suitable dielectric constant. A further restriction is the assumption that no photoconductivity occurs. Clearly none of these assumptions is universally valid, and certain additional effects will be discussed later.

The entire transfer process consists of five stages: (1) absorption of a photon of energy $\sim E_0$ by the sensitizer, (2) relaxation of the lattice surrounding the sensitizer by an amount such that the available electronic energy in a radiative transition from the sensitizer is $E_1 < E_0$, (3) transfer of energy E_1 to the activator, (4a) relaxation around the activator such that the available electronic energy in a radiative transition is $E_2 < E_1$, (4b) relaxation around the sensitizer to a state similar (but not necessarily identical) to its original unexcited state, (5) emission of energy E_2 .

Step 2 occurs in about 10^{-13} seconds or longer, the excess energy being dissipated to the lattice by phonons. This is the process associated with the Stokes' shift. Step 3 requires a time which depends on the distances to the surrounding activators, i.e., on the concentration x_a . If these distances are too large, we may expect the energy E_1 to appear: (a) as a photon which may or may not be absorbed by an activator atom depending on its absorption cross section and on the total number (not the concentration) of activators in the crystal, (b) as a photon which may be reabsorbed by another sensitizer, depending on whether or not the absorption and emission bands of the sensitizer overlap and upon the total number of sensitizers in the crystal, (c) as electronic excitation energy E_1 on a different sensitizer atom without a photon as intermediary, depending on the concentration x_s and on the overlap between emission and absorption bands of the sensitizer, or (d) as thermal energy following a nonradiative transition. For the present we shall not discuss these various processes, and

shall be concerned only with the probability of direct transfer to an activator.

Assuming that the latter transfer has occurred, step (4) again requires a time $\lesssim 10^{-13}$ seconds, and step (5) a time 10^{-8} seconds or much longer, depending on the forbiddenness of the transition. Since in almost all cases the Stokes' shifts are sizable, it is clear why the activator represents a "trap" for the electronic excitation energy: the activator, when excited, is not in resonance with the sensitizer, i.e., $E_2 < E_0$. Thus when appreciable relaxation occurs, as seems to be the case for most systems of interest in solids, the energy must stay on the activator atoms, and we need not concern ourselves with transfer in the opposite direction. A further stage or series of stages which may occur between steps 4 and 5, namely, radiative and nonradiative transitions to lower excited electronic states of the activator, may further decrease the probability of back-transfer, as would transfer to more distant activators. (If the activator and sensitizer are sufficiently close together, back-transfer may take place before relaxation, step 4, has time to occur. We shall not treat this case at the present time.)

We now consider the wave functions describing the above model. According to the time-dependent perturbation theory of quantum mechanics,²³ the well-known expression for the transition probability is $(2\pi/\hbar) |\langle H_1 \rangle|^2 \rho_E$ where \hbar is Planck's constant, ρ_E is the density of states, and $\langle H_1 \rangle$ is the matrix element of the perturbation to the Hamiltonian, between the initial and final states of the system. In our case, we ascribe the initial state Ψ_I to the configuration in which the sensitizer S is excited, ψ_s' , while the activator A is in its ground state, ψ_a ; and the final state Ψ_F to that in which S is in its ground state, ψ_s , while A is excited, ψ_a' . (Primed quantities will refer throughout to excited states.) Thus the probability that the energy is transferred from a particular sensitizer S to a particular activator A is of the form

$$P_{sa} = (2\pi/\hbar) \rho_E \left| \int \Psi_I^* H_1 \Psi_F d\tau \right|^2, \quad (1)$$

as long as the states Ψ_I and Ψ_F are of the same energy.

Because of lattice vibrations, of course, neither the initial nor final levels of S or A are well defined. We may therefore normalize our wave functions on an energy scale as we would for continuum wave functions²⁴ and absorb the density of states factor ρ_E within the normalization parameters. It will be convenient to normalize the initial (excited) state of S and the initial (ground) state of A in the usual manner and to introduce probability functions $p_s'(w_s')$ and $p_a(w_a)$ to ex-

²³ See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 189.

²⁴ For a discussion of this type of normalization see, for example, H. Bethe, *Handbuch der Physik* (1933), (2) 24/1, p. 273, and references contained therein. The discussion of normalization given below is similar to that in reference 19.

press the probabilities that S is in the particular energy state denoted by w_s' and that A is in the state w_a . Therefore consider

$$\int |\psi_s'(w_s')|^2 d\tau = \int |\psi_a(w_a)|^2 d\tau = 1, \quad (2)$$

$$\int_0^\infty p_s'(w_s') dw_s' = \int_0^\infty p_a(w_a) dw_a = 1.$$

For the final states we normalize the wave functions on an energy scale as follows:

$$\frac{1}{\Delta w} \int_w^{w+\Delta w} dw_s \int |\psi_s(w_s)|^2 d\tau = 1, \quad (3)$$

$$\frac{1}{\Delta w} \int_w^{w+\Delta w} dw_a' \int |\psi_a'(w_a')|^2 d\tau = 1.$$

Now the properly antisymmetrized initial and final states wave functions describing S and A can be written

$$\sqrt{2}\Psi_I(w_s', w_a) = \psi_s'(\mathbf{r}_1, w_s')\psi_a(\mathbf{r}_2, w_a) - \psi_s'(\mathbf{r}_2, w_s')\psi_a(\mathbf{r}_1, w_a) \quad (4)$$

$$\sqrt{2}\Psi_F(w_s, w_a') = \psi_s(\mathbf{r}_1, w_s)\psi_a'(\mathbf{r}_2, w_a') - \psi_s(\mathbf{r}_2, w_s)\psi_a'(\mathbf{r}_1, w_a'),$$

if only two electrons are involved in the transitions. If more than two electrons should be involved, Eq. (4) could easily be extended to express all of the possible permutations of the electrons; Eq. (4) as written will serve to show the type of term that enters because of antisymmetrization, i.e., the exchange term. The other terms, namely, Coulomb terms, are correctly given even without antisymmetrization of the wave functions. In the following \mathbf{r}_1 and \mathbf{r}_2 will be used to denote the coordinates of all the electrons involved. The atomic wave functions in (4) are normalized according to Eq. (2) and (3). If overlapping of the wave functions such as $\psi_s'(\mathbf{r}_1)$ and $\psi_a(\mathbf{r}_1)$ were appreciable, the squares of the normalization factors $\sqrt{2}$ should be reduced by quantities such as $(\int \psi_s'(\mathbf{r}_1) \psi_a(\mathbf{r}_1) d\tau_1 \int \psi_a(\mathbf{r}_2) \psi_s'(\mathbf{r}_2) d\tau_2)$; such effects are small and will henceforth be ignored. In general there will be several possible states Ψ_I and Ψ_F from and to which the system may make transitions contributing to the transfer process, depending, for example, on the polarization of the atomic functions. Then $\langle H_1(w_s', w_a; w_s, w_a') \rangle_{IF}$ is the matrix element of H_1 between particular states $\Psi_I(w_s', w_a)$ and $\Psi_F(w_s, w_a')$. It should be noticed that as a result of our type of normalization $\langle H_1 \rangle$ is now a dimensionless quantity, not an energy.

The electronic excitation energy on S in the state Ψ_I is $E = w_s' - w_s$, and that on A in the state Ψ_F is $w_a' - w_a$. According to the Franck-Condon principle, there is small probability of an electronic transition in which electronic excitation energy is lost to the lattice, so that the energy principle requires that the transi-

tion probability P_{sa} contain a Dirac delta-function $\delta[(w_s' - w_s) - (w_a' - w_a)]$. We therefore obtain for the total probability of energy transfer from S to A the result,

$$P_{sa} = (2\pi/\hbar) \sum_I \sum_F (g_s' g_a)^{-1} \times \int dw_a' \int dw_s \int dw_a p_a(w_a) \int dw_s' p_s'(w_s') \times |\langle H_1(w_s', w_a; w_s, w_a') \rangle_{IF}|^2 \times \delta[(w_s' - w_s) - (w_a' - w_a)],$$

where we omit the indices I and F on the energy parameters for the sake of brevity. The factor g_s' , the degeneracy of the level of the excited S atom or ion, is necessary to take account of the fact that only one of the possible excited states of S is occupied, whereas we subsequently sum over them all, similarly for g_a . The sums over I and F represent a sum over all possible transitions that can contribute to the transfer, that is, sums over i_s, i_a, f_s , and f_a . If the ground state of A is nondegenerate, the summation over i_a may be removed and g_a set equal to unity. Carrying out the integration over w_s by means of the delta-function and substituting $E = w_a' - w_a = w_s' - w_s$, we obtain

$$P_{sa} = (2\pi/\hbar) \sum_I \sum_F (g_s' g_a)^{-1} \times \int dE \int dw_a p_a(w_a) \int dw_s' p_s'(w_s') \times |\langle H_1(w_s', w_a; w_s' - E, w_a + E) \rangle_{IF}|^2. \quad (5)$$

III. ELECTRIC DIPOLE-DIPOLE INTERACTION

In order to compute the transfer probability [Eq. (5)] we require H_1 , the interaction between A and S . This interaction may be expressed as the sum of all the Coulomb interactions of the outer electrons and core of A with those of S , suitably reduced by the dielectric constant κ of the medium. When this sum is expanded in a Taylor series about the vector \mathbf{R} , the separation of the nuclei of A and S , the interaction energy is found to be

$$H_1(\mathbf{R}) = (e^2/\kappa R^3) \{ \mathbf{r}_s \cdot \mathbf{r}_a - 3(\mathbf{r}_s \cdot \mathbf{R})(\mathbf{r}_a \cdot \mathbf{R})/R^2 \} + (3e^2/2\kappa R^4) \{ \sum_{i=1}^3 (R_i/R) r_{ai}^2 r_{si} (-3 + 5R_i^2/R^2) + 10(XYZ/R^3)(x_a y_a z_s + x_a z_a y_s + y_a z_a x_s) + \sum_{i \neq j}^3 \sum_{j=1}^3 [(R_j/R) - 5R_i^2 R_j/R^3] \times [-r_{ai}^2 r_{sj} - 2r_{ai} r_{aj} r_{si}] \} + \dots \quad (6)$$

This is, of course, the interaction that gives rise to van der Waals' forces. The first curly brackets contain the

dipole-dipole interaction, and the second the dipole-quadrupole interaction; higher order interactions, including quadrupole-dipole, have been omitted. (We shall assume throughout that the sensitizer has an allowed transition, so that the dipole term for S gives the largest contribution.) In Eq. (6) $\mathbf{r}_s = \sum_m \mathbf{r}_{s,m}$ refers to all the electrons on S , measured from its nucleus, and similarly with $\mathbf{r}_a = \sum_n \mathbf{r}_{a,n}$; e is the magnitude of the electronic charge.

Inserting the first bracket of Eq. (6) into Eq. (5), we obtain

$$P_{sa}(dd) = (2\pi/\hbar) \sum_I \sum_F (e^4/\kappa^2 R^6) (g_s' g_a)^{-1} \\ \times \int dE \int dw_a p_a(w_a) \int dw_s' p_s'(w_s') \\ \times |\langle \mathbf{r}_s \rangle \cdot \langle \mathbf{r}_a \rangle - 3(\langle \mathbf{r}_s \rangle \cdot \mathbf{R})(\langle \mathbf{r}_a \rangle \cdot \mathbf{R})|^2, \quad (7)$$

where each matrix element, such as $\langle \mathbf{r}_s \rangle$, should be written as a function of two of the energy parameters, as $\langle \mathbf{r}_s(w_s', w_s' - E) \rangle_{i_s f_s}$. Note that the dimensions of $\langle \mathbf{r} \rangle^2$ are length squared per unit energy; note also the familiar R^{-6} dependence found in the van der Waals' energy. In Eq. (7) we have neglected all terms associated with the antisymmetrization of the wave functions. If we look at the interaction terms before expanding, we find we must compute the matrix elements of terms of the form e^2/R , $e^2/|\mathbf{R} + \mathbf{r}_a|$ and $e^2/|\mathbf{R} + \mathbf{r}_a - \mathbf{r}_s|$. Neither of the first two terms gives a nonzero matrix element in view of our neglect of overlap effects, i.e., the first two terms contain two and one factors, respectively, of the form $\int \psi_a^*(2) \psi_s(2) d\tau_2$. The third term gives rise to Eq. (7) and also to typical exchange integrals of the form $-e^2 \int \psi_s'(1) \psi_a(2) (1/r_{12}) \psi_s(2) \psi_a'(1)$. Such terms will be discussed in Sec. V; they are unimportant when dipole-dipole interactions are present. It should also be noted that each matrix element $\langle \mathbf{r} \rangle = \int \psi' \mathbf{r} \psi d\tau$ vanishes in the event that the electron spin flips during the transition. Spin-flip transitions will likewise be discussed in Sec. V.

We now average the absolute square of the matrix element in Eq. (7) over all possible orientations of \mathbf{R} and obtain

$$\langle |\langle \mathbf{r}_s \rangle \cdot \langle \mathbf{r}_a \rangle - (3/\mathbf{R}^2)(\langle \mathbf{r}_s \rangle \cdot \mathbf{R})(\langle \mathbf{r}_a \rangle \cdot \mathbf{R})|^2 \rangle_{\mathbf{R}} \\ = (2/3) |\langle \mathbf{r}_s \rangle|^2 |\langle \mathbf{r}_a \rangle|^2, \quad (8)$$

where

$$|\langle \mathbf{r} \rangle|^2 = |\langle x \rangle|^2 + |\langle y \rangle|^2 + |\langle z \rangle|^2.$$

Thus the transfer probability becomes

$$P_{sa}(dd) = \frac{4\pi e^4}{3\hbar \kappa^2 R^6 g_s' g_a} \sum_I \sum_F \int dE \\ \times \left\{ \int dw_s' p_s'(w_s') |\langle \mathbf{r}_s(w_s', w_s' - E) \rangle|^2 \right\} \\ \times \left\{ \int dw_a p_a(w_a) |\langle \mathbf{r}_a(w_a, w_a + E) \rangle|^2 \right\}. \quad (9)$$

An evaluation of these matrix elements as a function of energy is of course the foremost problem of luminescence, a problem which, as we have stated, we do not propose to discuss here. Knowing the wave functions, it would be a trivial matter to evaluate the integrals; not knowing them, it is expedient to evaluate the matrix elements directly from experiment. These same matrix elements determine oscillator strengths, absorption coefficients, and decay times, all of which are measurable quantities. We shall now express Eq. (9) in terms of these experimental parameters.

The probability of a spontaneous radiative transition of an isolated atom from a state i to a state f is given by²⁵

$$A(i f) = \frac{4e^2 E^3}{3\hbar^4 c^3} |\langle \mathbf{r}_{if} \rangle|^2, \quad (10)$$

where c is the velocity of light. For an atom in a crystalline medium this expression is to be changed in several ways. First, the energies of the initial and final states, because of vibrations of the surroundings, are not well defined, so that we introduce a probability function $p'(w')$, as in Sec. II, and normalize the final states on an energy scale. Second, we must change the expression to take account of the dielectric properties of the medium. Since the transition probability is proportional to the square of the matrix elements of the electric field dotted into the electric moment at the atom, the expression on the right-hand side of Eq. (10) is to be multiplied by the square of the ratio of the field within the crystal to that at an isolated atom, that is, by $(\mathcal{E}_c/\mathcal{E})^2$. The average value of \mathcal{E}_c within the crystal and the value of \mathcal{E} in a vacuum are to be chosen so as to correspond to the same photon density. Further, the transition probability is proportional to the density of states in momentum space, or to $k^2 dk$, where k is the propagation vector of photons in the medium. Since k is increased in a medium by the factor n (index of refraction), (10) is also to be multiplied by the factor n^3 .

In view of the above arguments, the probability of emission of a photon of energy E is

$$A(E) = \sum_i \sum_f \frac{4e^2 E^3}{3\hbar^4 c^3 g'} \left(\frac{\mathcal{E}_c}{\mathcal{E}} \right)^2 n^3 \\ \times \int |\langle \mathbf{r}_{if}(w', w' - E) \rangle|^2 p'(w') dw', \quad (11)$$

where the sum is over all transitions, and the degeneracy factor g' is introduced for the same purpose as in Eq. (5). The shape of the function $A(E)$ is given by the emission spectrum of the atom, and the integral $\int A(E) dE$ is equal to the decay constant of the level, $1/\tau$. Let the

²⁵ See, for example, N. F. Mott and I. N. Sneddon, *Wave Mechanics and Its Applications* (Oxford University Press, New York, 1948), p. 253 ff; note that there are several misprints on p. 257.

normalized function $f(E)$ represent the observed shape of the emission band, so that $\int f(E)dE=1$. Then from Eq. (11) we have the result,

$$\sum_i \sum_f \int |\langle \mathbf{r}_{if}(w', w' - E) \rangle|^2 p'(w') dw' = \frac{3\hbar^4 c^3 g'}{4\pi^3 e^2 E^3} \left(\frac{\mathcal{E}}{\mathcal{E}_c}\right)^2 \frac{1}{\tau} f(E). \quad (12)$$

Equation (12) is of course general and refers to either S or A . The left-hand side of Eq. (12), which refers to S in Eq. (9), may be evaluated experimentally by measuring the decay time and emission spectrum of S in a crystal containing a low concentration of S as its only impurity. Note that we assume no interactions between S and any other impurity in the derivation of Eq. (12). If interactions occur and change the band shape or decay time or if any competing processes occur to affect the decay time, Eq. (12) is not applicable. In general, Eq. (12) will be applicable if the concentration x_s is weak and if the quantum yield for luminescence of S is unity. If for some reason Eq. (12) cannot be applied, the left-hand side may be evaluated through absorption experiments as follows:

The usual expression for the Einstein B coefficient²⁵ for induced transitions in an isolated atom is

$$B(if) = \frac{2\pi e^2}{3\hbar^2} |\langle \mathbf{r}_{if} \rangle|^2.$$

In the event that the absorption band becomes broad, we may normalize the wave functions as previously and speak of the induced transition probability per unit energy range. Including the effect of the changed electric field in the medium, we obtain

$$B(E) = \sum_i \sum_f \frac{2\pi e^2}{3\hbar^2 g} \left(\frac{\mathcal{E}_c}{\mathcal{E}}\right)^2 \int p(w) dw |\langle \mathbf{r}_{if}(w, w + E) \rangle|^2.$$

The absorption cross section then becomes

$$\sigma(E) = \sum_i \sum_f \frac{4\pi^2 e^2 n E}{3\hbar c g} \left(\frac{\mathcal{E}_c}{\mathcal{E}}\right)^2 \int p(w) dw \times |\langle \mathbf{r}_{if}(w, w + E) \rangle|^2, \quad (13)$$

where the factor n appears because we have divided the transition probability B by a photon flux $v=c/n$. The absorption cross section, which will not in general be greatly distorted except by very large concentrations, can be measured as the ratio of the absorption coefficient (cm^{-1}) to the number density of impurities in the medium (cm^{-3}). Let us introduce therefore the normalized function $F(E)$ such that $\sigma(E)=QF(E)$, where

$\int F(E)dE=1$. Then we obtain from Eq. (13) the result,

$$\sum_i \sum_f \int p(w) dw |\langle \mathbf{r}_{if}(w, w + E) \rangle|^2 = \frac{3\hbar c g}{4\pi^2 e^2 n E} \left(\frac{\mathcal{E}}{\mathcal{E}_c}\right)^2 QF(E). \quad (14)$$

By applying this equation to the activator, if it has an observable absorption band, we may evaluate the remaining matrix elements in Eq. (9). $Q=\int \sigma(E)dE$ is measured as the area under the absorption band.

Equation (14) may also be useful for the evaluation of the sensitizer's matrix elements in the event that the quantum yield of S when present by itself is less than unity, or when the decay rate either cannot be measured or is not a simple exponential function. In such cases, we may still measure the (normalized) shape of the emission band $f_s(E)$ but may express the "strength" of the line in terms of the absorption area, Q_s . Thus we obtain the relation,

$$\sum_{i_s} \sum_{f_s} \int p_s'(w_s') dw_s' |\langle \mathbf{r}_{if}(w_s', w_s' - E) \rangle|^2 = \frac{3g_s \hbar c}{4\pi^2 e^2 n E} \left(\frac{\mathcal{E}}{\mathcal{E}_c}\right)^2 Q_s f_s(E). \quad (15)$$

It should be borne in mind that this last result is only approximate; the quantity Q_s is determined by the wave functions of S when its surroundings are in the positions characteristic of the unexcited state, whereas τ_s should be computed using wave functions in the "relaxed" lattice. Since these wave functions will in general be different in the two configurations of the lattice, the transition strength as measured by Q_s will be inexact.

Making use of Eqs. (12), (14), and (15), we may express Eq. (9) as

$$P_{sa}(dd) = \frac{3\hbar^4 c^4 Q_a}{4\pi R^6 n^4 \tau_s} \left(\frac{\mathcal{E}}{\kappa^3 \mathcal{E}_c}\right)^4 \int \frac{f_s(E) F_a(E)}{E^4} dE \quad (16)$$

with absorption data for A and emission data for S , or as

$$P_{sa}(dd) = \frac{3\hbar c^2 Q_a Q_s}{4\pi^3 n^2 R^6} \left(\frac{g_s}{g_s'}\right) \left(\frac{\mathcal{E}}{\kappa^3 \mathcal{E}_c}\right)^4 \int \frac{f_s(E) F_a(E)}{E^2} dE, \quad (17)$$

making use also of absorption data for S . We could similarly use an emission time τ_a to express the line strength for the activator, but if A has an allowed transition as assumed, Q_a can be easily measured.

The transfer probability is thus given by the strengths of the individual transitions in terms of decay times τ and absorption band areas Q and by the energy overlap of the absorption and emission bands of A and S . These quantities are all directly measurable optically except for the ratio $\mathcal{E}/\mathcal{E}_c$. We know that the average field

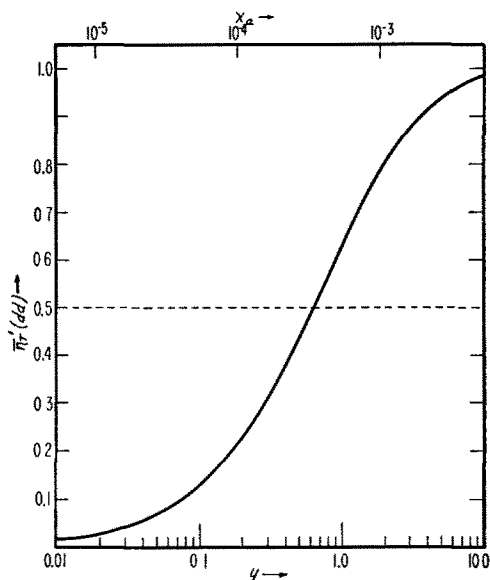


FIG. 1. Quantum yield for dd transfer as a function of the reduced concentration y of the activator. The upper abscissa represents the numerical value of the atomic concentration x_a in a typical case.

strength within the medium is reduced in the ratio $(\bar{\mathcal{E}}_c/\mathcal{E})^2 = 1/\kappa$, and we shall set the quantity $(\mathcal{E}/\kappa^{\frac{1}{2}}\mathcal{E}_c)^4$ equal to unity in the following numerical evaluation.

The foregoing discussion of the dipole-dipole transfer, based on a physical model similar to that of Förster,¹⁹ has proceeded in a manner similar to, although somewhat more general than, the development by him. It has been included here in detail for the sake of completeness and for the sake of clarity in the treatments of transfer by forbidden transitions.

Let us evaluate Eq. (16) for a typical pair of impurities. With good overlap we may expect $F_a(E)$ to overlap $f_s(E)$ with an overlap integral of $\sim 1/(3 \text{ eV})$, E to be about 5 eV, $n^4 \sim 6$, and $Q_a \sim 10^{-16} \text{ cm}^2 \text{ eV}$. Then P_{sa} becomes $(27/R)^6 (1/\tau_s)$, where R is expressed in Angstrom units. In order that appreciable transfer occur before S luminesces, $P_{sa}\tau_s$ must be $\gtrsim 1$, or transfer will occur if S and A are separated by not more than about 25 Å. For $\tau_s \sim 10^{-8} \text{ sec}$ and for S and A in adjacent positive ion sites in NaCl ($R = 3.97 \text{ Å}$), the jump time would be of the order 10^{-12} or 10^{-13} sec .

The experimentally significant quantity is the quantum yield for transfer, η_T . If we neglect nonradiative transitions in S and also neglect transfers from S to S , this quantity becomes $\eta_T = P_{sa}\tau_s / (1 + P_{sa}\tau_s)$. Defining $v = (4/3)\pi R^3$, we obtain $\eta_T = \beta^2 / (v^2 + \beta^2)$, where β is defined through the relation $P_{sa} = \beta^2 / \tau_s v^2$. In the typical case just discussed, β is $8.26 \times 10^{-20} \text{ cm}^3$, and η_T as defined is the quantum yield for transfer from an excited center S to an activator at distance $R = (3v/4\pi)^{\frac{1}{3}}$. To obtain the average yield $\bar{\eta}_T$ in a crystal, we require the integral over-all space of η_T times the probability that the nearest activator is at distance R . Let C^+ be the number density of lattice sites of the type that can ac-

commodate A , and let v_0 be the volume excluded by the presence of the sensitizer. Introducing the parameter $y = x_a C^+ \beta$, we find the average yield to be given by

$$\bar{\eta}_T = y e^{x_a C^+ v_0} \{ y^{-1} [e^{-x_a C^+ v_0} - 1] + \text{Ci}(y) \sin y - \text{Si}(y) \cos y + (\pi/2) \cos y \}, \quad (18)$$

where Ci and Si are the cosine- and sine-integral functions. For concentrations $x_a \gtrsim 1$ percent ($y \gtrsim 20$) we may set equal to unity the factors $\exp \pm (x_a C^+ v_0)$ and obtain a function of y alone,

$$\bar{\eta}_T' = y \{ \text{Ci}(y) \sin y - \text{Si}(y) \cos y + (\pi/2) \cos y \}. \quad (19)$$

A similar expression has been derived by Förster.^{19b} This function is shown in Fig. 1. For small concentrations ($y \ll 1$) $\bar{\eta}_T'$ varies as $y(\pi/2 + y \ln y - 0.4228y)$, thus demonstrating the expected linear dependence on concentration for small x_a . For $y \gg 1$, i.e., high concentrations, $\bar{\eta}_T' \rightarrow 1$, as may be seen from Eq. (18). Since $\bar{\eta}_T'$ is equal to $\frac{1}{2}$ for $y = 0.65$, according to Fig. 1, we may arbitrarily define a "critical" concentration by the relation $\bar{\eta}_T' = \frac{1}{2}$, or by

$$x_a^* = \frac{0.65}{C^+ \beta}. \quad (20)$$

For β equal to $8.3 \times 10^{-20} \text{ cm}^3$ and $C^+ = 2.25 \times 10^{22} \text{ cm}^{-3}$ (as in NaCl), x_a^* becomes 3.5×10^{-4} , and we may say that in this case S is able to sensitize 2900 sites. This large number will evidently be diminished if the overlap between emission of S and absorption of A is less than assumed above, if nonradiative processes in S reduce the natural lifetime τ_s , or if the strength of the transition in A is less than assumed above. It will clearly be further increased if S atoms are present in sufficient concentration that the excitation energy may be transferred from S to S until it resides nearer than average to an activator. For sufficiently weak concentrations x_a , of course, the transfer probability P_{sa} is independent of x_a .

Note that the critical concentration varies inversely as β , and hence as the inverse square root of the coupling integral $\int f_s(E) F_a(E) dE/E^4$ and as the inverse square root of the line strength of A . Thus even systems with poor overlap and with weak electric dipole transitions in A may take part in transfer with low concentration x_a .

It should be borne in mind that the above development is applicable not only to $S-A$ transfer, but also to $S-S$ and $A-A$ transfer. In the latter two cases the usual Stokes' shift will in general greatly reduce the overlap between emission and absorption, so that concentrations an order of magnitude higher than the above value of 3×10^{-4} may be required. The treatment is also applicable, of course, to liquid systems. The primary differences between solid and liquid systems seem to lie in the relative smallness of the index of refraction in liquid solutions and in the relative smallness of the Stokes' shifts in the liquids.

The temperature dependence of the transfer probability can be inferred from Eqs. (16) and (17). In general the strengths of the transitions as indicated by Q_a and τ_s or Q_s are roughly independent of temperature. Thus the main temperature dependence occurs in the amount of overlap between f_s and F_a . Both of these functions broaden with temperature, and in the event that they overlap perfectly at all temperatures the transfer probability will decrease with increasing temperature. However, if their centers are well separated, the broadening associated with increasing temperature will increase the overlap and hence the transfer probability. At low temperatures the broadening is negligible as compared with natural, zero-point widths, and the transfer probability should be independent of temperature. A further effect is the possible shift of the center of one function relative to the other, an effect which may either increase or decrease the probability. Such effects as these will vary from one case to the next, and are extremely difficult to calculate accurately from first principles.

Kröger⁸ has suggested that energy transfer be visualized on a "configurational coordinate" diagram, in which the energy of the center is plotted in the configuration space of the nuclear coordinates of the lattice neighbors. He presents such a diagram (in two dimensions) showing both the energy of a sensitizer and that of an activator as a function of the same configurational coordinate, and concludes that energy transfer can occur only at the point in configuration space where the curves cross, and that this point in general corresponds to specific excited vibrational states for both centers. He further concludes that the transfer process requires an activation energy and that the probability of transfer contains an exponential dependence on the reciprocal temperature, $P \sim \exp -W_s/kT$, where W_s is the energy difference between the crossing-point and the minimum of the curve representing the excited sensitizer atom. (See reference 8, p. 210.) These ideas have been developed in further detail by Botden.¹²

In two dimensions such a diagram is of course almost meaningless as is recognized by the authors. Specifically the one coordinate, if important for the sensitizer, will in general not be important for the activator, so that, whereas the sensitizer curve may be a rapidly varying function of the coordinate, the activator function will not; and the curves will in general not intersect. Also, the generalized energy surfaces for the two centers when plotted simultaneously in a multidimensional space will in general intersect at an infinite number of points with energy parameters, W_s , ranging from very close to zero (depending on the separation) up to infinity. Furthermore, these points do not represent the configurations for which transfer may occur.

With suitable modification, however, an interpretation based on configurational coordinate diagrams may be useful in some instances. The only restriction on the

transfer is that the virtual photon emitted by the sensitizer be equal in energy to that absorbed by the activator. That is, if one plots the *difference* between the energies of the excited electronic state and of the ground electronic state of the sensitizer center, and simultaneously the analogous energy difference for the activator, in the generalized coordinate space, transfer may occur with appreciable probability, according to the Franck-Condon principle, only at the intersections of these generalized surfaces of energy difference. Again there will in general exist an infinite number of such intersections; these intersections appear for all values of the energy W_s as defined above.

For example, if the low temperature emission band of S occurs at higher energy than the absorption band of A and if the centers are sufficiently far apart that the coordinates important to A do not greatly influence S , transfer may occur from S to A with no appreciable thermal activation W_s of S , but with activation only of A . The probability of achieving one of the possible configurations for transfer may in some cases be roughly proportional to $\exp -W_a/kT^*$, where $T^* = \theta \coth \theta/T$ is the "effective temperature" which takes account, through the Debye θ , of the zero-point broadening of the levels.²⁶ T^* and hence P_{sa} are independent of T for low T .

Transfer will also be possible for configurations corresponding to "activation energies" of all higher values than the minimum. Further, if S and A are close together, the minimum activation energy may be either greater or smaller than the above. In so far as the exponential dependence on W/T^* is valid, the value for W will be the smallest amount of thermal energy needed to bring S and A into resonance. The energy W_a , if present at A , may be sufficient to bring about resonance, whereas an energy W_s may be required at S . In general W_a and W_s will not be equal, and if S and A are not identical atoms, it is not possible *a priori* to say which of W_s and W_a is the smaller. If S and A are identical atoms, as in $S-S$ transfer, the least thermal energy sufficient to bring about resonance will usually be required at the excited atom, since the energy of the more spatially extended excited atom is not as strong a function of neighboring displacements as is that of the ground state. To repeat, in so far as W/kT^* represents the temperature dependence of P_{sa} , W will be the smaller of W_s and W_a . In the absence of detailed calculations we may not say which is the smaller. It should further be borne in mind that there exist many more configurations of all higher values of energy for which transfer may occur, so that the approximation by a single activation energy is expected to be valid only over a limited temperature range where W/kT^* is $\gg 1$. These complicated averaging processes over activation energies are taken account of empirically in Eqs. (5),

²⁶ K. Husimi, Proc. Phys. Math. Soc. Japan 22, 264 (1940).

(16), and (17). A transfer probability with simple exponential dependence on the reciprocal *absolute* temperature, $\exp(-W/kT)$, over a wide range of T , where W is independent of concentration x_a , seems extremely unlikely in view of the above considerations, whatever the interpretation given to W . A simple dependence on the *effective* temperature of the form $P_{sa} \sim \exp -W/kT^*$ could best be sought in systems of low concentration x_a and x_s having well-separated low temperature emission and absorption bands. It should be emphasized that all of the above considerations refer to the transfer probability itself and not to the quantum yield for the transfer process. The quantum yield will of course exhibit other temperature variation depending on non-radiative transitions within S .

An assumption that has been made throughout the foregoing treatment is that the presence of the activator does not alter the shape or position of the emission spectrum of the sensitizer. That this assumption is not precisely valid is clear both experimentally¹⁰ and theoretically. The reason for the changes in the spectra is based on the difference in the interaction between the activator and the sensitizer and that between the ion normally occupying the activator site and the sensitizer. This difference is of the same order of magnitude as each interaction alone. Each interaction is the difference between the energy perturbation to the ground state and that to the excited state of S by the other ion. Again the difference is of the same order as each energy perturbation. Thus the shift in the peak of the emission band of S must be of the same order as, or less than, the van der Waals' interaction between S and A at distance R . This energy is of the order of $\Delta E \sim E\alpha_a\alpha_s/R^6$, where E is the energy of the transition and α_a and α_s are the polarizabilities of A and S . Since α is of the order 10^{-24} cm³, it is clear that for separations R larger than nearest neighbor separations the perturbation by van der Waals forces is negligible. If A and S are nearest neighbors in the NaCl lattice, the relative energy shift $\Delta E/E$ is of the order $(2.8)^{-6} \sim 2 \times 10^{-3}$. Such a shift would be of importance in the case of very poor overlap between absorption and emission bands, but not otherwise. The perturbation for nearest neighbors and for nearest like neighbors might in some cases be somewhat larger than the above estimate as a result of exchange effects, particularly in crystals of high dielectric constant, but it seems safe to treat these perturbation effects on the spectra as of second-order importance.

IV. ELECTRIC DIPOLE-QUADRUPOLE INTERACTION

To determine the transfer probability when S makes an allowed transition and A makes a forbidden, quadrupole transition, we insert into Eq. (5) the absolute square of the matrix element $|\langle H_1 \rangle|^2$ computed from the second bracket of Eq. (6). Before inserting $|\langle H_1 \rangle|^2$ however we average over all orientations of \mathbf{R} . This

process results in

$$\begin{aligned} |\langle H_1 \rangle|^2_{\text{av}} = & \frac{9e^4}{4\kappa^2 R^8} |\langle \mathbf{r}_s \rangle|^2 \\ & \times \left\{ \frac{71}{36} [|\langle x_a^2 \rangle|^2 + |\langle y_a^2 \rangle|^2 + |\langle z_a^2 \rangle|^2] \right. \\ & + \frac{4}{3} [|\langle x_a y_a \rangle|^2 + |\langle y_a z_a \rangle|^2 + |\langle z_a x_a \rangle|^2] \\ & - \frac{8}{21} [|\langle x_a^2 \rangle \langle y_a^2 \rangle| + |\langle y_a^2 \rangle \langle z_a^2 \rangle| \\ & \left. + |\langle z_a^2 \rangle \langle x_a^2 \rangle|] \right\}, \quad (21) \end{aligned}$$

where, as before, we omit exchange terms. The usual expression for the quadrupole transition probabilities are given in terms of the double dot product of the dyadic²⁷

$$|\langle N \rangle|^2 = |\langle x^2 \rangle|^2 + |\langle y^2 \rangle|^2 + |\langle z^2 \rangle|^2 + 2|\langle xy \rangle|^2 + 2|\langle yz \rangle|^2 + 2|\langle zx \rangle|^2.$$

By summing $|\langle H_1 \rangle|^2_{\text{av}}$ and $|\langle N_a \rangle|^2$ over all D and S states we obtain the numerical relation between their matrix elements,

$$|\langle H_1 \rangle|^2_{\text{av}} = \frac{9e^4 \alpha}{4R^8 \kappa^2} |\langle \mathbf{r}_s \rangle|^2 |\langle N_a \rangle|^2, \quad (22)$$

where $\alpha = 1.266$. Thus we obtain the transfer probability from Eqs. (5) and (22):

$$\begin{aligned} P_{sa}(dq) = & \frac{9e^4 \pi \alpha}{2\hbar \kappa^2 R^8 g_s' g_a} \sum_I \sum_F \int dE \\ & \times \left\{ \int dw_s' p_s'(w_s') |\langle \mathbf{r}_s(w_s', w_s' - E) \rangle|^2 \right\} \\ & \times \left\{ \int dw_a p_a(w_a) |\langle N_a(w_a, w_a + E) \rangle|^2 \right\}. \quad (23) \end{aligned}$$

We may relate the quantities in the brackets in Eq. (23) to either absorption or emission data as in Sec. III. The first quantity, referring to the sensitizer, can be expressed either as in Eq. (12) or as in Eq. (15), depending on whether or not the decay time τ_s is known and meaningful. The quadrupole matrix elements should properly be expressed in terms of absorption curves, but unfortunately there is little hope of obtaining such data for the following reasons. The strength of a quadrupole transition is ordinarily weaker by a factor of $(a/\lambda)^2$ than an electric dipole transition, where a is the radius of the atom and λ the wavelength of the ab-

²⁷ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), p. 96.

sorbed light, or is weaker by a factor $\sim 10^{-7}$. Since the absorption coefficient resulting from a ten percent impurity with an allowed transition is of the order 10^4 cm^{-1} , ten atomic percent of the activator with a forbidden, quadrupole transition will have an absorption coefficient of only 10^{-3} per cm and thus will not be measurable. We may relate the matrix elements to the emission band, however, since decay times of the order $(10^{-8})/(10^{-7})=0.1$ sec can easily be observed. The spontaneous emission probability²⁷ is related to $|\langle N \rangle|^2$ through the relation,

$$\sum_a \sum_{f_a} \int p_a(w_a) dw_a |\langle N(w_a, w_a+E) \rangle|^2 = \frac{10\hbar^6 c^5 g_a'}{E^5 e^2 \tau_a n^3} \left(\frac{\mathcal{E}}{\mathcal{E}_c} \right)^2 F_a(E), \quad (24)$$

where we have included the effects of the medium and of broadening as in Eq. (11). Using Eqs. (22), (12), and (23), we find

$$P_{sa}(dq) = \frac{135\pi\alpha\hbar^9 c^8}{4n^6 R^8 \tau_a \tau_s} \frac{g_a'}{g_a} \left(\frac{\mathcal{E}}{\kappa^{\frac{1}{2}} \mathcal{E}_c} \right)^4 \int \frac{f_s(E) F_a(E)}{E^8} dE. \quad (25)$$

If τ_s is not obtainable or significant, we may use Eq. (15) instead of Eq. (12), with the result

$$P_{sa}(dq) = \frac{135\alpha\hbar^6 c^6 Q_s}{4\pi n^4 R^8 \tau_a} \times \frac{g_a' g_s}{g_a g_s'} \left(\frac{\mathcal{E}}{\kappa^{\frac{1}{2}} \mathcal{E}_c} \right)^4 \int \frac{f_s(E) F_a(E)}{E^6} dE. \quad (26)$$

Again it should be recalled that these line strengths are given only approximately by Q_s and τ_a for the same reason as that given following Eq. (15); that is, the strengths should be properly expressed in terms of τ_s and Q_a if these parameters were known. Note the inverse eighth-power dependence on R .

The ratio of the dipole-quadrupole transfer probability to the dipole-dipole probability is found from Eqs. (25) and (16) to be $(45\alpha/4\pi^2)(n\lambda/R)^2 \tau_a(d)/\tau_a(q)$, where we have made use of Eqs. (12) and (14). Now a quadrupole radiative transition [compare Eqs. (24) and (12)] has a probability of the order $(a/\lambda)^2$ times that for a dipole transition. Inserting $\tau_a(d)/\tau_a(q) \sim (a/\lambda)^2$, we find $P_{sa}(dq)/P_{sa}(dd)$ to be of the order $(a/R)^2$, which amounts to only an order of magnitude or so reduction for close neighbors. We see therefore that resonance transfer can easily occur from a sensitizer to a nearby activator if the latter has a quadrupole transition in the suitable frequency range; on the other hand, direct absorption of radiation in the activator occurs with a probability only $\sim 10^{-7}$ of that in an impurity with an allowed transition.

The dependence on concentration is found as in the last section. We define γ through the relation $P_{sa}(dq)$

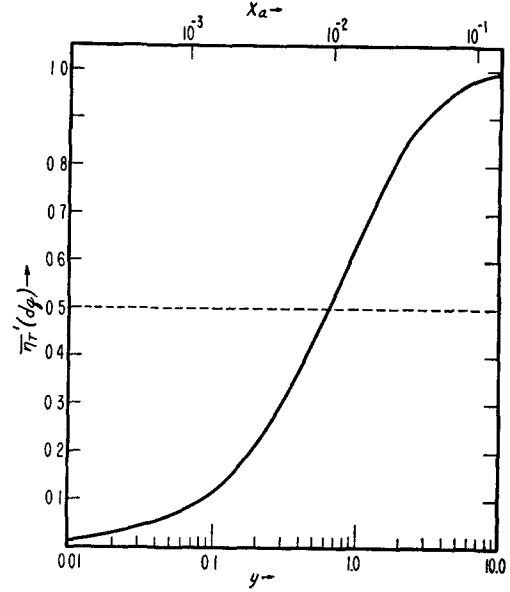


FIG. 2. Quantum yield for dq transfer as a function of the reduced concentration γ of the activator, as in Fig. 1. Typical atomic concentrations are shown on the upper abscissa scale. Note the more rapid variation of $\bar{\eta}_T'$ with concentration in the dq case than in the dd case.

$= \gamma^{8/3}/v^{8/3}\tau_s$, and letting $\gamma = \gamma C^+ x_a$, we find

$$\bar{\eta}_T = \gamma e^{x_a C^+ v_0} \left\{ \gamma^{-1} [e^{-x_a C^+ v_0} - 1] + \int_0^\infty \frac{e^{-vt}}{1+t^{8/3}} dt \right\}, \quad (27)$$

$$\bar{\eta}_T' = \gamma \int_0^\infty \frac{e^{-vt}}{1+t^{8/3}} dt. \quad (27')$$

The integral has been evaluated numerically as a function of γ and is shown in Fig. 2. Since concentrations x_a higher than 1 percent may be of interest in the dq transfer, it is not permissible to replace $\exp \pm (x_a C^+ v_0)$ by unity in the general case, and consequently $\bar{\eta}_T$ is not a function of γ alone in part of the range of interest. Figure 2 shows therefore the function $\bar{\eta}_T'(\gamma)$, and for high concentrations ($x_a > 1$ percent), $\bar{\eta}_T$ will require the indicated corrections. If we accept $\bar{\eta}_T' = \frac{1}{2}$ as the criterion for appreciable transfer, we find again that $\gamma = 0.65$ determines a critical concentration, $x_a^* = 0.65/\gamma C^+$. In a typical case [Eq. (25)] we may expect $E = 5$ ev, $n^6 = 13$, $\tau_a = 0.1$ sec, $g_a'/g_a = 5$, $\int f_s(E) F_a(E) dE = 1/(3 \text{ ev})$, and $C^+ = 2.25 \times 10^{22} \text{ cm}^{-3}$, so that γ becomes $3 \times 10^{-21} \text{ cm}^3$ and x_a is 0.96×10^{-2} . Thus S may be expected to sensitize about 100 sites. As is to be expected from the stronger R dependence in the dq case, $\bar{\eta}_T'$ is a somewhat more rapidly varying function of x_a in the dq case than in the dd case. The discussion of the temperature dependence given in the last section is also applicable to dq transfer.

One final remark should be made regarding the function $F_a(E)$, the absorption shape function for A . This function cannot be determined directly from experi-

ment because the absorption cannot be observed. Some idea as to its shape may be inferred in some cases from that of the observable emission band, but the energy of its center will still be unknown. The calculation of $F_a(E)$ is a difficult task, but some qualitative success may be expected from application of the methods of Lax, Huang and Rhys, Williams, and others.²⁸

V. EXCHANGE EFFECTS AND ADDITIONAL FORBIDDEN TRANSITIONS

We shall be concerned in this section with effects of the electron spin and shall therefore write out explicitly the matrix element of H_1 in terms of the wave functions $\psi(\mathbf{r}, \sigma) = \varphi(\mathbf{r})\chi(\sigma)$, where $\chi(\sigma)$ are the spin wave functions.

$$\begin{aligned} \langle H_1 \rangle = & \int \varphi_s'^*(\mathbf{r}_1) \varphi_a^*(\mathbf{r}_2) H_1 \varphi_s(\mathbf{r}_1) \varphi_a'(\mathbf{r}_2) \\ & \times \chi_s'^*(\sigma_1) \chi_a^*(\sigma_2) \chi_s(\sigma_1) \chi_a'(\sigma_2) \\ & - \int \varphi_s'^*(\mathbf{r}_1) \varphi_a^*(\mathbf{r}_2) H_1 \varphi_a'(\mathbf{r}_1) \varphi_s(\mathbf{r}_2) \\ & \times \chi_s'^*(\sigma_1) \chi_a^*(\sigma_2) \chi_a'(\sigma_1) \chi_s(\sigma_2). \end{aligned}$$

The first term in $\langle H_1 \rangle$ is the Coulomb term with which we have been concerned in the last two sections. Since in the approximation of Eq. (6) H_1 does not operate on the χ 's, we see the previously mentioned selection rule against spin-flip transitions, i.e., unless $\chi_s' = \chi_s$ and $\chi_a = \chi_a'$, the first integral vanishes. Thus all our results so far are applicable only to transitions in which all the spins are unchanged. The second integral is an exchange integral with $H_1 = e^2/\kappa r_{12}$. Ignoring the χ 's for the moment, we see that this integral merely represents the electrostatic interaction between the two charge clouds $Q'(\mathbf{r}_1) = \varphi_s'^*(\mathbf{r}_1) \varphi_a'(\mathbf{r}_1)$ and $Q(\mathbf{r}_2) = \varphi_a^*(\mathbf{r}_2) \varphi_s(\mathbf{r}_2)$; since each function φ dies off exponentially with distance from S or A , it is clear that each product Q will be very small throughout all space unless S and A have small separation. If the separation is small, both functions Q will be sizeable in the same region of space, namely, between S and A where r_{12} is small; thus the integral $\int Q'(\mathbf{r}_1) (1/r_{12}) Q(\mathbf{r}_2) d\tau_{12}$ may well be sizeable (for small R) even though the overlap integrals $\int Q(\mathbf{r}) d\tau$, which enter in normalization, are negligibly small.

Let us now look at the selection rules in the exchange integrals. Unless $\chi_s' = \chi_a'$ and $\chi_a = \chi_s$ the integral vanishes. However χ' is not necessarily equal to χ , so that the spin functions on both atoms may change simultaneously. If such a transition is forbidden on S (or A) by the Pauli principle, however, the spin function on A (or S) may not change either.

Other selection rules occur in the exchange integrals over the spatial variables, but in each case they forbid only specific transitions and do not preclude all transitions in any symmetry class. Thus, although all Cou-

lomb integrals may vanish, exchange will allow transfer to and excitation of A by all types of allowed and forbidden transitions, including, for example, $L=0$ to $L=0$ transitions.

The transfer probability by the exchange mechanism may be written in the form

$$P_{sa}(ex) = (2\pi/\hbar) Z^2 \int f_s(E) F_a(E) dE, \quad (28)$$

where Z^2 , a quantity that cannot be directly related to optical experiments, is defined by

$$Z^2 = \sum_I \sum_F \frac{e^4}{g_s' g_a k^2} \left| \int Q'(\mathbf{r}_1) \frac{1}{r_{12}} Q(\mathbf{r}_2) d\tau_{12} \right|_{IF}^2. \quad (29)$$

Note that the φ 's and Q 's are normalized over space (and not on an energy scale) so that Z^2 has the dimensions of energy squared. The separation and concentration dependences are hidden in Z^2 , which varies approximately as $Y(e^4/\kappa^2 R_0^2) \exp(-2R/L)$, where L is an effective average Bohr radius for the excited and unexcited states of the atoms S and A , and Y is a dimensionless quantity $\ll 1$ which takes account of the cancellation as a result of sign changes in the wave functions. If S and A occupy nearest like lattice sites in an ionic crystal such as NaCl, a typical transfer time would be of the order 10^{-10} – 10^{-11} seconds; if S and A occupy second nearest like lattice sites, the probability would be reduced by a factor of the order of 10^{-2} . In insulators with large dielectric constants the excited state wave functions may extend over very large volumes, so that Q' is sizeable even for R of the order 2 or 3 R_0 ; nevertheless the ground-state wave functions are relatively little influenced by the dielectric constant, are much more compact, and make Q negligibly small for $R \sim 2R_0$. Thus it seems unlikely even in a crystal of large κ that exchange may transfer excitation energy farther than the shell of third nearest like lattice sites. The NaCl structure contains, in the first shell, 12, in the second shell, 6, and in the third shell, 24 like lattice sites. Thus probably about 40 is an upper limit for the number of sites sensitizable by the exchange mechanism, or in other words the exchange mechanism is slightly less efficient than is dq transfer.

Another type of transfer mechanism may be investigated by including magnetic fields in the Hamiltonian. We may thereby obtain transfer by an electric dipole-magnetic dipole (em) process. The probability for this process will be seen to be negligibly small compared to that for exchange transfer when exchange is allowed by the spin selection rules.

The most important term in H_1 involving the magnetic field is of the form

$$\frac{e\hbar}{2mc} \mathbf{H} \cdot (\mathbf{r}_a \times \nabla_a + i\sigma_a),$$

²⁸ See M. Lax, J. Chem. Phys. **20**, 1752 (1952) for further references.

where \mathbf{H} is the magnetic field at A due to the motion of charge at S . The largest term in \mathbf{H} is of the order $(e/c)\mathbf{R} \times \mathbf{v}_s/R^3$, or $(eh/mc)\mathbf{R} \times \nabla_s/R^3$. Thus $\langle H_1 \rangle$ has the magnitude $(e^2\hbar^2/2m^2c^2R^2) \langle \nabla_s \rangle$ or, since $\langle \nabla_s \rangle = mE(\mathbf{r}_s)/\hbar^2$, we find

$$|\langle H_1(em) \rangle|^2 / |\langle H_1(dd) \rangle|^2 \sim (e^2/\hbar c)^4 E^2 / (e^2/R)^2. \quad (30)$$

For nearest neighbors therefore the em transfer probability is of the order 10^{-8} times that for the dd process, or of the order 10^4 sec^{-1} , and is clearly negligibly small.

VI. HOST-SENSITIZATION

From the viewpoint of the theory of solids, sensitization by the lattice itself rather than by impurities is the more interesting type, since such experiments are in principle capable of yielding information characteristic of the pure lattice, specifically information about excitons. Most of what has been said in the last four sections is likewise applicable to host-sensitization, except for the obviously nonvalid assumption that x_s is small enough that $S-S$ transfers do not occur. In general the transition in S will be an allowed, electric dipole transition as before; however, with concentrations x_s equal to unity a magnetic dipole transition in S having a probability $\sim 10^{-5}$ that of an allowed transition will give rise to an absorption coefficient of the order 10 per cm, so that appreciable radiation may be absorbed in a 1-mm thick crystal. In the latter case of course the transfer mechanism from S to S is by exchange, and similarly from S to A . If S has an allowed transition the transfer mechanism will usually be a dd process from S to S and, depending on the degree of forbiddenness of the transition in A , either a dd process, a competition between dq and exchange, or exchange from S to A . For the same reasons as previously mentioned, transfer from A to S will in many cases be highly improbable because of relaxation effects.

It is important to distinguish between two types of exciton propagation from S to S . In one case, where the transition in S is strong, with an oscillator strength of order unity, the jump time is of the same order as, or shorter than, nuclear readjustment times, namely, 10^{-13} sec [see Eq. (16)]; in this case step 2 in Sec. II, i.e., lattice relaxation, does not occur, and S' remains in resonance with all other S atoms so that P_{ss} is not greatly influenced by the temperature. (With the effective mass of the exciton independent of T and its kinetic energy proportional to kT for high T , its velocity and hence reciprocal jump time vary as $T^{1/2}$, after the exciton becomes thermalized.) For this type of transfer the use of configurational coordinates, based on the adiabatic approximation, is not justified.²⁹ Thus the exciton travels rapidly through the lattice, being scattered frequently by lattice vibrations, until it is thermally decomposed,³⁰ until it recombines optically

or thermally, or until it meets with an imperfection.²¹ If the transition in A is in resonance with that in S , the probability of transfer to A is large, $\sim 10^{13} \text{ sec}^{-1}$ for nearest neighbors if A has an allowed transition, $\gtrsim 10^{11} \text{ sec}^{-1}$ if not. In the former event there is likewise high probability for transfer back to some S before the occurrence of lattice relaxation which would end the transfer process. In the latter case the transfer probability P_{sa} will in general be less than, say, 10^{-1} or 10^{-2} times the probability that the energy will be transferred to another S ; on the other hand the distortion of the lattice associated with the presence of A may tend to keep the exciton in its vicinity, and of course if $S-A$ transfer should occur, nuclear readjustments would have time to occur and would assist in preventing transfer back to an S atom. Both of these effects will tend to keep the efficiency of sensitization high.

In the second type of propagation, where the oscillator strength for the transition in S is small, nuclear readjustment will take place on S before transfer occurs. In this case P_{ss} may be strongly temperature dependent (except at low T) since the excited atom S' in the relaxed lattice may be far from resonance with its neighbors S . The exciton will in this case move with an effective mass characteristic of nuclear masses, and P_{ss} may be reduced by many orders of magnitude from that for the other case discussed. If A is in resonance with the excited S in the relaxed lattice, however, P_{sa} may still be of the same magnitude as above, namely, $10^{13} - 10^{10} \text{ sec}^{-1}$ depending on the forbiddenness of the transition.

For either type of propagation S to S , the dependence of $\bar{\eta}_T$ on x_a is complicated greatly by the existence of other mechanisms for destroying the excitons. If thermal annihilation is unimportant, we might expect $\bar{\eta}_T$ to become and remain close to unity for $x_a \gg$ the concentration of other imperfections x_i since, experimentally, radiative processes in S are usually unimportant for x_i as small as attainable. For appreciable transfer to occur when thermal processes are important, however, the concentration x_a must be sufficiently large that $(x_a C^+)^{-1}$ is as small as the diffusion length of the exciton.

The temperature dependence of P_{sa} is about the same as was discussed in Sec. III, with the added complication that with increasing temperature the trapping of the exciton around A becomes less probable. The temperature dependence of P_{ss} may be weak, as in the first type of $S-S$ transfer above, or may be strong and complicated as for P_{sa} , in the second type. Botden¹² has presented an interpretation of host-sensitization data on Sm-activated CaWO_4 and SrWO_4 along the lines of Kröger's arguments⁸ discussed in Sec. III. His interpretation of the temperature dependence is as follows: At low temperatures he believes that only the radiative energy absorbed at the tungstate (S) sites nearest neighbors to the Sm (A) can be transferred to the Sm and that the transfer occurs without an activation energy. From all other WO_4 sites, he supposes an activation energy to be required in order to transfer to

²⁹ R. Peierls, Ann. Physik **13**, 905 (1932).

³⁰ Paul Leurgans, thesis, to be published.

the nearest WO_4 sites, so that at higher temperatures ($\gtrsim 200\text{K}$) the quantum yield increases. In order to explain the low temperature behavior Botden postulates *ad hoc* that in the $S-A$ transfer the Sm is raised to an excited electronic state exactly in resonance with the WO_4 transition, from which it jumps to a lower excited electronic state and from which finally the Sm emits. An alternative interpretation may be made which avoids the above assumption and still fits the temperature data: The postulate of more than one excited electronic state is unnecessary since relaxation around the Sm will prevent back-transfer, and the assumption of precise resonance to explain the absence of a temperature dependence at low temperature is unnecessary since thermal broadening of absorption and emission lines is small in comparison with zero-point widths at low T .

In the above system the oscillator strength for the transition in S is small, since the transition probability in the WO_4 group is $\sim 10^5$ per sec. Thus the second type of $S-S$ transfer is operative, and as we have seen above and in Section III, this type of transfer will also have a probability independent of T for low T . We might expect then a total probability of transfer from the initial tungstate ion to the Sm to depend on the temperature through a factor of the type $\exp-(W_{sa} + nW_{ss})/kT^*$, where n is the number of $S-S$ transfers required. A simple dependence such as this is to be expected only when complicating factors of the type discussed in Section III are unimportant.

VII. CONNECTION WITH EXPERIMENT

Sensitized luminescence experiments on the simplest transfer mechanism discussed above, namely, the dd transfer mechanism, do not seem to have been reported in the literature for simple inorganic systems. Probably this experiment has been neglected for two reasons: (1) If A has an allowed transition, it can absorb radiation itself and hence requires no sensitizer in order to be excited. It should be recalled, however, that the second reason for the practical interest in sensitization, namely, a double degradation of the energy, is still operative, so that, for example, the 2537 Hg line could be used to excite visible emission of short lifetime in the event that two sizeable Stokes' shifts (~ 1 ev each) can be employed. (2) In some experimental systems there might be difficulty in distinguishing dd transfer from a cascade phenomenon. In the latter process, where a photon is emitted by S and reabsorbed by A , the quantum yield for transfer depends not on the concentration x_a alone but also on the size and shape of the system. Neglecting dd transfer, we find the quantum yield for transfer by the cascade mechanism is equal to

$$\bar{\eta}_T(C) = A \nu \int f_s(E) [1 - e^{-C + x_a l \sigma(E)}] dE,$$

where the average is performed over the linear dimension l of the sample. $1 - \bar{\eta}_T(C)$ is the probability that a

photon emitted from S will leave the system. We neglect $S-S$ transfer of all types. Note that the critical concentration for this process varies inversely as the strength of the transition in A and inversely as the average size of the sample. See Eq. (20) for a comparison with dd transfer. The quantity $x_a C l$ represents the number of activators per cm squared projected on a plane perpendicular to the path of the photon. In a spherical system of a given volume containing a given concentration x_a the quantum yield will be much larger than for the same system flattened out into a thin film. We found $\bar{\eta}_T(dd)$ to be independent of the shape of the sample, or of its size. As an example to illustrate the orders of magnitude involved, let us consider a spherical sample of 1-mm radius, containing a concentration $x_a = 3 \times 10^{-4}$. Let us further assume the system to be characterized by those parameters given in Sec. III so that $\bar{\eta}_T(dd)$ is equal to $\frac{1}{2}$. For convenience let us assume that both $f_s(E)$ and $\sigma(E)$ are step functions each 1 ev wide, and that they overlap by $\frac{1}{2}$ ev. These specific assumptions are in agreement with the value of the overlap integral between emission and absorption assumed in Sec. III. We find $\bar{\eta}_T(C)$ to be $\frac{1}{3}$, as corresponds to the circumstance that practically all of the radiation emitted in a frequency range which can be absorbed by A is absorbed, and all the rest is transmitted. If the concentration x_a is increased to 3×10^{-3} , $\bar{\eta}_T(dd)$ is increased to almost 1 (see Fig. 1), but $\bar{\eta}_T(C)$ is still $\frac{1}{3}$. This example serves to illustrate the difference in the dependence of the two transfer mechanisms upon overlap of emission and absorption. If the emission band of S were 1 ev wide and the absorption band of A were 3 ev wide and covered the S emission range, the overlap integral $\int f_s(E) F_a(E) dE$ would be unchanged, and hence $\bar{\eta}_T(dd)$ would be unchanged. On the other hand the quantum yield $\bar{\eta}_T(C)$ would now be > 0.99 for $x_a > 3.1 \times 10^{-5}$. If the sphere were flattened out into a thin film, say 10^{-4} cm thick, $\bar{\eta}_T(dd)$ would still be $\frac{1}{2}$ for $x_a = 3 \times 10^{-4}$, but $\bar{\eta}_T(C)$ would be close to zero regardless of the particular shape of the overlap integrand.

Thus the two distinctions between cascade and resonant transfer occur in the dependence of the cascade transfer probability on the size and shape of the sample and on the details of the overlap of the absorption and emission spectra of A and S . Cascade effects can be made unimportant experimentally by dealing with thin samples of systems in which the overlapping of spectra is poor. For further discussion of this topic the reader is referred to reference 19(b), (c).

A second point should be emphasized in connection with the dd transfer: Because of the high efficiency of the transfer mechanism, it should be possible to utilize as a sensitizer an impurity which, even when present by itself, will not luminesce appreciably because of competing nonradiative processes. For example, let the thermal lifetime be denoted by τ_N , so that the quantum

yield for transfer becomes

$$\bar{\eta}_T' = \int_0^\infty \frac{\tau_s P_{sa} x_a C^+ dv e^{-x_a C^+ v}}{1 + \tau_s/\tau_N + P_{sa}\tau_s}.$$

The value of the integral is given by Eq. (19) in which y is to be replaced by $y(1 + \tau_s/\tau_N)^{-1}$. Hence if non-radiative processes within S are one hundred times more probable than emission from S , a concentration x_a ten times larger than the value of 3×10^{-4} obtained previously will result in efficient transfer. Thus though S , when present alone in the lattice, may luminesce with an efficiency as low as one percent, it may still serve as an excellent sensitizer for several hundred lattice sites. These considerations have only partial applicability to the dq and exchange processes. If $\tau_s/\tau_N \sim 10^2$, concentrations of the order ten percent are required for appreciable transfer.

An experimentally important process has so far been entirely neglected, i.e., concentration quenching.^{30a} Although the precise mechanism for this process is not understood, it is nevertheless clear experimentally that quenching effects occur for concentrations x_a as large as those required for efficient transfer by means of the dq and exchange mechanisms. Thus it is impossible in many cases to isolate experimentally the $S-A$ transfer process from quenching phenomena. This circumstance is a further argument for the investigation of simple dd systems in attempting to understand sensitized luminescence in general; such systems might consist of impurities such as Tl, Pb, Ag, Cu in the alkali halide lattices.

One of the commonly used luminescent impurities is Mn, which exhibits visible emission in a wide variety of host lattices,^{6-11,31} as well as in manganese salts.^{8,32} Klick and Schulman³² have compared the absorption spectrum of Mn^{++} in $MnCl_2$ with the atomic absorption spectrum, and have correlated the levels in solids with the corresponding levels in the isolated atoms. This correlation shows a number of spin-flip and quadrupole transitions in the wavelength range of 2370–5500Å; these transitions are probably those of importance in the process of transfer to Mn when used as an activator. It seems probable that the Mn ion when excited by any of these transitions is able to undergo nonradiative transitions into the lowest excited electronic state, from which it emits with a large Stokes' shift. It is difficult in practice to distinguish transfer by the dq process from that by the exchange process (which alone may excite the Mn in a spin-flip transition) since

the critical concentration of Mn would be of the same order of magnitude for both processes and since the absorption shape $F_a(E)$, and hence P_{sa} , are unknown. Quenching effects will also make difficult such a separation. If in any particular case the critical concentration turns out to be \gtrsim one percent, it would appear safe to assert that transfer is by the dq , rather than the exchange, process; if x_a is $>$ two percent it might *a priori* be either mechanism if both types of levels were known to exist in the general energy region capable of excitation by S . Critical concentrations of Mn of the order of three percent have been observed experimentally in $CaSiO_3:Pb+Mn$ ^{9,11} and in $Ca_3(PO_4)_2:Ce+Mn$.⁹ Botden and Kröger⁹ have assumed that transfer may occur only to nearest neighbors and have accepted the relatively low critical concentration of Mn as evidence for the preferential formation of pairs $Ce+Mn$ and $Pb+Mn$. Since transfer is not restricted to nearest neighbors, however, preferential pair formation is not necessarily indicated by these experiments.

From host-sensitization experiments one hopes to obtain information on several aspects of excitons: (1) From the use of activators with measurable absorption spectra can be determined the amount of Stokes' shift, if any, within the host-sensitizer. Since most pure lattices do not emit, the above information is not obtainable by direct means. (2) By varying the concentration x_a the diffusion length of the exciton may be found. (3) If such measurements are made as a function of temperature, indirect evidence may be inferred as to the thermal processes of the exciton. (4) Experiments that utilize directly the detecting properties of the activator for excitons may readily be imagined. For example, assume that a suitable activator has been found, say in the course of experiment (1) above, such that upon its introduction as an impurity some particular crystal becomes luminescent upon irradiation in the first fundamental absorption band. Then evaporate onto one face of a thin "perfect" crystal a layer of the same material containing the activator in high concentration, irradiate the other face of the crystal in the first fundamental absorption band, and measure the resulting luminescence. For a crystal of thickness much greater than 10^{-6} cm essentially none of the incident light will remain unabsorbed, and if luminescence is observed on the back face (and if photoconductivity is absent) the excitons must have travelled through the crystal. Such an experiment is in principle capable of measuring directly the diffusion length for an exciton, and if successful would be the first experimental proof of its motion. (The elegant experiments by Apker and Taft³³ on alkali halides were performed with a concentration of imperfections so large that, were there reasons to doubt the motion of excitons, the same interpretation²¹ which has been based on their motion could

^{30a} A manuscript is in preparation discussing concentration quenching from the point of view of resonance transfer of energy, i.e., $S-S$ transfer, in ordinary systems containing one impurity. It is concluded that $S-S$ transfer is the critical process for systems of low dielectric constant and small Stokes' shift.

³¹ F. A. Kroger, *Luminescence in Solids Containing Manganese* (Van Campen, Amsterdam, 1940).

³² C. C. Klick and J. H. Schulman, *J. Opt. Soc. Am.* **42**, 910 (1952).

³³ L. Apker and E. Taft, *Phys. Rev.* **83**, 479 (1951), and several earlier papers.

also be satisfactorily based on the nearness of every halide ion to a vacancy or F center.)

The difficulty of the above experiment of course resides in obtaining a "perfect" crystal sufficiently thin. An evaporated film would surely be so full of imperfections that the exciton's diffusion length would be less than or about the absorption depth of the incident light. If the diffusion length D in a good single crystal should be much larger than Heller and Marcus' estimate,²⁰ 10^{-4} cm, a crystal could probably be cleaved and annealed successfully, but if D is $<10^{-4}$ cm the experiment must await new methods of preparation of perfect thin films. Since the interaction between excitons and ionic crystals is large,^{21,30} the experiment might best be performed with non-ionic materials.

The most thoroughly investigated systems so far reported are the tungstates of Cd and Zn and the tungstate and molybdate of Ca, all activated with Sm.¹² The WO_4 and MoO_4 ions are the sensitizers in these crystals. The interpretation by Botden and Kroger of the temperature dependence has been discussed above in Section VI, and modifications have been presented. Several tentative conclusions may be drawn from these experiments. With a radiative decay time of $\sim 10^{-5}$ sec in the WO_4 ion, or an oscillator strength of the order 10^{-3} , the exchange mechanism is probably the operative method for $S-S$ transfer, and in the absence of relaxation effects, each jump time would be perhaps 10^{-10} sec. However, the tungstate excitation and reflection spectra¹² indicate that the tungstate absorption peaks at $\lesssim 2400\text{\AA}$, whereas the emission occurs at 4200\AA . Thus the lattice relaxation around the excited tungstate ion gives rise to a large Stokes' shift of 2.2 eV, throwing the excited tungstate ion far out of resonance with its neighbors. Consequently, we expect exceedingly slow migration of the energy from S to S , and, since the exciton must arrive within two or three shells of the Sm for $S-A$ transfer to occur, it is not surprising that the transfer yield is low (~ 5 percent) even for concentrations x_a as large as a tenth of a percent. The transfer to the Sm occurs by means of the short-range exchange mechanism since the transition within the Sm ion is forbidden, and that in the WO_4 ion is weak. That the Sm transition is a magnetic dipole transition is indicated by the decay time of the Sm luminescence, 10^{-3} sec, and by the weakness of the Sm absorption bands in the crystal. The relatively weak exchange mechanism is made still weaker by the poor overlap between the absorption of the Sm ion (centered at 3650\AA) and the WO_4 emission (4200\AA). We nevertheless expect a much

higher probability for energy transfer from WO_4' to a nearby Sm than from WO_4' to WO_4 because of the large Stokes' shift in the tungstate ion.

Subsequent to the preparation of this manuscript a paper by Botden³⁴ has appeared, containing new experimental results for the impurity-sensitized systems $\text{Ca}_3(\text{PO}_4)_2:\text{Ce} + \text{Mn}$, $\text{Sr}_3(\text{PO}_4)_2:\text{Sn} + \text{Mn}$, $3\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2:\text{Sb} + \text{Mn}$, $\text{Ca}_2\text{P}_2\text{O}_7:\text{Sn} + \text{Mn}$, and $\text{CaCO}_3:(\text{Pb or Tl}) + \text{Mn}$. Botden has analyzed his results on the basis of resonant transfer from S to A and includes S to S transfer in his interpretation. Experimentally he finds that about 30 or 40 sites may be sensitized by S , in agreement with our expectations above on the basis of the exchange mechanism (in the absence of an allowed transition in the Mn). He also finds experimentally that $S-S$ transfer may occur to one of the 150 nearest neighbors. Using Eq. (17) one may predict a critical separation of 23A. From the $\text{Ca}_3(\text{PO}_4)_2$ molecular weight (310) and macroscopic density (3.14 gm/cm^3), the present writer estimates the cation site concentration to be $1.8 \times 10^{22} \text{ cm}^{-3}$, and thus about 1000 sites to be within 23A of the sensitizer. Such a discrepancy, about a factor of 6, would be too large to overlook in a careful interpretation. Since Botden's determination of the number of sites depends on the zeroth, first and second derivatives of the experimental curves of transfer efficiency *versus* S concentration, and depends in a complicated and unknown way on a number of drastic simplifying assumptions, it is probably not profitable to emphasize the discrepancy at this time.

In addition to the statistical analysis to obtain the number of sites sensitized by S , Botden³⁴ discusses the temperature dependence of the transfer probability along the same lines as in references 8 and 12. The same modifications are suggested here as were made to references 8 and 12 in Secs. III and VI.

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³⁴ Th. Botden, Philips Research Rept. 7, 197 (1952).