

photographic registration have been checked with higher resolution and Geiger counter registration of intensities. This structure is all so close to the edge as to be affected by, if not governed entirely by, atomic optical levels modified by heteropolar (HCl) and homopolar (Cl_2) binding. Extended structure solely dependent upon electron scattering was not observed.

There is no agreement between theory and experiment in the case of Cl_2 for which the best chance of checking theory and experiment is expected. This serves to point up other discrepancies cited in the Introduction and to indicate that the theory of the structure to be found for absorption in molecular gases, within several tens of volts immediately on the short wavelength side of the main edge, is unsatisfactory.

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A Note on the Propagation of Excitation in an Idealized Crystal*†

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It is shown that, in insulators, overlapping of the electronic wave functions of near-by crystal constituents is not necessary for effective transfer of excitation energy by the "exciton" mechanism. The electromagnetic interaction of the "virtual" dipoles of the transition is sufficient to give rise to such transfer characterized in cubic crystals by a wave number \mathbf{k} , and an anisotropic effective mass, given in order of magnitude by the ratio electronic mass/oscillator strength of transition. Implications and limitations of the calculation are discussed.

I. INTRODUCTION

DURING the past year, a basic advance has been made in the understanding of the processes of migration of energy in ionic crystals,¹ through the experimental work of Apker and Taft. Although these workers dealt with photoelectric emission, an inescapable conclusion from their results is that part of the emitted electrons derive their energy only by some intermediate transfer process from the energy of the incident photons. Since the energy distribution of this group of electrons (called the *S*-group by Apker and Taft) does not display the characteristics one would expect if the electrons were directly released by absorption of light, one is led to the hypothesis that, in an intermediate stage, the energy is carried by what have been called "excitons." These entities were first introduced as a theoretical concept by Frenkel,² and signify a moving state of electronic excitation energy in the lattice. That electronic states of this kind must in general be characterized by a wave number, rather than by a label corresponding to the atom on which they reside, is a consequence of the strong coupling between adjacent constituents of the lattice; in the alkali halides the participating units may presumably be considered to be the halide ions.

An important purpose of the present paper is to show that the use of the term "exciton" (for electronic excitation energy traveling in an insulating solid) is appropriate to a situation in which there is "strong coupling" of any type between an excited atom and its neighbors. In particular, appreciable overlapping of their electronic wave functions is not necessary to insure "strong coupling" of the crystal constituents. It will be seen as a principal result, that energy transfer by electromagnetic "near zone" interactions may take place very quickly in certain crystals.³ Thus, because of this interaction alone, one must characterize the wave functions of the excitation by a wave number (and hence one is obliged to use the term exciton), rather than view the excitation as well localized on single atoms or molecules. This does not require the appearance of a new band in the spectrum of atoms when they are placed into condensed systems. The structure in absorption spectra due to the doublet levels characteristic of the bromide and iodide ions, for example, is observed also in the solid state. The work of the present paper demonstrates that one has every reason to believe that these levels become typical exciton levels when the ions mentioned are made the anions of ionic crystals.

Further discussion of the implications of our calculation will be given in later publications. The authors wish to thank Professor Frederick Seitz for suggesting that a suitably simplified model of an insulating crystal

* A preliminary report of this work was given at the New York meeting of the American Physical Society, February, 1951, *Phys. Rev.* **82**, 315 (1951).

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¹ L. Apker and E. Taft, *Phys. Rev.* **82**, 814 (1951); **81**, 698 (1951); **72**, 964 (1950); M. Hebb, *Phys. Rev.* **81**, 702 (1951).

² J. Frenkel, *Phys. Rev.* **37**, 17 (1931); **37**, 1276 (1931); *Physik. Z. Sowjetunion* **9**, 158 (1936).

³ This is analogous to the mechanism of "sensitized fluorescence" in gases. G. Cario and J. Franck, *Z. Physik* **17**, 202 (1923), and many later papers.

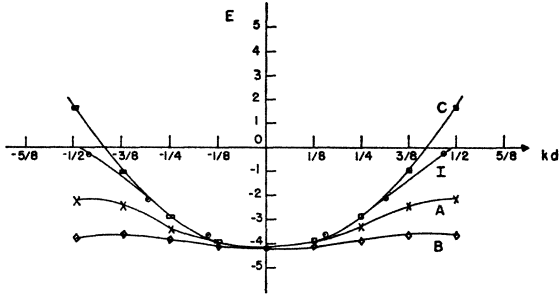


Fig. 1. Dependence of exciton energy on wave numbers for $(\mathbf{u}, \mathbf{k})=90^\circ$, in a face-centered crystal. Ordinate: $(E_{\mathbf{k}^n} - E_{JJ^n})/|\mathbf{u}|^2 n^0 = E$. Abscissa: $|\mathbf{k}|d$, where $d = (2n_0)^{-1}$. I : Integral Approximation (same for all directions of k). A : \mathbf{k} in 100 direction. B : \mathbf{k} in 110 direction. C : \mathbf{k} in 111 direction.

be chosen, with the problem of electromagnetic "near zone" exciton propagation in mind.

II. CALCULATIONS AND CONCLUSIONS

A suitable framework for this study was proposed long ago by Frenkel² and Peierls,⁴ but they do not appear to have emphasized the relative importance of the electromagnetic coupling between atoms. This leads to several important conclusions which are discussed in the latter part of this section, and form the principal content of the present work.

We consider a cubic crystal of effectively infinite size, on the lattice sites of which are arranged identical one-electron atoms, whose thermal vibration we shall leave out of the computation. As a starting approximation, we may take a determinant wave function of all the atoms, which ignores spin effects and neglects the overlapping of the ground-state wave functions on different atoms. This does not mean that exchange effects are to be totally ignored, as we shall see, and hence does not exclude the kind of band formation characteristic of a quantum theoretical approach (although we do assume that the effects of overlap, and hence exchange, on the normalization, are secondary).

As a convenience we shall assume that the ground-state atomic functions are S -type, and that the corresponding excited state wave functions have P -character. Since the lattice has cubic symmetry, we need not concern ourselves with the orbital degeneracy of the excited state; (i.e., it is not lifted by the cubic symmetry), this has an important corollary the fact the state may in principle have an arbitrary direction of polarization.

Thus the ground-state wave function is⁵

$$\Psi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1^0(\mathbf{r}_1) & \cdots & \psi_1^0(\mathbf{r}_N) \\ \vdots & & \vdots \\ \psi_N^0(\mathbf{r}_1) & \cdots & \psi_N^0(\mathbf{r}_N) \end{vmatrix}$$

and a typical zero'th order excited state wave function will be

$$\Psi_{J^n} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1^0(\mathbf{r}_1) & \cdots & \psi_1^0(\mathbf{r}_N) \\ \vdots & & \vdots \\ \psi_J^n(\mathbf{r}_1) & \cdots & \psi_J^n(\mathbf{r}_N) \\ \vdots & & \vdots \\ \psi_N^0(\mathbf{r}_1) & \cdots & \psi_N^0(\mathbf{r}_N) \end{vmatrix}$$

Here the superscript n refers to the n th excited atomic state of energy ϵ_n , the subscript labels the nucleus involved, the vector argument refers to the electron in question. The energy corresponding to Ψ_0 , is found to be:

$$E^0 = N\epsilon_0 - \frac{1}{2}e^2 \sum'_{I,J} \int \psi_I^0(\mathbf{r}_1) \psi_J^0(\mathbf{r}_2) \times \frac{1}{r_{12}} \psi_I^0(\mathbf{r}_2) \psi_J^0(\mathbf{r}_1) d\tau_1 d\tau_2. \quad (1)$$

where the prime acts to exclude the case in which $I=J$. Consistently with the assumption that no overlapping of the ground-state wave function takes place, we have neglected here the total coulomb interaction of neighboring atoms. We have used the hamiltonian

$$H = \sum_I H_I + \sum_{I,J} H_{IJ}$$

$$H_I = \frac{-e^2}{r_{iI}} - \frac{\hbar^2}{2m_{e1}} \nabla_i^2, \quad H_{IJ} = \sum'_{I,J} \frac{e^2}{R_{IJ}} - \sum_{i,I} \frac{e^2}{r_{iI}} + \sum'_{i,i} \frac{e^2}{r_{ij}}$$

where ∇_i^2 refers to the i th electron, associated with the I th atom, and the small letters refer to the electrons, the large to the nuclei.

The energy of the excited state wave function Ψ_{J^n} is computed to be

$$E_{JJ^n} = N\epsilon_0 + \epsilon_n - \epsilon_0 - e^2 \sum_{L \neq 0} \times \int \psi_{L+J^0}(\mathbf{r}_2) \psi_{L+J^0}(\mathbf{r}_1) \frac{1}{r_{12}} \psi_{J^n}(\mathbf{r}_1) \psi_{J^n}(\mathbf{r}_2) d\tau_1 d\tau_2$$

$$- \frac{e^2}{2} \sum'_{\substack{I \neq M \\ I \neq J \\ J \neq M}} \int \psi_I^0(\mathbf{r}_1) \psi_M^0(\mathbf{r}_2) \times \frac{1}{r_{12}} \psi_I^0(\mathbf{r}_2) \psi_M^0(\mathbf{r}_1) d\tau_1 d\tau_2. \quad (2)$$

Here ϵ_0 = energy of the isolated atom in its ground state, ϵ_n = energy of the isolated atom in its excited state, and N = total number of atoms or electrons. The excited state wave functions do not diagonalize the hamiltonian, and, of course, are degenerate. The off-diagonal

⁴ R. Peierls, Ann. Physik 13, 905 (1932).

⁵ For a brief summary of Peierls' and Frenkel's work, see F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 415-417.

matrix elements are typified by E_{JL} ,

$$E_{JL} = \int \cdots \int \Psi_J^n H \Psi_L^n d\tau_1 \cdots d\tau_N.$$

$i=1, \dots, N$

These reduce to

$$E_{JL} = e^2 \int \psi_J^n(\mathbf{r}_1) \psi_L^0(\mathbf{r}_2) \frac{1}{r_{12}} \psi_J^0(\mathbf{r}_1) \psi_L^n(\mathbf{r}_2) d\tau_1 d\tau_2$$

"coulomb"

$$- e^2 \int \psi_J^n(\mathbf{r}_1) \psi_L^0(\mathbf{r}_2) \frac{1}{r_{12}} \psi_J^0(\mathbf{r}_2) \psi_L^n(\mathbf{r}_1) d\tau_1 d\tau_2. \quad (3)$$

"exchange"

In order to obtain a correct zero'th order wave function from the degenerate set Ψ_J^n , the following linear combination is chosen

$$\Psi_{\mathbf{k}}^n = 1/\sqrt{N} \sum_J \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_J) \Psi_J^n.$$

It may be verified that the off-diagonal matrix elements of two wave functions with quantum numbers \mathbf{k} and \mathbf{k}' do indeed vanish, if one uses the δ -function relation:

$$\sum_J \exp[2\pi i (\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}_J] = \delta_{\mathbf{k}-\mathbf{k}', 0}.$$

The new diagonal energy is found to be

$$E_{\mathbf{k}}^n = E_{JJ}^n + \sum_{L'} E_{JL} \exp[2\pi i \mathbf{k} \cdot (\mathbf{r}_J - \mathbf{r}_L)]. \quad (4)$$

The prime signifies that $J \neq L$, and the sum is to be taken over all lattice points.

It is at this stage of the calculation, we wish to stress, that previous treatments diverge in emphasis, as well as in the physical conclusions drawn. In order to evaluate the lattice sum in Eq. (4), it is expedient to examine the terms in the expression (3) for E_{JL} , as functions of lattice parameter. For convenience we proceed in reverse order; i.e., we shall first consider the "exchange" term. This will depend exponentially on lattice parameter, somewhat in the fashion $(e^2/R) \times \exp(-2R/a)$ where a = equivalent Bohr radius of the excitation; R = nearest neighbor distance. Hence, only the nearest neighbors, if we consider the important lower excited states, will contribute to the lattice sum. Furthermore, even this contribution will be small, because of the exponential dependence, at a density characteristic of many ionic and molecular crystals. Further discussion will be given this term later. The other term in E_{JL} , the coulomb part, is nothing more than an expression for the interaction of two charge clouds, each with density equal to the product of the excited and ground-state wave functions of an isolated atom. Such an integral can be expanded in the lattice parameter, or, more conveniently, in the distance between the atoms R . One obtains

$$\frac{Q_1 Q_2}{R} + \left(\frac{Q_1 \mathbf{R} \cdot \mathbf{u}_2}{R^3} - \frac{Q_2 \mathbf{R} \cdot \mathbf{u}_1}{R^3} \right) - \left(\frac{\mathbf{u}_1 \cdot \mathbf{u}_2}{R^5} (\mathbf{R} \cdot (-\mathbf{R})) - 3 \frac{(\mathbf{u}_1 \cdot \mathbf{R})(\mathbf{u}_2 \cdot \mathbf{R})}{R^5} \right) + \cdots$$

Here

$$Q_1 = \int \psi_J^n(\mathbf{r}_1) \psi_J^0(\mathbf{r}_1) d\tau_1, \quad Q_2 = \int \psi_L^n(\mathbf{r}_2) \psi_L^0(\mathbf{r}_2) d\tau_2$$

$$\mathbf{u}_1 = e \int \psi_J^n(\mathbf{r}_1) [\mathbf{r}_1 - \mathbf{r}_J] \psi_J^0(\mathbf{r}_1) d\tau_1,$$

$$\mathbf{u}_2 = e \int \psi_L^n(\mathbf{r}_2) [\mathbf{r}_2 - \mathbf{r}_L] \psi_L^0(\mathbf{r}_2) d\tau_2.$$

Thus the first two terms cancel, and we are left with the third term. Because we have neglected thermal effects, the vectors $\mathbf{u}_1, \mathbf{u}_2$ have the same direction and magnitude for all atoms, and hence the final expression for the lattice sum of the coulomb parts of the original off diagonal matrix element is

$$\sum_{L'} E_{JL} = - |\mathbf{u}|^2 \sum_{L'} \left(\frac{3 \cos^2(\mathbf{u}, \mathbf{r}_J - \mathbf{r}_L) - 1}{|\mathbf{r}_L - \mathbf{r}_J|^3} \right) \times \exp[2\pi i \mathbf{k} \cdot (\mathbf{r}_J - \mathbf{r}_L)].$$

Note that the contributions of distant neighbors, especially for $|\mathbf{k}| \approx 0$, cannot be neglected, as previous treatments have done.^{2,4,5}

It remains to consider the relative magnitude of the coulomb and exchange terms. A rough idea may be obtained by considering the excitation of the lowest level (exciton level) in an alkali halide. The excitation may be regarded as characteristic of the halide ion lattice, and thus R may be chosen to be the nearest like neighbor distance, for purposes of comparison. When this is done, and an oscillator strength of order unity is assigned to the dipole transition represented by $|\mathbf{u}|$, one sees that the relative order of magnitude is about

$$\frac{\exp(-2R/a)/R \cdot \exp[-(2)(3.14)\sqrt{2}/(1.5)]}{a^2/R^3} \sim \frac{((1.5)/(3.14)\sqrt{2})^2}{((1.5)/(3.14)\sqrt{2})^2}$$

a number of the order of 1/10. A more precise comparison will certainly not invert the relative importance of the two terms.⁶ It is seen that the dipole-dipole term is

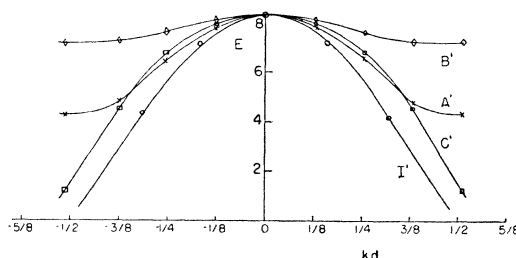


FIG. 2. Dependence of exciton energy on wave number for $(\mathbf{u}, \mathbf{k}) = 0^\circ$, in a face-centered crystal. The symbols have the same meaning as in Fig. 1.

⁶ The writers are indebted to Dr. D. Dexter for making available to us his results on the "spread" of exciton wave functions in NaCl. See Phys. Rev. **83**, 435 (1951). It is shown there that most of the charge density of the excited state is concentrated on the Cl^- ion (not on the Na^+ ions as is commonly supposed).

the important one. The sum, when carried out for $|\mathbf{k}| \approx 0$ (i.e., $|\mathbf{k}|R \ll 1$) is nothing more than the interaction energy of a lattice of static dipoles of magnitude $|\mathbf{u}|$. If we neglect the contribution of outer surface (depolarization) terms, and replace the summation by an integral, both of these operations being permissible when $|\mathbf{k}| \approx 0$ (i.e., of order $1/\lambda_{op}$) we obtain

$$E_{\mathbf{k}}^n = E_{JJ}^n + 8\pi/3 P_2(\cos(\mathbf{u}, \mathbf{k})) n_0 |\mathbf{u}|^2 \{j_0(\rho) - j_2(\rho)\},$$

where P_2 is the Legendre polynomial of order two, n_0 the density of atoms and j_0 and j_2 are spherical bessel functions⁷ of argument $\rho = 2\pi|\mathbf{k}|R_0$, where R_0 is determined by the condition that $(4\pi/3)R_0^3 = 1/n_0$.

It should be specifically mentioned that the summation method used breaks down when $|\mathbf{k}|$ precisely equals zero, because then the outer surface terms are just as important as contributions from nearest neighbors. In practice, however, $|\mathbf{k}|$ never exactly equals zero (except possibly when, under the influence of lattice polarization, the exciton may become trapped. Our treatment is not appropriate for such situations). This result applies to any centro-symmetric cubic lattice, but the integral is a good approximation only for $|\mathbf{k}|$ small, but not zero. It is to be noted that if $|\mathbf{k}| \rightarrow 0$, $(\mathbf{u}, \mathbf{k}) = 90^\circ$, we obtain a factor $4\pi/3$ which bears a strong resemblance to the Lorentz-Lorenz polarization contribution. The relevance of this fact for a consideration of the problem of "local fields" is discussed in a paper by Heller and Dexter.⁸ Figures 1 and 2 illustrate the goodness of approximation of the integral to the sum for the particular directions relative to the cubic axes (in a face-centered crystal) which are indicated. It is to be stressed that the angle (\mathbf{u}, \mathbf{k}) is completely arbitrary, and thus that anisotropy of exciton motion may be expected even in a cubic lattice. Although only the state $(\mathbf{u}, \mathbf{k}) = 90^\circ$ will be excited by light waves if the simultaneous creation of phonons is neglected, others may arise through interaction with lattice modes, and during creation of excitons by α -particles or β -rays.

The sums were carried out by use of an extension of Ewald's method of theta-functions given by Born and Bradburn.⁹ The method is very elegant (although it would have to be revised for $|\mathbf{k}| = 0$ in our problem in which case, fortunately, the answer is known). Convenient numerical tables are given in the articles of Born and Misra.¹⁰

The significance of the qualitative results presented is seen most strikingly if we find the reciprocal effective mass of the exciton near (but not at) the base of the energy curve, by the usual method, taking a second de-

rivative. This gives

$$\begin{aligned} \left(\frac{1}{m_{\text{eff}}}\right)_{|\mathbf{k}| \approx 0} &= \left(\frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}\right)_{|\mathbf{k}| \approx 0} \\ &= \frac{8\pi}{3} P_2(\cos(\mathbf{u}, \mathbf{k})) \frac{|\mathbf{u}|^2}{\hbar^2} n_0 (j_0'' - j_2'')_{|\mathbf{k}|=0} (2\pi R_0)^2 \\ &= \frac{8\pi}{3} P_2(\cos(\mathbf{u}, \mathbf{k})) \frac{|\mathbf{u}|^2}{\hbar^2} n_0 \cdot 4\pi^2 R_0^2 \left(-\frac{1}{5}\right). \end{aligned}$$

Changing to the oscillator strength f_{n0} by use of the relation:

$$f_{n0} = \frac{(\epsilon_n - \epsilon_0) m_{el} |\mathbf{u}|^2}{3\hbar^2 e^2}$$

one has

$$\begin{aligned} \left(\frac{1}{m_{\text{eff}}}\right)_{|\mathbf{k}| \approx 0} &= -\frac{16\pi}{3 \times 15} \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} P_2(\cos(\mathbf{u}, \mathbf{k})) \\ &\quad \times \left(\frac{e^2 n_0^{\frac{1}{2}}}{\epsilon_n - \epsilon_0}\right) \frac{f_{n0}}{m_{el}} \end{aligned}$$

In other words, the effective mass will be positive or negative depending upon the relative orientation of \mathbf{u} and \mathbf{k} (and, incidentally, the effective mass can become infinite for certain relative orientations), but, in general we may say that $m_{\text{exciton}} \sim (m_{\text{electron}}/f_{n0})(R_0/a)$, and is positive when the exciton is created by light (since $P_2(\cos 90^\circ) = -\frac{1}{2}$). Thus the smaller the oscillator strength, the slower is the propagation of excitation, for a given kinetic energy of the exciton.

These findings should be compared with Foerster's¹¹ result that the speed of migration of excitation from one molecule to another in a dilute solution of dye molecules varies as the inverse sixth power of the mean separation. Our picture of exciton migration deals with a different limiting case, that in which the density is so high that the stationary states cannot be well approximated by imagining only one atom excited at a time. Thus, throughout the region of high concentration, the appropriate model is much more like that of the electron wave packets in metals, in which collisions (changing \mathbf{k} and, in general, \mathbf{u}) will take place during the lifetime of the excitation. This approach suggests that a typical "maximum diffusion distance" of an exciton wave packet will be given by d , where

$$\begin{aligned} d &\leq (\langle v_{\text{thermal}}^2 \rangle \tau_{\text{thermal}} \tau_{\text{opt}})^{\frac{1}{2}} \\ &\approx (10^{14} \times 10^{-14} \times 10^{-8})^{\frac{1}{2}} = 10^{-4} \text{ cm}, \end{aligned}$$

although the total path length covered may be of the order of centimeters. Of course a competing process, such as creation of F -centers, may rob the exciton of its energy long before the optical lifetime is up.

¹¹ T. Foerster, *Ann. Physik* 2, 55 (1948), and references to earlier work there given.

⁷ P. M. Morse, *Vibration and Sound* (McGraw-Hill Book Company, Inc., New York, 1948), second edition, p. 316.

⁸ W. R. Heller and D. L. Dexter (to be published).

⁹ M. Born and M. Bradburn, *Proc. Cambridge Phil. Soc.* 39, 104 (1943).

¹⁰ R. D. Misra, *Proc. Cambridge Phil. Soc.* 36, 173 (1940); M. Born and R. D. Misra, *Proc. Cambridge Phil. Soc.* 36, 466 (1940).

It is interesting to realize that the lattice sum which leads to the main conclusions is a very sensitive function (for $|\mathbf{k}| \approx 0$) of the distant configuration of atoms. This implies that if the crystal has dimensions of the order of the diffusion distance or smaller, one may notice peculiar effects (due to the consequent anisotropy and increase in magnitude of the effective mass) in fluorescence or other phenomena associated with energy transfer by this mechanism. It was pointed out to the authors¹² that Vavilov¹³ has observed unusually well developed luminescence phenomena in very fine capillaries, using dye solutions which do not display such effects in bulk. The fact that the atoms in solution are not arranged in a cubic lattice should not change the qualitative prediction.

One may emphasize that all our conclusions follow from the premise that there is only a small amount of actual overlapping of the excited state wave functions of the electrons. While this premise will not hold in some cases (obviously not in the case of strong valence bonds between the crystal constituents) it should be qualitatively appropriate in certain ionic and molecular crystals in which the electronic wave functions are large at the sites of relatively widely spaced crystal constituents and small in between them. Qualitatively similar conclusions should hold for pure liquids and solutions in both the solid and liquid states, since the only difference will lie in the random arrangement of the excited atoms or molecules in these systems.

An important point to be settled before the present results can be applied to actual crystals is that of the effect of lattice vibrations on the calculations. Reasoning from an argument based on the use of the customary plots of total energy *versus* nuclear configuration coordinate, one might expect that "resonant transfer" of electromagnetic energy must await a favorably similar disposition of the configuration coordinates of a neighboring atom. But, as was stressed in Peierls' fundamental paper,⁴ such curves are appropriate only when the energy levels of the electronic system are very widely spaced relative to the interaction energy with the important lattice vibrations. Otherwise, (as is the case for strong coupling) the adiabatic approximation on which the use of the energy curves is based, must break down, and, in fact, one should solve the problem of the states generated by the "mixture" of the two quasi-continuous spectra of the excitons and of the phonons.

Difficult as this is, one sees that such a mixture will allow the resonant interaction to have its effect without waiting, so to speak, because the nuclear displacement coordinates no longer correspond to precise points on the curve of total energy. We may thus see that the resonant near-zone interaction should make possible a well-developed band structure with its quantum-

mechanical implications as regards the nonlocalization of energy, even when the lattice vibrations are taken into account. A criterion, then, which allows us to reason as in this paper, without taking specific account of the lattice vibrations, is simply that the band widths due to electromagnetic coupling be large (and hence that the spacing between levels be small) compared to the lattice vibration energies which are relevant for the particular electronic transitions. In ionic lattices this criterion should be satisfied, if f_{n_0} is not much less than 1, at practically all temperatures. In molecular crystals however, especially for small oscillator strengths and at low temperatures the argument based on energy curves may apply; the excitation mass will then be limited to values effectively of the order of nuclear masses, i.e., propagation will be relatively slow.

SUMMARY

It is shown that overlapping of electronic wave functions on nearby atoms or molecules in crystals is not necessary for effective transfer of excitation energy by the exciton mechanism. This is due to the fact that the principal interaction, varying as $1/R^3$, is characteristic of electromagnetic oscillators in their quasi-static zone. For an idealized cubic crystal, the results are obtained that anisotropy exists, in general, in the motion of excitons, and that the effective mass of an exciton corresponding to a dipole transition is given in order of magnitude by

$$m_{eff} \sim (m_{el}/f_{n_0})(R_0/a),$$

where m_{el} = mass of electron, f_{n_0} = oscillator strength of corresponding isolated atomic transition, a = equivalent Bohr radius of internal exciton orbit in crystal $R_0 = (\frac{3}{4}\pi n_0)^{\frac{1}{3}}$, and n_0 = atomic density.

The qualitative conclusion is pointed out that for sample dimensions small relative to the "diffusion distance" of an exciton, one should observe characteristic changes in the effective mass. Also, the whole discussion should have qualitative value for energy transfer in liquids or concentrated solutions, under suitable restrictions, although the atomic arrangement here has no long range order. A discussion is given of the effect on the results of accounting for lattice vibrations.

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¹² In private conversation with Mr. E. Jacobs and Professor E. Rabinowitch.

¹³ S. Vavilov, *Doklady Akad. Nauk. S.S.S.R.* **67**, 811 (1949).