Optical Absorption in Ionic Crystals Involving Small Polarons*†

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A theory of optical absorption by electrons in ionic crystals is given for two cases: (1) for transitions from a wide valence band to a narrow conduction band; (2) for transitions from one narrow band to another. All coupling of electrons in the wide valence band with the phonons is ignored while for the narrow bands coupling with the longitudinal optical phonons is treated by use of the wave functions of small polaron theory. Dispersion of phonon frequencies, interaction with acoustical modes, and all effects involving spin are neglected. Transition probabilities between states are obtained by standard time-dependent perturbation theory with the electron-radiation interaction as a perturbation. Indirect transitions via a third band and exciton absorption are qualitatively discussed. Consideration of the effects of an interaction quadratic in the normal coordinates is given for the case of electronic interaction with a single mode of lattice vibration, and Urbach's rule is discussed using this model. The applicability of the theory to the transition metal oxides and alkali halides is considered.

I. INTRODUCTION

MANY difficulties occur in the theoretical treatment of the properties of electrons in ionic crystals because of the strong coupling of electrons with the longitudinal optical modes of lattice vibration. An electron in these crystals has to be thought of as carrying around with it a cloud of lattice polarization. The complex of electron plus surrounding polarization is usually called a polaron.

The problem of calculating the self-energy and increase of effective mass of a low-energy electron (with an effective mass which may differ from the free-electron mass) due to its interaction with a vibrating polarization continuum has been quite well treated by variational techniques, as may be seen from Fröhlich's[1] and Allcock's[2] review articles. Calculations on the mobility of electrons in this model have also been made (see Schultz's review[3]) but there is some disagreement about results for intermediate strengths of the coupling. One reason for difficulties is that little is known about the properties of polarons of energies of the order of the phonon energy above the bottom of the band.

An alternative approach to the polaron problem, which is usually known as small polaron theory, and is applicable to electrons in narrow bands, for which the above-mentioned effective mass model will not be valid, has been developed by Yamashita and Kurosawa,[4]

Sewell,[5] and Holstein.[6] In this approach the polaron states at low temperatures consist of linear combinations of states in which the electron is localized on one lattice site, with the centers of the lattice vibration harmonic oscillators suitably displaced by an amount depending on the strength of the coupling. The coupling with the phonons gives rise to a band narrowing, which gets more extreme as the temperature is raised. (In this connection see the note added in proof at the end of the paper.) Above a certain transition temperature (of the order of half the optical phonon temperature if the main interaction is with the optical phonons) the band picture breaks down and a picture in which the electron hops from site to site with an activation energy takes its place. Neglecting impurity scattering, the mobility decreases with temperature at low temperatures, when the band model applies, but increases exponentially with an activation energy above the transition temperature.

The optical properties of ionic crystals are also difficult to investigate theoretically because of the strong coupling with the lattice polarization. Absorption of a photon is normally accompanied by the absorption or emission of many phonons.

Optical properties of solids are determined by the refractive index n and extinction coefficient κ as a function of frequency. These quantities are simply related to the complex dielectric constant or complex conductivity, and so one method of finding them is to calculate the electronic current as a function of time induced by a small electric field of arbitrary time variation. Feynman et al.[7] have calculated the complex impedance of a polaron in the effective-mass model by writing down the quantum-mechanical expression for the expected current, eliminating phonon coordinates by standard field-theoretical techniques, and then introducing some approximations. Sewell[8] has given

[1] H. Fröhlich, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 325.

[2] G. R. Allcock, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 412.

[3] T. D. Schultz, Phys. Rev. **116**, 526 (1959).

[4] J. Yamashita and T. Kurosawa, J. Phys. Chem. Solids **5**, 34 (1958).

[5] G. L. Sewell, Phil. Mag. **3**, 1361 (1958).

[6] T. Holstein, Ann. Phys. (N. Y.) **8**, 325 and 343 (1959).

[7] R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127**, 1004 (1962).

[8] G. L. Sewell, Phys. Rev. **129**, 597 (1963).

formal expressions for the conductivity in a small polaron model at high temperatures for frequencies less than $(kT/\hbar)$ and less than the phonon frequencies, by making use of a modification for open systems of Kubo's formalism for the linear response of a closed system to an applied field.

In this paper, instead of calculating both n and κ by finding the complex conductivity, we shall assume that the refractive index is known and then calculate the absorption coefficient by use of perturbation theory.

For a process in which n phonons assist in the absorption of a photon, one method of treatment is to take the electron-phonon interaction plus the electron-radiation interaction as a perturbation, and use $(n+1)$st-order perturbation theory (see, e.g., Meyer's[9] and Dumke's[10] articles for one- and two-phonon processes treated by this method), while a second approach is to consider the effect of the electron-phonon interaction on the lattice and electron wave functions first, and then calculate the absorption using first-order perturbation theory with just the electron-radiation interaction as the perturbation. It seems likely that in many cases the second method will provide advantages over the first, as it avoids the consideration of large numbers of intermediate states,[11] and it also offers the possibility of being used when the electron-phonon interaction is too strong to be treated by perturbation theory. For optical phonons it has the additional advantage that use may be made of the extensive literature on the theory of polarons.

This second method is used in this paper to deal with transitions involving polarons in narrow bands for which "small" polaron theory applies. Much of the work is similar to that of Pekar[12] and of Perlin and Palistrant[13] on optical transitions in and from F centers in the alkali halides.

In Sec. II the theory of absorption is given for two cases: (1) for transitions of electrons from a wide valence band for which the coupling with the phonons is neglected, to a small polaron conduction band; (2) for transitions between two small polaron bands. Indirect transitions via a third band and exciton absorption are briefly discussed.

In Sec. III the range of validity of the theory of Sec. II is discussed, estimates of the parameters of the theory and of the importance of some neglected factors are made, and some simplifications of the results at low and high temperatures are indicated.

In Sec. IV a model involving interaction with a single harmonic oscillator is used to give a discussion of the effects on absorption of an interaction between an electron and lattice vibrations quadratic in the vibrational coordinates. The connection between this type of interaction and Urbach's rule is shown for this model.

In Sec. V the applicability of the theory to the transition metal oxides (in particular, NiO) and the alkali halides is considered.

II. THEORY OF ABSORPTION

A. General

In this section we shall be concerned with a system with a Hamiltonian H^{tot} given by

$$H^{\mathrm{tot}}=H+H^{r}+H^{e-r}, \tag{1}$$

where H^r and H^{e-r} are the radiation Hamiltonian and electron-radiation interaction for a radiation field which has already been modified from the free radiation field by the introduction of a refractive index, and

$$H=H^{e}+H^{p}+H^{e-p}, \tag{2}$$

where H^e is the electron Hamiltonian for a crystal with the atoms in their lattice sites, H^p is the phonon Hamiltonian, and H^{e-p} represents the electron-phonon interaction.

If the eigenfunctions of H are given by

$$H|s\rangle=E_{s}|s\rangle, \tag{3}$$

then standard absorption theory gives the following expression for the electronic absorption coefficient K for electromagnetic radiation polarized in the x direction as a function of photon energy Ω, provided that the wave vector of the radiation is negligibly small:

$$K(\Omega)=\frac{A}{n\Omega}\operatorname{Av}_{s}\sum_{s'}|\langle s|\sum_{i}(\partial/\partial x_{i})|s'\rangle|^{2}$$
$$\times\delta(E_{s'}-E_{s}-\Omega). \tag{4}$$

Here n is the refractive index (which may be a function of Ω), x_i denotes the x component of the ith electron coordinates; the sum inside the matrix element is over all electron suffixes i, $\operatorname{Av}_s \sum_{s'}$ denotes a thermodynamic average over all initial states $|s\rangle$ energy E_s and a sum over final states $|s'\rangle$, energy $E_{s'}$, and

$$A=\frac{1}{V}\frac{4\pi^{2}e^{2}\hbar^{3}}{m^{2}c}, \tag{5}$$

where V is the volume of the system, m and $(-e)$ are the mass and charge of an electron, and c is the velocity of light in vacuo. The refractive index n may depend to a large extent on the same electronic processes considered here as contributing to the absorption. Thus, our theory cannot be used to predict the absorption

[9] H. J. G. Meyer, Phys. Rev. **112**, 298 (1958).

[10] W. P. Dumke, Phys. Rev. **108**, 1419 (1957); **118**, 938 (1960).

[11] An alternative method of avoiding explicitly considering intermediate states, convenient in some problems, is to use the generating function method, applied to a calculation of the line shapes of exciton absorption lines by Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **20**, 53 (1958).

[12] S. I. Pekar, *Untersuchungen über Die Elektronentheorie der Kristalle* (Akademie-Verlag, Berlin, 1954). Also available in Russian.

[13] Yu. E. Perlin and M. E. Palistrant, Opt. Spectr. **9**, 320 (1960).

coefficient K itself but only a relation between n and K. However, we should remember that K will vary over many orders of magnitude near an absorption edge while n normally remains of order unity, and so the general form of the dependence of K on photon energy Ω may be obtained by supposing n is constant.

In the following subsections we shall specialize to the case where H^e and H^{e-p} can be expressed as a sum of one-electron Hamiltonians, shall ignore all branches of the phonon spectrum except one, and shall take wave functions which are approximate eigenfunctions of the part of H referring to a single electron for the special cases of narrow bands for which small polaron theory applies, or of a wide band with H^{e-p} neglected.

B. Wide Band to Narrow Band Absorption

In this subsection, we shall consider absorption of radiation in an ionic crystal due to transitions from states consisting of an electron in a wide valence band plus free phonons, to states containing an electron in a narrow conduction band, whose wave functions are given to a good approximation by a linear combination of states with the electron localized on a lattice site and surrounded by the lattice polarization induced by such a localized electron cloud.[14] Only one branch of the phonon spectrum will be considered.

Thus, we take initial and final states $|a\rangle$ and $|f\rangle$ given by

$$|a\rangle \equiv |vk\{n\}\rangle = \frac{1}{N^{1/2}} u_k(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r}) \prod_w |n_w\rangle, \quad (6)$$

$$|f\rangle \equiv |ck'\{n'\}\rangle = \frac{1}{N^{1/2}} \sum_{\mathbf{R'}} \exp(i\mathbf{k'}\cdot\mathbf{R'})\phi(\mathbf{r}-\mathbf{R'})$$
$$\times \prod_w |n_w',f_w(\mathbf{R'})\rangle. \quad (7)$$

In (6) and (7) v and c stand for valence and conduction band, $\{n\}$ and $\{n'\}$ denote the sets of phonon occupation numbers n_w and $n_{w'}$, N is the number of unit cells in the crystal, $\mathbf{r}$ is the electron coordinate, $u_k(\mathbf{r})$ is the periodic part of the Bloch function of wave vector $\mathbf{k}$ in the valence band (normalized within one unit cell), $|n_w\rangle$ denotes the n_wth excited state of the normal mode of wave vector $\mathbf{w}$ of the branch of the phonon spectrum being considered, the set of $\phi(\mathbf{r}-\mathbf{R'})$ are normalized, orthogonalized wave functions localized about lattice sites $\mathbf{R'}$, being orthogonalized atomic functions slightly modified by a deepening of the atomic potential well by the lattice polarization. The sum in (7) is over all lattice vectors $\mathbf{R'}$, the products are over all phonon wave vectors $\mathbf{w}$, and $|n_w',f_w\rangle$, a displaced harmonic

oscillator state, is defined by

$$|n_w',f_w\rangle = \exp\{-\tfrac{1}{2}|f_w|^2\}\frac{1}{(n_w'!)^{1/2}}(b_w^\dagger+f_w^*)^{n_w'}$$
$$\times\exp(-f_w b_w^\dagger)|0_w\rangle, \quad (8)$$

where $b_w^\dagger$ is the creation operator for a phonon of wave vector $\mathbf{w}$, f_w is a complex number, and we use an asterisk to denote the complex conjugate of any number or function.

For more realistic wave functions the ϕ's should depend on the instantaneous position of the ions on which they are concentrated and perhaps of their neighbors, but we shall not attempt to consider this dependence. There is a similar neglect of the dependence of electron wave function on nuclear positions in the valence band functions (6), and, using the semiclassical argument that absorption takes place so quickly that the ions do not have time to change their position during the absorption, and remembering that a first improvement on the electron wave function in (6) and (7) would allow the ϕ on one ion and the part of u nearest this ion to follow rigidly the motion of the ion concerned, we might expect that the two errors have a tendency to cancel each other.

Since the eigenfunctions of the Hamiltonian of a crystal must simply multiply by a phase factor on translation of all coordinates through one lattice distance, we require

$$f_w(\mathbf{R'}) = d_w \exp(-i\mathbf{w}\cdot\mathbf{R'}), \quad (9)$$

where d_w is independent of $\mathbf{R'}$.

We shall assume an electron-phonon interaction Hamiltonian H^{e-p} linear in the phonon creation and annihilation operators of the form

$$H^{e-p} = \sum_w V_w(b_{-w}^\dagger-b_w)s_w(\mathbf{r})\exp(i\mathbf{w}\cdot\mathbf{r}), \quad (10)$$

where the $s_w(\mathbf{r})$ are periodic functions of electron position $\mathbf{r}$ (normalized in unit volume), and the V_w's are constants with the dimensions of energy. If we now find the d_w's by taking just one term of the sum over $\mathbf{R'}$ in (7), and minimizing the expectation value of the Hamiltonian as in strong coupling effective mass polaron theory,[1] we find that

$$d_w^* = -\left(\frac{V_w}{\hbar\omega_w}\right)\int \phi^*(\mathbf{r})\phi(\mathbf{r})\exp(i\mathbf{w}\cdot\mathbf{r})s_w(\mathbf{r})d^3r, \quad (11)$$

where ω_w is the angular frequency of the phonon of wave vector $\mathbf{w}$, and ϕ is a localized electron wave function which is of the type occurring in (7) for the case when the lattice point is at the origin. If the electron-phonon interaction arises from long-range forces only, then $s_w(\mathbf{r})=1$, and, since we are supposing ϕ is sufficiently localized for overlap between nearest neighbor ϕ's to be small, it will be a fair approximation to put

[14] Although more often than not we expect valence bands to be narrower than conduction bands, we have chosen the reverse case in view of possible applications to the transition metal oxides (see Sec. V). The results, however, are expected to apply equally well to transitions between a small polaron valence band and a wide conduction band.

$\exp(i\mathbf{w}\cdot\mathbf{r})\simeq1$ inside the integral in (11). Thus, in this case, we have

$$d_{\mathbf{w}}\simeq V_{\mathbf{w}}/\hbar\omega_{\mathbf{w}}. \qquad (12)$$

The matrix element of $(\partial/\partial x)$ between the initial and final states of (6) and (7) may now be written down

$$M_{\mathbf{k}\mathbf{k}'\{n\}\{n'\}}\equiv\langle v\mathbf{k}\{n\}\,|\,(\partial/\partial x)\,|\,c\mathbf{k}'\{n'\}\rangle$$

$$=\frac{1}{N}\int d^3\mathbf{r}\sum_{\mathbf{R}'}[\exp(i\mathbf{k}'\cdot\mathbf{R}')\{u_{\mathbf{k}}^*(\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{r})$$

$$\times(\partial/\partial x)\phi(\mathbf{r}-\mathbf{R}')\}]\prod_{\mathbf{w}}\langle n_{\mathbf{w}}|n_{\mathbf{w}'},f_{\mathbf{w}}(\mathbf{R}')\rangle, \quad (13)$$

where the $\mathbf{r}$ integration is over the whole crystal.

We next restrict ourselves to a consideration of sets $\{n\}$ and $\{n'\}$ related by

$$\begin{aligned} n_{\mathbf{w}'}&=n_{\mathbf{w}}+1, \quad &\mathbf{w}\in\{A\},\\ n_{\mathbf{w}'}&=n_{\mathbf{w}}-1, \quad &\mathbf{w}\in\{B\}, \qquad (14)\\ n_{\mathbf{w}'}&=n_{\mathbf{w}}, \quad &\mathbf{w}\notin\{A\}\text{ or }\{B\}. \end{aligned}$$

Here $\{A\}$ and $\{B\}$ denote distinct sets of phonon wave vectors. The quantities f and f' are of the order of $N^{-1/2}$, and hence are small. Thus, we can make use of the approximate relations

$$\begin{aligned} \langle n,f\,|\,n,f'\rangle&\simeq1-(n+\tfrac{1}{2})hh^*-\mathrm{Im}(fh^*),\\ \langle n,f\,|\,(n+1),f'\rangle&\simeq(n+1)^{1/2}h^*, \qquad (15)\\ \langle n,f\,|\,(n-1),f'\rangle&\simeq-n^{1/2}h, \end{aligned}$$

where h is defined by $h=(f'-f)$, and Im denotes the imaginary part. Writing

$$\phi(\mathbf{r}-\mathbf{R}')=\sum_{\mathbf{k}''}a_{\mathbf{k}''}\exp[i\mathbf{k}''\cdot(\mathbf{r}-\mathbf{R}')], \qquad (16)$$

we find, using (9), that integration over $\mathbf{r}$ followed by summation over $\mathbf{R}'$ in (13) gives a zero result for the matrix element unless

$$\mathbf{k}'-\mathbf{k}+\sum_A\mathbf{w}-\sum_B\mathbf{w}=2\pi\mathbf{L}, \qquad (17)$$

where $\mathbf{L}$ is a reciprocal lattice vector and $\sum_A$, $\sum_B$ denote sums over all $\mathbf{w}$ belonging to $\{A\}$ and $\{B\}$, respectively, and that when (17) is satisfied

$$M_{\mathbf{k}\mathbf{k}'\{n\}\{n'\}}=Q_{\mathbf{k}}\prod_A\{d_{\mathbf{w}}^*(n_{\mathbf{w}}+1)^{1/2}\}\prod_B\{d_{\mathbf{w}}n_{\mathbf{w}}^{1/2}\}$$

$$\times\exp\{-\sum_{\mathbf{w}}(n_{\mathbf{w}}+\tfrac{1}{2})|d_{\mathbf{w}}|^2\}. \qquad (18)$$

Here $\prod_A$ and $\prod_B$ denote products over all $\mathbf{w}$ which belong to $\{A\}$ and $\{B\}$, respectively, and the summation in the exponential, although strictly containing modified terms for $\mathbf{w}$'s in $\{A\}$ or $\{B\}$, may be taken over all wave vectors, since the fraction of these in $\{A\}$ and $\{B\}$ will be negligible for cases of interest. $Q_{\mathbf{k}}$ is

defined by

$$Q_{\mathbf{k}}=\sum_{\mathbf{L}'}a_{\mathbf{k}+2\pi\mathbf{L}'}i(k_x+2\pi L_x')$$

$$\times\int d^3\mathbf{r}\,u_{\mathbf{k}}^*(\mathbf{r})\exp(2\pi i\mathbf{L}'\cdot\mathbf{r}). \quad (19)$$

Here the sum is over all reciprocal lattice vectors $\mathbf{L}'$, and the suffix x on a quantity denotes its component in the x direction. We expect $Q_{\mathbf{k}}$ to vary slowly with $\mathbf{k}$ for small $\mathbf{k}$ provided that it does not vanish at $\mathbf{k}=0$.

The absorption coefficient due to transitions between states given by (6) and (7) may now be obtained by using the extension of (4) to apply to our case, i.e.,

$$K(\Omega)=\frac{A}{n\Omega}\mathrm{Av}_n\sum_{n'}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}|M_{\mathbf{k}\mathbf{k}'\{n\}\{n'\}}|^2\delta(\text{energy}), \quad (20)$$

where A is given by (5) and M by (13), specialized to (18) for states which (14) and (17) hold, and the wave-vector summations are over all occupied $\mathbf{k}$ in the valence band and all unoccupied $\mathbf{k}'$ in the conduction band. We shall assume that the valence band is completely full and the conduction band completely empty. Transitions in which occupation numbers of individual oscillator states change by two or more play a negligible part in the absorption for macroscopic crystals, and so (18) and (20) give sufficient information to determine the absorption coefficient in principle. However, the mathematics involved is very complicated even for simple functions $Q_{\mathbf{k}}$ and $d_{\mathbf{w}}$. We shall concentrate on the features of the absorption which can be obtained without too many calculations.

We shall restrict our considerations to optical phonons from now on, and neglect dispersion of phonon frequencies.

We first split K up into parts according to the net number of phonons emitted during the photon absorption process,[15] i.e., we write

$$K(\Omega)=\sum_{p=-\infty}^{p_0}K_p(\Omega), \qquad (21)$$

where $K_p(\Omega)$ represents the part of the absorption taking place with a simultaneous net emission of p phonons, and p_0 is the largest integer less than $(\Omega/\hbar\omega)$.

Next we note that, since the matrix element of (18) does not depend on $\mathbf{k}'$, if we forget about the δ function of energy on the right-hand side of (20), the summation over $\mathbf{k}'$ just selects the $\mathbf{k}'$ which satisfies the wave-vector

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[15] The method used here of splitting the absorption coefficient into parts involving given numbers of phonons is useful only when phonon dispersion is small. For this case, the split-up enables us to obtain certain details of the shape of the absorption fairly simply. For a more general case use of the method of moments as developed in detail for electronic transitions between impurity levels in semiconductors and insulators by M. Lax [J. Chem. Phys. **20**, 1753 (1952)] and by R. Kubo and Y. Toyozawa [Prog. Theoret. Phys. (Kyoto) **13**, 160 (1955)] would perhaps be advisable, at least for transitions between two narrow bands.

conservation condition. For a given $\{n\}$ summation over the $\{n'\}$ which contribute to $K_p(\Omega)$ may be performed by summing over all sets $\{A\}$, $\{B\}$ containing $(m+p)$ and m members, respectively, and then over all m. The summation over sets $\{A\}$, $\{B\}$ of a given size may be expressed in terms of a multiple sum over w's or, if $(2m+p)\ll N$, as a product of simple sums over w's. Finally, since all n_w's are independent, averaging over $\{n\}$ just replaces all the n_w's by $\bar{n}$, where $\bar{n}$ is the thermal occupation number of the phonon states.

Bearing in mind that the results of the last paragraph, we can show from (18), (20), and (21) that

$$\int nK_p(\Omega)\Omega d\Omega = A \sum_{k} |Q_k|^2 R_p, \qquad (22)$$

where

$$R_p = \sum_{m=m_1}^{\infty} \frac{D^{2m+p}}{(m+p)!\,m!}(\bar{n}+1)^{m+p}(\bar{n})^m$$
$$\times \exp[-(2\bar{n}+1)D], \qquad (23)$$

with

$$D = \sum_{w} |d_w|^2, \qquad (24)$$

and m_1 is zero if p is positive but equals $(-p)$ if p is negative.

If $\bar{n}\neq 0$ we can also write R_p in the alternative form

$$R_p = (1+1/\bar{n})^{p/2} I_p(Z) \exp[-(2\bar{n}+1)D], \qquad (25)$$

where I_p denotes a Bessel function of imaginary argument and

$$Z = 2[\bar{n}(\bar{n}+1)]^{1/2}D. \qquad (26)$$

It is of interest to note that the absorption without assistance of phonons is decreased by the exponential factor in (23) due to the electron-phonon interaction, but that the total integral of $nK\Omega$ is unaltered by the interaction.

By writing down double summations over m and p and summing over p first it is straightforward to show from (23) that

$$\sum_{p=-\infty}^{\infty} R_p = 1; \qquad \sum_{p=-\infty}^{\infty} pR_p = D = \bar{p} \quad \text{(say)};$$

$$\sum_{p=-\infty}^{\infty} (p-\bar{p})^2 R_p = D(2\bar{n}+1) = \langle (p-\bar{p})^2 \rangle_{\text{av}}. \qquad (27)$$

Thus, the mean net number of emitted phonons contributing to the integrated absorption equals D, while the mean square departure from this number is equal to $[D(2\bar{n}+1)]$. At low temperatures the mean number of phonons emitted multiplied by the phonon energy in some sense gives the length of the tail of the absorption, since there is always some absorption without assistance of phonons, but most of the absorption is due to processes involving net emission of about $\bar{p}$ phonons. Alternatively, however, we may say that any absorption which would occur without electron-phonon interaction is spread into an energy region such that the root-mean-

square energy change is $\{\langle (p-\bar{p})^2 \rangle_{\text{av}}\}^{1/2}\hbar\omega$. Thus, at low temperatures, according to which definition of the width of the absorption tail we use, we may say that this width is equal either to $D\hbar\omega$ or to $D^{1/2}\hbar\omega$.

To obtain information about the shapes of the individual bands, we first make a further splitting of the absorption coefficient into parts $K_{p,m}(\Omega)$ due to processes where $(m+p)$ phonons are emitted and m phonons absorbed. Thus, we have

$$K_p(\Omega) = \sum_{m=m_1}^{\infty} K_{p,m}(\Omega), \qquad (28)$$

with $m_1 = \max(0, -p)$ as before.

Now going back to (20) and (18) and using some of the arguments presented before Eq. (22), we see that if p and m are not both zero the dependence on Ω of $K_{p,m}$ is given by

$$n\Omega K_{p,m}(\Omega) \propto \int \rho_v(E)\rho_c(\Omega-E_G-p\hbar\omega-E)$$
$$\times B_{p,m}(E,\Omega)dE, \qquad (29)$$

where E_G is the energy gap, ρ_v and ρ_c are the densities of states per unit energy in the valence and conduction bands, and

$$B_{p,m}(E,\Omega) = \text{Av}\{|Q_k|^2 \prod_{A,B} |d_w|^2\}. \qquad (30)$$

Here $\prod_{A,B}$ denotes a product over all w's in $\{A\}$ and $\{B\}$, and the average is over all k, k' and sets $\{A\}$, $\{B\}$ which contain $(m+p)$ and m members, respectively, subject to the conditions that wave-vector conservation is satisfied and that

$$E_{ck'} = \Omega - E_G - p\hbar\omega - E, \qquad (31)$$

$$E_{vk} = E, \qquad (32)$$

where $E_{ck'}$ and E_{vk} are the energies above the bottom of the conduction band and below the top of the valence band of polarons and bare electrons of wave vectors k' and k, respectively (see Fig. 1).

Now if we neglect the conduction bandwidth entirely, i.e., if we put

$$\rho_c(E) = N\delta(E), \qquad (33)$$

then (29) is considerably simplified, as may be seen by the following argument. Finding the average in (30) involves summations over k, k' and sets $\{A\}$, $\{B\}$ which satisfy the wave-vector conservation conditions and (31) and (32); the summation over $\{A\}$ and $\{B\}$ gives a result which depends only on $(k-k')$; for the correct E the summation over k' will extend over all k' and hence over all $(k-k')$ (regarding wave vectors differing by 2π times a reciprocal lattice vector as identical); thus the summation over k', $\{A\}$, and $\{B\}$ of $\prod_{A,B} |d_w|^2$ gives a result independent of k, and we find

$$B_{p,m}(E,\Omega) \propto Q^2(E) \equiv \text{Av}_k |Q_k|^2, \qquad (34)$$
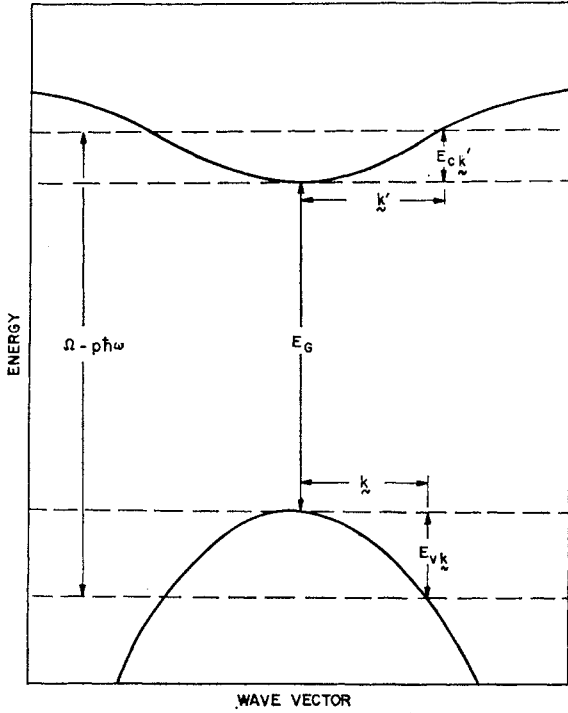
FIG. 1. Energy band diagram for Sec. II B.

where the average is over all $\mathbf{k}$ which satisfy Eq. (32).

Hence, when (33) is satisfied, using Eqs. (21), (22), (28) to (32), and (34), we find

$$K(\Omega) = (A/n\Omega) \sum_{p=-\infty}^{p_1} F(\Omega - E_G - p\hbar\omega) R_p, \qquad (35)$$

where p_1 is the positive or negative integer defined by

$$0 < \Omega - E_G - p_1\hbar\omega \leqslant \hbar\omega, \qquad (36)$$

i.e., it is the largest integer less than $\{(\Omega - E_G)/\hbar\omega\}$, and

$$F(E) = Q^2(E)\rho_v(E). \qquad (37)$$

If the width of the conduction band is not negligible, calculations become much more difficult. However, it is worth noting that for large $(2m+p)$ the averaging of $\prod_{A,B} |d_w|^2$ in (30) gives a result independent of $\mathbf{k}$ and $\mathbf{k}'$ (see Appendix I). Thus (34) holds, and so the shapes of the large p, m bands can be obtained by simple integrations if $Q(E)$ and the density-of-states functions are known.

C. Narrow Band to Narrow Band Absorption

1. Direct Process

In this subsection we shall consider absorption due to transitions induced by the electron-radiation interaction between states of two narrow polaron bands, the states being of the type used for the conduction band in Sec. II B. The process considered here will be direct in the

sense that no intermediate state in a third band is involved, but indirect in the sense that phonon occupation numbers will change during the transitions.

Thus, for initial and final states $|a\rangle$ and $|f\rangle$ we take

$$|a\rangle \equiv |\alpha\mathbf{k}\{n\}\rangle = \frac{1}{N^{1/2}} \sum_{\mathbf{R}} \exp(i\mathbf{k}\cdot\mathbf{R})\phi_\alpha(\mathbf{r}-\mathbf{R})$$
$$\times \prod_w |n_w, f_{\alpha w}(\mathbf{R})\rangle, \quad (38)$$

$$|f\rangle \equiv |\beta\mathbf{k}'\{n'\}\rangle = \frac{1}{N^{1/2}} \sum_{\mathbf{R}'} \exp(i\mathbf{k}'\cdot\mathbf{R}')\phi_\beta(\mathbf{r}-\mathbf{R}')$$
$$\times \prod_w |n_w', f_{\beta w}(\mathbf{R}')\rangle, \quad (39)$$

where ϕ_α and ϕ_β are localized, orthogonalized functions of the electron coordinate for the bands α and β, concentrated near lattice points $\mathbf{R}$ and $\mathbf{R}'$,

$$f_{iw}(\mathbf{R}) = d_w \exp(-i\mathbf{w}\cdot\mathbf{R}), \quad i = \alpha, \beta, \qquad (40)$$

where the d_{iw}'s are independent of $\mathbf{R}$, and the other notation is as in Sec. II B, i.e., $|n,f\rangle$ is defined as in (8), N is the number of unit cells in the crystal, $\mathbf{k}$ and $\mathbf{k}'$ are electron wave vectors, and the $\mathbf{w}$'s are phonon wave vectors.

Calculation of the matrix element of $(\partial/\partial x)$ between these states involves integrations over $\mathbf{r}$ and the phonon coordinates, and summations over $\mathbf{R}$ and $\mathbf{R}'$. We have to distinguish two cases, one an electron transfer process where the main contribution to the matrix element is from $\mathbf{R} \neq \mathbf{R}'$ and the other a single site process where the main contribution is from $\mathbf{R} = \mathbf{R}'$.

Transitions by electron transfer. For bands made up of localized functions of the same parity, such as the d bands in the transition metal oxides, or of functions of other suitable symmetry properties,

$$\int \phi_\alpha^*(\mathbf{r}-\mathbf{R})\frac{\partial}{\partial x}\phi_\beta(\mathbf{r}-\mathbf{R})d^3r = 0, \qquad (41)$$

and so the terms with $\mathbf{R} = \mathbf{R}'$ in the summations over lattice vectors in the matrix element of $(\partial/\partial x)$ between the states of (38) and (39) vanish.

The terms in the matrix element from $\mathbf{R} \neq \mathbf{R}'$ depend on differences of $f_{\alpha w}$ on one lattice site and $f_{\beta w}$ on a different site. Before proceeding further we shall make the simplifying assumption that

$$d_{\alpha w} = d_{\beta w} = d_w \text{ (say)}. \qquad (42)$$

This equation will hold if the electron-phonon interaction is due to Coulomb interaction with ions, and if the ϕ's are sufficiently localized for overlap to be neglected and are also small enough for variations of the Coulomb field across ϕ to be negligible. These assumptions are likely to be valid for the long-wavelength modes where the d's are determined mainly by the long-range interaction; but for the short-wavelength

modes, considerable departures from (42) might occur (see the discussion on NiO in Sec. V).

We shall next suppose that contributions to the matrix element from $\mathbf{R}$ and $\mathbf{R}'$ differing by more than one lattice distance are negligible. Defining $a(\mathbf{G})$ by

$$a(\mathbf{G}) \equiv \int \phi_\alpha^*(\mathbf{r}-\mathbf{R})\frac{\partial}{\partial x}\phi_\beta(\mathbf{r}-\mathbf{R}-\mathbf{G})d^3\mathbf{r}, \qquad (43)$$

where $\mathbf{G}$ is any one of the set of smallest nonzero lattice vectors, using Eqs. (15) and (40), we can now show that, if $\{n\}$ and $\{n'\}$ are connected by the relations (14), and the wave-vector conservation condition and (41) and (42) are satisfied, then the matrix element of $(\partial/\partial x)$ between the states (38) and (39) is given by

$$M_{\alpha\beta\mathbf{k}\mathbf{k}'\{n\}\{n'\}} \equiv \langle \alpha\mathbf{k}\{n\} \mid (\partial/\partial x) \mid \beta\mathbf{k}'\{n'\} \rangle$$

$$= \sum_{\mathbf{G}} \big[a(\mathbf{G}) \exp(i\mathbf{k}\cdot\mathbf{G})$$

$$\times \prod_A \{[1-\exp(-i\mathbf{w}\cdot\mathbf{G})]d_\mathbf{w}^*(n_\mathbf{w}+1)^{1/2}\}$$

$$\times \prod_B \{[\exp(i\mathbf{w}\cdot\mathbf{G})-1]d_\mathbf{w}(n_\mathbf{w})^{1/2}\}$$

$$\times \exp\Big[-\sum_\mathbf{w} 2(2n_\mathbf{w}+1)\mid d_\mathbf{w}\mid^2 \sin^2\Big(\frac{\mathbf{w}\cdot\mathbf{G}}{2}\Big)\Big]. \quad (44)$$

Here the summation is over all nearest-neighbor lattice vectors $\mathbf{G}$, $\prod_A$ and $\prod_B$ denote the products over all $\mathbf{w}$ in $\{A\}$ and $\{B\}$, and, as before, the sum in the exponential can be taken over all $\mathbf{w}$, since the fraction of $\mathbf{w}$'s in $\{A\}$ and $\{B\}$ is negligible for cases of interest. The exponential in (44) should be independent of $\mathbf{G}$ for a thermal distribution of phonons.

To pass from the matrix element to the absorption coefficient, we again use (20), putting the band suffices α and β on the matrix element and remembering to restrict the sum over $\mathbf{k}$ and $\mathbf{k}'$ to occupied $\mathbf{k}$ in band α and unoccupied $\mathbf{k}'$ in band β. For a general set of occupied $\mathbf{k}$ and unoccupied $\mathbf{k}'$ progress is difficult but, since we are concerned with narrow bands, at not too low temperatures any set of electrons in thermal equilibrium in bands α and β should be randomly distributed over the wave vectors $\mathbf{k}$ and $\mathbf{k}'$ of the bands. If this is the case, we find that we can ignore cross terms between different $\mathbf{G}$ in a sum over initial and final electron wave vectors of squares of matrix elements in (20). Thus, dividing K into partial absorption coefficients K_p due to processes involving the net emission of p phonons as before,[15] assuming that all phonon frequencies are equal, and using arguments similar to those used in Sec. II B to assist in the performance of the various summations in the expression for the absorption coefficient, we can show that

$$\int nK_p(\Omega)\Omega d\Omega = An_\alpha\Big(1-\frac{n_\beta}{N}\Big)\sum_\mathbf{G} \mid a(\mathbf{G})\mid^2 H_p, \quad (45)$$

where A is given by (5), n_α and n_β are the numbers of electrons in the bands α and β, and

$$H_p = \sum_{m=m_1}^\infty \frac{S^{2m+p}}{(m+p)!m!}(\bar{n}+1)^{m+p}(\bar{n})^m$$
$$\times \exp[-(2\bar{n}+1)S], \quad (46)$$

where

$$S = \sum_\mathbf{w} \{4\mid d_\mathbf{w}\mid^2 \sin^2(\mathbf{w}\cdot\mathbf{G}/2)\}, \quad (47)$$

and $m_1 = \max(0, -p)$ as before. S can be identified with the constant S in Yamashita and Kurosawa's article.[4]

Equations similar to (27) give the mean net number of phonons emitted $\bar{p}$, and the mean square deviation of this number from $\bar{p}$, i.e., we have

$$\bar{p} = S, \qquad \langle(p-\bar{p})^2\rangle_{av} = S(2\bar{n}+1). \quad (48)$$

Since our polaron bands are narrow in this case, the quantity $[2\hbar\omega\{\langle(p-\bar{p})^2\rangle_{av}\}^{1/2}]$ gives a type of measure of the width of the envelope of the set of sharp lines for $n\Omega K$ predicted on our model.

Another case of interest where some simplifications in the expressions for the integrated partial absorption coefficients can be made is that in which all the occupied $\mathbf{k}$ are so small that $\exp(i\mathbf{k}\cdot\mathbf{G})$ can be replaced by unity in the matrix element. For this case we shall make the additional assumptions that all states in β are empty, and that cross terms between different $\mathbf{G}$'s except equal and opposite ones do not contribute to the integrated absorption, either because all except a pair of $a(\mathbf{G})$'s are zero or possibly for some other reason. Since for electrons in thermal equilibrium the condition that all occupied $\mathbf{k}$ be small requires temperatures such that kT is much less than the polaron bandwidth, we shall restrict our considerations to $T=0$. Then, writing

$$a(\mathbf{G}) = b(\mathbf{G}) + ic(\mathbf{G}), \quad (49)$$

where b and c are real, we can show that

$$\int nK_p(\Omega)\Omega d\Omega$$

$$= An_\alpha \sum_\mathbf{G}' (1/p!)[\{\mid a(\mathbf{G})\mid^2 + \mid a(-\mathbf{G})\mid^2\}S^p$$
$$+2\{b(\mathbf{G})b(-\mathbf{G})+c(\mathbf{G})c(-\mathbf{G})\}U^p]$$

$$\times \exp(-S), \quad (50)$$

where $\sum'$ denotes a sum over half the $\mathbf{G}$'s, and

$$U = \sum_\mathbf{w} \{4\mid d_\mathbf{w}\mid^2 \sin^2(\mathbf{w}\cdot\mathbf{G}/2)\cos(\mathbf{w}\cdot\mathbf{G})\}. \quad (51)$$

We notice that $U < S$, and so the expression (50) reduces to (45), (specialized to the case $T=0$) if p is large, or for any p if

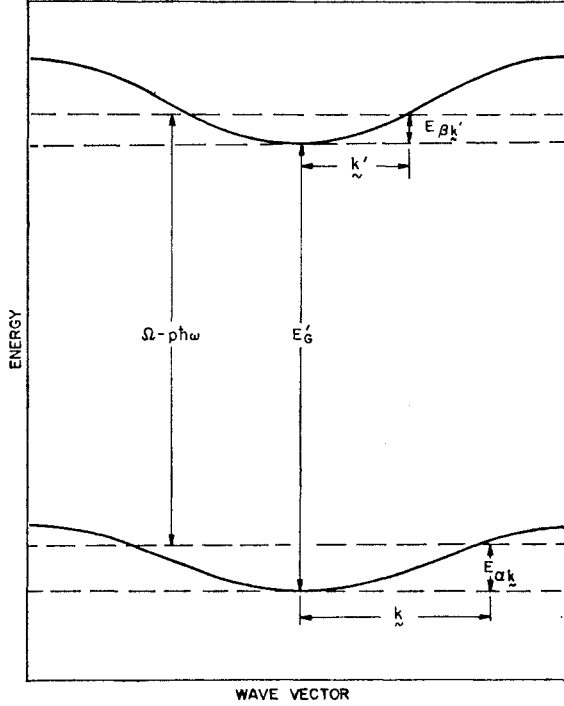$$b(\mathbf{G})b(-\mathbf{G})+c(\mathbf{G})c(-\mathbf{G})=0. \quad (52)$$

FIG. 2. Energy band diagram for Sec. II C.

To calculate the shapes of the individual absorption bands, whether or not our simplifications for the integrated absorption (45) to (47) or (50) and (51) can be used, we further subdivide K_p into $K_{p,m}$'s as in (28), and we see from the expressions for the matrix element and the absorption coefficient that

$$n\Omega K_{p,m}(\Omega) \propto \int \rho_\alpha(E)\rho_\beta(\Omega - E_G - p\hbar\omega + E)$$

$$\times C_{p,m}(E,\Omega)dE, \quad (53)$$

where ρ_α and ρ_β are the densities of states with respect to energy for the bands α and β, and

$$C_{p,m}(\Omega) = \text{Av} \left| \sum_G a(G) \exp[i(\mathbf{k}+\mathbf{k}')\cdot G/2] \right.$$

$$\times \prod_A \{2id_w^* \sin(\mathbf{w}\cdot G/2)\}$$

$$\left. \times \prod_B \{2id_w \sin(\mathbf{w}\cdot G/2)\} \right|^2. \quad (54)$$

Here the average is over occupied $\mathbf{k}$ and unoccupied $\mathbf{k}'$, and sets $\{A\}$, $\{B\}$ containing $(m+p)$ and m members, respectively, subject to the conditions that wave-vector conservation holds and that $\mathbf{k}$ and $\mathbf{k}'$ satisfy

$$E_{\beta\mathbf{k}'} = \Omega - E_G' - p\hbar\omega + E, \quad (55)$$

$$E_{\alpha\mathbf{k}} = E, \quad (56)$$

where E_G' is the energy gap between the bottoms of the bands, and $E_{\alpha\mathbf{k}}$ and $E_{\beta\mathbf{k}'}$ are the energies of polarons of wave vectors $\mathbf{k}$ and $\mathbf{k}'$ above the minima of bands α

and β (see Fig. 2). For large $(2m+p)$ we can show that $C_{p,m}$ is independent of E and Ω (see Appendix II), and so the shape of the large p, m bands depends only on the density-of-states functions.

It is of interest to note that the expressions (45) and (46) for the integrated absorption for a random distribution of initially occupied wave vectors are just the same as would have been obtained by taking localized polaron wave functions as initial and final states. Thus, when the polaron bandwidth is negligibly small, the actual absorption coefficient can be obtained by using localized functions, as we should expect. At temperatures above the critical temperature when the band picture breaks down, it seems probable, for photon frequencies greater than the probability per unit time of site jumps, that the absorption calculated by first-order perturbation theory with localized initial and final states will give correct results, and so it appears that, except at very low frequencies, there will not be any sharp change in the absorption spectrum at the transition temperature.

Transitions on one site. If the integral on the left-hand side of (41) is not zero, or if the electric quadrupole or magnetic-dipole contribution to the single site matrix element is greater than the overlap integrals $a(G)$ of (43), then the main contribution to the matrix elements of the electron-radiation interaction between the states of (38) and (39) will come from $\mathbf{R} = \mathbf{R}'$. The calculation of the absorption is rather simpler in this case than for electron transfer, and we find a set of absorption bands commencing at energies $(E_G' + p\hbar\omega)$ whose integrated absorption is proportional to a quantity defined as is H_p in (46), but with S replaced by a quantity T such that

$$T = \sum_w |(d_{\alpha w} - d_{\beta w})|^2. \quad (57)$$

Hence we expect a smaller total width to the absorption if transitions on one site are dominant than for absorption by electron transfer.

2. Indirect Transitions via an Allowed Band

If (41) holds under our assumption of neglect of the dependence of the ϕ's on the positions of the atoms about which they are localized, then the absorption due to the direct process considered in the last section will not be large, since electric dipole transitions are precluded from the single-site absorption, and the quantity $a(G)$ of (43) occurring in the electron transfer absorption theory will be small because it is necessary that there be little overlap between different ϕ's for our small polaron wave functions to be applicable. Thus, in some cases the main absorption may arise from a breakdown of the relation (41) due to changes of the ϕ's when the atoms on which they are localized move from their perfect lattice positions.

Since the change of electronic matrix elements with atomic position arises from a mixing in of electronic

states of higher bands with the original state, one may regard absorption arising from this change as indirect phonon-assisted absorption via a band to which dipole transitions are allowed. The effective matrix elements for a second-order process will be equal to an allowed dipole matrix element times an interband electron-phonon matrix element, over an energy denominator equal to the difference in energy between the initial state and a state containing an electron in the intermediate band. Thus, we may estimate that the oscillator strength f for this type of transition satisfies

$$f \sim f_0 (\bar{E}/\bar{E}_G)^2, \qquad (58)$$

where f_0 is the oscillator strength to the allowed intermediate band, $\bar{E}$ is a typical interband electron-phonon matrix element, and $\bar{E}_G$ is an average band gap. We may also deduce this result from Kubo and Toyozawa's work[15] on this type of transition between impurity levels. The oscillator strength increases with temperature in this model.

Since the interband electron-phonon matrix elements are likely to be smaller than the intraband ones, the width of the absorption will probably be determined by a quantity depending on the $d_{\alpha w}$'s and $d_{\beta w}$'s. If the main contribution to the matrix element between two states comes from ϕ's on the same atomic site, then the width will depend on the quantity T of (57), while if it comes from ϕ's on different sites, then the parameter determining the width will be of the order of S of Eq. (47).

Apart from the different constant determining the width, the shape of the absorption should be similar to that found for the direct process.

D. Exciton Absorption

1. Excitons from a Wide and a Narrow Band

The problem of absorption by excitons formed from electrons in a small polaron band and holes in a wide valence band would be difficult to treat properly, since all the usual difficulties occurring in polaron theory, as to what extent the lattice polarization can follow the motion of the hole, will arise. However, some insight into the sort of thing to be expected may be obtained by supposing that the exciton wave functions are composed of linear combinations of states whose electron-hole part represents an electron localized on one lattice site with a hole moving in orbit around it, and that this complex is surrounded by a lattice polarization which depends only on the lattice point about which the electron is localized, and not on the instantaneous positions of the electron or hole. In this case, if we write the exciton-lattice interaction as the difference of two terms of the form (10), the first containing the electron coordinate $\mathbf{r}$, and the second the hole coordinate $\mathbf{r}'$, we can show by the usual variational

method that the oscillator displacements $d_w{}'$ satisfy

$$(d_w{}')^* = -\left(\frac{V_w}{\hbar\omega_w}\right) \int \phi_e{}^*(\mathbf{r},\mathbf{r}')\phi_e(\mathbf{r},\mathbf{r}')$$

$$\times [\exp(i\mathbf{w}\cdot\mathbf{r})s_w(\mathbf{r}) - \exp(i\mathbf{w}\cdot\mathbf{r}')s_w(\mathbf{r}')]d^3rd^3r', \qquad (59)$$

where ϕ_e represents the electron-hole part of the exciton wave function when the electron is localized about the origin.

If we expand the exponentials in (59) in powers of $\mathbf{w}$, we see that the terms independent of $\mathbf{w}$ cancel. The terms linear in $(\mathbf{w}\cdot\mathbf{r})$ and $(\mathbf{w}\cdot\mathbf{r}')$ will vanish from symmetry reasons if ϕ_e has a definite parity with respect to inversion about the origin and if $s_w(\mathbf{r})$ is even with respect to this inversion. [For interaction with longitudinal optical modes in a continuum polarization model $s_w(\mathbf{r})=1$.] Hence in such cases the first terms contributing to $d_w{}'$ are those proportional to $(\mathbf{w}\cdot\mathbf{r})^2$ and $(\mathbf{w}\cdot\mathbf{r}')^2$. With an exciton of radius r_e the second of these terms will give a contribution to $d_w{}'$ of the order of $(wr_e)^2$ times that from the term unity in the exponential, while the contribution from the $(\mathbf{w}\cdot\mathbf{r})^2$ term will be negligible for small w, and so for $w<(1/r_e)$ we expect $|(d_w{}'/d_w)| \sim (w^2r_e^2)$.

On the other hand, for $w>(1/r_e)$ the second of the two terms in (59) will be small, since the hole wave function will have small Fourier coefficients at these wave vectors, while the first term is approximately equal to d_w. Thus, for $w>(1/r_e)$, $|(d_w{}'/d_w)| \sim 1$.

If the phonons with which the exciton is interacting all have the same frequency ω, then the absorption should consist of a series of bands commencing at energies $(E_e+p\hbar\omega)$, where E_e is the energy of the lowest exciton state of the band measured relative to the ground state, and p is any positive integer or zero. The integrated absorption for the pth band should be proportional to $R_p{}'$, where $R_p{}'$ is defined as is R_p in Eqs. (23) and (24), but with D and d_w replaced by D' and $d_w{}'$, where $d_w{}'$ is given by (59). From the remarks of the previous paragraph about the magnitude of the displacements $d_w{}'$ we can see that the ratio of the width of the tail of the band-to-band absorption to that of the exciton absorption will be larger for small exciton radii. On the other hand, judging from a hydrogen-like exciton model, the ratio of the oscillator strengths of the band-to-band and exciton absorption should be of the order of $(r_e/G)^3$, where G is a lattice distance.[16]

If we subdivide the absorption coefficient into parts $K_{p,m}$ due to processes in which $(m+p)$ phonons are emitted and m phonons absorbed, then $K_{0,0}$ will be a line absorption, while expressions analogous to those for the band-to-band absorption of Sec. II B with one of the bands of negligible width should be obtainable for the shapes of the other $K_{p,m}$ bands.

[16] R. J. Elliott, Phys. Rev. 108, 1384 (1957).

2. Excitons from Two Narrow Bands

Two types of excitons can be formed from states of a full and an empty narrow band: (1) linear combinations of states where an electron is transferred from one ion to a neighboring ion; (2) linear combinations of states where a single ion is excited. In both cases the system of excited electron and associated hole will be accompanied by displacements of the lattice vibration oscillators.

Electron transfer exciton. If the bands are very narrow we should be able to forget about taking linear combinations of the states where one electron is transferred from one site to another. The absorption problem then reduces to finding the absorption due to transitions from a polaron state localized on one lattice site with an electron wave function associated with one band, to a state localized on another site with an electron wave function associated with the other band. Since overlap integrals between anything but nearest neighbors will be negligible we need only consider excitons formed by transfer to a nearest-neighbor site. Our results are then formally just the same as those for electron transfer band-to-band absorption of Sec. II C in the limit of negligible bandwidth, i.e., we expect a set of absorption lines at energies $(E_e' + p\hbar\omega)$, where E_e' is the energy to form an exciton without change of phonon occupation numbers, with the strengths of the lines given by (45), (46), and (47) with n_α put equal to the total number of electrons in the full band and $n_\beta = 0$.

The complementarity of the exciton absorption described here and the band-to-band absorption of Sec. II C may be seen as follows. If the initial band α is nearly empty, then exciton states will not exist since formation of excitons is a manifestation of correlation which will be negligible for nearly empty bands. Thus, in this case, the absorption will be to band states as in Sec. II C. On the other hand, if α is nearly full, the requirement of orthogonality of the continuum states to the localized exciton states will drastically reduce the electron wave function of the final band near a hole, and hence will make absorption to the continuum states negligible. If α is about half-full, a localized electron model predicts that there will be two types of absorption, one at the energy at which it would occur if α were nearly empty and the other at a larger energy equal to the exciton energy for α full. The ratio of the strengths for absorption of these two types will be of the order of $\{n_\alpha/(N-n_\alpha)\}$, where n_α is the number of electrons in α. A band picture gives different results for partially full bands, but, if the bandwidth for a single electron in α is sufficiently small, the localized electron model should be best as soon as more than a few electrons are put into the band, since the gain of correlation energy by the use of localized electron states will easily overcome the small decrease of kinetic energy obtained by the use of spread out one electron wave functions.

Single site exciton. If (41) holds for the relevant localized wave functions, electric dipole transitions to a single-site exciton state will be forbidden. Hence, in this case the absorption will probably be due to transitions via a third allowed band, with the order of magnitude of the oscillator strength given by (58) and the width determined by the parameter T of (57). Calculation of the oscillator strength for this type of transition for ions in solid solutions have been performed by Liehr and Ballhausen.[17]

III. DISCUSSION

A. Conditions of Validity of Theory

The conditions under which the polaron wave functions used for the narrow bands in Sec. II represent a fair approximation to the stationary states of a system containing an electron in interaction with optical phonons may be best seen from a study of Holstein's articles,[6] in which a one-dimensional molecular crystal model is studied in some detail.

In these articles an examination is made of a set of differential-cum-difference equations for the amplitudes of electron wave functions at particular lattice sites as a function of coordinates describing the separation of nuclei in individual molecules. A first necessary condition for any sort of small polaron theory to hold is that these equations have stationary solutions, when nuclear kinetic energy is neglected, in which the electron is mainly concentrated on one site. It is shown [see Eqs. (43), (46), and (36) of Part I of reference 6] that such solutions will exist if

$$2J \ll E_b, \qquad (60)$$

where J is the overlap integral of the electron Hamiltonian between nearest-neighbor molecular wave functions and E_b is the polaron binding energy for $J=0$. In our model for the conduction band in Sec. II B, making use of a general result of adiabatic polaron theory[12] that the polaron binding energy is equal to half the increase of lattice energy arising from the displacements of the oscillators, we can show that

$$E_b = \tfrac{1}{2}D\hbar\omega, \qquad (61)$$

where D is defined by (24).

However, Holstein has shown that the simple perturbation approach of using basic states consisting of an electron on one lattice site together with a set of displaced harmonic oscillators, and either forming linear combinations of these to form polaron bands at low temperatures or considering the probabilities of site jumps between these states by perturbation theory at high temperatures, is not valid except under stricter conditions than (60). These stricter conditions were found by comparing the above-mentioned perturbation approach in a two-site model with a different method of

[17] A. D. Liehr and C. J. Ballhausen, Phys. Rev. 106, 1161 (1957).

solving the differential-cum-difference equations for the amplitudes of the electron wave functions, which is analogous to the adiabatic method of solving Schrödinger's equation for a set of electrons and nuclei. The conditions are

$$2J < (E_b)^{1/2}(\hbar\omega)^{1/2}, \quad T < T_c \quad (62)$$

$$J < \pi^{-3/4}(E_b)^{1/4}(kT)^{1/4}(\hbar\omega)^{1/2}, \quad T > T_c \quad (63)$$

where T_c is the transition temperature above which the band picture is replaced by the site-jumping picture.

Although, if (62) or (63) are not satisfied, the adiabatic approach is more appropriate than the perturbation method, the wave functions in the two cases do not appear to be drastically different provided that (60) holds. Quantities that do differ considerably in the two models are the relative binding energies of states of different wave vector at low temperatures, a greater bandwidth being obtained in the adiabatic approach, and the site-jump probability at high temperatures, also greater in the adiabatic theory. Thus, provided that we do not attempt to calculate polaron bandwidths by the perturbation method, we expect the theory of Sec. II to give fair results for the absorption under the condition (60), subject to reservations noted in Sec. III C.

B. Estimates of the Parameters D and S

The breadth of the tail of the absorption as predicted in Sec. II B and the total breadth predicted in Sec. II C depend on the parameters D and S of Eqs. (24) and (47). Yamashita and Kurosawa[4] have estimated the quantity S using a continuum polarization model and replacing summation over all wave vectors by an integration over a spherical region. We obtain their results and also calculate D by using (12) with the standard value of the continuum polarization model for V_w (see, e.g., reference 1), which gives $|d_w| \propto (1/w)$,

$$D = \frac{1}{\pi}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right)\frac{e^2 w_{max}}{\hbar\omega}, \quad (64)$$

and

$$(S/D) = 2 - \frac{1}{w_{max}G}\int_0^{w_{max}G} \frac{\sin x}{x}dx. \quad (65)$$

Here ϵ_∞ and ϵ_s are the high-frequency and static dielectric constants of the crystal, G is the modulus of the nearest-neighbor lattice vectors of Sec. II, and w_{max} is defined by

$$\tfrac{4}{3}\pi(w_{max}/2\pi)^3 = 1/V_c, \quad (66)$$

where V_c is the volume of a unit cell of the crystal. If $w_{max}G = \pi$, then $(S/D) \simeq 0.82$.

In most materials $(e^2 w_{max}/\hbar\omega) \sim 10^2$ to 10^3, and so D and S can be quite large.

C. Some Neglected Factors

Leaving aside a discussion of effects connected with electron spins and of the difficult problem of determining how far a one-electron model is valid, the following factors neglected in the theory of Sec. II should be noted.

1. At low photon energies, the probability of induced emission of photons can become comparable with that of absorption. For a thermal distribution of electrons and phonons in the initial state, induced emission can be taken into account by multiplying the expression for the absorption coefficient obtained previously by a factor $[1 - \exp(-\Omega/kT)]$. This factor reduces to (Ω/kT) if $\Omega \ll kT$ and will thus cancel any $(1/\Omega)$ dependence of the absorption coefficient in this region.

2. The frequency spectrum of the phonons, instead of being concentrated at ω, will normally be spread over a region of width $\Delta\omega$. We expect that the main effect of this dispersion on the absorption curves will be to spread the absorption at a particular energy for the p,mth band of the theory over an energy region of width of the order of $(2m+p)^{1/2}\hbar\Delta\omega$. Thus, a spread of $\hbar\omega$ will be obtained if the number of phonons concerned is of the order of $(\omega/\Delta\omega)^2$.

3. Even when small polaron functions do represent a fair approximation to eigenfunctions of the Hamiltonian without radiation, the residual interaction which gives matrix elements between different small polaron states can modify our results slightly. If the residual interaction gives a lifetime τ to our basic band or localized states, then we expect that the main effect of the interaction is to produce a smearing out of the absorption coefficient calculated at any given energy into a region of width $(\hbar/\tau)$. Phonon dispersion or polaron bandwidth below the transition temperature will normally bring about a larger broadening than $(\hbar/\tau)$ to all peaks except perhaps the zero-phonon one, and so in general the residual interaction will just add slight tails to the absorption round peaks which are sufficiently narrow not to have merged with the ones at energies $\hbar\omega$ above and below. The only case where more drastic alterations to the absorption can occur is at low photon energies and low temperatures. For this case we should note two points (1) For $\Omega < (\hbar/\tau)$ any $(1/\Omega)$ dependence of the absorption will be flattened off if not already flattened by induced emission. (2) For transitions within one small polaron band in Sec. II C the main absorption at low temperatures for any photon energy well below $\hbar\omega$ will be due to the smearing out of the fictitious infinitely sharp peak at zero frequency. To calculate the detailed shape of the absorption in this region we should have to use the second-order perturbation approach,[9] but with the residual interaction plus the electron-radiation interaction as the perturbation rather than the total electron-phonon interaction plus the electron-radiation interaction as used by Meyer in reference 9.

4. The effect of the interaction of the electrons in the wide valence band with the phonons, neglected in Sec. II B, would be difficult to take into account properly, but, since holes near the top of the valence band will interact quite strongly with the long-wavelength longitudinal optical phonons, the effective parameter D determining the relative magnitude of the various partial absorption coefficients $K_{p,m}(\Omega)$, will be decreased for the absorption just above the threshold for any partial absorption band. This reduction in effective D for transitions producing low-energy holes will increase the absorption just above the threshold for absorption bands involving less than the average number of phonons, while the opposite will hold if the number of phonons contributing is above average.

An order-of-magnitude estimate for the amount of the decrease of effective D may perhaps be obtained by assuming that we can treat the electron-phonon interaction in the valence band by introducing oscillator displacements $d_{\mathbf{w}}$ for the low-energy holes as obtained in weak or intermediate coupling effective mass polaron theory. This theory gives $d_{\mathbf{w}}$'s for these holes nearly equal to those for a small polaron band in the continuum polarization model for $w < u$, where $u = (2m^*\omega/\hbar)^{1/2}$, m^* being the "bare" effective mass of holes in the valence band, and predicts a rapid decrease of the $d_{\mathbf{w}}$'s for $w > u$. Thus, using the continuum polarization model for all our $d_{\mathbf{w}}$'s, we estimate that D is reduced by a factor $(1 - u/w_{\max})$, where $w_{\max}$ is given by (66). If $m^* \sim m$, $(u/w_{\max}) \sim 10^{-1}$ in most materials.

5. Only one branch of the phonon spectrum was considered in Sec. II, and this branch was specified as an optical one for most of the section. Neglect of interaction of electrons with acoustical phonons is probably a fairly good approximation in ionic crystals which are not piezoelectric except perhaps for exciton absorption, where the effects of the electron and hole tend to cancel each other in the polar interaction.

In piezoelectric crystals, if interaction with the polarization due to the acoustical modes is taken into account, one finds, using, e.g., Meijer's and Polder's article on piezoelectric scattering[18] and Eq. (11), that $d_{\mathbf{w}}$ depends very much on the direction of $\mathbf{w}$, but that for directions for which it is largest

$$|d_{\mathbf{w}}| \sim 2\pi g / V^{1/2} w^{3/2}, \tag{67}$$

where V is the volume of the crystal and g is a dimensionless constant given by

$$g = \left(\frac{V}{N}\right)^{1/2} \frac{e^* e_{ij}}{\hbar^{1/2} s^{3/2} \epsilon_s M_c^{1/2}}. \tag{68}$$

Here e^* is the effective charge on an ion, s is the velocity of sound in the material, e_{ij} is a piezoelectric constant relating polarization and strain, ϵ_s is the static dielectric

[18] H. J. G. Meijer and D. Polder, Physica **19**, 255 (1953).

constant of the crystal, and M_c is the total mass of the ions in a unit cell.

Hence, an order-of-magnitude estimate of the total extent W of the tail of the band-to-band absorption which would arise for piezoelectric coupling may be found by putting

$$W \sim \sum_{\mathbf{w}} |d_{\mathbf{w}}|^2 \hbar s w, \tag{69}$$

assuming $d_{\mathbf{w}}$ is given by (67) for all $\mathbf{w}$ in one branch of the spectrum, and replacing the summation over $\mathbf{w}$ by an integration over a sphere of radius $w_{\max}$ given by (66). The result is

$$W \sim 2g^2 (\hbar s w_{\max}). \tag{70}$$

This width should be compared with the corresponding quantity $D\hbar\omega$ for interaction with optical phonons, where D is given by (64) for a continuum polarization model.

D. Simplifications at Low and High Temperatures

It is of interest to notice that the dependence on p of the integrated absorption of the bands with net emission of p phonons, contained in the expressions for R_p of (23) and H_p of (46) is very simple at $T = 0$ and for high temperatures. At $T = 0$ we have

$$R_p \propto D^p / p!, \tag{71}$$

while if D is large, using (25) and (26) and an asymptotic form for the Bessel function in (25), we can show that at temperatures such that $kT > \hbar\omega$ the dependence of R_p on p is approximately given by

$$R_p \propto \exp[-(\hbar\omega/4DkT)(p - D)^2]. \tag{72}$$

Thus, for the wide to narrow band case of Sec. II B, if we consider the conduction band to be of negligible width and replace the function $F(E)$ of (37) by a step function (F is likely to start to rise as $E^{1/2}$ and then flatten off), the dependence on energy of $n\Omega K(\Omega)$ as given by (35) will be contained in the sum

$$\sum_{p=0}^{p_1} (D^p / p!)$$

at low temperatures, with p_1 defined by (36), while at high temperatures $n\Omega K$ will behave like an error function.

Expressions for H_p of (46) at $T = 0$ and at high temperatures are the same as (71) and (72) except that S replaces D. Hence, from (45), we have a series of absorption peaks whose strengths have a roughly Gaussian envelope at high temperatures while at $T = 0$, the strengths of the peaks at $(E_G + p\hbar\omega)$ are proportional to $(1/p)(S^p/p!)$. To obtain realistic absorption curves we must remember to allow for spontaneous emission, dispersion of phonon frequencies and residual interaction as discussed in Sec. III C.

To see the sort of absorption spectrum expected due to transitions within one narrow band we introduce the function $g(u)$ by the defining equation

$$g(u) \equiv (1/u)H_u[1-\exp(-u\hbar\omega/kT)], \qquad (73)$$

where H_u is defined as in (46) for integral u, and this definition is extended to nonintegral u in a natural manner. The function $g(u)$ will be proportional to the absorption coefficient as modified by spontaneous emission at photon energy $u\hbar\omega$ when polaron bandwidth or dispersion of phonon frequencies is just sufficient to merge individual absorption peaks into a continuous curve, while when the individual peaks maintain their identity, $g(u)$ for nonzero, integral values of u should be roughly proportional to the integrated absorption for the peaks at the corresponding photon energies.

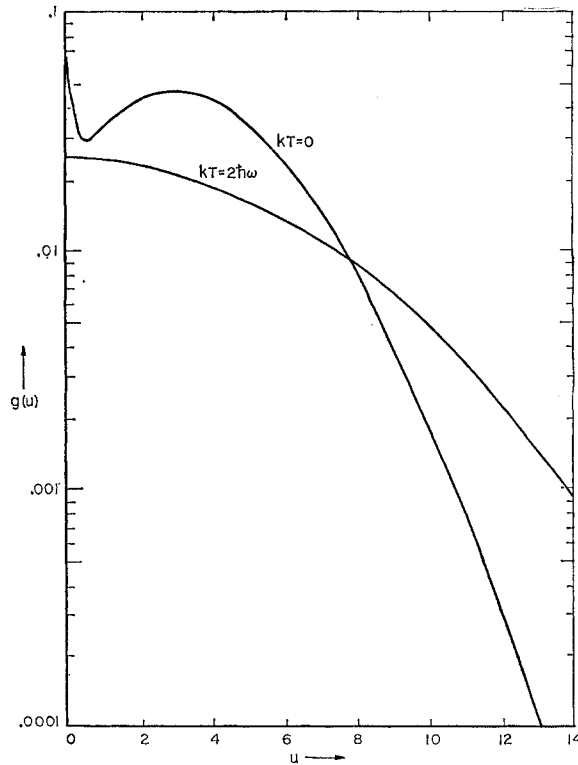On Fig. 3 we have plotted $g(u)$ against u for two

FIG. 3. Plot of the function $g(u)$ of (73) against u for the temperatures $T=0$ and $T=(2\hbar\omega/k)$, with the parameter S of (47) satisfying $S=5$. This function is expected to be proportional to the refractive index times the absorption coefficient at photon energy $u\hbar\omega$ due to transitions within one small polaron band (or between localized polaron states) when dispersion of phonon frequencies or polaron bandwidths are just sufficient to broaden the set of lines predicted with no dispersion and negligible bandwidth into a smooth curve, while, when individual absorption peaks are distinguishable, $g(u)$ for nonzero integral values of u should be roughly proportional to the absorption strengths of the peaks at the corresponding photon energies. However, the only similarity between the behavior of $g(u)$ for $u<1$ on the $T=0$ curve and the expected absorption in the corresponding region is the fact that both $g(u)$ and the absorption start to rise with decreasing u for some value of $u<1$.

temperatures $T=0$ and $T=(2\hbar\omega/k)$ with the parameter S of (47) given by $S=5$. When $kT=2\hbar\omega$, $\bar{n}\simeq1.56$, and the parameter Z' analogous to Z of (26) (with D replaced by S) satisfies $Z'\simeq4S=20$. The behavior of the absorption at low photon energies at $T=0$ will not be closely related to $g(u)$ in the corresponding region. However, we do expect a steep rise with decreasing photon energies starting somewhere below the $u=1$ peak and flattening off at energies $\Omega<(\hbar/\tau)$, where τ is the scattering time associated with the residual interaction.

The minimum in the low-temperature curve for $g(u)$ would become more pronounced for larger values of S. It should be noted that this minimum is of a different type from the minima in the absorption by polarons in the effective-mass model obtained by Feynman et al.[7] Their minima are more analogous to those which we should obtain in our theory if we were to suppose that absorption to a polaron band of higher energy caused the falling absorption for large u in Fig. 3 to start rising again. However, even here the analogy is not very good, as, in the effective mass type of polaron theory, for strong coupling the potential well due to the polarization can introduce a number of bound electron states radically different from the states with no coupling, whereas in small polaron theory a deep well is already present, and the polarization merely effects a slight increase in the depth of this well, and hence is not likely to drastically alter the electronic part of the polaron wave function.

IV. MODEL WITH INTERACTION QUADRATIC IN VIBRATIONAL COORDINATES

In the last two sections we have considered optical absorption by electrons when the electron-phonon interaction is linear in the vibrational normal coordinates. However, for some cases, particularly for exciton absorption, interaction quadratic in these coordinates may be important. We can get some idea of what will happen under these circumstances by considering a model where the interaction is with one localized vibrational mode only, and is entirely quadratic in the coordinate describing this mode.

For this case, if we use the adiabatic method to find the vibrational potential energy for two electron states a and b, then in general we shall have potential energy curves as functions of nuclear position which have different curvatures for the two states; thus we might have a configurational coordinate diagram as shown in Fig. 4. If we neglect the variation of the electronic matrix element with change of the configurational coordinate ξ, then the energy dependence of the absorption may be obtained entirely in terms of matrix elements and energy differences between the vibrational energy eigenstates for the two potential curves. At high temperatures one may then obtain correct results for absorption by imagining that the lower curve is occupied
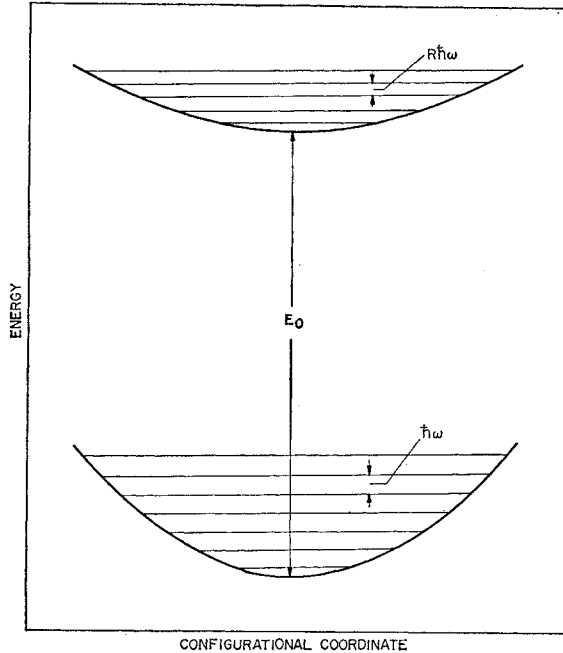
FIG. 4. Configurational coordinate diagram with vibrational Hamiltonians given by (74) and (75).

with a probability according to classical statistical mechanics, and that transitions take place vertically on the configurational coordinate diagram (i.e., with no change of ξ).[15] If we choose a dimensionless ξ such that the vibrational Hamiltonians H_{va} and H_{vb} for the two curves are given by

$$H_{va}=\left(-\frac{1}{2}\frac{\partial^2}{\partial\xi^2}+\tfrac{1}{2}\xi^2\right)\hbar\omega \tag{74}$$

and

$$H_{vb}=\left(-\frac{1}{2}\frac{\partial^2}{\partial\xi^2}+\tfrac{1}{2}R^2\xi^2\right)\hbar\omega+E_0 \tag{75}$$

(H_{vb} has eigenstates separated by energies $R\hbar\omega$), then the classical probability $P(E)dE$ for the energy on the lower curve to have values between E and $(E+dE)$ satisfies

$$P(E)\propto E^{-1/2}\exp(-E/kT) \tag{76}$$

and the vertical energy difference ΔE_v between the two curves at energy E on the lower one is given by

$$\Delta E_v=E_0-E(1-R^2). \tag{77}$$

Hence we obtain the dependence of the absorption coefficient K on photon energy Ω

$$n\Omega K(\Omega)\propto(E_0-\Omega)^{-1/2}\exp\{(\Omega-E_0)/[(1-R^2)kT]\} \tag{78}$$

for $\Omega<E_0$, with a sharp drop at higher photon energies.

At low temperatures, when the system is initially in the ground state on the lower curve, there should be one large peak in the absorption, due to transitions to the ground state on the upper curve, followed by peaks

of rapidly decreasing magnitude at energies $2R\hbar\omega$ above the first one. (Matrix elements to every other level will be zero because the wave functions are alternately even and odd about the center.)

The above arguments about the absorption should be valid for a quadratic interaction with a single normal coordinate up to a certain strength. However, for very strong interaction the point $\xi=0$ on the upper curve could turn into a maximum instead of a minimum; when we take into account some terms in the electron-phonon interaction of higher order in ξ we might expect a configurational coordinate diagram as shown in Fig. 5, where the vibrational Hamiltonian for the lower curve is given by (74) as before, while the potential for the upper curve $V(\xi)$ has the form

$$V(\xi)=E_0-\tfrac{1}{2}\xi^2L^2\hbar\omega+O(\xi^3). \tag{79}$$

At high temperatures we can again calculate absorption by assuming classical occupation probabilities on the lower curve and vertical transitions. If the ξ's of importance are within the central quadratic portion of the upper curve we obtain

$$n\Omega K(\Omega)\propto(E_0-\Omega)^{-1/2}\exp[(\Omega-E_0)/(1+L^2)kT], \tag{80}$$

for $\Omega<E_0$, with a sharp drop at higher photon energies.

It is not possible to find the exact form of the absorption at low temperatures without knowing the wave functions for the vibrational states for the upper curve. However, if we assume that the matrix element between the ground state of the lower curve and a state of energy E_1 on the upper curve, such that E_1 cuts the center portion of the upper curve at ξ_1, is proportional to $\exp(-B\xi_1{}^2)$, where B is a constant, and also assume a uniform distribution in energy of the states of the upper curve, then the envelope $K'(\Omega)$ of the absorption peaks at $T=0$ is given by

$$n\Omega K'(\Omega)\propto\exp[(\Omega/\hbar\omega)(4B/L^2)]. \tag{81}$$

If we assume that the upper state wave function is of order unity at $\xi=\xi_1$, and decays inwards at the same rate as a no-phonon harmonic oscillator wave function of frequency $L\hbar\omega$, then the overlap of the ground-state harmonic oscillator function χ_g and upper state wave function χ_u at ξ will satisfy

$$\chi_g{}^*(\xi)\chi_u(\xi)\sim\exp[-\tfrac{1}{2}\xi^2-\tfrac{1}{2}L(\xi-\xi_1)^2]. \tag{82}$$

Hence, by integrating over all ξ, we may obtain an approximate value for B,

$$B\simeq\tfrac{1}{2}L/(1+L). \tag{83}$$

This is the same as the value we obtain if we put the matrix element equal to the overlap at the value of ξ at which this overlap reaches a maximum.

The estimate (83) for B may serve as a rough guide for regions of photon energy such that the upper level reached lies well away from the maximum and minima in the upper state curve of Fig. 5, but detailed calcu-

lations of wave functions would certainly be necessary to deal with levels near these extremes, and would be desirable for all levels.[19] Numerical results for particular cases of the potentials of the form of Fig. 5 have been carried out by Somorjai and Hornig.[20]

If an attempt to describe a combination of interactions linear and quadratic in the normal coordinates by a single vibrational coordinate were made, we should expect the shape associated with the linear terms near the peak of the absorption but that associated with the quadratic terms well away from the peak on the low-energy side.

A possible mechanism for giving a quadratic interaction with vibrational modes which produce electric fields has been proposed by Toyozawa in a note on Urbach's rule.[21] This mechanism is simply the reduction in energy ΔE of a polarizable electron or exciton state in an electric field of magnitude $\mathcal{E}$. This reduction satisfies

$$\Delta E = -\tfrac{1}{2}\alpha \mathcal{E}^2, \tag{84}$$

where α is the polarizability of the state.

The relation between $\mathcal{E}$ and the vibrational coordinate ξ for a localized mode will depend on details of the form of vibration. However, we may obtain rough estimates of the fields associated with localized modes in ionic crystals by imagining that we have a crystal composed of point charges, and considering a mode in which two nearest-neighbor ions of opposite charge move back and forth along the line joining them. We now suppose that there are no fields acting on the ions when they are in their equilibrium positions, and make the simple assumption that the field produced by the relative vibration of the two ions is equal to the change in Coulomb attractive field between them. Then, if we introduce the dimensionless vibrational coordinate ξ for the mode of motion by writing $\xi = (M\omega/\hbar)^{1/2}x$, where M is the reduced mass of the ions, ω is the angular frequency of vibration, and x is their relative displacement, we find that, in terms of ξ, the electric field at one ion due to the vibrational notion of the other relative to it satisfies

$$\mathcal{E} = (2e^*\xi/a^3)(\hbar/M\omega)^{1/2}, \tag{85}$$

where a is the equilibrium separation of the ions. Hence, from (84) and (85), if we have an excited electronic state localized at the site of one ion, the polarizability α of this state required to give an upper configurational coordinate potential described by (79) is given by

$$4\alpha(e^*)^2 = a^6(L^2+1)M\omega^2. \tag{86}$$

By putting $L=0$ in (86) we obtain the critical value for the polarizability at which the upper curve first becomes flat. The polarizability of the electron part

of the exciton wave functions in the alkali halides may perhaps approach or exceed this value (see Sec. V), and so it is possible that our model will apply to exciton absorption in these materials.

V. PARTICULAR MATERIALS

A. Transition Metal Oxides

The most striking group of ionic materials containing electrons in states made up from electronic functions of unfilled shells of ions such that the overlap integrals with neighboring ions of the same type are small but not negligible are the transition metal oxides which contain from 1 to 9 electrons in the $3d$ shell of the transition metal ions. A review of the properties of these oxides has been written by Morin.[22] The five $3d$ one-electron orbitals in a cubic environment such as seen by the transition metal ions in the monoxides with the NaCl structure are split by the cubic field by an amount of the order of 1 eV into three lower ϵ levels whose wave functions are mainly directed in between the anions, and two upper γ levels, directed towards the anions. In a trigonal field there is a further slight splitting of one of the ϵ levels below the other two. The first excited state of any ion in a cubic environment may be considered as produced from the ground state by excitation of an electron from an ϵ to a γ orbital. In many of the oxides there is a wide filled band formed from $2p$ oxygen wave functions a few electron volts in energy below the d bands. Thus, it would appear that the theories of absorption in Secs. II B and II C might both find application in these oxides. However, at
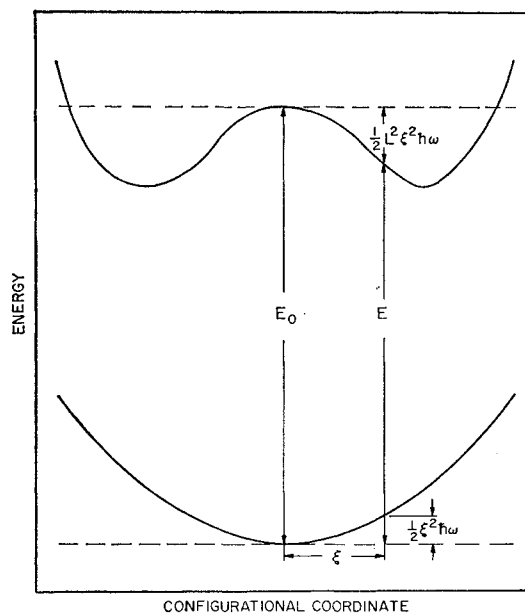
FIG. 5. Configurational coordinate diagram with an upper state vibrational potential of the form (79).

[19] See footnote 31 at the end of Sec. V.
[20] R. L. Somorjai and D. F. Hornig, J. Chem. Phys. **36**, 1980 (1962).
[21] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **22**, 455 (1959).

[22] F. J. Morin, in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), Chap. 14, p. 600.

present there does not seem to be any clear-cut indication of absorption of the type predicted in Sec. II C. This type of absorption is more likely to be noticeable in the oxides of the lighter transition metals Sc, Ti, and V, where overlap integrals are comparatively large, but more experimental information is available in NiO, and so we shall concentrate on this substance, first making estimates of the orders of magnitude of the parameters involved in the theory and then commenting on optical absorption results obtained by Newman and Chrenko.[23]

We should note that the overlap integrals determining the width of the d bands in these oxides are not simple overlaps between electron states of the transitional metal ions, but involve transfer of electrons between the cations via oxygen ions. Complications would occur in our theory if we attempted to take this fact into account in a realistic way, but we shall not consider these. We shall also ignore difficulties associated with magnetic properties.

NiO

Taking the values $\epsilon_\infty = 5.4$, $\epsilon_s = 12$, and $\hbar\omega = 0.076$ eV from reference 23, using the value 4.18 Å for the lattice constant, and noting that for the NaCl structure of NiO there are four unit cells in a cube of the dimension of the lattice constant we find from (66) that $w_{max} = 1.5 \times 10^8$ cm^{-1}, and from (64) that on the continuum polarization model $D \simeq 9$. Hence, if we take $w_{max}G = \pi$, hoping that the error introduced by choosing a too small value of G will partly compensate that arising from taking a spherical Brillouin zone, we find from (65) that $S \simeq 7$.

There are eight d electrons per nickel ion in NiO and it is almost insulating when stoichiometric, showing, however, slight p-type conduction which can be increased by doping. It is thought that a filled $2p$ oxygen band lies at an energy slightly below the filled $3d^8$ levels, while the empty $3d^9$ levels lie a few electron volts higher in energy than the filled d states.

According to Morin[22] the mobility of d holes, deduced from a combination of thermoelectric power and conductivity data, increases sharply with temperature in the region investigated, i.e., room temperature and above, and so, if small polaron theory applies, the transition temperature T_c between the band and jumping region must be below room temperature. By interpreting the temperature dependence of the mobility according to their model[24,4] Yamashita and Kurosawa estimate $S \sim 15$ for samples with fairly small carrier concentrations and $S \sim 4$ or 5 for highly doped material. They also find that the correct order of magnitude for the mobilities is obtained if the matrix

element of the electronic Hamiltonian between electron states on adjacent sites, which we call J, satisfies $J \sim \hbar\omega$. If we use the value $D \simeq 9$ estimated above then from (61) $E_b \simeq 4.5$ $\hbar\omega$. Thus, (62) is satisfied, (63) does not hold except at very high temperatures, while (60) is true if we allow a rather liberal interpretation of much less than. Hence, we seem to be about on the borderlines of applicability of small polaron theory in NiO. The site jump probability values at room temperature are of the order of 10^{11} sec^{-1}, hence, the polaron energy levels are lifetime broadened by only about 10^{-4} eV at this temperature.

We are now in a position to discuss the optical absorption results of Newman and Chrenko which are reproduced in Fig. 6. The rise in absorption at very low energies on the figure is due to reststrahlen absorption, the 0.24-eV peak has been interpreted by Newman and Chrenko as connected with antiferromagnetic ordering, the peaks between 1 and 4 eV occur at positions close to those for Ni^{++} ions in a cubic environment in MgO,[25] and are thought to be due to transitions within one ion, while the long rise in absorption to the plateau above 4 eV is probably due to transitions from a filled oxygen p band to empty Ni$^+$ d levels. The various peaks between 1 and 4 eV are superimposed on a continuous background absorption which rises as $1/(E-E_0)^4$, where $E_0 = 4$ eV. The magnitude of the absorption background increases with increasing im-
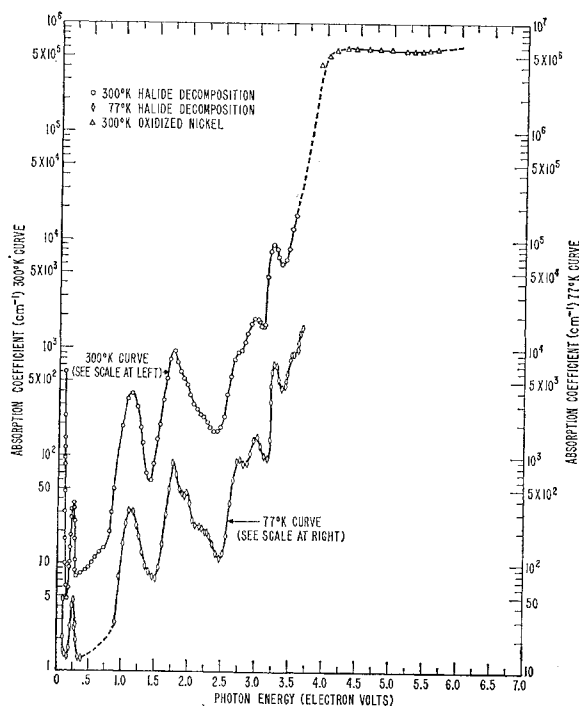

Fig. 6. Absorption spectrum of NiO at 300°K, 77°K. Dashed lines are interpolations. (This figure is reproduced from Fig. 2 of reference 23.)

[23] R. Newman and R. M. Chrenko, Phys. Rev. 114, 1507 (1959).
[24] Holstein (reference 6) has pointed out an error in Yamashita and Kurosawa's derivation of the jumping mobility, but has shown that this error produces negligible deviations in their results from the true ones for most cases of interest.

[25] W. Low, Phys. Rev. 109, 247 (1958).

purity concentration, but, as far as the author is aware, the details of its origin are still obscure.

Since there are indications that the mobilities of holes in the filled oxygen p band are quite large,[21] this band is probably wide, while we have shown above that small polaron theory should hold for the d^8 bands, and so may hold for the d^9 bands as well. Thus, the theory of Sec. II B might apply to the long absorption rise and plateau above 4 eV in the figure. The optical phonon temperature corresponding to $\hbar\omega = 0.076$ eV is 880°K, hence the phonon occupation numbers at room temperature are very small, and the theory with $T=0$ should give approximately the correct shape of the curve. We can fit the observed absorption in this region quite well by using our theory for $T=0$, assuming the function $F(E)$ of (37) is a step function as suggested in Sec. III D, and adjusting the constant D, and the absolute magnitude and position in energy of the absorption to give the best fit to experiment. The energy gap required for this fit is 3.25 eV while the value of the constant D used is $D=8$. This value is in reasonable agreement with $D=9$ estimated on the continuum polarization model. One would have expected to see signs of one or more exciton peaks somewhere near the low-energy tail of the curve, but perhaps these are too broad and weak to be noticeable.

The main difficulty in accepting this interpretation of the absorption in this high-energy region is to reconcile having $D=8$ with the value of $S=15$ for holes in d^8 shells deduced from mobility results. However, the two values may not be incompatible since (1) D is probably associated with the oscillator displacements brought about by an electron in an Ni^+ d level, while S is connected with electrons in Ni^{++} d levels; (2) departures from the continuum polarization model will affect the oscillator displacements for large w most, and these displacements can give a larger contribution to S than to D even for electrons in the same d states. (The maximum ratio of the contributions to S and D is 4, for $\mathbf{w} \cdot \mathbf{G} = \pi$.) The oscillator strengths of the absorption peaks between 1 and 4 eV are of the order of 10^{-5}, that of the narrow peak at 3.5 eV being slightly larger than the others. These peaks are probably due to transitions within a single Ni^{++} ion taking place via an intermediate p band. The shape of the individual peaks on the 77°K curve can be fitted quite well by an envelope of absorption lines at energies $(E_i + p\hbar\omega)$, with $\hbar\omega = 0.076$ eV, of strengths proportional to $(T_i{}^p/p!)$, where E_i and T_i are energies and width constants associated with the ith peak. The parameters T_i required are about equal to 3 or 4 for all the peaks except that at 3.5 eV for which $T_i = 1$ is better.

This form of absorption shape is expected for single-site excitons at low temperatures if the coupling with the longitudinal optical modes determines the width, and dispersion of phonon frequencies or lack of resolution in the experiments is sufficient to smear out the

individual lines into a smooth curve. As mentioned at the end of Sec. II D the oscillator strengths for this type of transition should be of the order of magnitude given by (58) and the parameters T_i should be identified with T of (57) for the relevant electronic states. Values of T as high as four are not surprising, since, if we accept the value $S \simeq 15$ from mobility results, which value is about twice that estimated on the continuum polarization model, then a large fraction of the contribution to S must come from the short-wavelength modes. Thus, the short-wavelength modes are likely to be important in determining D too, and the d_w's for these modes will depend on short-range forces which are sensitive to the details of the electron wave functions concerned. Hence T, which depends on differences of d_w's for two bands, can be an appreciable fraction of D.

We notice from Fig. 6 that the magnitude of the absorption at the peaks is decreased by a slight amount in passing from 300 to 77°K while the width is not noticeably altered, in agreement with the expected proportionality of the oscillator strength of the absorption for indirect phonon-assisted transitions via an allowed band to $(2\bar{n}+1)$, where $\bar{n}$ is the thermal occupation number of the phonons concerned. If we assume it is the longitudinal optical phonons which bring about the transitions, then the decrease of f in passing from 300 to 77°K should be by a factor 0.90.

It is of interest to try to see why electron transfer exciton absorption does not seem to be observed. Using the theory of Sec. II C, expected to be applicable to electron transfer excitons as discussed in Sec. II D, we can estimate the oscillator strength f for formation of this type of exciton on the assumption that the ratio of $a(\mathbf{G})$ of (43) to the reciprocal of the ionic radius is of the same order as the ratio of nearest-neighbor off-diagonal matrix elements J of the electron Hamiltonian to some energy E associated with the wave function on one lattice site. This gives $f \sim (J/E)^2$. Taking the value $J \sim \hbar\omega$ estimated by Yamashita and Kurosawa and $E \sim 36$ eV (the ionization energy of a free ion), we find $f \sim 4 \times 10^{-6}$, which is not much less than the strengths of the observed single-ion exciton peaks. However, the larger width of the electron-transfer type of band could make it more difficult to see, and also the transitions will occur at higher energies than the free ion transitions, and so may be mainly submerged under the large plateau above 4 eV.

B. Alkali Halides

The conduction band of the alkali halides is built up from alkali s states, and is thought to be quite wide, while there is evidence from the spin resonance work of Castner and Känzig[26] that the valence band, composed of halogen p functions, is very narrow, and Nettel[27] has shown theoretically that this is likely to

[26] T. G. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957).

[27] S. J. Nettel, Phys. Rev. **121**, 425 (1961).

be the case. Hence, the theory of Sec. II B might be expected to apply to the valence to conduction band absorption (the wide band is now the conduction band, but this should not affect the theory) and that of Sec. II C to the absorption by holes. We should note however that, as for d bands in the transition metal oxides, one may expect modifications of the theory to be needed to take into account the fact that the narrow band is not made up entirely from functions on one type of ion. It is also worth remarking that Toyozawa has suggested that the most important interactions in the valence band may be between holes and acoustical phonons.[28]

The valence band p states in the alkali halides are normally all filled, and so to observe absorption involving transitions within the p bands requires the production of holes in the valence band by some means, such as irradiating with ultraviolet or x radiation, and then looking at the modification of the longer wavelength absorption by the presence of holes. The situation is complicated by the fact that the holes distort the lattice very anisotropically in their vicinity, forming a molecular ion with two nearest-neighbor halogen atoms lying in a [110] direction relative to each other. Delbecq et al.[29] have performed absorption experiments on x-ray irradiated KCl and detect two absorption bands associated with holes, but we have not attempted to interpret their results.

As far as the valence to conduction-band absorption is concerned, we find that experimentally, because of the high absorption coefficients in the band-to-band absorption region, the best absorption results have been obtained for the first exciton band. The absorption in the tail of this band can be described over many orders of magnitude of the absorption coefficient by Urbach's rule, i.e.,

$$K(\Omega) \propto \exp[\sigma(\Omega - E_0)/kT], \qquad (87)$$

where E_0 is a fixed energy and σ is a constant of order unity. Departures from this law are obtained at low temperatures when T is replaced by a constant temperature T_0. Near the peak of the absorption the shape is Gaussian.

The validity of (87) over a large energy region indicates, as suggested by Toyozawa,[20] that the terms in the electron-phonon interaction quadratic in the normal coordinates are dominant in determining the shape of this absorption. As the energy of the peak is not far from that for free molecules, we might expect a localized exciton model to be a good approximation, and so we use our single vibrational coordinate model with an excited state vibrational potential energy given by (79) or (75).

Extensive measurements of the absorption rise in

[28] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **26**, 29 (1961).
[29] D. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958).

KI have been made by Haupt,[30] who obtains a value $\sigma \simeq 0.8$ in Eq. (84) and finds that T must be replaced by $T_0 \simeq 66°K$ at low temperatures. To explain an exponential rise at low temperatures we must suppose that the configurational coordinate model of Fig. 5 applies with a potential energy given by (79). From (78) ignoring variations in $(n\Omega)$ on the left-hand side and in $(\Omega - E_0)^{-1/2}$ on the right-hand side of the equation, the value of L required to give $\sigma = 0.8$ in (87) is $L = 0.5$. If we use (81) and (83), then the parameter describing the low-temperature absorption satisfies $kT_0 \simeq 0.3 \ \hbar\omega$. Taking the frequency of the mode concerned as that of the long-wavelength longitudinal optical phonons, and using the approximate value of 200°K for the longitudinal optical phonon temperature deduced from the results for KI for dielectric constants, refractive index, and restrahlen frequency given by Pekar,[12] we find $T_0 \sim 60°K$. The agreement of this value with the experimental value of 66°K is better than one would expect in view of the many uncertainties in the theory.[31]

If we ignore effects associated with the hole part of the exciton wave function, and apply (86) to the electron part, using $e^* = e$ (electronic charge), $a = 3.53$ Å, $M = 30$ amu (reduced mass of potassium and iodine atoms), and $\hbar\omega = k \times 200°K$, we find that the value for the electronic polarizability required to make $L = 0.5$ is $\alpha = 1.0 \times 10^{-22}$ cm^3. This value may be compared with the potassium atom value of $\alpha = 4.6 \times 10^{-23}$ cm^3.

VI. CONCLUSION

In Sec. II use was made of the wave functions of small polaron theory to calculate optical absorption coefficients in ionic crystals due to electron transitions to states of a small polaron band: (1) from Bloch states in a band for which coupling to the phonons is neglected; (2) from another small polaron band. In both cases the squares of the moduli of matrix elements for transitions without change of phonon-occupation numbers are decreased by the electron-phonon coupling by the negative exponents of parameters depending on the temperature and on the sums of squares of the lattice-oscillator displacements occurring in small polaron theory. The absorption lost because of this factor reappears in processes where phonons are emitted and absorbed, usually in such a way that the integral over energy of the product of refractive index, absorption coefficient, and photon energy remains constant, independent of coupling strength. The preferred occupation-

[30] U. Haupt, Z. Physik **157**, 232 (1959).
[31] *Note added in proof.* Use of the WKB method to find the upper state vibrational wave functions increases B from the value given by (83), and hence decreases the value of $(kT_0/\hbar\omega)$ from that calculated above. For $L = 0.5$ we now find that $(kT_0/\hbar\omega) \simeq 0.2$. Thus, there is no longer good agreement with the observed T_0 in KI. This discrepancy may perhaps be understood in terms of a model involving interaction with two vibrational coordinates ξ_1 and ξ_2, the interaction being linear in ξ_1 and quadratic in ξ_2, but with the strength of the quadratic interaction in ξ_2 depending on the value of ξ_1.

number changes during the absorption are of the order of the parameter occurring in the exponential mentioned above. If the absorption is split into sub-bands for which $(m+p)$ phonons are emitted and p phonons absorbed, then the shape of the sub-bands for large $(2m+p)$ is determined by electronic matrix elements and density of states functions alone, while for small $(2m+p)$ details of the electron-phonon interaction need to be known, unless one of the polaron bands concerned has negligible width.

The theory of Sec. II B for absorption due to transitions from a wide band where electrons are uncoupled to the phonons to a small polaron band, specialized to low temperatures, negligible width for the polaron band and a step-function density of states for the valence band, predicts absorption roughly proportional to a sum

$$\sum_{p=0}^{p_1} (D^p/p!),$$

where D is a constant given by (24) and p_1 increases by one when the photon energy increases by the phonon energy $\hbar\omega$. With a value for D only slightly different from that estimated on a continuum polarization model this form of the theory appears to give a satisfactory account of the tail to the absorption plateau above 4 eV in NiO, and is likely to be applicable to the corresponding absorption tails in other transition metal oxides.

The theory of absorption due to transitions between narrow polaron bands developed in Sec. II C predicts rather weak absorption. In its simplest form, for negligible polaron bandwidth, it predicts a series of absorption lines at energy $(E_G'+p\hbar\omega)$ (where E_G' is the band gap and p is an integer), such that the integrated absorption over these lines weighted by the photon energy and refractive index is proportional at low temperatures to $[(\text{constant})^p/p!]$, where the constant is either S of (47) or T of (57), according to whether electron transfer or single site processes are dominant. In practical cases phonon dispersion or other broadening mechanisms are likely to smear these lines into a smooth curve. This theory might apply to some results on absorption by holes in x-ray-irradiated KCl,[28] but no attempt has been made to interpret these results in detail here.

The theory of Sec. II does not predict absorption edges following a simple exponential rise with photon energy, and so cannot be used to explain Urbach's rule. However in Sec. IV a configurational coordinate model has been used to apply to localized excitons an idea of Toyozawa[21] for estimating the line shape of absorption due to an exciton-phonon interaction quadratic in the coordinates of a single normal mode, and this model seems to be able to account for results on Urbach's rule in[29] KI if rather large polarizabilities for exciton states are assumed.

The use of approximate energy eigenstates of the electron-phonon system obtained from polaron theory to calculate the absorption with the assistance of many phonons offers great advantages over a many-order perturbation type of approach, and is conceptually simpler than the more sophisticated method used by Feynman et al.[7] However, before the present method could be extended to polarons in a wide band, a further study of the stationary states of the electron-phonon system containing electrons of energy of the order of the phonon energy above the bottom of the band would have to be made.

Note added in proof. The author has recently read some work of É. L. Nagaev [Soviet Phys.—Solid State 4, 1611 (1963)], who points out that, except at $T=0$, wave functions of the type occurring in Eq. (7), with fixed numbers of phonons in each displaced oscillator state, are not the best small polaron wave functions to use. One should first form suitable linear combinations of states containing an electron localized on one site together with a given total number of phonons, but with various occupation numbers for the individual oscillator states. Bloch-type combinations of these new localized states may then be taken. Using this approach a distribution of effective overlap integrals is obtained at any given temperature. The mean value of these overlaps is equal to the overlap occurring in the usual small polaron theory, but the mean square value increases with increasing temperature. Thus, in some sense, the bandwidth becomes larger as the temperature rises, instead of becoming smaller as in conventional small polaron theory.

The consequences of these considerations on the work presented here have not been examined in detail yet, but it seems probable that the results of Sec. II B will not be altered significantly, since the parameter D describing the shape of the absorption tail there is simply related to the binding energy for zero overlap, which is not changed by the use of Nagaev's states. The present author is of the opinion that the results of Sec. II C will not be altered much either, except perhaps at photon energies less than the polaron bandwidth. However, this matter requires further study.

ACKNOWLEDGMENTS

APPENDIX A

Any dependence on E and Ω of the average of $\prod_w |d_w|^2$ in (30) will arise from the dependence on $\mathbf{k}$ and $\mathbf{k}'$ of the sums $S_{\mathbf{kk}'}$ of $\prod_{A,B} |d_w|^2$ over all sets

$\{A\}$, $\{B\}$ containing $(m+p)$ and m members and subject to the wave-vector conservation condition (17) for given $\mathbf{k}$ and $\mathbf{k}'$. This sum $S_{\mathbf{kk}'}$ satisfies

$$S_{\mathbf{kk}'} \propto \sum_{\mathbf{L}} \int d^3\mathbf{w}_1 \cdots d^3\mathbf{w}_{2m+p}$$

$$\times \prod_{i=1}^{2m+p} |d_{\mathbf{w}_i}|^2 \delta(\mathbf{k}' - \mathbf{k} + \sum_A \mathbf{w} - \sum_B \mathbf{w} - 2\pi\mathbf{L}), \quad (A1)$$

where the summation is over all reciprocal lattice vectors $\mathbf{L}$ and the integrations over $\mathbf{w}$'s are over the first Brillouin zone. We can simplify (A1) by noting that

$$N \sum_{\mathbf{L}} \delta(\mathbf{a} - \mathbf{L}) = \sum_{\mathbf{R}} \exp(i\mathbf{a} \cdot \mathbf{R}), \quad (A2)$$

where $\mathbf{a}$ is any given wave vector and the summation on the right is over all lattice vectors $\mathbf{R}$. Using (A2) the integration over individual $\mathbf{w}$'s can be performed independently. Writing

$$\int |d_{\mathbf{w}}|^2 \exp(i\mathbf{w} \cdot \mathbf{R}) d^3\mathbf{w} = f(\mathbf{R}), \quad (A3)$$

we find

$$S_{\mathbf{kk}'} \propto \sum_{\mathbf{R}} \exp[i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}][f(\mathbf{R})]^{2m+p}. \quad (A4)$$

Inspecting (A3) we see that

$$|f(0)| > |f(\mathbf{R})|, \quad \mathbf{R} \neq 0 \quad (A5)$$

and so for large $(2m+p)$ the main contribution to $S_{\mathbf{kk}'}$ in (A4) comes from $\mathbf{R}=0$. Hence $S_{\mathbf{kk}'}$ is independent of $\mathbf{k}$ and $\mathbf{k}'$.

APPENDIX B

Let us consider the sum $T_{\mathbf{kk}'}$ defined by

$$T_{\mathbf{kk}'} = \sum_{\{A\},\{B\}}' \left| \sum_{\mathbf{G}} a(\mathbf{G}) \exp[i(\mathbf{k}+\mathbf{k}') \cdot \mathbf{G}/2] \right.$$

$$\times \prod_A [2id_{\mathbf{w}}^* \sin(\mathbf{w} \cdot \mathbf{G}/2)]$$

$$\left. \times \prod_B [2id_{\mathbf{w}} \sin(\mathbf{w} \cdot \mathbf{G}/2)] \right|^2, \quad (B1)$$

where $\sum_{\{A\},\{B\}}'$ denotes a sum over all sets $\{A\}$, $\{B\}$ containing $(m+p)$ and m members and satisfying the wave-vector conservation condition (17) for given $\mathbf{k}$, $\mathbf{k}'$. Suppose we separate the sums in (B1) into sums of terms for the individual $\mathbf{G}$'s and sums of cross terms between different $\mathbf{G}$'s we find that the ratio of magnitudes of the contribution from the cross term between $\mathbf{G}_1$ and $\mathbf{G}_2$ to that from the sum of terms for $\mathbf{G}_1$ and $\mathbf{G}_2$ separately is of the order of r, where

$$r \lesssim (S'/S)^{2m+p}, \quad (B2)$$

with S defined by (47) and

$$S' = \sum_{\mathbf{w}} \{4|d_{\mathbf{w}}|^2 \sin(\mathbf{w} \cdot \mathbf{G}_1/2) \sin(\mathbf{w} \cdot \mathbf{G}_2/2)$$

$$\times \cos[\mathbf{w} \cdot (\mathbf{G}_1 - \mathbf{G}_2)/2]\}. \quad (B3)$$

Now it is apparent that $|S'| < S$, and so r is small for large $(2m+p)$. Thus, for large $(2m+p)$ the terms from the individual $\mathbf{G}$'s contribute independently to $T_{\mathbf{kk}'}$, and so the arguments used in Appendix I to show that $S_{\mathbf{kk}'}$ is independent of $\mathbf{k}$ and $\mathbf{k}'$ for large $(2m+p)$ can be applied to $T_{\mathbf{kk}'}$.

Any dependence of the average in (54) on E and Ω would come in through a dependence of $T_{\mathbf{kk}'}$ on $\mathbf{k}$ and $\mathbf{k}'$. Hence we have proved our assertion that this average is independent of E and Ω for large $(2m+p)$.