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Interaction of a Polarizable Potassium Chloride Crystal with a Valence-Band Hole*

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The interaction of a valence-band hole with a potassium chloride crystal, when crystal-hole correlations are considered, is studied by variational means. Initially a crystal trial wave function is constructed which allows for the ionic polarizability of the crystal by means of a correlation between the crystal configuration and the motion of the hole. The expectation value of the Hamiltonian operator for the crystal is found by integrating over both electronic and nuclear coordinates. The necessary matrix elements of the electronic energy operators are taken from a previous calculation by Howland. The total energy expectation is minimized with respect to a single parameter in the wave function that measures the hole-lattice correlation. One finds that the valence bands obtained when the crystal lattice is treated as rigid become completely flat, a result which implies that the hole is self-trapped.

The modifications that are introduced by the addition of the electronic polarizability are studied by repeating the previous calculation with a refined wave function. Only a rough treatment drawing on the experimental electronic polarizabilities of the crystal ions is given. Information on self-trapped holes in KCl derived from the electron-spin resonance experiments of Castner and Känzig is briefly considered.

1. INTRODUCTION

A SLOW conduction electron or a valence-band hole in an ionic crystal interacts strongly with the crystal by inducing ionic and electronic polarizations. Theories of the polaron are generally based on a model in which the extra charge is treated as a free particle with a definite effective mass interacting with a continuous polarizable medium.[1] However, Sewell[2] and Holstein[3] have recently explored a tight-binding approach in which the interaction between charge and crystal is built into the wave function from the start. This approach is suitable when the interaction of the charge with the undeformed lattice is particularly strong.[2]

Making use of a suggestion by Koster[4] of an Ansatz similar to that considered by Sewell, the writer studied the behavior of a valence-band hole in potassium chloride in an attempt to extend the careful numerical calculation of the band structure of potassium chloride for a nonpolarizable lattice made by Howland.[5] Unlike the investigations of Sewell and Holstein the present study is based on an *ab initio* many-electron Hamiltonian, and is thus also able to take electronic polarization into account. Its basic result, a flattening of the energy bands brought on by the crystal polarization, has been anticipated by their calculations, with which it shares a number of features.

The valence band in potassium chloride has been selected for study because it is better suited for a tight binding treatment than, say, a conduction electron, and because many requisite data are available from Howland's calculation. Also, this investigation is related to two interesting observations: the study by Parratt and Jossem[6] of the x-ray emission spectrum in KCl which accompanies electronic transitions from the valence to the K band, and the study by Castner and Känzig[7] and others of electron-spin resonance spectra in a number of alkali halides, including KCl, that can be associated with self-trapped holes.

The main subject of this paper will be the modifications undergone by the band structure as a result of the crystal polarizations. Two calculations are carried out: In the first a wave function which takes account of only the ionic polarizability is considered. This portion of the work can be carried out with relative precision, and thus forms a reliable basis for the second calculation, where the modifications to the problem introduced by the addition of the electronic polarizability are treated in a rough way. A brief attempt is then made to explain the experimental findings of Castner and Känzig within the framework of the investigation. The relation of the present study to the x-ray emission spectra observed by Parratt and Jossem will be taken up in a subsequent paper.

In the present treatment the ground state of the crystal with the hole is sought by variational means. The only *a priori* assumptions are those made when

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[1] For a review of the polaron problem see H. Fröhlich, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 325. For references to very recent work, see T. D. Schultz, Phys. Rev. **116**, 526 (1959). A fuller review by Schultz will be found in Technical Report No. 9, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, 1956 (unpublished).

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

[3] T. Holstein, Ann. Phys. **8**, 325 (1959).

[4] G. F. Koster, Department of Physics, Massachusetts Institute of Technology (private communication).

[5] L. P. Howland, Phys. Rev. **109**, 1927 (1958).

[6] L. G. Parratt and E. L. Jossem, Phys. Rev. **97**, 916 (1955).

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

constructing the trial functions.[8] These are allowed to depend on the coordinates of the nuclei, treated as regular coordinates rather than as parameters, and on the coordinates of the valence electrons. The expectation value of the Hamiltonian is then found by integrating over both sets of coordinates. The energy is minimized with respect to a single parameter built into the crystal trial function as a measure of the hole-lattice coupling. The optimum crystal functions and energies are dependent on the propagation vector **k**, so that the calculation must be repeated at representative points throughout the Brillouin zone.

In terms of a simplified system of a single electron and $2N$ ion cores the tight-binding Ansatz basic to this paper can be written as:

$$W=\sum_{g=1}^{2N}\left[e^{i\mathbf{k}\cdot\mathbf{R}_g}w_g(\mathbf{r})\chi_g(X)\right], \tag{1-1}$$

where $w_g(\mathbf{r})$ is a free-ion orbital on the ion g, which is located in the lattice at $\mathbf{R}_g$, $\mathbf{k}$ the Bloch propagation vector, and $\chi_g(X)$ a function of the nuclear coordinates only, which in some way takes cognizance of the location of the electron at the ion g. The nature of the electron-lattice correlation contained in Eq. (1-1) can be understood by imagining the electron to be in the immediate vicinity of, say, the ion h. Then, because of the localized nature of the orbitals w, χ_h will be multiplied by a coefficient far in excess of that of any of the other χ's. The point of the Ansatz (1-1) is that it manages to display an electron-lattice correlation without sacrificing necessary Bloch symmetry.

2. IONIC POLARIZATION

(a) Wave Function

The trial functions for the crystal with a hole are to be based on a description of perfect ionic crystals studied by Löwdin[9] and on Howland's related calculation.[5] The crystal is considered to consist of the valence electrons, and of potassium and chlorine ion cores carrying charges of plus seven and nine, respectively, i.e., the nuclei and their ten inner electrons are treated as single point charges in accordance with the well-founded approximations made by Howland. When the crystal does not contain the hole, its charge is balanced; thus, if there are N ion cores of each type and a total of $2M$ valence electrons, $16N=2M$. The function constructed by Löwdin, which will be denoted as Φ, represented the perfect potassium chloride crystal as an array of K^+ and Cl^- ions. The crystal wave functions were built from real free-ion orbitals, which for KCl are available from the calculations of Hartree and Hartree.[10] To build up the ions, eight orbitals, three $3p$ and one $3s$ orbital of each spin, must be associated with each of the crystal ion cores. It is convenient to number these orbitals $w_1, w_2, \cdots, w_{2M}$, or to distinguish them by capital italic subscripts, $G, H\cdots$. The corresponding small letters will denote the relevant crystal ions. It is assumed that the orbitals w also contain the spin dependence. Following Löwdin, the hole-free electronic function Φ will be chosen as a single Slater determinant of all the $2M$ free-ion orbitals w.

In this study it will be necessary to extend Φ to describe the crystal when the ion cores assume arbitrary configurations. Let X stand for an arbitrary assignment of values to the Cartesian coordinates of all the ion cores making up the crystal, and $X=X_0$ mean that the crystal occupies its usual periodic configuration. It will always be assumed that X does not depart too radically from X_0. In this section one postulates that all the free-ion orbitals follow the motion of their ion cores without deformation; that is, if $\mathbf{x}_g$ is the arbitrary location of the ion g,

$$w_G(\mathbf{r},X)=w_G(\mathbf{r}-\mathbf{x}_g). \tag{2-1}$$

This simplification means that no explicit account is being taken of the electronic polarizability. Φ for arbitrary X is formed from $\Phi(X_0)$ by giving all the component free-ion orbitals the X dependence of (2-1). Accordingly,

$$\Phi(X)=\left[(2M)!\,|\Delta(X)|\right]^{-\frac{1}{2}}\det\left[w_g(\mathbf{r}_j-\mathbf{x}_g)\right];\quad j,g=1,2,\cdots,2M, \tag{2-2}$$

where $|\Delta(X)|$ in the normalizing factor is the determinant of the overlap matrix.

To arrive at a complete wave function for the hole-free crystal, $\Phi(X)$ must be multiplied by an appropriate function of the nuclear coordinates. One begins by defining a potential energy for the entire crystal, $U(X)$, as

$$U(X)=\int\Phi(X)H_U(X)\Phi(X)d\tau_1,\,\cdots,\,d\tau_{2M}. \tag{2-3}$$

H_U is the "static Hamiltonian" of the crystal; it contains the Coulomb interactions of all the charges making up the crystal as well as the kinetic energy of the valence electrons. It does not, however, include the kinetic energy of the ion cores. $U(X)$ is to be found by integrating over space and spin coordinates of all the $2M$ valence electrons in the crystal.

The next step is to expand $U(X)$ in a Taylor series about $U(X_0)$ up to quadratic terms in X. This expansion can be reduced to a quadratic form by a linear transformation from nuclear Cartesian coordinates to normal coordinates Q_ϕ.[11] If the $6N$ Cartesian coordinates of the

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[8] However, the analytic treatment of certain quantities characteristic of a hole-free lattice has had to be somewhat rough, and an appeal is here made to physical intuition for additional justification.

[9] P. O. Löwdin, thesis, Uppsala, 1948 (unpublished); *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.

[10] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936) for Cl^-; **A166**, 450 (1938) for K^+.

[11] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), Chap. IV.

ion cores are written as x_{hi}, where h denotes an ion, i the direction of the coordinate, and R_{hi} its equilibrium value, the transformation can be written as:

$$Q_\phi = \sum_{i=1}^{3} \sum_{h=1}^{2N} e(\phi|h,i)(x_{hi}-R_{hi}), \qquad \phi=1, 2, \cdots, 6N, \qquad (2\text{-}4)$$

where the e's are the coefficients that effect the transformation. Finally one defines a nuclear function $\chi_0(X)$ as the ground-state solution to the well-known harmonic-oscillator equation[12]:

$$[T_N+U(X)]\chi_0(X) = \sum_{\phi=1}^{6N} \left[\frac{-\hbar^2}{2M} \frac{\partial^2}{\partial Q_\phi^2} + U(X_0) + \frac{M}{2}\omega_\phi^2 Q_\phi^2 \right] \chi_0(X) = \mathcal{E}\chi_0(X), \qquad (2\text{-}5)$$

where T_N is the nuclear kinetic-energy operator, the ω_ϕ's are the natural frequencies, M is the reduced core mass, and $\mathcal{E}$ the eigenvalue. The complete function for the hole-free crystal is just $\Phi(X)\chi_0(X)$.

The nuclear trial functions for the crystal with a hole will be restricted to their ground state (absolute zero of temperature). Elevated temperatures have, however, been studied by Sewell and by Holstein. The normal modes for a real alkali halide crystal with a single vacant Bloch orbital are difficult to find,[13] so that it will be desirable to base the nuclear functions on the normal modes of the hole-free crystal as just defined.

The trial function for the crystal with a valence-band hole adopted by Howland, to be denoted as $\Psi_H(X_0)$, may be obtained by first converting the determinantal function $\Phi(X_0)$ into an equivalent determinant of Bloch orbitals,[14] and then deleting the row corresponding to the vacant Bloch orbital and the column corresponding to the missing electron. With the help of Eq. (2-1), $\Psi_H(X_0)$ can be extended to arbitrary configurations X. $\Psi_H(X)$ can then be made to satisfy an equation of the form

$$\Psi_H(X) = \sum_{g=1}^{2N} e^{i\mathbf{k}\cdot\mathbf{R}_g} w_g'(1, 2, \cdots, 2M-1, X), \qquad (2\text{-}6)$$

where $w_g'(1,2,\cdots,2M-1,X)$, a function of the coordinates of the $(2M-1)$ valence electrons remaining in the crystal and of X, describes an electronic configuration in which the hole is localized on the ion g. The precise definition of the "hole orbitals" w_g' will be given shortly.

The trial function for a crystal with a hole to be studied here is

$$W = \sum_g [e^{i\mathbf{k}\cdot\mathbf{R}_g} w_g'(1.2,\cdots,2M-1,X)\chi_g(X)], \qquad (2\text{-}7)$$

where the hole orbitals w_g' are the same as in Eq. (2-6). As in Eq. (1-1), the nuclear functions χ_g take cognizance of the location of the hole on the ion g. Accordingly, Eq. (2-7) differs from Eq. (1-1) only in the replacement of the electron orbitals $w_g(\mathbf{r})$ by the hole orbitals w_g', and, consequently, displays a hole-lattice correlation.

To arrive at a definition of the nuclear trial functions $\chi_g(X)$, one must first associate with each ion g of the crystal a separate, displaced, ion-core configuration, to be denoted as X_g. Roughly speaking, X_g is the configuration which the hole-free crystal will assume under the action of an extraneous, positive, point charge $|e|$ fixed in the crystal at $\mathbf{R}_g$, i.e., added to the charge of the ion-core g; (e is the electronic charge). A more precise definition of X_g will be given later. The configuration X_g can be specified in terms of appropriate values, $S(\phi,g)$, of the $6N$ normal coordinates Q_ϕ. Let $x_{hi}'(g)$ be the value assumed by the nuclear Cartesian coordinate x_{hi} when $X=X_g$. Then, from Eq. (2-4),

$$S(\phi,g) = \sum_{i=1}^{3} \sum_{h=1}^{2N} e(\phi|h,i)[x_{hi}'(g)-R_{hi}], \qquad \phi=1, 2, \cdots, 6N. \qquad (2\text{-}8)$$

In the present study the hole-lattice correlation is to be determined by variational means. Consequently, a more general configuration, to be denoted as ΓX_g, will be introduced, in which the individual Cartesian displacements of the ions that make up the configuration X_g are all taken proportional to a single parameter Γ. Equation (2-8) shows that the normal amplitudes $S(\phi,g)$ must also be multiplied by Γ. The nuclear functions χ_g are to differ from the harmonic oscillator function χ_0 defined by Eq. (2-5) only in that they describe oscillations about the displaced configurations ΓX_g, rather than about X_0. One has the definition

$$\chi_g(X) = \prod_{\phi=1}^{6N} \left(\frac{2M\omega_\phi}{h}\right)^{\frac{1}{4}} \times \exp\{-(M\pi/h)\omega_\phi[Q_\phi-\Gamma S(\phi,g)]^2\}. \qquad (2\text{-}9)$$

It is to be noted that the functions χ_g for all ions g in the crystal depend on the same variable Γ, which is to be a variational parameter of the over-all calculation. An important property of the crystal function W is that

$$W \rightarrow \Psi_H(X)\chi_0(X) \quad \text{as} \quad \Gamma \rightarrow 0. \qquad (2\text{-}10)$$

Remaining to be treated is the definition of the hole orbitals w_g'. It was found more convenient to work directly with the nonorthogonal ionic orbitals, rather than first combining the ionic orbitals into Bloch functions. In consequence of Eq. (2-6) the definition

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[12] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1949), Chap. IV.

[13] E. W. Montroll and R. B. Potts, Phys. Rev. **102**, 72 (1956).

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

of w_g' in terms of free-ion orbitals is

$$w_g'(1,2,\cdots,2M-1,X)=\left[\frac{1}{[(2M-1)!|\Delta|]^{\frac{1}{2}}}\right]\times{\sum_G}^{(g)}\sum_{I=1}^{2M}(-1)^{I+1}A_{\alpha G}\Delta_{IG}w(I|2M). \quad (2\text{-}11)$$

$w(I|2M)$ is obtained from the Determinant (2-2) by removing the normalizing constant in front of the determinant and deleting the Ith row and $2M$th column. Δ_{IG} is the overlap element $\int w_I(\mathbf{r}_1-\mathbf{x}_i)\times w_G(\mathbf{r}_1-\mathbf{x}_g)d\tau_1$. Since the integration is to imply a summation over spins as well, Δ_{IG} vanishes unless I and G correspond to the same spin. $|\Delta|$ is again the determinant of the overlap matrix. ${\sum_G}^{(g)}$ means a summation over the eight orbitals belonging to the ion g. The variational problem eventually reduces to secular equations with $2M$ eigenfunctions α, there being for a given spin and a given vector $\mathbf{k}$ eight independent solutions. For a particular α the wave function is determined by the eigenvector $A_{\alpha G}$. There is a separate complex coefficient $A_{\alpha G}$ for each of the eight orbitals of a given spin in a crystal cell.

If I and G correspond to orbitals on separate ions, Δ_{IG} is small compared to unity.[5] Thus, to first order w_g' is, as one might expect, a linear combination of determinantal functions $w(G'|2M)$, where G' is one of the orbitals on the ion g. Equations (2-7), (2-9), and (2-11) define the desired trial function.

(b) The Integration

The expectation value of the energy is to be found by integrating over the spin and space coordinates of the $(2M-1)$ valence electrons as well as over the coordinates of the $2N$ ion cores. The integration over electronic coordinates requires the calculation of matrix elements between determinantal functions of nonorthogonal orbitals. Löwdin has given a number of relationships for carrying through such calculations.[15] Since the reductions are straightforward, the final results will be given directly.

First one needs an expression for $U(X)$, the potential energy of the hole-free crystal defined by Eq. (2-3). Integration over electronic coordinates only yields

$$U(X)=C(X)+\sum_{IJ}\langle H_1\rangle_{IJ}\Delta_{JI}^{-1}+\sum_{IKJL}\left\langle\frac{e^2}{2r_{12}}\right\rangle_{IKJL}\times(\Delta_{JI}^{-1}\Delta_{LK}^{-1}-\Delta_{JK}^{-1}\Delta_{LI}^{-1}), \quad (2\text{-}12)$$

where $\langle H_1\rangle_{IJ}=\int w_I(1)w_J(1)d\tau_1$, and

$$\left\langle\frac{e^2}{r_{12}}\right\rangle_{IKJL}=e^2\int\int\frac{w_I(1)w_k(2)w_J(1)w_L(2)}{r_{12}}d\tau_1 d\tau_2.$$

Δ_{JI}^{-1} is an element in the inverse overlap matrix $\mathbf{\Delta}^{-1}$, a matrix defined by the relation

$$\mathbf{\Delta}\mathbf{\Delta}^{-1}=\mathbf{1}, \quad (2\text{-}13)$$

where $\mathbf{\Delta}$ is the overlap matrix and $\mathbf{1}$ the unity matrix.

The Hamiltonian for the crystal, H, is given by

$$H=T_N+C(X)+\sum_{i=1}^{2M-1}H_i+\frac{1}{2}\sum_{i\neq j}^{2M-1}\sum_{j=1}^{2M-1}\frac{e^2}{r_{ij}}. \quad (2\text{-}14)$$

Here T_N is again the nuclear kinetic energy operator, $C(X)$ the Coulomb interaction energy between the ion cores, H_i a single-electron Hamiltonian consisting of a kinetic energy and a Coulomb interaction with the ion cores, and $\frac{1}{2}\sum_{i\neq j}^{2M-1}\sum_{j=1}^{2M-1}(e^2/r_{ij})$ is the Coulomb interaction between the valence electrons.

The nuclear kinetic energy is conveniently split into two terms:

$$\int\int W^*T_NWd\tau_1,\cdots,d\tau_{2M-1}dX$$

$$=\int\int W^*\sum_g e^{i\mathbf{k}\cdot\mathbf{R}_g}W_g'(1,2,\cdots,2M-1,X)\times T_N\chi_g(X)+\langle T_N\rangle_B; \quad (2\text{-}15)$$

this defines a new term $\langle T_N\rangle_B$.

It is also helpful to define a quantity ϵ_{GH} as follows:

$$\epsilon_{GH}=\langle H_1\rangle_{GH}+\sum_{I,J}\Delta_{JI}^{-1}\times\left[\left\langle\frac{e^2}{r_{12}}\right\rangle_{GIHJ}-\left\langle\frac{e^2}{r_{12}}\right\rangle_{IGHJ}\right]. \quad (2\text{-}16)$$

With the help of Eqs. (2-12), (2-14), and (2-15) one obtains the final result:

$$E(\Gamma,\alpha)=\int\int W^*HWd\tau_1,\cdots,d\tau_{2M-1}dX=\langle T_N\rangle_B+\sum_{g,h}e^{i\mathbf{k}\cdot(\mathbf{R}_g-\mathbf{R}_h)}{\sum_G}^{(g)}{\sum_H}^{(h)}A_{\alpha G}A_{\alpha H}^*\int\chi_H\times\{\Delta_{GH}[U(X)+T_N]-\epsilon_{GH}\}\chi_g dX, \quad (2\text{-}17)$$

where $E(\Gamma,\alpha)$ is the total energy of the crystal. Equation (2-17) can be viewed as an extension of Koopman's theorem,[14] the terms ${\sum_G}^{(g)}{\sum_H}^{(h)}A_{\alpha G}A_{\alpha H}^*\epsilon_{GH}$ being analogs of the Fourier coefficients of the Hartree-Fock energy parameter.

The integration over nuclear coordinates indicated in Eq. (2-17) may be carried out by expressing the integrand in terms of the normal mode amplitudes Q_ϕ. In view of (2-5) and (2-9) it is only necessary to expand ϵ_{GH} in a Taylor series about X_0 in the normal coordinates. The expansion is again terminated at the quadratic terms. Δ_{GH} may be taken independent of

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[15] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

X. The result is:

$$E(\Gamma,\alpha)=U(X_0)+\sum_{\phi}\tfrac{1}{2}\hbar\omega_\phi+\langle T_N\rangle_B$$
$$+\sum_{g,h}e^{i\mathbf{k}\cdot(\mathbf{R}_g-\mathbf{R}_h)}Y_{gh}\sum_{G}{}^{(g)}\sum_{H}{}^{(h)}A_{\alpha G}A_{\alpha H}{}^*$$
$$\times\left[\Delta_{GH}\frac{M}{2}\sum_{\phi}\Gamma^2S(\phi,g)S(\phi,h)-\bar{\epsilon}_{GH}\right], \quad (2\text{-}18)$$

where $\bar{\epsilon}_{GH}=[\epsilon_{GH}(\Gamma X_g)+\epsilon_{GH}(\Gamma X_h)]/2$ and

$$Y_{gh}=\int\chi_g\chi_h dX$$
$$=\exp\{-(M/4\hbar)\sum_{\phi}\omega_\phi\Gamma^2[S(\phi,g)-S(\phi,h)]^2\}. \quad (2\text{-}19)$$

$\epsilon_{GH}(\Gamma X_g)$ is the value which $\epsilon_{GH}(X)$ assumes in the crystal configuration ΓX_g. The normalizing condition becomes

$$\int W^*Wd\tau dX=\sum_{g,h}e^{i\mathbf{k}\cdot(\mathbf{R}_g-\mathbf{R}_h)}Y_{gh}$$
$$\times\sum_{G}{}^{(g)}\sum_{H}{}^{(h)}A_{\alpha G}A_{\alpha H}{}^*\Delta_{GH}=1. \quad (2\text{-}20)$$

Of the terms appearing on the right of (2-18), $U(X_0)$ will be recognized as the cohesive energy of the hole-free undeformed crystal, essentially as calculated by Howland, and $\sum_\phi (\hbar/2)\omega_\phi$ as the zero-point vibrational energy of the lattice. A negligible correction to the zero-point vibrational energy stemming from the Taylor expansion of $\epsilon_{GH}(X)$ has been omitted.[16] Such a term arises because the normal modes were selected so as to diagonalize only $U(X)$.

The term $\langle T_N\rangle_B$ arises from the dependence of the electronic parts of the wave function on nuclear coordinates. A similar small contribution to the nuclear kinetic energy T', would be encountered if the crystal were described by the simpler adiabatic function $\Psi_H(X)\chi_0(X)$.[14] It is possible to show that the difference $(\langle T_N\rangle_B-T')$ is negligible.[16] In other words, $\langle T_N\rangle_B$ is an additive constant in the energy expectation, virtually independent of k and of Γ, which a wave function derived from the adiabatic approximation is bound to introduce.

(c) Evaluation of Terms

A large portion of ϵ_{GH}, defined in (2-16), is the Coulomb interaction of the charge distribution $-|e|w_G(1)w_H(1)d\tau_1$ with all the crystal ions considered as single positive and negative point charges. Let $V_{GH}(X)$ be the portion of this interaction which is sensitive to the crystal deformation $(X-X_0)$. If a displaced crystal ion is thought of as an electric dipole superimposed on the undisplaced ion, then $V_{GH}(X)$ can be envisaged as an interaction of the charge distribution with the electric field of those crystal dipoles that are implied by the configuration X. It is convenient to split V_{GH} off from ϵ_{GH}, leaving a remainder h_{GH}. One has:

$$\epsilon_{GH}(X)=V_{GH}(X)+h_{GH}(X). \quad (2\text{-}21)$$

Equation (2-21) is helpful because V_{GH} contains the greater part of the X dependence of ϵ_{GH}. It will be noticed that h_{GH} still contains the Madelung energy.[17]

The easiest terms in the fourth term on the right-hand side of Eq. (2-18) to understand intuitively are those for which g and h correspond to the same ion. From (2-19) one sees that if $g=h$, Y_{gh} is unity. As a consequence of the symmetry of the free ion orbitals and of the fact that the configurations will be chosen spherically symmetric, the matrix elements $h_{GH}(\Gamma X_g)$, V_{GH}, Δ_{GH} vanish for $g=h$, unless also $G=H$. Furthermore, the symmetry of the ionic orbitals leads to the result that $V_{GG}(\Gamma X_g)$, to be abbreviated as $V(\Gamma X_g)$, is just equal to the interaction of a negative point charge e located at $\mathbf{R}_g$ with the crystal polarization. That is,

$$V(\Gamma X_g)=\sum_{j}{}'e^2(-1)^j\left[\frac{1}{|\mathbf{R}_g-\mathbf{x}_j'(g)|}-\frac{1}{|\mathbf{R}_g-\mathbf{R}_j|}\right], \quad (2\text{-}22)$$

where $x_j'(g)$ is the location of the ion j when $X=\Gamma X_g$, the even indices j belong to the negative ions, and the prime indicates that the term $j=g$ has been omitted from the summation. Since it turns out that the matrix elements h_{GG} are essentially independent of $(X-X_0)$ for all G, one sees that the energy difference $[\frac{1}{2}M\sum_\phi\Gamma^2\times\omega_\phi{}^2S^2(\phi,g)-V(\Gamma X_g)]$ virtually contains the X dependence of the diagonal terms. This observation leads one to define the displaced equilibrium configuration associated with the ion g for Γ equal to unity, $(X=X_g)$, as that configuration for which

$$[\tfrac{1}{2}M\textstyle\sum_\phi\omega_\phi{}^2S^2(\phi,g)-V(X_g)]$$

assumes its minimum value.

The Expansion (2-3) for $U(X)$ shows

$$[\tfrac{1}{2}M\textstyle\sum_\phi\omega_\phi{}^2S^2(\phi,g)]$$

to be the stored elastic energy $[U(X_g)-U(X_0)]$. The minus sign that accompanies $V(X_g)$ occurs because one is dealing with a hole as opposed to an electron. Thus, the exact definition of X_g is compatible with the previous less formal statement that X_g is the configuration assumed by the crystal under the action of a positive point charge $|e|$ fixed at R_g. It will be seen that in essence one first solves the problem of a self-trapped charge as posed in classical physics. This solution corresponds to a value of unity for Γ; Γ is then adjusted

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[16] For more details see Technical Report 146, Laboratory for Insulation Research, Massachusetts Institute of Technology (unpublished). The writer's thesis filed with the Library at M.I.T. contains a complete account of the work.

[17] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, New York, 1956), 2nd ed.

so as to compensate for whatever additional effects are introduced by the quantum-mechanical formulation.

To determine the configuration X_g one must know how to evaluate $U(X)$ for arbitrary configurations X. Because direct substitution into the analytic Eq. (2-12) is very involved, one constructs a mode of the hole-free crystal that has an internal energy which coincides sufficiently well with $U(X)$ for all X. It turns out that the final conclusions of the calculation of the band-structure remain unaffected by changes of the order of 25% in the quantities to be calculated on the basis of the crystal model, so that some latitude is permitted in its construction.

If $\Phi(X)$ is a good description of the hole-free crystal, then it appears that $U(X)$, the associated energy expectation, will be rendered sufficiently faithfully by a model such as was postulated in the rather successful classical treatments of the alkali halides.[8,14] In the model to be used here the ions are replaced by point charges with consequent long-range Coulomb interactions. In addition, each ion is considered to be under the action of the central, independent (two-body) forces of its six nearest neighbors. Repulsive forces of more distant ions are omitted. If the crystal is assumed elastic, then a knowledge of the compressibility and lattice constant is sufficient to determine the repulsive forces.[17] Such a model has, for example, been used by Kellermann[18] to study the vibrational spectrum of sodium chloride. It will be noticed that, in harmony with the crystal function $\Phi(X)$, the model takes no account of the electronic polarizability. Use of the model can be justified further by showing that it leads to results that agree asymptotically with the analytic Eq. (2-21), providing that theoretical values are used for the lattice constant and compressibility.[16] That is, for a given crystal configuration the model yields approximately the same result as (2-18) for the elastic energy stored in that part of the crystal, not in the immediate vicinity of the deforming charge, where a slowly varying polar deformation can be assumed.

In view of Eq. (2-22) for $V(\Gamma X_g)$, the configurations X_g are just the equilibrium configurations of the model under the action of a virtual charge $|e|$. Two distinct configurations are needed, corresponding to the location of the charge at positive and negative ions, respectively. One begins by assuming that ions outside of the central four shells have radial displacements satisfying the appropriate asymptotic inverse-square law.[16] Individual equilibrium conditions in the form of four simultaneous equations are then set up for the displacements of the inner shells. The electrostatic forces on the inner ions are obtained from a calculation by Mott and Littleton,[19] who found for an alkali halide crystal, likewise polarized by a point charge, the dipole forces exerted on any one ion in the first four shells by the first twenty-three shells of the crystal. The largest of the displacements obtained in this way amount to about 20% of the equilibrium interionic distance.

Once the equilibrium configurations are determined, the potentials $V(\Gamma X_g)$, the matrix elements V_{GH}, and the stored energy $\frac{1}{2}M\sum_\phi \omega_\phi^2 S^2(\phi,g)$ are easily approximated. In accordance with the treatment of Howland,[5] the only two center matrix elements that are retained are those between all nearest neighbors, and those between next nearest halogen ions. Consequently, only two energies $\frac{1}{2}M\sum_\phi \omega_\phi^2 S(\phi,g)S(\phi,h)$, where g and h correspond to different ions, are required. They are are found by first determining energies

$$\tfrac{1}{2}M\sum\nolimits_\phi \omega_\phi^2[S(\phi,g)-S(\phi,h)]^2,$$

which, since the transformation from normal to Cartesian coordinates is linear, are just the energies stored in the crystal when $X=X_g-X_h$, and then substituting the known values of the diagonal terms, i.e., of $\frac{1}{2}M\sum_\phi \omega_\phi^2 S^2(\phi,K^+)$, etc.

The two required overlap integrals Y_{gh}, defined in (2-19), are replaced by approximate overlap integrals,

$$Y_{gh}'=\exp-\left\{\Gamma^2\frac{M}{2}\sum_\phi \omega_\phi^2 \times[S(\phi,g)-S(\phi,h)]^2/\hbar\omega_{\max}\right\}. \qquad (2\text{-}23)$$

Here $\omega_{\max}$ is the largest vibrational frequency of the crystal, estimated by Iona[20] to be 4.73×10^{13} sec^{-1}. The validity of these replacements will be explained when the results are discussed. Their point is that the Y_{gh}' can be determined without carrying through explicit normal mode analysis of the configurations X_g, since the numerator in the exponent of (2-23) is one of the energies stored in the configurations (X_g-X_h). Results for the various quantities calculated with the help of the crystal model are listed in Table I. The matrix elements h_{GH},[21] defined by (2-21), are deduced from Howland's calculation.[5] Scrutiny of his results shows that if H and G correspond to different ions, about 95% of each matrix element $h_{GH}(X_0)$ stems from contributions involving only orbitals centered on the ions g and h. $h_{GH}(X)$ is, accordingly, taken to depend only on the displacement of the ion g relative to h. In this way $h_{GH}(\Gamma X_g)$ can be found as a function of Γ from Howland's analytic expressions for the variation of the elements h_{GH} with the lattice constant. It turns out to be a good approximation to take the diagonal elements h_{GG} for all G independent of X. Thus all the terms on the right of Eq. (2-18) can be found without undue difficulty.

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[18] E. W. Kellermann, Phil. Trans. Roy. Soc. (London) **A238**, 513 (1940).

[19] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[20] M. Iona, Phys. Rev. **60**, 822 (1941).

[21] The elements $h_{GH}(X_0)$ are identical with elements designated by Howland as $H(mR|n)$.

TABLE I. Quantities calculated using the crystal model.

$\sum_{\phi} \frac{M}{2}\omega_{\phi}^2\Gamma^2 S^2(\phi,\mathrm{Cl}^-)$	$2.83\Gamma^2$ ev	$V_{\mathrm{Cl}^-}(\Gamma X_{\mathrm{Cl}^-})$	5.83Γ ev
$\sum_{\phi} \frac{M}{2}\omega_{\phi}^2\Gamma^2 S^2(\phi,\mathrm{K}^+)$	$5.36\Gamma^2$ ev	$V_{\mathrm{K}^+}(\Gamma X_{\mathrm{K}^+})$	$7.59\Gamma+1.23\Gamma^2$ ev
$\sum_{\phi} \frac{M}{2}\omega_{\phi}^2\Gamma^2 S(\phi,\mathrm{K}^+)S(\phi,\mathrm{Cl}^-)$	$2.00\Gamma^2$ ev	$Y_{\mathrm{Cl}^-\mathrm{K}^+}{}'$	$\exp(-67\Gamma^2)$
$\sum_{\phi} \frac{M}{2}\omega_{\phi}^2\Gamma^2 (\phi,\mathrm{Cl}^-)_g S(\phi,\mathrm{Cl}^-)_h$	$1.40\Gamma^2$ ev	$Y_{\mathrm{Cl}^-\mathrm{Cl}^-}{}'$	$\exp(-46\Gamma^2)$

(d) The Secular Equations and Their Solutions

It is necessary to consider the determination of eigenvectors $A_{\alpha G}$ that make the contribution to the crystal energy given by the fourth term of (2-18) a minimum. The nondiagonal terms in (2-18) depend only on the relative positions of the ions in the lattice, so that the identicated summation over all ions g and h can be readily carried out.[5] It will be recalled that only matrix elements between nearest neighbors and between next-nearest Cl^- neighbors are to be retained. Since there is no mixing between ionic orbitals of opposite spin, one is left with a quadratic form in eight coefficients $A_{\alpha G}$, there being one coefficient for each orbital of a given spin in the crystal cell. Minimization with respect to these coefficients, subject to the normalizing Eq. (2-20), gives rise to a secular equation. The resulting eigenvalues, $E'(\Gamma,\alpha)$, of which there are eight for fixed values of **k** and Γ are the desired energies.

Secular equations were set up and solved at representative points within the central Brillouin zone. For ready comparison these points were chosen to coincide with the first twenty-two points indicated in Howland's calculation. The energy eigenvalues were obtained as functions of Γ by setting up at each of the points in the Brillouin zone secular equations for a series of sixteen values of Γ chosen to span the range $\Gamma=0$ to $\Gamma=1.1$. An electronic computer was used to solve the resulting 352 secular equations. At $\Gamma=0$ the results coincided with the eigenvalues determined by Howland.

The results of the calculation can best be understood by defining energies $E_C(\Gamma,\alpha)$ and $h_C(\Gamma,\alpha)$ by the relations:

$$\sum_{g}\sum_{G}{}^{(g)} |A_{\alpha G}|^2\left[\frac{M}{2}\sum_{\phi}\omega_{\phi}^2\Gamma^2 S^2(\phi,g)-V(\Gamma X_g)\right]$$
$$=E_C(\Gamma,\alpha)\sum_{G=1}^{2M}|A_{\alpha G}|^2, \quad \text{(2-24A)}$$

$$\sum_{g}\sum_{G}{}^{(g)}|A_{\alpha G}|^2 h_{GG}(\Gamma X_g)=h_C(\Gamma,\alpha)\sum_{G=1}^{2M}|A_{\alpha G}|^2. \quad \text{(2-24B)}$$

When the energies E_C and h_C are subtracted out from the second line of the energy Eq. (2-18), one is left, in view of the normalizing Relation (2-20), with only off-diagonal terms, $g\neq h$, which are very sensitive to Γ by virtue of the factors Y_{gh}. It is these remnant terms that are responsible for the band structure. h_C, which it will be recalled contains the Madelung energy, is relatively insensitive to Γ. In view of its definition, E_C can be thought of as the "classical energy" involved in the hole-crystal interaction.

E_C, which roughly equals $(3\Gamma^2-6\Gamma)$ ev (see Table I), reaches its minimum value in the vicinity of $\Gamma=1$, as expected. However, for some values of **k**, the band-structure terms lower the total energy. Their sum, though, decays rapidly as Γ is raised from zero in conjunction with the behavior of Y_{gh}. There is, thus, a conflict between two mechanisms for lowering the energy: a polarization of the crystal about the hole, and a spreading of the hole charge in the crystal. The resulting variation of the total energy for the highest-lying $3p$ Cl^- eigenvalue at the point $k_x=k_y=k_z=\pi/2a$ is illustrated in Fig. 1. This curve is typical for $3p$ Cl^- eigenvalues that lie near the top of the band. Lower-lying $3p$ Cl^- eigenvalues and the eigenvalues making up all the other bands decrease monotonically as Γ is raised from zero to unity. All the energy minima thus occur in the vicinity of unity.

The dependence on Γ of the over-all bandwidths, except that of the K^+ $3s$ band, is illustrated in Fig. 2, where the maximum and minimum energies of each band at the specified value of Γ are plotted. At $\Gamma=1$ the overlaps Y_{gh} are, respectively, less than e^{-46} and e^{-67}. The off-diagonal terms, therefore, essentially vanish, the secular determinants factor, and the energy bands are flat, as can be seen from Fig. 2. It is now evident that the replacement of the true overlaps Y_{gh} by their upper limits Y_{gh}' was permissible. The studies of Sewell[2] and Holstein[3] suggest that the overlaps Y_{gh} decrease as the temperature is raised, so that similar results can be expected even at elevated temperatures.

In general, for a given value of Γ the effective mass will be a very involved function of **k**. Nevertheless, since the k-dependent portion of the energy is proportional to the overlaps Y_{gh}, the effective mass, $\hbar^2/(d^2E/dk_x^2)$, say, will be roughly proportional to Y_{gh}^{-1}, so that it will have a Γ dependence of the form $\exp(n\Gamma^2)$,

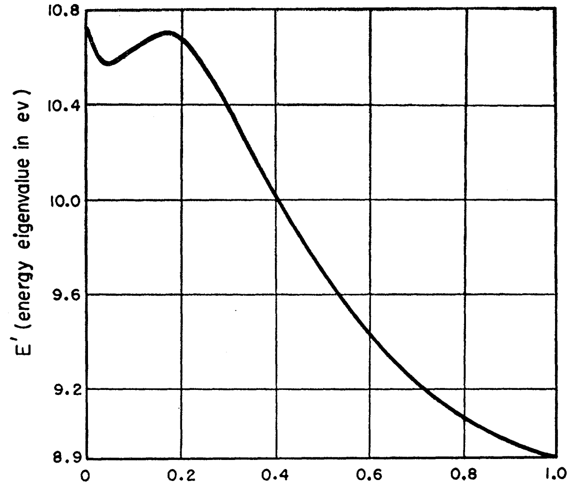

FIG. 1. Γ dependence of highest $3p\text{Cl}^-$ eigenvalue at $k_x=k_y=k=\pi/2a$.

where $n\sim 60$. The physical meaning of the narrow bands will be touched on again later.

3. ELECTRONIC AND IONIC POLARIZATION

The hole-crystal interaction described in the previous section must be regarded as suggestive rather than conclusive, since no account is taken of the electronic polarizability. Modifications introduced by the electronic polarizability will now be explored by retracing the earlier calculation with a refined trial wave function that allows for both polarizabilities. Since the calculation involves polarized ionic orbitals, it is not feasible to match the accuracy of the previous section. Only a rough treatment drawing on the experimental dielectric constants and the known behavior of the free-ion orbitals will be undertaken. As the work is in parallel with the first calculation, it will be presented in less detail.[16]

The modified trial function for the crystal with a hole continues to satisfy Eq. (2-7). However, the hole orbitals w_g' are now built from polarized ionic orbitals $w_I(r,X)_g$ in essentially the same way as they were previously built from free-ion orbitals $w_I(\mathbf{r}-\mathbf{x}_i)$. $w_I(r,X)_g$, $I=1, 2, \cdots, 2M$, is defined as the free-ion eigenfunction $w_I(\mathbf{r}-\mathbf{x}_i)$ modified to take into account a perturbation of its free-ion Hartree-Fock potential by the electric field of a positive point charge $|e|$ located at the ion g, i.e., at $\mathbf{R}_g$. The orbitals $w_I(r,X)_g$ are understood to depend on the crystal configuration X, in that the perturbing field is as given by classical electrostatics when due account is taken of the crystal polarization set up by the deformation $(X-X_0)$ of the polar crystal. This definition is sufficiently complete for the present treatment of the problem. The result is that, instead of dealing with a single family of free-ion orbitals $w_I(\mathbf{r}-\mathbf{x}_i)$, one must work with an entire set of families of polarized orbitals, there being a separate $2M$-fold family of polarized orbitals $w_I(r,X)_g$ for every ion g in the crystal. With the new crystal function one finds that if the hole is localized at a particular ion, each of the surrounding ions will not only shift its equilibrium position but will acquire an appropriate electronic dipole moment as well.

The integration over electronic and nuclear coordinates that yields the expectation value of the Hamiltonian proceeds in much the same way as in the previous section. The result is an expression for the energy which is indeed similar to Eq. (2-18), but which does differ from the earlier expression in a number of interesting respects.

As a result of the interaction of different families of polarized orbitals, the matrix elements ϵ_{GH} and Δ_{GH} are replaced when (and only when) G and H correspond to different ions by relatively complicated combinations of elements $\epsilon_{G'H'}$ and $\Delta_{G'H'}$, respectively, $G', H'=1, 2, \cdots, 2M$. The combination coefficients depend on increments in overlap elements between ionic orbitals arising from polarization of the orbitals, for example on

$$\left[\int w_J(r,\Gamma X_g)_h w_H(r,\Gamma X_g)_h d\tau_r - \int w_J(r,\Gamma X_g)_h w_H(r,\Gamma X_g)_g d\tau_r\right].$$

To calculate these increments one replaces the polarized ionic orbitals by unpolarized free-ion orbitals shifted without deformation through appropriate displacements. The displacements of the orbitals $w_I(r)_g$ on an ion i are those which, if undergone by all the valence electrons on the ion, would give rise to an electronic dipole moment prescribed by experiment for the ion i when under the action of a charge $|e|$ at $\mathbf{R}_g$. Data given by Howland on the variation of electronic matrix elements with lattice constant then allow one to find the increments. In this way it is possible to estimate upper limits on the modifications of the elements ϵ_{GH} and Δ_{GH} arising from the electronic polarization. One finds that in themselves these modifications are capable of at most doubling the $3p$ Cl$^-$ bandwidth as obtained when all polarization effects are omitted, and are capable of broadening the other bandwidths by at most half their original widths.

Of greater significance is that in the energy Expression (2-18) the nuclear overlap integrals Y_{gh} are everywhere multiplied by many-electron overlap integrals Z_{gh}, between functions describing the hole-free crystal polarized by virtual charges at different locations. That is, if Φ_g and Φ_h are determinantal wave functions of order $2M$ constructed from polarized orbitals $w_I(r)_g$ and $w_I(r)_h$, respectively, in the same manner as Φ was constructed from the free-ion orbitals $w_I(r)$, then Z_{gh} is defined as $\int \Phi_g \Phi_h d\tau_1, \cdots, d\tau_{2M}$. The factors Z_{gh}, which are taken to be independent of X, are estimated by again representing the polarized orbitals as free-ion orbitals appropriately shifted relative to their ionic cores. It is then necessary to transform the ionic orbitals into sets of localized orthogonal orbitals of the type suggested by Landshoff.[14] In the end one finds that $Z_{gh}\sim 0.1$ when g and h are nearest neighbors, and Z_{gh} ~ 0.06 when g and h are next-nearest Cl^- neighbors.

The behavior of the energy bands when only the electronic polarizability is active, i.e., when $\Gamma=0$, is of special interest. For this case an indication of the bandwidths can be obtained from the experimental emission spectra that accompany electronic transitions from the $3p$ bands to the $1s$ state.[6] The experimental bands are found to be much narrower than those predicted by Howland's calculation, where the electronic polarizability is not considered.[5] Since the factors Z_{gh} have the effect of drastically reducing bandwidths, they may be expected to shed some light on the discrepancy between theory and experiment. This matter is still undergoing study.

One would again like to know the behavior of the total energy as Γ is raised from zero to unity. The shielding action of the electronic polarization scales down the ionic displacements characteristic of the configurations X_g. This has the effect of raising the nuclear overlap integrals Y_{gh}. By drawing on the dielectric constants one can estimate that $Y_{\mathrm{Cl^-Cl^-}}'$ is increased from $\exp(-46\Gamma^2)$ to $\exp(-12\Gamma^2)$, and $Y_{\mathrm{Cl^-K^+}}'$ is increased from $\exp(-67\Gamma^2)$ to $\exp(-18\Gamma^2)$. The numerical values of the exponents for the true nuclear overlaps, Y_{gh}, will again be appreciably larger.

The last important modification introduced by the electronic polarizability concerns the new classical energy E_C', which can again be separated out. The approximate behavior of E_C' can be inferred by identifying it with the classical electrostatic volume integral $-\frac{1}{2}\int \mathbf{P}\cdot\mathbf{D}dv$, where $\mathbf{P}$ is the polarization and $\mathbf{D}$ the displacement induced by a point charge $|e|$ in the crystal, considered as a continuum. This allows one to estimate the values assumed by E_C' at Γ equal to zero and unity, respectively, in terms of $E_C(\Gamma=1)$, the classical energy calculated in the previous section to be roughly 3 ev, as follows:

$$E_C'(\Gamma=0)=(1-\epsilon^{-1})(1-\epsilon_M^{-1})^{-1}E_C(\Gamma=1) \\ =-2.1\text{ ev}, \quad (3\text{-}1)$$

$$E_C'(\Gamma=1)-(1-\epsilon_S^{-1})(1-\epsilon_M^{-1})^{-1}E_C(\Gamma=1) \\ =-3.1\text{ ev}. \quad (3\text{-}2)$$

Here ϵ and ϵ_S are the experimental optical and static dielectric constants of a KCl crystal. ϵ_M, $(=4.16)$, is the effective dielectric constant for the crystal model of Sec. 2.

It will be seen that as Γ is raised from zero to unity, E_C' decreases by an increment of only 1 ev as compared o the corresponding decrease of 3 ev in E_C observed in he earlier treatment. Nevertheless, estimates indicate hat, because the band-dependent terms are so greatly reduced by the overlaps Z_{gh}, the total energy minima will again coincide with the minima of the classical energy everywhere in the Brillouin zone; i.e., the minima will lie in the vicinity of $\Gamma=1$, where the Y_{gh} are so small as to lead to essentially flat bands, or very large effective masses.

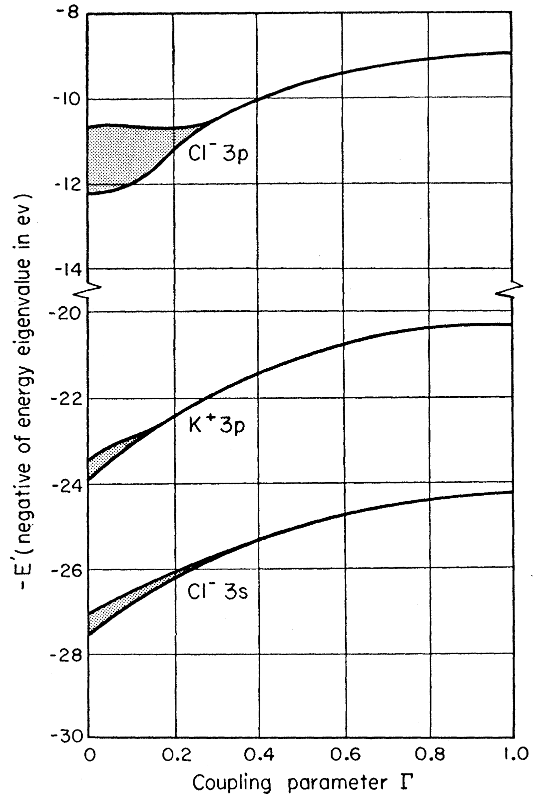

FIG. 2. Destruction of energy bands by ionic polarization.

4. EXPERIMENTAL MODEL FOR TRAPPED HOLE

Castner and Känzig, in their study of a number of the alkali halides including KCl, obtained electron-spin resonance data which they were able to associate with self-trapped holes.[7] The experiments of Delbecq, Smaller, and Yuster[22] further confirm that the trapped holes are not associated with either ion vacancies or impurities. The last two sections help to understand how valence-band holes in the alkali-halides come to be "self-trapped." A hole localized at a particular ion can be described by a wave packet of crystal functions $W(\mathbf{k})$ corresponding to all the vectors $\mathbf{k}$ in the first Brillouin zone. Since the valence bands are so narrow, the difference in the energies associated with a localized hole and a Bloch state $W(\mathbf{k})$, respectively, will be minute ($\sim 10^{-14}$ ev). Consequently, any small nonperiodic electric fields in the crystal, such as those associated with even distant crystal imperfections, will

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[22] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958).

cause the holes to become localized at optimum lattice sites.

A second point is that Castner and Känzig's data show the hole to be localized on two adjacent halogen ions rather than on a single ion, as has been assumed. An attempt has been made to evaluate, within the framework of the previous calculation, the energy associated with this mode of trapping. Since the hole is to be localized on two adjacent ions, a transformation is carried out which converts the determinant of free-ion orbitals (2-2) into an equivalent determinant in which the ionic orbitals on halogen ions are replaced by molecular orbitals. The hole orbitals, w_g', are constructed in the same way as before from determinantal functions which, however, are missing one molecular rather than one atomic orbital. In addition, with a vacant molecular orbital one associates a displaced crystal configuration that is allowed to depart from spherical symmetry. The previous restriction of crystal deformations to spherical symmetry led to a threefold degeneracy among the states corresponding to a vacant $2p$ orbital localized on a given ion. Since according to a theorem proved by Jahn and Teller[23] the ground state of a molecular system does not have an orbital electronic degeneracy, the earlier crystal functions suffered from a lack of generality, a lack which is now removed in part.

It has already been established that the lowest energy state of a KCl crystal with a hole is one in which the crystal polarizations induced by the hole assume their full classical value. Consequently, the assumption is here made from the beginning that in the crystal function the parameter Γ, which was a measure of the ionic polarization, can be set equal to unity. Since this has the result that terms in the wave function corresponding to separate trapping configurations have negligible interactions, it becomes permissible to construct a function in which the hole is confined to a particular region of the crystal.

Accordingly, the crystal wave function is written:

$$W=(2M-1)!|\Delta|^{-\frac{1}{2}}\chi_g\sum_{I=1}^{2M}(-1)^{I+1}\Delta_{IG}w(I|2M). \tag{4-1}$$

The meaning of the symbols is the same as in Sec. 2. However, the component orbitals are now polarized molecular orbitals rather than free-ion orbitals. The "vacant" orbital w_G is taken to be the odd molecular orbital $w_{1Z'}+w_{2Z'}$, where $w_{1Z'}$ and $w_{2Z'}$ are polarized ionic orbitals centered, respectively, on the two trapping centers, ions (1) and (2), and directed along the line joining the centers. In accordance with the earlier treatment, the single displaced equilibrium configuration X_q, associated with the orbital w_G, is taken to be the configuration assumed by the crystal under the action of two-point virtual charges $|e|/2$, located, respectively, on the ions (1) and (2). The component molecular orbitals are similarly assumed to be polarized by these virtual charges.

While the first three terms of the Expression for the energy, (2-18), remain unchanged, the fourth term now becomes more simply:

$$E'=U(X_g)-U(X_0)-V(X_g)-h_{GG}. \tag{4-2}$$

The meaning of the symbols again corresponds to that of Sec. 2.

The stored energy $[U(X_g)-U(X_0)]$ and $V(X_g)$ are first found by the methods of Sec. 2; the electronic polarization is then allowed for by corrections of the same sort as those shown in Eqs. (3-1) and (3-2). One finds for the "classical energy," E_C'', that

$$E_C''=U(X_g)-U(X_0)-V(X_g)=-2.0\text{ ev}. \tag{4-3}$$

This result is to be compared with a corresponding value of -3.1 ev for a one-center Cl$^-$ trap. The difference between these results can be understood by again identifying E_C'' with $-\frac{1}{2}\int\mathbf{P}\cdot\mathbf{D}dv$, where $\mathbf{P}$ and $\mathbf{D}$ are fields induced in the crystal imagined as a continuum. This integral will be numerically smaller when the fields are induced by two charges $|e|/2$ spread apart somewhat (it will be just half when they are infinitely far apart) than when the fields are induced by a single point charge $|e|$. To find the hole interaction h_{GG} one again approximates polarized orbitals by free-ion orbitals appropriately shifted without deformation. The odd molecular orbitals turn out to be somewhat more stable than a $3p$ Cl$^-$ free-ion oribtal (h_{GG} is numerically smaller), leading to an energy for the two-center trap 0.7 ev higher than that associated with a single-center trap.

It is thought that this contradiction between theory and experiment may well originate with the arbitrariness of the trial function. The experiments furnish an indication of the electronic configuration of the hole. If, in accordance with Castner and Känzig, one assumes that the orbital corresponding in essence to the unpaired electron is a $3p$ odd molecular orbital mixed with a $4s$ orbital, the magnitude of the $4s$ admixture can be inferred from the resonance frequencies. This admixture is found to be many times greater than that assumed in the present trial function, where, as in Sec. 3, the free-ion orbitals are being polarized by the virtual charges to an extent compatible with the experimental electronic polarizabilities.

The trial functions were chosen on the basis of the expected behavior of a hole-free crystal under the action of virtual charges that simulate the charge distribution of the hole. It was this arbitrariness in the function that allowed one to evaluate the energy of the crystal in a relatively simple way. For the present aspect of the problem, however, the strength of the quasi-molecular bond between two trapping centers, measured by the element h_{GG}, assumes considerable

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

importance, as has been suggested by Castner and Känzig, and ought to influence the construction of the trial function, especially the nature of all the polarized orbitals in the vicinity of the hole. The proper way of dealing with the problem is presumably to set up a quite general wave function in which both the positions of the ions that determine the displaced equilibrium configuration and the linear combinations of ground and excited free-ion functions that determine the polarized orbitals are left free to be determined by an over-all variational calculation, instead of being specified from the beginning. Such a procedure would be very much more difficult since it would no longer be possible to isolate terms characteristic of a hole-free crystal, whose behavior can be calculated from the experimental properties of the macroscopic crystal. Furthermore, neither the excited orbitals for the K^+ and Cl^- ions nor multicenter matrix elements involving these orbitals are available. It will be seen that such a calculation lies outside the scope of the present work.

In conclusion, it has been possible to show that one can expect a valence-band hole in its ground state to be self-trapped; however, the details of the associated electronic and ion core configurations cannot be predicted without additional calculation.

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Frequency-Dependent Hall Effect in Normal and Superconducting Metals*†‡

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The Hall current flow occurring in a normal and a superconducting metal when both a static magnetic field (H_0) and an electromagnetic wave are applied on the metal is calculated. The entire frequency range of the electromagnetic wave is discussed although the emphasis is on the microwave range. The nonlocal, transverse Hall current in a normal metal is calculated by solving the Boltzmann equation. It is shown that the microwave Kerr rotation in a circular cylindrical cavity provides a good test for the nonlocal Hall current in a normal metal. The relation between a longitudinal and a transverse Hall current in a superconductor is briefly discussed. A detailed theory of the transverse Hall current in a superconductor based on the Bardeen-Cooper-Schrieffer model and including the effect of collective excitations is presented. The field H_0 is assumed constant in space and a general result for the Hall current in Q space is derived. When the electric field is constant in space ($Q\rightarrow 0$), it is shown that the Hall current is proportional to the microscopic analog of the fraction of normal electrons of a two-fluid model.

I. INTRODUCTION

THE Hall effect at audio frequencies is a well understood phenomenon in both metals and semiconductors. The experimental method used at these very low frequencies is a simple measurement of the Hall emf developed across the sample when a current flows in the sample and a static magnetic field is applied perpendicular to the current flow. The theory of this effect yields the simple and well-known result (we neglect any effect of band structure throughout),

$$j_{\mathrm{Hall}}=-R_0\sigma_0^2\mathbf{E}\times\mathbf{H}_0, \qquad (1)$$

where

$$\sigma_0=ne^2\tau/m, \quad R_0=-(nec)^{-1}, \qquad (2)$$

and where H_0 is the static magnetic field applied and n is the number of carriers per unit volume. We use the convention that R_0 is positive for electrons and negative for holes.

In general a Hall current or a Hall electric field will be produced by a microwave or an optical electric field with a static magnetic field perpendicular to the applied electric field. A simple measurement of a Hall emf is no longer feasible at these high frequencies. If a plane polarized electromagnetic wave is incident on a sample and if there is a static magnetic field present which is perpendicular to the incident electric field then both the

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