for iron,[1] as expected on the basis of the electron concentration,[1] while for the Sb alloy it is slightly higher. These differences are well outside of the experimental error.

It is interesting to observe that for Re in iron the effective field is of the same order of magnitude as that previously found for Au in iron,[4] but that the value for Sb is much smaller. On the basis of γ-ray anisotropy measurements, Samoilov et al.[4] give $H_{eff} \geq 280$ kOe for

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[4] B. N. Samoilov, V. V. Sklyarevskii and E. P. Stepanov, J. Exptl. Theoret. Phys. U.S.S.R. **38**, 359 (1960) [translation: Soviet Phys.—JETP **11**, 261 (1960)].

Sb in Fe. According to a note added to their paper by those authors, this should be corrected to $H_{eff} \geq 180$ kOe, which is not inconsistent with the value obtained in the present work. H_{eff} for Re in Fe apparently has not been previously measured.

Relation between Absorption and Emission Probabilities in Luminescent Centers in Ionic Solids

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It is pointed out that the Einstein relationship between spontaneous emission probability and induced absorption probability for radiative transitions is not generally valid for impurity centers in condensed media. An alternative approach to the problem is available by which estimates of the possible discrepancies can be made. Several mechanisms are discussed, particularly the Jahn-Teller effect, which depend on the existence of the phonon field and the lattice relaxation following absorption of a photon. In some simple cases, such as the F center in KCl and LiF, the decay time predicted from the integrated absorption cross section may differ by an order of magnitude from that observed. In other simple and cubic systems, where the atomic symmetries are appropriate, the discrepancy may be even larger. In noncubic crystals similar discrepancies may be expected.

I. ABSORPTION AND LUMINESCENCE IN ATOMIC SYSTEMS

BECAUSE of the common occurrence of absorption and luminescence of light in physical systems, and because of similar characteristics of these two phenomena, it has long seemed natural to discuss them in terms of related concepts. The development of the Bohr theory of the atom, together with the Planck radiation law, made it possible for Einstein[1] to establish simple relationships between absorption and emission parameters in atomic systems. In his famous work Einstein considered a simple two-state system and showed that when such a system is in equilibrium with a set of Planck oscillators (i.e., a radiation field), the principle of detailed balancing leads to a predicted spontaneous emission probability per unit time, A_{21}, which is related to the induced absorption (or emission) probability per unit energy density per unit time, times unit frequency, B_{12} ($=B_{21}$), by the expression

$$A_{21} = \frac{1}{\tau}\bigg|_{21} = \frac{8\pi h \nu_{12}^3}{c^3} B_{12}, \qquad (1)$$

where $h\nu_{12}$ is the energy separation between the two states. The frequencies of absorbed and emitted light (ν_{12}) are equal in this case.

Quantum-mechanical considerations applied to simple systems lead to the same conclusions.[2,3] Semiclassical radiation theory is sufficient to compute the (induced) B coefficient, and although it does not predict the existence of spontaneous emission, quantum electrodynamics does; therefore, although the Einstein relationship *must* be used in connection with semiclassical theory to predict A_{21}, it is not necessary if the problem is treated by quantum electrodynamics, and so in principle one could forget it. In connection with isolated atomic systems, the two schemes may be used equivalently; however, as we shall see, in solids there are particular precautions which must be taken.

In the simple atomic case, either of the above schemes yields the following results for allowed (electric-dipole)

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[1] A. Einstein, Physik. Z. **18**, 121 (1917).

[2] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), Chaps. 10 and 14. W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed.

[3] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), Chap. 4.

transitions[3]:

$$B_{ij} = \frac{2\pi e^2}{3\hbar^2} \frac{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\delta\gamma} \rangle|^2}{2J_i+1}, \qquad (2)$$

$$A_{ji} = \frac{4e^2 \omega_{ji}^3}{3\hbar c^3} \frac{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\gamma\delta} \rangle|^2}{2J_j+1}. \qquad (3)$$

Here B_{ij} per unit frequency is the induced transition probability per unit energy density per unit time,[4] while A_{ji} is the spontaneous emission probability per unit time; the dipole matrix element is

$$\langle \mathbf{r}_{\delta\gamma} \rangle = \langle \mathbf{r}_{\gamma\delta} \rangle = \int \Psi_\delta^* \left(\sum_k \mathbf{r}_k \right) \Psi_\gamma d\tau, \qquad (4)$$

expressed in terms of the electronic wave functions of the initial and final states δ, γ of the levels i, j.[5]

The probabilities in Eqs. (2) and (3) may be conveniently expressed in terms of the dimensionless "oscillator strength,"[6] a tensor which in simple cases may be treated as a scalar quantity,

$$f_{i \to j} = \frac{2m}{3\hbar} \omega_{ij} \frac{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\delta\gamma} \rangle|^2}{2J_i+1}, \qquad (5)$$

where m is the electronic mass. In terms of the oscillator strength, then,

$$B_{ij} = \frac{\pi e^2}{m\hbar\omega_{ij}} f_{ij}, \qquad (6)$$

and

$$\frac{1}{\tau}\bigg|_{ji} = A_{ji} = \frac{2e^2 \omega_{ij}^2}{mc^3} f_{ij} \frac{(2J_i+1)}{(2J_j+1)}. \qquad (7)$$

These equations may be considered as indicating two experimental methods for the determination of the oscillator strength, f_{ij}, connecting a pair of levels i and j.

We may also express other measurable quantities in terms of A_{ji} and B_{ij}. In the absence of competing processes, the reciprocal decay time A_{ji} is evidently directly proportional to the (integrated over energy) absorption cross section, Σ_{ij}, with a proportionality constant depending on fundamental constants and on the energy of the transition. The total absorption cross section, Σ_{ij}, is equal to the probability of the induced transition, multiplied by the energy absorbed in the transition, divided by the energy flux corresponding to

one photon per unit volume,[6] that is,

$$\Sigma_{ij} = B_{ij}(\hbar\omega_{ij})(2\pi\hbar/c). \qquad (8)$$

In terms of the oscillator strength and decay times, we have

$$\Sigma_{ij} = \frac{2\pi^2 e^2 \hbar}{mc} f_{ij}, \qquad (9)$$

or

$$\Sigma_{ij} = \frac{\pi^2 c^2 \hbar}{(\omega_{ij})^2} \left(\frac{1}{\tau_{ji}} \right) \left(\frac{2J_j+1}{2J_i+1} \right). \qquad (10)$$

These relationships and generalizations of them have been widely used in atomic and molecular spectroscopy for decades. It is natural that their use should have been extended to imperfections in solids. It is this, generally unwarranted, extension which is the subject of this paper.

II. ABSORPTION AND LUMINESCENCE IN IMPERFECTIONS IN SOLIDS

In order to gain some insight into the treatment of this problem, we consider first in some detail the Schrödinger equation of the solid. The total crystal Hamiltonian, neglecting spin-dependent terms, is

$$\mathcal{H} = T_e + T_N + U(\mathbf{r},\mathbf{x}). \qquad (11)$$

Here T_e is the electronic kinetic energy, T_N the nuclear kinetic energy, and $U(\mathbf{r},\mathbf{x})$ the (electron-electron) + (electron-nucleus) + (nucleus-nucleus) potential energy. The symbol $\mathbf{r}$ will be used to denote the set of electronic coordinates and $\mathbf{x}$ the nuclear coordinates. The total wave function Ψ is thus a function of electronic and nuclear coordinates, which is commonly separated, following the Born-Oppenheimer approximation,[7] into electronic and nuclear factors

$$\Psi_{n\eta}(\mathbf{r},\mathbf{x}) \cong \phi_{n,\mathbf{x}}(\mathbf{r}) \chi_{n,\eta}(\mathbf{x}). \qquad (12)$$

The rationale behind this approximation is that the heavy nuclei move so much more slowly than the electrons that for all nuclear positions there is effectively a stationary electronic state ϕ_n which depends parametrically on the set $\mathbf{x}$. The nuclear wave function χ in turn depends not on the electronic positions, but only on the electronic state n.

Using this approximation, one obtains the following Schrödinger equations for the electronic and nuclear systems[8]:

$$[T_e + U(\mathbf{r},\mathbf{x})]\phi_{n,\mathbf{x}}(\mathbf{r}) = E_n(\mathbf{x})\phi_{n,\mathbf{x}}(\mathbf{r}), \qquad (13)$$

$$[T_N + E_n(\mathbf{x})]\chi_{n,\eta}(\mathbf{x}) = \mathcal{E}_{n,\eta}\chi_{n,\eta}(\mathbf{x}). \qquad (14)$$

In these equations, $E_n(\mathbf{x})$ is an adiabatic electronic eigenvalue. It is important to note that both ϕ and χ form a complete set of eigenfunctions.

[4] $\hbar\omega_{ij} = |E_i - E_j|$. The factors $(2J+1)$ in Eqs. (2) and (3), and in those following, arise from the degeneracy of the atomic levels; J is the angular momentum quantum number. The summations over the states δ, γ represent summations over the components of the levels i, j.

[5] Note that our B_{ij} differs from that of reference 2; in the derivation, B_{ij} always occurs as a multiple of the energy density $\rho(\nu)$, and there are constants which may be absorbed by either $\rho(\nu)$ or B_{ij}. Our expression for B_{ij} leads to Eq. (1).

[6] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

[7] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

[8] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 14.

We now write $\mathbf{x}=\mathbf{x}_0+\mathbf{u}$, $\mathbf{x}_0$ representing the equilibrium nuclear positions, and $\mathbf{u}$ the displacements from these equilibrium positions. Of course, in principle, we cannot know what the values $\mathbf{x}_0$ are until we have solved Eqs. (13) and (14). Since $\chi(\mathbf{x})$ depends parametrically on the electronic state n, we must think of the set $\mathbf{x}_0$ as being dependent on n. Nevertheless, it is useful to introduce this separation and treat the set $\mathbf{x}_0(n)$ as if they were known. Next, we formally make a linear transformation on $\mathbf{u}$ and, thereby, introduce a new set of displacement parameters $\mathbf{q}$, the normal coordinates of the crystal, which have the property that $[\partial^2 E_n(\mathbf{x})/\partial q_i\partial q_j]_{q_i=q_j=0}=0$ for $i\neq j$. We note the important fact that the set of $\mathbf{q}$ depends on $\mathbf{x}_0$, and will thus, in general, be different for different $\mathbf{x}_0$.

We then expand the adiabatic electronic energy $E_n(\mathbf{x})$ in a Taylor series in $\mathbf{q}$,

$$E_n(\mathbf{x})=E_n(\mathbf{x}_0)+\sum_\mu [C_\mu{}^n q_\mu+D_\mu{}^n q_\mu{}^2+\cdots], \quad (15)$$

where

$$C_\mu{}^n=[\partial E_n(\mathbf{x})/\partial q_\mu]_{q_\mu=0}$$

and

$$D_\mu{}^n=[\partial^2 E_n(\mathbf{x})/\partial q_\mu{}^2]_{q_\mu=0}.$$

The nuclear equation, Eq. (14), may then be approximately written

$$[T_N+E_n(\mathbf{x}_0)+\sum_\mu(C_\mu{}^n q_\mu+D_\mu{}^n q_\mu{}^2)]\chi_{n,\eta}(\mathbf{x})$$
$$= \mathcal{E}_{n,\eta}\chi_{n,\eta}(\mathbf{x}). \quad (14')$$

Equation (14′) may be transformed into a set of harmonic oscillator equations.[9] The "force constants" of these oscillators will depend on $D_\mu{}^n$, and the equilibrium positions on $C_\mu{}^n$. The lattice relaxation parameters $C_\mu{}^n$ are thus of utmost importance. In generalized treatments of optical centers, one finds that $C_\mu{}^n$ account for Stokes' shifts (that is, differences in energy between absorption and emission peaks) and bandwidths.[10] Most important for this discussion, the potential U in the electronic equation, Eq. (13), is a function of the equilibrium positions of the nuclei, $\mathbf{x}_0(n)$ (as well as the set of normal coordinates $\mathbf{q}$), which are, in turn, dependent on the electronic state through the lattice relaxation parameter $C_\mu{}^n$; thus a self-consistent procedure must be employed. This may be expressed in another way by saying that after absorption of a photon, when the charge distribution of the excited electronic state is different from what it was in the ground state, the lattice will relax to a new equilibrium state, and the lattice vibrations will change, i.e., there will be a new set of $\mathbf{x}_0$ and $\mathbf{q}$. The point we wish to emphasize is that as a result of this lattice relaxation and the consequent change of U, the analytical form of the set of electronic wave functions, as well as the energies of the stationary states, will, in general, be different from those which existed when the lattice was in its original configuration.

It is evident, then, that in general the states involved in absorption and emission, although they may occupy the same relative positions on an energy level diagram, and *may* possess unchanged symmetry properties, are *not precisely the same electronic states.*

Since the importance of the above discussion hinges on how $C_\mu{}^n$ will change for states of interest, it is important to investigate the properties of $C_\mu{}^n$, and thus find out how lattice relaxation occurs. $C_\mu{}^n$ may, in fact, be calculated for a given electronic state through application of the so-called Hellmann-Feynman theorem,[11] which states that

$$\partial E_n(\mathbf{x})/\partial q_\nu=\langle\phi_{n,\mathbf{x}}(\mathbf{r})| \partial U/\partial q_\nu|\phi_{n,\mathbf{x}}(\mathbf{r})\rangle. \quad (16)$$

Investigation of Eq. (16) has been carried out by group-theoretical methods[12–15] and we may state the result in terms of the Jahn-Teller theorem.[12] This theorem states that $\partial E_n(\mathbf{x})/\partial q_\nu$, Eq. (16), will be nonzero if the electronic state n is degenerate. [Exceptions can only occur if (a) all of the nuclei are on a straight line, or (b) the system contains an odd number of electrons and the only degeneracy is the twofold Kramers[16] degeneracy, neither of which exceptions is of interest here.] Furthermore, lattice relaxation will occur, the effect being to remove the degeneracy. Obviously, this relaxation must be such as to change the symmetry properties of the potential $U(\mathbf{r},\mathbf{x})$, as well as its "size." Then, the symmetry properties of the electronic wave functions ϕ will also change, in a self-consistent way. We see that the Jahn-Teller theorem says nothing about nondegenerate states; in such a case Eq. (16) must be explicitly evaluated.

We note the fact that for many physical situations the pertinent physics involved in the electronic equation, Eq. (13), depends primarily upon the equilibrium position of the nuclei, $\mathbf{x}_0$, and not on the details of the lattice vibrations. There are several reasons for this, the main one being that the amplitudes of lattice vibrations *are* small, and the changes in the potential associated with them may be treated by perturbation theory. Thus, in a zero-order approach one may write

$$[T_e+U^0(\mathbf{r},\mathbf{x}_0)]\phi^0{}_{n,\mathbf{x}_0}(\mathbf{r})=E_n{}^0(\mathbf{x}_0)\phi^0{}_{n,\mathbf{x}_0}(\mathbf{r}). \quad (13')$$

If the instantaneous vibrations $\mathbf{q}$ involve no important change in the symmetry of the zero-order potential, U^0, use of Eq. (13′) is adequate. However, there *are* important cases in which one must consider the perturbation caused by the vibrations. This is particularly true if matrix elements for a transition are identically zero when the $\phi_n{}^0$ are used, and if the perturbation makes the

[9] K. Huang and A. Rhys, Proc. Roy. Soc. (London) A204, 406 (1950).

[10] S. I. Pekar, Uspekhi Fiz. Nauk 50, 197 (1953).

[11] H. Hellmann, *Einfuhrung in die Quanten Chemie* (B. G. Teubner, Leipzig, 1937), p. 285; R. P. Feynman, Phys. Rev. 56, 340 (1939); Theodore Berlin, J. Chem. Phys. 19, 208 (1951).

[12] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A161, 220 (1937).

[13] W. L. Clinton and B. Rice, J. Chem. Phys. 30, 542 (1959).

[14] U. Opik and M. H. L. Pryce, Proc. Roy. Soc. (London) A238, 425 (1957).

[15] N. N. Kristofel, Optika i Spektroskopiya 9, 324 (1960).

[16] H. A. Kramers, Proc. Acad. Sci. Amsterdam 33, 959 (1930).

matrix elements involving first-order ϕ_n's nonzero. Such cases will be discussed later; for the most part we shall assume that $U^0(\mathbf{r},\mathbf{x}_0)$ is the important term in the potential, $\phi^0_{n,\mathbf{x}_0}$ is a good approximation to the wave function, and $E_n^0(\mathbf{x}_0)$ is an accurate eigenvalue.

Let us illustrate the above concepts by a simple example. (For a more quantitative discussion of the type of center we are about to discuss, see Sec. IV, B.) We assume that we have a center which is a substitutional impurity in a cubic crystal. This center, as a free ion, will be assumed to have an S state and a P level, between which electric dipole transitions may occur. The effect of a cubic crystal field will be essentially to leave these as S and P levels. Suppose now that the center is in the S state; i.e., $\phi = \phi_S$. Consistent with this, the surrounding ions execute small vibrations about an equilibrium position $\mathbf{x}_0$ with $C_\mu^S = 0$, and $U^0(\mathbf{r},\mathbf{x}_0)$ equal to a cubic potential. Now, according to the Jahn-Teller theorem, the P level consistent with U^0, being orbitally degenerate, will be such that $C_\mu^P \neq 0$; thus if the center is excited to the P level, lattice relaxation will occur to remove the degeneracy of the excited states. The lattice configuration consistent with the P level will then no longer have cubic symmetry, and in turn the P and S states will not remain purely P- and S-like but will be mixed with other angular terms. The new set of electronic wave functions, consistent with the new set of $\mathbf{x}_0(P)$ is thus expected to be quite different from the original set, and matrix elements for emission may be expected to be different from those for absorption.

We may describe the above processes in terms of "configurational coordinate" diagrams whose interpretation, however, differs somewhat from the usual one.[6] Suppose that the important mode of vibration when the center is in the S ground state is a breathing mode, i.e., neighboring ions are vibrating radially, in phase. Then the potential $U(\mathbf{r},\mathbf{x})$ will always have cubic symmetry. We may then plot the energy of the system vs q_1, where q_1 is the coordinate corresponding to this mode of vibration (Fig. 1a). This energy vs q_1 curve is drawn as a solid line, labeled "$1S$." Consistent with the system's being in this state, $C_\mu^{1S} = 0$. Also consistent with this nuclear configuration, there exist the rest of the complete set of electronic states ϕ_n, whose E vs q_1 curves are symbolically drawn as dashed lines. These curves will, in general, have different minima and curvature than those of the $1S$ state. We may think of the higher states as "virtual" states, in the sense that they exist only when the electronic system is in the $1S$ state, consistent with the particular set of $\mathbf{x}_0$ and $\mathbf{q}$ existing at that time. The dashed P-state curve passing through B actually is triply degenerate under the q_1 mode of vibration.

Suppose now that a photon is absorbed and the system excited to the P_z state; this is represented in Fig. 1(a) as a transition from A to B. A Jahn-Teller lattice relaxation will occur; the new potential after relaxation will be $U[\mathbf{r},\mathbf{x}_0(P_z),\mathbf{q}_2]$, with a new set of $\mathbf{x}_0(P_z)$ and a corresponding new set of normal modes, the
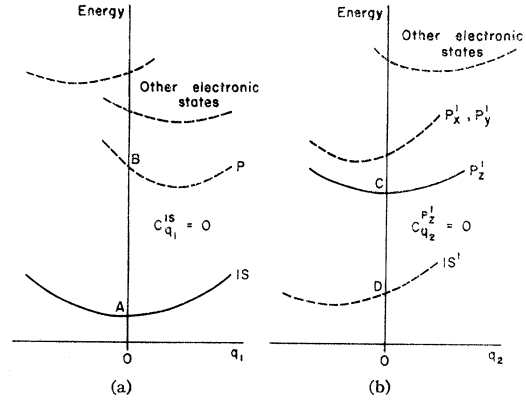

FIG. 1. (a) Configurational coordinate curves of energy vs q_1 for various electronic states. The electronic system is in the $1S$ state; i.e., $C_{q_1}^{1S} = 0$. $1S - P$ absorption takes place with an energy peak corresponding to $(B-A)$. (b) Configurational coordinate curves of energy vs q_2. The electronic system is in the P_z' state; i.e., $C_{q_2}^{P_z'} = 0$. The Jahn-Teller effect has removed the degeneracy of P_z' with P_x' and P_y'. $P_z' - 1S'$ emission takes place with an energy peak corresponding to $(C-D)$.

"important" one being q_2. (For simplicity, we assume that there exists a single important mode, q_2.) U no longer has cubic symmetry.

Since the q_1 mode no longer exists after relaxation, we must draw a new configurational coordinate curve, Fig. 1(b). In this figure the P_z' state will be represented as a solid line, with $C_\mu^{P_z'} = 0$. All the other states are "virtual" states, in the sense used above. We call the excited state P_z' because it will not be strictly P-like, but will contain other angular momentum components; similarly with the new P_x', P_y', $1S'$. Note that P_x' and P_y' are no longer degenerate with P_z'; they may or may not be degenerate with each other, depending on the nature of q_2. Emission will now occur between C and D, and there will be a Stokes' shift given by $E_{AB} - E_{CD}$.

On the basis of the above discussion, we must conclude that Einstein's relationship between A_{ji} and B_{ij} will, in general, not be valid in the case of imperfections in solids, because, among other things, it will no longer be true that $\omega_{ij} = \omega_{ji}$ and $\sum_{\delta,\gamma}|\langle \mathbf{r}_{\delta\gamma}\rangle|^2 = \sum_{\delta,\gamma}|\langle \mathbf{r}_{\gamma\delta}\rangle|^2$. (We note here, in order to avoid confusion, that we are not including in this discussion the possibility of cascade processes, in which absorption occurs to a level j, and a separate, e.g., nonradiative process sends the system into a distinctly different electronic level k, from which it emits. Such processes do occur in certain cases, of course, but consideration of them is beyond the scope of this discussion.)

It is, in principle, possible to derive something analogous to the Einstein $A - B$ relationships for solids. As we may infer from the above discussion, however, this problem is much more complicated than that for the 2-level atom. The point is, basically, that the electronic system is interacting not only with a blackbody radiation field, but also with a vibrational field whose characteristics in general depend on the electronic state. Not only

must the *existence* of Planck photon and phonon oscillators be taken into account, but also the dependence of the electronic wave functions on the configurations of the nuclei, the equilibrium values of which in turn depend on the electronic state. Thus, this entire problem must be treated in a self-consistent way.

Fortunately, it *is* possible to eliminate the use of detailed balance arguments, and to arrive at separate expressions for absorption and emission parameters (by using quantum electrodynamics); accordingly, we feel that it is wisest in principle to abandon the $A-B$ coefficients approach entirely, and to think of absorption and emission as generally separate processes which in some simple cases may be directly related. In this connection we note that in non-ionic condensed systems it might well be sufficient to consider deviation from the Einstein relation as a small perturbation. However, in ionic systems this cannot be a satisfactory approach, and in neither case is it necessary.

We should emphasize that usually, in ionic systems, it is still pertinent, useful, and desirable to specify purely electronic transitions $i \to j$ and $j \to i$. Several factors are involved in this statement. The most important is that, because of the large difference in electronic and nuclear masses, we can "follow" an electronic state as relaxation occurs after an optical transition. In addition, lattice relaxation can be expected to occur in times very short compared with τ, perhaps in 10^{-10} sec rather than $\gtrsim 10^{-8}$ sec. Another factor is that, because of the strong interactions in ionic systems, it frequently is impossible to distinguish particular vibrational transitions during an electronic transition, and only a broadened electronic transition can be observed. The broadening can be described in terms of an appropriate average over the vibrational transitions, a unique set of which can be ascribed to a given electronic transition.

With this philosophy we specialize Eqs. (2) and (3) to the case of absorption and emission in a dielectric medium; following the notation of reference 6, we obtain for the spontaneous emission probability

$$A_{km}(E) = \left[\frac{\mathscr{E}_{\mathrm{eff}}(E_{km})}{\mathscr{E}_0} \right]^2 n(E_{km})$$

$$\times \frac{4e^2 E_{km}{}^3}{3\hbar^4 c^3} \sum_{\delta,\gamma} |\langle \mathbf{r}_{\delta\gamma} \rangle|^2 \frac{S_{km}{}^e(E)}{2J_k+1}, \quad (17)$$

and for the absorption cross section (as a function of energy)

$$\sigma_{mk}(E) = \left[\frac{\mathscr{E}_{\mathrm{eff}}(E_{mk})}{\mathscr{E}_0} \right]^2 \frac{1}{n(E_{mk})}$$

$$\times \frac{4\pi^2 e^2 E_{mk}}{3\hbar c} \sum_{\delta,\gamma} |\langle \mathbf{r}_{\delta\gamma} \rangle|^2 \frac{S_{mk}{}^a(E)}{2J_m+1}. \quad (18)$$

In these equations, as in the ones following, we use the subscripts k and m to denote electronic levels in a particular way. The first letter in a subscript refers to the electronic level of the system before a transition takes place, and the second refers to the level into which the transition is made. Thus, for example, in Eq. (17) A_{km} signifies a transition from level k to level m, while in Eq. (18) σ_{mk} signifies one from levels m to k. It is to be noted that because of lattice relaxation the states in the two levels m, Eqs. (17) and (18) are not exactly the same, although they are related adiabatically.

The ratio of the integrated absorption coefficient $\Sigma_{mk} \equiv \int \sigma_{mk} dE$ and the reciprocal decay time $\tau_{km}{}^{-1} = \int A_{km} dE$ is given by an expression analogous to Eq. (10),

$$\frac{\Sigma_{mk}}{\tau_{km}{}^{-1}} = \left[\frac{\mathscr{E}_{\mathrm{eff}}(E_{mk})}{\mathscr{E}_{\mathrm{eff}}(E_{km})} \right]^2 \frac{\pi^2 \hbar^3 c^2}{n(E_{mk})n(E_{km})}$$

$$\times \frac{E_{mk}}{E_{km}{}^3} \frac{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\gamma\delta} \rangle|^2}{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\delta\gamma} \rangle|^2} \frac{(2J_k+1)}{(2J_m+1)}. \quad (19)$$

In terms of the oscillator strength,

$$\Sigma_{mk} = \left[\frac{\mathscr{E}_{\mathrm{eff}}(E_{mk})}{\mathscr{E}_0} \right]^2 \frac{1}{n(E_{mk})} \frac{2\pi^2 e^2 \hbar}{m^{(*)} c} f_{mk}, \quad (20)$$

so we also have a relationship between f_{mk} and $\tau_{km}{}^{-1}$ analogous to Eq. (7),

$$\frac{f_{mk}}{\tau_{km}{}^{-1}} = \left[\frac{\mathscr{E}_0}{\mathscr{E}_{\mathrm{eff}}(E_{km})} \right]^2 \frac{\hbar^2 c^3 m^{(*)}}{2e^2 n(E_{km})} \frac{E_{mk}}{E_{km}{}^3}$$

$$\times \frac{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\gamma\delta} \rangle|^2}{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\delta\gamma} \rangle|^2} \frac{(2J_k+1)}{(2J_m+1)}. \quad (21)$$

If the system is tightly bound, $m^* = m$ and $\mathscr{E}_{\mathrm{eff}}/\mathscr{E}_0 = 1 + (n^2-1)/3$ (as we shall see); in this case,

$$\frac{f_{mk}}{\tau_{km}{}^{-1}} = \left(\frac{3}{n^2+2} \right)^2 \frac{\hbar^2 c^3 m}{2e^2} \frac{E_{mk}}{E_{km}{}^3} \frac{1}{n(E_{mk})}$$

$$\times \frac{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\gamma\delta} \rangle|^2}{\sum_{\delta,\gamma} |\langle \mathbf{r}_{\delta\gamma} \rangle|^2} \frac{(2J_k+1)}{(2J_m+1)}. \quad (22)$$

Equation (19) is the modified Einstein relation, in analogy with Eq. (10). In these equations, $\mathscr{E}_{\mathrm{eff}}$ is the effective field at the absorption or emission center, while $\mathscr{E}_0$ is the average field in the medium. E_{km} and E_{mk} are the absolute values of the energies of emission and absorption, respectively; they will not, in general, be equal. The indices of refraction $n(E_{mk})$ and $n(E_{km})$ are evaluated at the peak energies of absorption and emission; they may be expected to be different, although usually not by a great amount. $S_{mk}{}^a(E)$ and $S_{km}{}^e(E)$ are shape functions centered close to E_{mk} and E_{km}, respectively, and normalized such that $\int S dE = 1$. For some purposes, as in atomic spectroscopy, they may be replaced by delta functions. The parameter m^* is the

appropriate value of the effective mass of the electron undergoing transition.

Equations (17)–(22) involve an implied assumption; namely, we assume that the factors $\mathcal{E}_{eff}$, n, E, and $\sum_{\delta,\gamma}|\langle \mathbf{r}\rangle|^2$, which all are functions of E, vary sufficiently little with E over the width of the band that the explicit E dependence may be absorbed into the shape factor $S(E)$, and the other quantities may be replaced with their values at the line peak. This is essentially equivalent to a generalized Condon approximation and is a reasonable procedure for our purposes. $S(E)$, which is commonly close to a Gaussian in shape, is primarily determined by the "appropriate average" over vibrational transitions referred to above, but deviations of the order 25% can easily occur because of variations with E of $\mathcal{E}_{eff}$, n and $\sum_{\delta,\gamma}|\langle \mathbf{r}\rangle|^{2}$.[17]

III. MACROSCOPIC PARAMETERS

We now investigate the effects of the macroscopic factors $n(E)$, $\mathcal{E}_{eff}$, ω, and m^* on the transition probabilities, i.e., the difference between Eq. (10) and Eq. (19).

A. Indices of Refraction

The presence of the indices of refraction in our equations comes from the following considerations[6]: The absorption cross section is obtained by dividing the transition probability for absorption by the rate of energy flux corresponding to one photon per unit volume, that is, by $n^2 \mathcal{E}_0^2 v/4\pi$. In this expression, n is the index of refraction of a transparent medium, while v is the energy velocity. In this case, then, $v=c/n$ and we see that the absorption cross section must be divided by n. In the case of emission the transition probability is divided not by an energy flux but by an energy density, that is, by n^2. But further, the emission probability is proportional to the density of photon states, i.e., to the cube of the photon momentum. This means that we must further multiply by n^3, leaving a net factor of n for the emission probability. This leaves a factor of $[n(E_{mk})n(E_{km})]^{-1}$ in our ratio of $\sum_{mk}$ to τ_{km}^{-1}, Eq. (19); in typical cases this represents a factor of $(1.9)^{-1}$ for LiF to $(5.4)^{-1}$ for TlBr, for wavelengths in the visible region.

The indices of refraction used here are those characterizing the bulk medium at the energies corresponding to the energy of the photon involved in the transition, and in general n will not be the same for absorption and emission. In one typical case (i.e., the F center in KBr), the difference in emission and absorption energies is such that the index of refraction for absorption is 1.57, while that for emission is 1.54.[18] It is thus accurate to use the listed average value for n in such a case. For Ag^+ in NaCl the corresponding values are 1.73 and 1.65. In some other cases the change will be considerably larger, up to a factor of 2, but only when absorption

occurs in a center near the region of fundamental absorption of the host crystal and emission appears with a sizable Stokes' shift.

B. Effective Field

In calculating transition probabilities one must consider the actual field at the center, $\mathcal{E}_{eff}$, which in general will be different from the average field in the medium, $\mathcal{E}_0$. For an extremely diffuse center, $\mathcal{E}_{eff} \approx \mathcal{E}_0$; on the other hand, for an extremely tightly bound center,[6]

$$\mathcal{E}_{eff} \approx \mathcal{E}_0 \left[1 + \frac{n^2-1}{3} + O((n^2-1)/3)^2 + J + X + K \right]. \quad (23)$$

In Eq. (23), $[1+(n^2-1)/3]$ constitutes the Lorentz local-field ratio, and would be the only important term for an extremely well-localized center in a tightly bound matrix; the next term is of the order of the square of the Lorentz correction; J, X, K represent corrections arising from overlap of neighboring atom wave functions, exchange effects, and higher multipole interactions, respectively.

In many cases of interest neither of these extremes applies. The effective field will be an explicit function of the electronic state and the positions of the nuclei, and must be evaluated in a self-consistent fashion. For example, if the ground electronic state of the impurity is well localized, as is also the excited state immediately after excitation, $\mathcal{E}_{eff}(E_{mk})$ may be considerably greater than $\mathcal{E}_0$. If, after relaxation occurs, the excited state and/or ground state electronic wave functions change to more diffuse charge distributions, the ratio $\mathcal{E}_{eff}(E_{km})/\mathcal{E}_0$ may become considerably smaller. Therefore, it is not to be expected that $\mathcal{E}_{eff}(E_{km})=\mathcal{E}_{eff}(E_{mk})$. It is reasonable to expect, however, that the square of the ratio of these is of the order of unity, with a change of no greater than a factor of 4 in most cases of interest.

C. Frequency of Absorbed or Emitted Light

In a fundamental calculation based upon a complete solution of the crystal Schrödinger equation along the lines of Sec. II, one would, in the process, calculate the energy levels as a function of lattice configuration, and thus the frequency of absorption and emission peaks (as modified by the considerations in the last paragraph of Sec. II). In the absence of such a computation, however, and no completely satisfactory calculation has as yet been performed, one may still make use of the observed frequencies in our equations concerning transition probabilities. As we have mentioned before, in most cases these frequencies will not be equal (i.e., there will be a Stokes' shift to lower energy in emission), and this effect must be accounted for in the calculation of transition probabilities. In most cases, the absorption peak frequency exceeds the emission peak frequency by a factor of order 2, usually somewhat less. A semi-quantitative argument predicts an upper limit of a

[17] D. L. Dexter, Phys. Rev. **96**, 615 (1954).

[18] See C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 115 for curves of n vs energy.

factor of 2, but deviations can be expected in any particular case.[10] All other parameters being unchanged, a Stokes' shift of a factor of two would lead to a decrease of a factor of $2^3 = 8$ in the emission probability computed from Eq. (19) as compared with Eq. (10).

D. Effective Mass

The mass m^* appearing in Eqs. (20) and (21) will for diffuse centers be the effective mass, which may be experimentally determined by cyclotron resonance or other methods. For very tightly bound centers, $m^* = m$, the electronic mass.

IV. CHANGE OF MATRIX ELEMENT

We have seen that factors of the order $(10)^{\pm 1}$ may be expected to modify the Einstein $A - B$ relationship, Eq. (10), in typical cases because of changes in "macroscopic" parameters. However, more interesting and larger effects might be sought which are specifically related to the changes in electronic wave functions as lattice relaxation occurs. These should be manifested as differences in the optical transition matrix elements between absorption and emission, i.e., as "matrix element effects." This topic has not previously been discussed to our knowledge, and a major purpose of this paper is to point out some of the phenomena which may be expected to occur.

In applying our discussion of matrix element effects we will use Eq. (19), which expresses the ratio of quantities which may be experimentally determined, i.e., τ and Σ, in terms of the summed squared matrix element ratio. In principle, this may be done exactly, in line with our prior discussion; in practice, the effective fields are not known, and approximations must be made. In the use of Eq. (19) we shall always assume that $\mathcal{E}_{\text{eff}}(E_{km}) = \mathcal{E}_{\text{eff}}(E_{mk})$. As mentioned in Sec. III, this might possibly introduce an error as large as a factor of 4 into the ratio. The reader should keep this point in mind as we later look at the sizes of matrix element effects.

The preceding discussion has been quite general and applies to any center in any type of environment. In what follows, we discuss only substitutional centers in cubic crystals, except where noted. It is evident that similar effects will occur for interstitial impurities, where the crystal field might very well not have inversion symmetry.

For convenience, we shall divide the "matrix element effects" into the following categories and discuss several systems as examples: (A) Matrix elements for absorption and emission are essentially the same. (B) Matrix elements are larger for absorption than for emission. (C) Matrix elements are larger for emission than for absorption. In (D) we shall briefly discuss centers in noncubic environments.

A. Matrix Elements Practically Unchanged

This would be expected to occur in at least two extreme cases in solids: (1) In tightly bound, quasi-atomic centers in which either $U(\mathbf{r}, \mathbf{x})$ is not strongly dependent on $\mathbf{x}$, or $\mathbf{x}$ is not strongly dependent on the electronic state. In this case $C_\mu{}^n$ would be the same for states of interest, i.e., independent of n, and there would be little or no Stokes' shift in luminescence. (2) In continuum treatments of very loosely bound centers, such as some theories of the F center.[10] In this case the electron involved in the transition is assumed to "see" a spherically symmetrical dielectric continuum in both ground and excited states to a sufficient degree that hydrogenlike wave functions are valid for both cases.

An example of a system of type (1) would be rare earth ions having transitions involving inner, shielded electrons.[19] (Typical transitions of this type have an oscillator strength $\approx 10^{-7}$.) Because of the shielding effect of outer electrons, lattice relaxation is expected to be very small, and emission is expected to have a decay time calculable on the assumption that the matrix elements do not change to any appreciable degree.

We mention again that we are considering only cases in which emission occurs between the same levels as does absorption. Undoubtedly there are cases of important cascade processes involving the rare-earth transitions. These may be complex and of several types, and deviations from Eq. (19) should by no means always be attributed to matrix element effects of the type considered here.

As an example of (2), we have performed a calculation using Pekar's wave functions[10] in the following way: We used his hydrogenic $1s$ wave function, appropriate to the lattice in the ground-state configuration, and a hydrogenic $2p$ function with damping length determined by the Coulombic potential consistent with this $1s$ function to calculate the dipole matrix element for absorption. We then took his $2p$ wave function, appropriate to the lattice in the relaxed configuration, and a hydrogenic $1s$ function with damping length consistent with this $2p$ function to calculate the dipole matrix element for emission. We found that the ratio of these is given by

$$\frac{\langle r \rangle_{\text{emis}}}{\langle r \rangle_{\text{abs}}} = \frac{1 + 0.312[\epsilon/n^2 - 1]}{1 + 0.3914[\epsilon/n^2 - 1]}. \tag{24}$$

In this equation, ϵ is the static dielectric constant of the system, while n is the index of refraction. The ratio varies from 0.94 for $[\epsilon/n^2 - 1] = 1$ to 0.86 for $[\epsilon/n^2 - 1] = 6$, a range which includes all the alkali halides; so we see that the ratio of the square of the dipole matrix elements will be between 0.7 and unity on the basis of this model. We might comment here, however, that this model of the F center is for several reasons not considered valid,[20] and so these results are not to be taken as accurately indicative of the expected values of the F-center dipole matrix elements.

As another example of a spherically symmetric system

[19] For examples of optical properties of such centers, see L. J. F. Broer, C. J. Gorter, and J. Hoogschagen, Physica 11, 231 (1945).
[20] W. Beall Fowler and D. L. Dexter, Physica Status Solids 2, 819 (1962).

of type (2), we consider a purely hydrogenic system whose characteristics are solely determined by the effective nuclear charge, Z. It is easily shown that for such a system, the square of the dipole matrix element is proportional to Z^{-2}, while the energy of a $1s \leftrightarrow 2p$ transition is proportional to Z^2; thus, $|\langle r \rangle|^2$ is proportional to E^{-1}. If we assume that a Stokes' shift may occur through a lattice relaxation expressible solely in a change in Z, we have

$$|\langle r \rangle|_{\text{abs}}^2 / |\langle r \rangle|_{\text{emis}}^2 = E_{\text{emis}}/E_{\text{abs}}. \qquad (25)$$

Thus we see that a normal Stokes' shift with $E_{\text{emis}} < E_{\text{abs}}$ would yield $|\langle r \rangle|_{\text{abs}}^2 < |\langle r \rangle|_{\text{emis}}^2$. The predicted Stokes' shifts in ionic crystals on the basis of the theory of a polarizable dielectric continuum range from about 50 to 90% for most ionic crystals, so that on this basis we might expect the squared matrix element ratio of Eq. (25) to be between 0.6 and 0.1.

It is likely that in most cases of imperfections in ionic crystals case (A), when it applies, is not very interesting. Changes of the order 10 or less are all that can be expected in the squared matrix elements between absorption and emission.

B. Matrix Elements Larger for Absorption than for Emission

This effect is expected to be important for centers which have allowed absorptions (such as $S \rightarrow P$) and a fairly strong interaction with, say, nearest-neighbor ions. (We use "allowed" and "forbidden" in the sense of the one-electron, electric dipole moment selection rules.) In this case $U(\mathbf{r},\mathbf{x})$ will be a strong function of the $\mathbf{x}$, which in turn will be strongly dependent upon n through $C_\mu{}^n$; furthermore, since dipole transitions involve a change in symmetry of n (from $1s \rightarrow 2p$, say), one would expect lattice relaxation to occur via the Jahn-Teller effect which could change the angular dependence of U, as well as its radial dependence. Accordingly, the electronic wave functions would have different angular dependence, and the emission matrix elements might be smaller than those for absorption.

The importance of an effect of this sort will depend strongly on the magnitude of the electron-lattice coupling, which is indicated by such things as Stokes' shifts and line widths. Thus, for example, we would expect that this effect could be of some importance in the case of the F center, as well as in other systems which manifest allowed $S \rightarrow P$ absorptive transitions (i.e., Tl+ in KCl).

We may extend our brief discussion of the Jahn-Teller effect (Sec. II) in considering the point-ion model of the F center.[21] According to this simple model, the potential "seen" by the F-center electron is

$$V(\mathbf{r}) = \sum_i \frac{e_i}{|\mathbf{r} - \mathbf{R}_i|}, \qquad (26)$$

where $\mathbf{R}_i$ is the position of the ith point ion. One may investigate the symmetry properties of this potential by expanding $|\mathbf{r} - \mathbf{R}_i|^{-1}$ in spherical harmonics; if the ions are at perfect-cubic-lattice positions, one finds that

$$V(\mathbf{r}) = g(r) + h(r)Y_4(\theta,\phi) + \cdots. \qquad (27)$$

Here $g(r)$ and $h(r)$ are functions only of $|\mathbf{r}|$, and further, $h(r)$ is considerably smaller than $g(r)$. Thus, to a good approximation, the F-center ground state is an s state, the first excited level is a p level, and transitions between them are allowed. However, the p level has threefold orbital degeneracy; therefore, when the system is in the excited p state the Jahn-Teller effect will occur. This will remove the orbital degeneracy of the p level in destroying the cubic symmetry of the system. This is intuitively reasonable and corresponds to a noncubic lattice relaxation under the influence of the non-spherically symmetric p field, say along the z axis. Calculations have been carried out on various aspects of this effect; for example, it has been predicted that in LiCl, the nearest neighbors along the z axis move outward, while those on the x and y axes move inward.[22]

Accordingly the potential field "seen" by the electron is different in the two electronic states. In particular, we find that this type of distortion not only changes $g(r)$, the spherically symmetric term of $V(\mathbf{r})$, but it also introduces a term $l(r)Y_2(\theta,\phi)$. Thus the potential, even in our static, point-ion approximation, is no longer of cubic symmetry. This means that the excited state ψ_e will contain p- and f-like components, while ψ_g, the ground electronic state, will have, after relaxation, s- and d-like characteristics. The change in the spherically symmetric part of $V(\mathbf{r})$ will alter the amount of p-like function in the excited state and the amount of s-like function in the ground state, while the $P_2(\cos\theta)$ term in the potential will introduce f-like function to the excited state and d-like function to the ground state. Thus, the electronic wave functions after relaxation will be of the form

$$\psi_g(\mathbf{r}) = \varphi_s(r) + \varphi_d(r)P_2(\cos\theta),$$
$$\psi_e(\mathbf{r}) = \varphi_p(r)\cos\theta + \varphi_f(r)P_3(\cos\theta). \qquad (28)$$

The dipole matrix element in emission will then be

$$\langle \varphi_s + \varphi_d P_2(\cos\theta) | r\cos\theta | \varphi_p\cos\theta + \varphi_f P_3(\cos\theta) \rangle$$
$$= \langle \varphi_s | r\cos^2\theta | \varphi_p \rangle + \langle \varphi_d P_2(\cos\theta) | r\cos\theta | \varphi_p\cos\theta \rangle$$
$$+ \langle \varphi_d P_2(\cos\theta) | r\cos\theta | \varphi_f P_3(\cos\theta) \rangle. \qquad (29)$$

For several reasons this matrix element can be changed from that involved in absorption: First, φ_s and φ_p for emission may be "smaller" than for absorption as a result of normalization. Second, the analytic form of φ_s and φ_p will change, as mentioned above, because of the change in the spherically symmetric part of the potential. That is, the radial parts of the wave functions will change, as discussed in (A), above. Third, it should be pointed out that in the sum of the three matrix

[21] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

[22] R. F. Wood and J. Korringa, Phys. Rev. **123**, 1138 (1961).

elements, Eq. (29), the *signs* may not all be the same and cancellation may occur. It is apparent, then, that it is quite possible for s and p functions to be "subtracted out" of the ground-configuration functions to an extent which could reduce the matrix elements considerably (apart from the effect of noncubic relaxation). Noncubic effects could also be such as to cause cancellation of the matrix elements in Eq. (29).

This is all very well and good; even a simple model of the F center might well predict a matrix element effect such that emission matrix elements are smaller than those for absorption. However, it is not all clear whether this simple model provides a valid description of this system. Before discussing this further, let us investigate the experimental situation regarding the F center. We may do this by comparing the measured F-center oscillator strength[6,23] (actually, the measured Σ) with the reciprocal lifetime (or A coefficient).[24] Using Eq. (19), let us assume that $\mathcal{E}_{\rm eff}$ and $\sum_{\delta,\gamma} |\langle \mathbf{r} \rangle|^2$ are the same for absorption and luminescence of the F center in KCl. We also assume that the measured oscillator strength is due to both the $^2S_{1/2} \rightarrow {}^2P_{1/2}$ and $^2S_{1/2} \rightarrow {}^2P_{3/2}$ transitions; thus the sum of the factors $(2J_k+1)(2J_m+1)^{-1}$ in Eq. (19), corresponding to the two transitions becomes $(2\times\frac{1}{2}+1+2\times\frac{3}{2}+1)/(2\times\frac{1}{2}+1)=3$. Under these assumptions, using the measured values $E_{\rm abs}=2.3$ eV, $E_{\rm emis}=1.0$ eV,[25] we compute a decay time $\tau=9.3\times10^{-8}$ sec, as compared with the measured value of 60×10^{-8} sec. There is thus a discrepancy of a factor of seven.[26] This discrepancy may, qualitatively, be explained in terms of our previous discussion. A factor of 7 is not surprising on the basis of matrix element effects.

However, it is not at all clear, in the case of the F center, whether the mechanisms which we have been discussing are the primary ones. This is true because we have neglected the effect of the presence of any other levels in the system, in particular, the existence of a "$2s$" state.

There are several ways in which the $2s$ state could affect the primary optical processes in the F center:

(1) If the $2s$ state were much higher in energy than the $2p$ level (before and after relaxation), there would be very little effect.

(2) If, in the relaxed lattice, the $2s$ state were *below* the $2p$, the excited system would spend most of its time

in the $2s$ state, and emission would be largely forbidden. Further, there would be a definite temperature dependence of the decay time, probably quite strong, indicative of the Boltzmann probability of occupation of the higher state.

(3) If, in the relaxed lattice, the $2s$ state were *above* the $2p$ level, low temperature emission would be primarily from a $2p$ state and thus be largely allowed. Furthermore, there could also be a temperature dependence here of the decay time up to a factor of 2.

(4) The $2s$ and $2p$ levels could also be mixed via oddparity lattice vibrations. This would be a dynamic effect which will be discussed below.

It is easy to show that, in a spherically symmetric potential well (which is quite close to the point-ion potential for a perfect cubic lattice) the $2s$ state lies much higher in energy than the $2p$ level. It is not clear, however, how this will change after lattice relaxation. In any quasi-hydrogenic model, the $2s$ state will be much closer to the $2p$; however, only in the pure hydrogenic potential would they be expected to coincide. Thus, it seems likely that the $2s$ state lies somewhere above the $2p$ level in energy.

The data of reference 24 do not help much in interpreting the situation. According to reference 24, the decay time for F-center luminescence in KCl goes from approximately 0.85×10^{-6} sec at $0°$K to 0.6×10^{-6} sec at $100°$K. The behavior is approximately linear on a plot of $\ln\tau$ vs T. This type of curve may be explained in several ways: (a) It is consistent with a center having 2 slightly separated excited levels, the radiative transition probability from each being close to the same; however, no change in emission spectrum with temperature has been reported. (b) It might also be explained by the normal temperature-dependence of the quantities in the expression for τ^{-1}, Eq. (17), on the assumption of only one excited level. This would, in fact, require a slightly larger temperature dependence of the matrix elements than one might expect for an "allowed" transition. However, if dynamic mixing is at all important, this might not be too surprising.

It is evident, then, that the F-center decay time is subject to several independent interpretations. It is perhaps unfortunate that this is not a clearcut case, since it *is* one of the very few for which data exist on *both* Σ and τ^{-1}. As a general rule, if Σ has been large enough to measure, τ^{-1} has been too large to measure, and *vice versa*.

At any rate, the data of reference 24, although not unambiguously interpreted, certainly serve to reinforce the point of view presented in this paper. Equation (19) is *not* valid if the matrix elements are cancelled, and certainly Eq. (10) is not.

We have performed a similar calculation (for τ^{-1} on the basis of the measured Σ) on the "allowed" transition, $^1P_1 \rightarrow {}^1S_0$, in KCl:Tl. This has an absorption peak

[23] R. H. Silsbee, Phys. Rev. **103**, 1675 (1956). The oscillator strengths quoted in our paper are actually calculated from measured absorption cross sections, using Eq. (20) with $\mathcal{E}_{\rm eff}/\mathcal{E}_0 = 1+(n^2-1)/3$ and $m^*=m$, and thus our use of Eq. (22) with such oscillator strengths is equivalent to the use of Eq. (19).

[24] R. K. Swank and F. C. Brown, Phys. Rev. Letters **8**, 10 (1962).

[25] P. J. Botden, C. Z. van Doorn, and Y. Haven, Philips Research Repts. **9**, 469 (1954).

[26] A calculation along the lines of Eq. (22) has apparently been carried out by J. J. Markham, Bull. Am. Phys. Soc. **7**, 197 (1962), assuming matrix elements to be the same. He calculates $\tau=5\times10^{-9}$ sec for the F center in KCl; it is not clear to us how he gets this figure, but the ratio of his and our predicted results corresponds roughly to $(E_{\rm abs})^{-3}$, so that perhaps he equated all factors of $E_{\rm emis}$ to $E_{\rm abs}$ in Eq. (22).

at 6.3 eV, and an emission peak at 5 eV.[27] Measurement of Σ leads to an oscillator strength of 0.5; if the matrix elements do not change, Eq. (19) predicts a decay time of 2×10^{-9} sec. To our knowledge the decay time for this transition has not been measured.

We may point out that this system is more complicated than we have indicated. First, more than one emission peak is associated with the 6.3-eV absorption, and second, there is still some question as to the assignment of energies to transitions (that is, does the 5-eV emission occur between the same levels as the 6.3-eV absorption?), and it also appears that metastable trapping states occur near the excited states.[28]

C. Matrix Elements Smaller for Absorption than for Emission

We shall discuss two cases of this: (1) Transitions involving change of multiplicity, or spin flip. Matrix elements for such transitions depend upon the spin-orbit interaction and on the electrostatic splitting between terms of different multiplicity. (2) Transitions for which the matrix elements would be zero in absorption if only the equilibrium positions $x_0(0)$ of neighboring ions were considered. Such matrix elements may become nonzero when the fluctuating Coulomb potential due to lattice vibrations is considered.

(1) Since this effect is largely governed by the spin-orbit and electrostatic interactions, we must investigate how strongly these interactions depend on the equilibrium positions of the lattice ions. This dependence will, of course, vary from center to center; the properties of a very tightly bound center might be largely insensitive to the positions of neighboring nuclei, a more loosely bound center might interact strongly with the neighbors, and an extremely diffuse center might ignore completely the details of the locations of its neighbors. Again, as an indicator, we may observe the size of the Stokes' shift. We may also investigate whether free-ion wave functions adequately describe the electronic properties of the center. If there is a sizeable Stokes' shift, or if free-ion wave functions prove inadequate in describing the center, we might expect a rather large matrix element effect in ionic systems.

As an example of this, we consider the familiar $^1S \rightarrow {}^3P$ transition in thallium-activated alkali halides. This system has been studied extensively, both experimentally and theoretically, and several tentative conclusions have been drawn concerning it.[27-30] First, the $^1S \rightarrow {}^3P$ transition apparently has a moderate Stokes' shift; $E_{abs} \cong 1.2 E_{emis}$. Second, it was shown in references 26 and 29 that free-ion wave functions do not adequately describe the system; it was proposed that

mixing of wave functions centered on nearest neighbors is necessary for a complete description of the system. Dipole matrix elements involving such functions will generally be strongly dependent on the positions of the neighboring ions, since they will involve two-center integrals, and if the contribution to the wave functions by the near neighbors is large, the matrix element effect will also be large. However, we must remember that in this case the matrix element effect is not essentially a symmetry effect. That is, the transition probability is largely governed by the magnitude of the spin-orbit and electrostatic interactions, which, in turn, depend on the distances to the neighboring ions. The symmetry of a distortion will not affect these interactions nearly as much as the size of the distortion. Furthermore, the importance of nearest-neighbor positions on the above quantities is small enough that we might expect, say, an effect of a factor of 5 in the squared matrix element ratio from these considerations, but probably not a factor of 50.

Performing a calculation similar to that of Sec. B, we find, accepting the assignment that the $^1S \rightarrow {}^3P$ absorption is at 5.0 eV and the corresponding emission at 4.2 eV, that if the matrix elements do not change, the decay time for this emission should be of the order of 10^{-8} sec.

The decay time for this transition has apparently been measured[27]; in the range of 22 to 72°C, it varies as $\tau^{-1} = S e^{-\epsilon/kT}$, where $S = 2.9 \times 10^9$ sec^{-1} and $\epsilon = 0.66$ eV. There is some question as to the interpretation of this, but one thing *is* clear: Such behavior is not consistent with a model of a simple "two-level" system. However, the temperature at which measurements were made is high (F-center measurements have been made at 0–150°K), and low-temperature measurements might well reveal different behavior.

(2) In this case, static lattice considerations [i.e., setting $x(0) = x_0(0)$] do not act to make allowed absorptive transitions which are forbidden in the free ion (that is, when the lattice is in its ground-state configuration). However, even at 0°K the ions of the lattice are vibrating, and if one considers this *dynamic* effect, one may find that modes exist which make the matrix elements non-zero. That is, matrix elements involving $\phi_n{}^0$ [Eq. (13′)] may be zero, while those involving ϕ_n [Eq. (13)] may be nonzero. This, of course, is consistent with our Born-Oppenheimer wave functions of Sec. II. Thus, there may be a small probability for absorption; after absorption, there are at least three possible situations:

(a) Lattice relaxation in the excited state does not, from *static* considerations [i.e., setting $x(exc) = x_0(exc)$], make emission dipole matrix elements nonzero. Thus, the mechanism for emission is also the dynamic effect, which may or may not become much more effective than it was in absorption. It is apparent that after lattice relaxation there will exist a new set of vibrational

[27] R. S. Knox and D. L. Dexter, Phys. Rev. **104**, 1245 (1956).
[28] W. Bunger and W. Flechsig, Z. Physik **67**, 42 (1931).
[29] For a bibliography of experimental work, see F. Stockmann, *Landolt-Bornstein Tables* (Springer-Verlag, Berlin, 1955), Vol. I, Part IV, pp. 999–1007.
[30] Robert S. Knox, Phys. Rev. **115**, 1095 (1959).

modes, whose effect might be quite different from that of the original set. In particular, the number and effectiveness of odd-parity modes could change greatly. Undoubtedly, the modes of the perfect lattice will be perturbed by an impurity center, and localized modes might appear. There are at least two cases in which one would expect a significant change in the number and effectiveness of odd-parity modes: (i) if the angular part of the electronic charge distribution changes greatly during an optical process, and (ii) if the "size," or effective radius, of the charge distribution changes much.

(b) Lattice relaxation does, from purely *static* considerations, make emission dipole matrix elements nonzero. Then the emission mechanism is a static effect, and emission probabilities are expected to be much greater than the corresponding absorption probabilities.

(c) Lattice relaxation may occur to one of two or more configurations, whose energy difference in equilibrium is small. The lowest in energy of these static configurations might not be consistent with nonzero matrix elements, but another might. This would then be equivalent to having a metastable trap, only slightly lower in energy than that of a luminescent center. The familiar Boltzmann factor would govern the relative probability of occupation of these levels, and would thus also govern the decay time.

Case (a), then, insofar as the dynamic effect is slight, is essentially a situation in which matrix elements do not change appreciably, and as such belongs in Sec. A.

For case (b) to occur, lattice relaxation must introduce a perturbing potential of the correct symmetry to make transitions allowed. This lattice relaxation, of course, must be consistent with the charge distribution causing it. Clearly, this case will not be operative in all instances of forbidden absorptions, and one must investigate each particular system separately.

One could not predict case (c) except on the basis of detailed calculation; its occurrence would seem to be less likely in cubic systems than in noncubic systems. Because of the Boltzmann factor dependence of the decay time, one might hope to detect this effect by measuring the decay time as a function of temperature. Interpretation of such an experiment might be rather difficult, however, since case (a) decay times will also be temperature dependent, as will be other aspects of emission.

As an example of the above discussion, we consider NaCl:Ag. It has been found that this system has several weak absorption lines, with oscillator strength $\cong 0.001$.[31] These have been attributed to $S \rightarrow D$ transitions, which are forbidden from static lattice considerations, but which become weakly allowed through

the dynamic considerations of odd-parity lattice vibrations.[32-34]

After absorption, lattice relaxation will occur; we investigate which of the cases (a), (b), and (c) will apply in emission.

For case (b) to occur, relaxation would have to be such as to mix P state into either (or both) S and D levels. This would come about through a perturbing potential proportional to $\cos\theta$, which is odd under inversion. However, the D-level charge distribution *does* possess inversion symmetry (as do all hydrogenic charge distributions), so it is difficult to see how a case (b) equilibrium distortion could occur in a way consistent with a D-type charge distribution. Case (b) thus is probably not operative here.

From our general discussion above, it seems unlikely that case (c) occurs here either. If the matrix elements do not change, and if the important absorption and emission energies are 5.7 and 4.96 eV, respectively,[35] NaCl:Ag should have a decay time $\tau \cong 2.1 \times 10^{-7}$ sec, assuming $\Delta J = 0$, according to Eq. (19), at absolute zero. As far as we know, this decay time has not been measured.[35a] Knowledge of its value and of its temperature dependence could add greatly to our knowledge of the nature of this system's lattice relaxation. A most interesting effect is demonstrated in this system, namely, a change in absorption strength with temperature, because of the amount of odd-parity lattice vibration present.[31]

As another instance of case 2 it is apparent that an $S \rightarrow F$ transition in an impurity ion imbedded in a crystal would probably show a strong effect. The F-level charge distribution has inversion symmetry; when the electronic system is in the excited state, one would expect a Jahn-Teller distortion to occur which would introduce a perturbing potential $l(r)Y_2(\theta,\varphi)$. This has inversion symmetry and so is consistent with the F-level charge distribution. This distortion would mix P state into the F level and D state into the S state. Thus, purely static considerations would yield nonzero radiative transition probabilities in emission.

It is not clear whether any systems exist in which $S \rightarrow F$ transitions are of paramount importance. Divalent manganese in solids is thought to undergo transitions from a ^6S state to states made up of ^4D, ^4G, ^4F, and ^4P states,[36] but as far as we know a detailed and

[32] J. M. Conway, D. A. Greenwood, J. A. Krumhansl, and W. Martienssen (to be published).

[33] R. S. Knox (private communication).

[34] F. Seitz, Revs. Modern Phys. 23, 328 (1951).

[35] H. W. Etzel, J. H. Schulman, R. J. Ginther, and E. W. Claffy, Phys. Rev. 85, 1063 (1952).

[35a] *Note added in proof.* Recently the decay time of the 4.51 eV emission in KCl:Ag has been measured by Tomura and Nishimura [Masao Tomura and Hitoshi Nishimura, Paper IG-11, International Conference on Crystal Lattice Defects, Kyoto, Japan, 1962]. They find that $\tau = 1.36 \times 10^{-5}$ sec. This is larger than that roughly estimated by us for NaCl:Ag and is consistent without conjecture that the emission process in these substances is phonon assisted, and that there is no large static matrix element effect.

[36] C. C. Klick, Suppl. Brit. J. Appl. Phys. 4, S74 (1954).

[31] W. Martienssen (private communication reported by reference 32).

trustworthy analysis of this system has not been made. There are several experimental clues which make us suspect that the matrix element effect is not important in at least the most familiar transitions, however. A consistent model of the Mn^{++} center in Zn_2SiO_4 links the 5200 Å emission band to a 4700 Å absorption band.[37] Thus there is a small Stokes' shift, indicating that the interaction with the lattice may not be great. Further, the decay time is largely temperature independent, and of the order of 10^{-3} sec[36]; if the matrix element effect were not important, this would be consistent with an oscillator strength of about 10^{-6}. This is, in fact, quite close to the oscillator strength ($\cong 10^{-7}$) observed for Mn^{++} ions from $MnSO_4$ in solution in H_2O.[38] We must emphasize, however, that it is far from clear that the phenomena which we describe are connected with $S \rightarrow F$ transitions.

D. Centers in a Noncubic Environment

The considerations of the preceding sections will be applicable in the case of centers in noncubic environments. In most cases, however, it is not likely that there will be a spectacular increase in matrix elements after absorption and lattice relaxation. This is true because in most noncubic fields of interest practically all transitions with $\Delta m_S = \Delta m = 0$ will be allowed in absorption, from static considerations. For example, in a tetrahedral environment both D and F atomic states acquire some P-like character, and thus transitions are allowed to a ground state (without having to involve lattice vibrations).[39]

[37] C. C. Klick and J. H. Schulman, J. Opt. Soc. Am. 42, 910 (1952).

[38] CHR. Klixbull Jørgensen, Acta Chem. Scand. 8, 1495 (1954), and accompanying articles.

[39] Note added in proof. There exists a fairly sizeable amount of literature on crystal field theory with regard to complex ions, such as Mn^{++} and Co^{++}. The case of Mn^{++} in a cubic crystal field is reviewed by McClure [D. S. McClure, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 9, pp. 499–502], who gives references to the

Absorption of this type is apparently observed in AgI, in which the Ag^+ ion is in a tetrahedral environment.[33]

V. CONCLUSION

We have shown that the Einstein relation is not in general valid in the case of imperfections in solids. Several types of mechanisms are suggested, in particular, the Jahn-Teller effect, which might introduce discrepancies into results derived through the use of the Einstein relation. The F center is the system in which the most clear-cut case of discrepancy is known. Other systems are discussed, and it is expected that failure of the Einstein relation will manifest itself in important ways in instances other than the F center, when additional experiments are performed.

original work. The interesting transitions in Mn^{++} occur between a ^6S ground state and an excited level which in the free ion is ^4G, but which splits into several components in the crystal field. The considerations of our paper should help to understand this system.

Another interesting system is Co^{++} in a tetrahedral field. As we point out in Sec. IV D, a tetrahedral field will make transition probabilities between almost any two levels nonzero; however, such a field also splits the levels, and there will be components of these levels between which transition probabilities will be zero. Thus interesting effects may indeed occur. In the particular case of Co^{++} there exist atomic levels ^4P and ^4F which under the influence of a tetrahedral field becomes $^4T_1$, and $^4T_1$, $^4T_2$, $^4A_2$, respectively [A. D. Liehr and C. J. Ballhausen, J. Mol. Spectroscopy 2, 342 (1958)]. Absorption is observed from the $^4A_2$ ground state to both $^4T_1$ states, but not to $^4T_2$ [R. Pappalardo and R. E. Dietz, Phys. Rev. 123, 1188 (1961)]. In fact, crystal field theory predicts zero matrix elements between $^4A_2$ and $^4T_2$ [see A. D. Liehr and C. J. Ballhausen]. Garlick [G. F. J. Garlick (private communication)], however, has informed us of a preliminary study of emission between these levels for Co^{++} in ZnS. The decay time appears to be $\gtrsim 10^{-4}$ sec. If matrix elements for absorption and emission are the same, Eq. (19) predicts a decay time $\gtrsim 10^{-2}$ sec (assuming $f \lesssim 10^{-6}$). A detailed analysis of this system may show that the apparent discrepancy is due to effects of the type which we have discussed.

We are grateful to Professor Garlick for permission to quote his unpublished results.