PHYSICAL REVIEW VOLUME 162, NUMBER 3 15 OCTOBER 1967

Electronic Structure of the *U* Center. II. Force-Constant Changes and Local Modes*

R. F. WOOD AND R. L. GILBERT
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 7 June 1967)

The force constants and local-mode frequencies of the *U* center in KCl, KBr, and KI have been obtained from a detailed quantum-mechanical calculation. The model which has been used corresponds to the "static-well" approximation. It takes into account both the electronic structure of the first-nearest-neighbor ions and the polarization of the H^- ion during the local-mode oscillations. The agreement of the calculated local-mode frequencies with the experimental values is greatly enhanced when the polarization of the H^- ion is included.

I. INTRODUCTION

IN the first paper[1] (I) of this series, a report was given of calculations on the electronic structure, optical absorption, and lattice relaxation of the *U* center. In this paper, we present the results of calculations on the force-constant changes and localized vibrational mode associated with the H^- ion using the first model described in I. In this model, the electronic structure on the H^- ion and its first nearest neighbors (1nn) is taken into account quantum mechanically, but all other ions are treated as point charges. One very important feature is that polarization effects associated with the deformation of the H^- ion can be introduced into the calculations.

Shaefer's[2] experimental work on the infrared absorption of the *U* center in KCl revealed a sharp peak lying well above the upper band edge of the longitudinal optical modes. This localized mode is accompanied by much weaker side bands which evidently arise from the anharmonic interaction of localized and band modes. Shaefer's work was carried out at a time when theoretical interest in the effect of an impurity atom on the vibrational structure of a crystal was rapidly increasing. Lifshitz's[3] early papers on localized perturbations using Green's-function techniques were becoming better known, as was the work of Lax[4] and of Montroll and co-workers.[5] Among the recent work connected more directly with the *U* center, we mention that of Jaswal and Montgomery,[6] Lengler and Ludwig,[7] Klein,[8] and Fieschi *et al.*[9] The early work usually assumed that the substitution of an H^- ion for a negative ion of the perfect lattice could be represented by a simple mass change. This assumption ensures a very well localized perturbation for which the theoretical analysis simplifies considerably. It was subsequently realized that a force-constant change was also needed to explain the experimental frequency. More recently, the question has arisen about the extent to which the H^- ion is polarized when displaced from equilibrium. We believe the results reported here largely answer this question.

As far as we know, the work reported here is the first attempt to calculate the force-constant changes and polarization effects from a truly quantum-mechanical calculation. The *U* center appears to be uniquely suited for this type of calculation for several reasons. First, the local-mode frequency is so much higher than the band frequencies that a "static-well" approximation in which the neighboring ions are held fixed at or near their equilibrium positions during the calculation is expected to be quite a good one. This is discussed in Sec. II. Second, the H^- ion has only two electrons to account for quantum mechanically. Third, the *U* center occurs in the most ionic of all crystals and its nearest neighbors are positive ions. This means that it is probably adequate to use free-ion HF orbitals even in the crystal and to neglect the polarization of the positive ions. Fourth, since even in a perfect alkali-halide crystal repulsive forces between second-nearest neighbors are not great, we can expect the force-constant changes between negative ions to be relatively unimportant in determining the local-mode frequency.

The electronic wave function associated with the H^- ion in the ground state of the system is surely quite compact, and therefore we expect the first model described in I to give fairly good results. Thus, in carrying out the calculations, we hold the 1nn positive ions in their new equilibrium positions as found in I and displace the H^- ion in a [100] direction in small steps. At each displaced position, the electronic energy is recalculated assuming that the 1nn alkali free-ion orbitals are undistorted and that all other ions are point ions. Polarization of the H^- ion is allowed by admixing in the wave function a component of *p*-like symmetry in a variational calculation. This is all described in Sec. III, and in Sec. IV the results of the calculations are given and discussed.

---

* Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

[1] R. F. Wood and U. Öpik, preceding paper, Phys. Rev. **162**, 736 (1967).

[2] G. Shaefer, J. Phys. Chem. Solids **12**, 233 (1960).

[3] I. M. Lifshitz, Nuovo Cimento **3**, Suppl. 4, 716 (1956), and references therein.

[4] M. Lax, Phys. Rev. **94**, 1392 (1954).

[5] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); A. A. Maradudin, P. Mazur, E. W. Montroll, and G. H. Weiss, Rev. Mod. Phys. **30**, 175 (1959).

[6] S. S. Jaswal and D. J. Montgomery, Phys. Rev. **135**, A125 (1964).

[7] B. Lengler and W. Ludwig, Z. Physik **171**, 273 (1963).

[8] M. V. Klein, Phys. Rev. **131**, 1502 (1963).

[9] R. Fieschi, G. F. Nardelli, and N. Terzi, Phys. Rev. 138, A203 (1965).

II. LOCALIZED PERTURBATIONS

We review here very briefly the theory of lattice dynamics and localized perturbations for the case in which a true localized mode occurs.

The equation of motion for the jth Cartesian component of the displacement from equilibrium of the αth ion in the νth unit cell of a perfect crystal is given by

$$M_\alpha \ddot{u}_{j\alpha}(\nu) = -\sum_{k\beta\mu} A_{j\alpha,k\beta}(\nu,\mu) u_{k\beta}(\mu)\,, \tag{1}$$

where the A's are the force constants; they depend only on the relative positions of the νth and μth unit cells. More specifically,

$$A_{j\alpha,k\beta}(\nu,\mu) \equiv [\partial^2 V/\partial u_{j\alpha}(\nu)\partial u_{k\beta}(\mu)]_0\,, \tag{2}$$

where V is the potential energy of the system and the derivatives are evaluated at the equilibrium positions.

It is convenient to introduce mass-reduced quantities by writing

$$w_{j\alpha} = M_\alpha^{1/2} u_{j\alpha}, \quad A'_{j\alpha,k\beta} = (M_\alpha M_\beta)^{-1/2} A_{j\alpha,k\beta}$$

in terms of which Eq. (1) becomes, in matrix form,

$$d^2\mathbf{w}/dt^2 = -\mathbf{A}'\mathbf{w}\,. \tag{3}$$

Expressing the transformation to normal coordinates $\mathbf{d}$ by

$$\mathbf{w} = \mathbf{bd}\,, \tag{4}$$

and considering the resulting time dependence with $\lambda \equiv \omega^2$, Eq. (3) becomes

$$\lambda \mathbf{Id} = \mathbf{b}^T \mathbf{A}'\mathbf{bd}\,, \tag{5}$$

where T means the transpose. The matrix elements of $\mathbf{b}$ are given by

$$b_{j\alpha\nu,s\mathbf{q}} = (NM_\alpha)^{-1/2} \sigma^*{}_{j\alpha}{}^{s\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{R}_\nu}\,, \tag{6}$$

in which $\sigma^*{}_{j\alpha}{}^{s\mathbf{q}}$ is a component of the polarization vector and $\exp(-i\mathbf{q}\cdot\mathbf{R}_\nu)$ accounts for the translational periodicity of the system. The normal coordinate going with the s, $\mathbf{q}$ normal mode is

$$\begin{aligned} d_s(\mathbf{q}) &= \sum_{j\alpha\nu} b^T{}_{s\mathbf{q},j\alpha\nu} w_{j\alpha}(\nu) \\ &= N^{-1/2} \sum_{j\alpha\nu} \sigma_{j\alpha}{}^{s\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_\nu} M_\alpha{}^{1/2} w_{j\alpha}(\nu)\,. \end{aligned} \tag{7}$$

Equation (3) after the elimination of the time dependence but before diagonalization is given by

$$(\mathbf{A}' - \lambda)\mathbf{v} = 0\,. \tag{8}$$

Let us assume that a single defect of mass M_0' has been introduced into the lattice at a site which we label with a zero and that its influence is given by the perturbation matrix

$$\boldsymbol{\Delta} = \Delta\mathbf{A}' + \epsilon\lambda\mathbf{I}\,, \tag{9}$$

where $\epsilon = (M_0 - M_0')/M_0$ is the relative mass change of the defect. We have then

$$(\mathbf{A}' - \lambda\mathbf{I} + \boldsymbol{\Delta})\mathbf{v} = 0\,, \tag{10}$$

which can be written, for a true local mode, as

$$\mathbf{v} = -\mathbf{G}\boldsymbol{\Delta}\mathbf{v}\,, \tag{11}$$

where

$$\mathbf{G} \equiv (\mathbf{A}' - \lambda\mathbf{I})^{-1} \tag{12}$$

is the Green's-function matrix for the perfect crystal. It is nonsingular for a local mode which is not degenerate with any band modes. Its matrix elements in terms of those of $\mathbf{b}$ are given by

$$G(j\alpha\nu,k\beta\mu) = \sum_{s,\mathbf{q}} \frac{\sigma_{j\alpha}{}^{s\mathbf{q}} \sigma^T{}_{k\beta}{}^{s\mathbf{q}}}{\lambda_{s\mathbf{q}} - \lambda} e^{i\mathbf{q}\cdot(\mathbf{R}_\nu - \mathbf{R}_\mu)}\,. \tag{13}$$

In many cases, the influence of the defect on the crystal will be quite local and therefore the dimension of $\boldsymbol{\Delta}$ will be much smaller than that of $\mathbf{A}'$, thus simplifying enormously the solution of Eq. (11). The theory of localized perturbations has been thoroughly covered in the recent literature. It is now well known that a simple mass defect can introduce both true localized modes (light mass) lying outside the band and quasilocalized or resonant modes (heavier mass) lying within the band. It is often possible to obtain useful information without considering force-constant changes, but in most cases this approach should be considered only as a first rough approximation.

Intuitively, one feels that when the local-mode frequency lies well outside the band, as in the case of the U center, a static-well approximation in which only the defect ion is allowed to move should be a good starting approximation. That is, during the period of an in-band normal-mode oscillation of the crystal the local oscillator carries out several complete periods, and therefore during any one of them sees the neighboring ions as though they were fixed. Since λ for the local mode is outside of the band, G can be expanded in powers of $\lambda_{s\mathbf{q}}/\lambda$ or, equivalently, $\mathbf{A}'/\lambda$. Keeping terms of order $(\lambda_{s\mathbf{q}}/\lambda)^2$ leads to a quadratic for λ which can be expanded in terms of approximately M_0'/M_0 to give

$$\begin{aligned} \lambda = {} & (A_{j1,j1}(0,0) + \Delta A_{j1,j1}(0,0))/M_0' \\ & + \epsilon \sum_{k\beta\mu}{}' A^2{}_{j1,k\beta}(0,\mu)/M_\mu (\epsilon A_{j1,j1}(0,0) + \Delta A_{j1,j1}(0,0))\,. \end{aligned} \tag{14}$$

The prime on the summation is meant to exclude the diagonal element which has been incorporated into the first term. The first term gives just the static-well approximation, whereas the sum gives the first corrections, of order $1/M_\mu$, to it. Since $M_\mu \simeq 40$ in KCl, we expect the static-well approximation to be quite adequate.

Virtually the same result as that contained in Eq. (14) can be derived by applying Eq. (8) directly to the imperfect crystal. We imagine the vector $\mathbf{v}$ to have components $\mathbf{v}_d$ in a subspace associated primarily with the defect and component $\mathbf{v}_c$ associated with the rest of the crystal. This induces a partitioning of Eq. (8) into two equations

$$(\mathbf{A}_{dd}'-\lambda\mathbf{I})\mathbf{v}_d+\mathbf{A}_{dc}'\mathbf{v}_c=0\,, \tag{15a}$$

$$\mathbf{A}_{cd}'^{T}\mathbf{v}_d+(\mathbf{A}_{cc}'-\lambda\mathbf{I})\mathbf{v}_c=0\,, \tag{15b}$$

from which $\mathbf{v}_c$ can be eliminated to give

$$(\mathbf{A}_{dd}'-\lambda\mathbf{I}-\mathbf{A}_{dc}'\mathbf{G}_{cc}\mathbf{A}_{cd}'^{T})\mathbf{v}_d=0\,, \tag{15c}$$

with $\mathbf{G}_{cc}\equiv(\mathbf{A}_{dc}'-\lambda\mathbf{I})^{-1}$. In the static-well approximation, we have just $\mathbf{A}_{dd}'-\lambda\mathbf{I}=0$, whereas the correction terms of Eq. (14) can be obtained by again expanding $\mathbf{G}_{cc}$ in terms of A_{cc}'/λ and M_0'/M_0 and keeping appropriate terms.

Our problem, then, is to calculate the force constant

$$A_{j1,j1}(0,0)+\Delta A_{j1,j1}(0,0)\equiv[\partial^2V/\partial u_{j1}^2(0)]_0\equiv k\,, \tag{16}$$

where V is the potential energy of the system with the defect present.

III. ELECTRONIC STRUCTURE AND FORCE CONSTANTS

According to Born,[10] in the highest approximation in which the total wave function of the crystal can be written as the single product of a nuclear part $\chi(\mathbf{R})$ and an electronic part $\psi(\mathbf{r},\mathbf{R})$, the equation for the former is given by

$$(T_N+U(\mathbf{R}))\chi(\mathbf{R})=E\chi(\mathbf{R})\,. \tag{17}$$

Here $\mathbf{r}$ and $\mathbf{R}$ represent all of the electronic and nuclear coordinates, respectively. We shall assume the crystal to be in its electronic ground state. T_N is the kinetic energy of the nuclei and $U(\mathbf{R})$ is given by

$$U(\mathbf{R})=E_{\mathrm{el}}(\mathbf{R})+\langle\psi(\mathbf{r},\mathbf{R})|T_N|\psi(\mathbf{r},\mathbf{R})\rangle\,. \tag{18}$$

For the system we are considering in this paper, the second term on the right is expected to represent only a slight extension beyond the adiabatic approximation, and so we shall ignore it. Thus, the potential energy V of the preceding section is here given by E_{el}. The first term is the eigenvalue of the electronic Hamiltonian obtained from

$$H_{\mathrm{el}}(\mathbf{r},\mathbf{R})\psi(\mathbf{r},\mathbf{R})=E_{\mathrm{el}}(\mathbf{R})\psi(\mathbf{r},\mathbf{R})\,. \tag{19}$$

It can be taken to include the nuclear repulsion energy for the values of the nuclear coordinate $\mathbf{R}$. The notation here is meant to emphasize that the electronic-eigenvalue problem must be solved for each set of values of the nuclear coordinates. In this, the adiabatic approximation, the electrons are able to adjust completely to each change in the positions of the nuclei. In the harmonic approximation, on the other hand, the effective nuclear potential is obtained as an expansion through quadratic terms of the electronic energy about the equilibrium position of the nuclei.

To calculate the effective nuclear potential, then, we need to know the solution of Eq. (19) as a function of $\mathbf{R}$. In the static-well approximation for the U center, $\mathbf{R}$ refers only to the displacement of the H^- ion from its equilibrium position. Since the motion of the H^- ion in a cubic well will be threefold degenerate, we need consider displacements along only one direction, which we choose to be the [100]. In I, approximate solutions to Eq. (19) for the ground and first excited states were obtained by a variational method with the H^- ion fixed at a perfect crystal site. In order to determine the new equilibrium positions of the neighboring ions, the variation calculation was carried out for values of $\mathbf{R}$ representing the positions of the six 1nn ions in a "breathing-mode" type of displacement and a minimum was obtained. With the 1nn ions fixed in their new positions, we must now carry out the same type of calculation for displacements of the H^- ion in the [100] direction.

For convenience, we repeat here the principal equations from I. The Hamiltonian $H(\equiv H_{\mathrm{el}})$ is given by

$$H=H_U+H_{\mathrm{cr}}+H_{\mathrm{int}}\,, \tag{20}$$

$$H_U=\sum_{i=1}^{2}\{-\tfrac{1}{2}\nabla_i^2-r_i^{-1}\}+r_{12}^{-1} \tag{21}$$

in which $\mathbf{r}_i$ is the distance of the ith electron from the proton and $\mathbf{r}_{12}^{-1}$ is the interaction of the two electrons (in a.u.).

$$H_{\mathrm{int}}=\sum_{i=1}^{2}\{-\sum_{\nu}Z_\nu|r_i-\mathbf{R}_\nu|^{-1}+\sum_{j=3}^{M}|r_i-r_j|^{-1}\}\,, \tag{22}$$

where Z_ν is the nuclear charge, $\mathbf{R}_\nu$ is the position of the νth ion, and $\mathbf{r}_j$ is the position vector of the jth electron.

H_{cr} is the Hamiltonian of the rest of the crystal, including nuclear interactions, but it is not used explicitly in our calculations and will not be given here. That part of the wave function of the crystal plus defect which refers to the U center is given by

$$\psi_U(1,2)=N_U[\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)]\theta(s_1,s_2)\,. \tag{23}$$

Here θ is a normalized singlet spin function and N_U is a spatial normalization factor. ψ_a and ψ_b are normalized one-electron functions suitably orthogonalized to the free-ion HF orbitals on the 1nn ions. For example,

$$\psi_a=N_a[\phi_a+\sum_{\nu,j}c_{\nu,j}a_{\nu,j}(\mathbf{r}-\mathbf{R}_\nu)]\,, \tag{24}$$

with $c_{\nu,j}=-(a_{\nu,j}|\phi_a)$, $\phi_a=(\beta_a^3/\pi)^{1/2}\exp(-\beta_a r)$, and $N_a=(1-\sum_{\nu,j}c_{\nu,j}^2)^{-1/2}$. These same free-ion orbitals occur in the Coulomb and exchange parts of H_{int}. Corresponding to Eq. (20), we obtain from Eq. (19)

$$E_{\mathrm{el}}=E_U(\beta_a,\beta_b,\mathbf{R})+E_{\mathrm{int}}(\beta_a,\beta_b,\mathbf{R})+E_{\mathrm{cr}}(\mathbf{R})\,. \tag{25}$$

---

[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), p. 406.

We assume $E_{\mathrm{cr}}(\mathbf{R})$ to be independent of the small displacements of the H$^-$ ion and therefore in the static-well approximation it is a constant and can be neglected. In I, E_U+E_{int} was given by

$$E_U+E_{\mathrm{int}}=2N_U^2\{(a|h|a)+(b|h|b)+2S_{ab}(a|h|b)+(ab|ab)+(ab|ba)\}\,, \quad (26)$$

with

$$(a|h|b)\equiv\int\psi_a^*(1)h\psi_b(1)d\tau_1\,, \quad (27\mathrm{a})$$

$$(ab|cd)\equiv\int\psi_a^*(1)\psi_b^*(2)r_{12}^{-1}\psi_c(1)\psi_d(2)d\tau_1d\tau_2\,, \quad (27\mathrm{b})$$

$$S_{ab}=\int\psi_a^*\psi_b d\tau\,, \quad (27\mathrm{c})$$

$$N_U=[2(1+S_{ab}^2)]^{-1/2}\,, \quad (27\mathrm{d})$$

and

$$h=-\tfrac{1}{2}\nabla_1^2-r_1^{-1}-\sum_\nu\{Z_\nu|\mathbf{r}_1-\mathbf{R}_\nu|^{-1}+\int r_{13}^{-1}(\rho_{c\nu}(3,3)-2^{-1}\rho_{c\nu}(1,3)P_{13})d\tau_3\}\,. \quad (27\mathrm{e})$$

Here $\rho_{c\nu}$ is that part of the Fock-Dirac density matrix for the νth ion and P_{13} acting to the right interchanges the roles of 1 and 3 in Eq. (26). 1 is the integration variable for ψ_U and 3 that for the rest of the crystal. It is to be understood that since the electronic structure on just the 1nn ions is considered, the sum over ν in Eq. (27e) reduces to the point-ion approximation for all other neighbors.

Introducing ψ_a from Eq. (24) into $(a|h|a)$, we get

$$(a|h|a)=N_a^2\{(\phi_a|h|\phi_a)+2\sum_{\nu,j}c_{\nu,j}(\phi_a|h|a_{\nu,j})+\sum_{\nu,j}c_{\nu,j}^2(a_{\nu,j}|h|a_{\nu,j})\} \quad (28)$$

and corresponding terms for $(b|h|b)$ and $(a|h|b)$. The first term yields the kinetic, point-ion, Coulomb, and exchange energy for the trial function ϕ_a. The second and third terms arise from the orthogonalization of the trial functions to the ion core orbitals.

Neglecting polarization of the H$^-$ ion for the present, we proceed with the calculation by evaluating the terms in Eq. (26) for each different ion in the sum over ν. From symmetry the contributions from the (0,1,0), (0, −1, 0), (0,0,1), and (0,0, −1) ions are identical, whereas the contributions from the (1,0,0) and (−1, 0,0) ions differ from each other and from those of the other four ions. It is interesting to note that the normalization factor N_U prevents the forces between the H$^-$ ion and any given 1nn ion from being strictly two-body and central.

In I, it was found that

$$(\phi_a|h|a_{\nu,j})=(\epsilon_{\nu j,}+a_MR^{-1})(\phi_a|\phi_{\nu,j})-2(\phi_a|r^{-1}|a_{\nu,j}) \quad (29)$$

and

$$(a_{\nu,j}|h|a_{\nu,j})=\epsilon_{\nu,j}+a_MR^{-1}-2(a_{\nu,j}|r^{-1}|a_{\nu,j})\,. \quad (30)$$

The last terms on the right side of both of these expressions present some problems. The origin of the factor of 2 in front of them is difficult to see unless one goes into considerable detail, but the conclusion is that one integral should be associated with the proton and one with the effective charge of a negative-ion vacancy. The latter does not move when the H$^-$ ion is displaced, while the former does. Thus, there are really two distinct integrals occurring in both Eqs. (29) and (30), and we have taken this into account in the calculations.

A. Inclusion of H$^-$ Polarization

As the H$^-$ ion is displaced from its equilibrium position, we expect some deformation or polarization of its electronic-charge cloud. In a shell-model calculation, this would be interpreted in terms of the displacement (without deformation) of the electronic charge relative to the proton. We can do somewhat better than this by a straightforward but tedious calculation which allows the admixture of a function of p-like symmetry into the wave function as the H$^-$ ion is displaced.

We now write

$$\psi_{\mathrm{pol}}(1,2)=N_{\mathrm{pol}}\{\psi_U(1,2)+\eta\psi_U'(1,2)\}\,, \quad (31)$$

with $\psi_U(1,2)$ given by Eq. (23) and

$$\psi_U'=N_U'[\psi_a'(1)\psi_b'(2)+\psi_a'(2)\psi_b'(1)]\theta(s_1,s_2)\,. \quad (32)$$

Here

$$\psi_b'=N_b're^{-\beta_b'r}\cos\gamma \quad (33)$$

and ψ_a' has the same form as ψ_a. γ is the angle between the principal symmetry axis of the p function and the vector $\mathbf{r}$.

Substituting into the Hamiltonian, we have

$$(E_U+E_{\mathrm{int}})_{\mathrm{pol}}=N_{\mathrm{pol}}^2\{\langle\psi|H'|\psi\rangle+2\eta\langle\psi|H'|\psi'\rangle+\eta^2\langle\psi'|H'|\psi'\rangle\}\,, \quad (34)$$

with

$$H'\equiv H_U+H_{\mathrm{int}}\,.$$

In general, there are five variational parameters involved in Eq. (34). These are the two nonlinear parameters (β_a and β_b) in ψ, the two (β_a' and β_b') in ψ' and the coefficient η. In practice, it turns out that there is little point in either varying β_a and β_b from their values when polarization is not included or in putting $\beta_a'\neq\beta_a$. Thus, we have only two parameters to deal with, i.e., β_b' and η. To cut down still further on the large amount of computer time involved in the calculation, we determined the value of β_b' which approximately minimized the energy in KCl for an H$^-$ displacement of 4% of the new 1nn distance. This value was then used for both 2 and 6% displacements, so that η was the only remaining variation parameter. For KBr and KI the value of β_b'

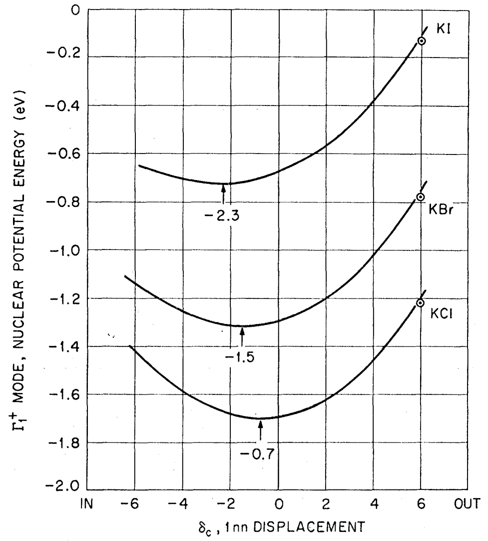

FIG. 1. The nuclear potential-energy curve for the six nearest-neighbor ions in the Γ_1^+ mode. δ_c is given as a percent of the nearest-neighbor distance in the perfect crystal.

was simply estimated by a scaling procedure from the KCl value.

B. Polarizability

The electrical polarizability α is defined by

$$\boldsymbol{\mu}=\alpha\mathbf{E}, \tag{35}$$

where $\boldsymbol{\mu}$ is the dipole moment induced by the electric field $\mathbf{E}$. In analogy with this equation, we define a mechanical polarizability by

$$\boldsymbol{\mu}=\alpha_m\mathbf{F}, \tag{36}$$

in which $\mathbf{F}$ is a mechanical force per unit charge. In terms of the force constant k (Eq. 16) and the percentage displacement δ of the H^- ion, we take

$$\mathbf{F}=k(\delta\mathbf{R}_c) \tag{37}$$

and evaluate the dipole-moment operator using the wave function of Eq. (31). R_c is the new position of the 1nn ions after the cubic (Γ_1^+) relaxation. Thus, we get

$$\begin{aligned}\boldsymbol{\mu}&=e\langle\psi_{\mathrm{pol}}|\,\mathbf{r}_1+\mathbf{r}_2\,|\psi_{\mathrm{pol}}\rangle\\&=N_{\mathrm{pol}}{}^2 2\eta\langle\psi_U(1,2)\,|\,\mathbf{r}_1+\mathbf{r}_2|\psi_U{}'(1,2)\rangle,\end{aligned} \tag{38}$$

since the diagonal terms vanish from symmetry. Therefore,

$$\alpha_m=2\eta(k\delta R_c)^{-1}N_{\mathrm{pol}}{}^2\langle\psi_U(1,2)\,|\,\mathbf{r}_1+\mathbf{r}_2|\psi_U{}'(1,2)\rangle. \tag{39}$$

In using this equation, we shall always assume that the mechanical force $k(\delta R_c)$ operates on unit charge and that e in Eq. (38) is unity. Also, in evaluating the integral in Eq. (39), we shall ignore contributions from the overlap terms in the wave functions. We do not expect this to introduce an error of more than 10%.

TABLE I. Various quantities obtained from the KCl calculation. The symbols are defined in the text. The experimental value of k is 14.43×10^3 dyn/cm.

	No polarization		Polarization			
δ	E_U+E_{int} (a.u.)	$k\times10^{-3}$ dyn cm^{-1}	E_U+E_{int} (a.u.)	$k\times10^{-3}$ dyn cm^{-1}	η	$100\eta/\delta$
0	−1.071241		−1.071241			
2	−1.071139	23.54	−1.071181	13.77	0.01195	0.5975
4	−1.070832	23.54	−1.071003	13.69	0.02396	0.5991
6	−1.070316	23.66	−1.070707	13.65	0.03611	0.6018

C. Second-Nearest-Neighbor Interactions

We attempted to estimate the effects of interaction with the 2nn ions by using a Born-Mayer potential of the form

$$V_{\mathrm{BM}}=A_{\mu\nu}\exp(r_\mu-r_\nu-r)/\rho, \tag{40}$$

with

$$A_{\mu\nu}=b(1+Z_\mu/n_\mu+Z_\nu/n_\nu). \tag{41}$$

Here, Z_μ, n_μ, and r_μ are, respectively, the ionic charge, the number of outer electrons, and the radius of ion μ. The parameters b and ρ are taken from Tosi and Fumi[11] and are assumed to have the same values for the interaction between the H$^-$ ion and a negative halogen ion as they have for the interaction between two similar halogen ions. Polarization of the H$^-$ ion is taken into account by reducing the 2nn interaction in the same ratio that the 1nn interaction was reduced by polarization effects.

IV. RESULTS AND DISCUSSION

All of the input data used in the calculations are given in Table I of paper I.

In Fig. 1, we show the potential-energy curves for the motion of the six 1nn ions in a Γ_1^+ mode with the H$^-$ ion fixed at its equilibrium position. The displacement δ_c is given in terms of the percentage of the 1nn distance. The calculation of these curves is discussed in I. The values of δ_c at equilibrium are shown together with arrows marking the minima of the curves. The equilibrium values of δ_c used in the local-mode calculations were somewhat larger than these, namely, −2 for KCl, −2.5 for KBr, and −3 for KI. The larger values were obtained from an earlier calculation using only $3s$ and $3p$ Slater orbitals to represent the outer electrons of the K$^+$ ion and neglecting the inner electrons completely. Because of this discrepancy and because the classical ionic-crystal part of the calculations must be somewhat limited in accuracy, we tested the effect in KCl (before polarization of the H$^-$ ion) of small changes in the 1nn positions. In fact, although 1 and 2% inward displacements gave considerably different total energies, the energy difference between any two points on the "no-polarization" curve in Fig. 2, dis-

---

[11] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids 25, 45 (1964).

TABLE II. Results for the local-mode frequency in various approximations discussed in the text and for the mechanical polarizability calculated by Eq. (39). All frequencies are given in units of 10^{13} rad/sec.

	ω_{expt}	ω_{np}	ω_{p}	ω_{ri}	$\omega_{\mathrm{p}}^{2\mathrm{nn}}$	α_m (in Å^3)
KCl	9.29	11.87	9.05	14.8	9.37	6.95
KBr	8.27	10.27	7.99	$\cdots$	8.44	8.00
KI	7.31	8.37	6.65	12.7	7.37	10.04

cussed in the next paragraph, was hardly affected. The curves in Fig. 1 were calculated with constant values of the variation parameters β_a and β_b appropriate for values of δ_c near the equilibrium position. The validity of this approximation was checked by varying β_a and β_b at $\delta_c=6$ until a new minimum in E_U+E_{int} was obtained. The encircled points on the graph show how little difference this makes.

In Fig. 2, the potential-energy curves for the displacement of the H$^-$ ion in a [100] direction in KCl are given in various approximations. In this case, δ is given as a percent of the *new* 1nn distance. The point-ion calculation (the results are shifted to coincide with the other curves at $\delta=0$) neglects the electronic structure of all the ions and is obviously quite inadequate. However, it is already seen from this figure that the calculation which neglects polarization of the H$^-$ ion will give a frequency considerably higher than the experimental value. The dashed curve is obtained by using the "experimental" force constant in Eq. (42) below.

Some of the data plotted in Fig. 2 are also given in columns 2 and 4 of Table I along with the resulting force constants k, calculated from the equation

$$\Delta E_{\mathrm{el}}=\tfrac{1}{2}k[(1-\delta_c/100)R_0(\Delta\delta)]^2. \qquad (42)$$

Here R_0 is the 1nn distance in the perfect crystal and $(1-\delta_c/100)R_0$ is the 1nn distance when the U center is present. ΔE_{el} was taken as the value of E_{el} at $\delta=0$ minus its value at the other δ's listed in the first column. The purpose of showing several calculated values of each k is to demonstrate the consistency of the results. In the last two columns are shown the values of the p-function mixing parameter η, and the ratio $100\eta/\delta$, which, like the force constants, is very nearly constant.

In Table II we show various values of the local-mode frequency and the polarizability for the three crystals. ω_{np} is the frequency without polarization, ω_{p} is that with polarization, and ω_{expt} is the experimental value. The values given by Fieschi *et al.* in Ref. 9 for a pure mass defect in a rigid-ion-model calculation are shown in column 5, and those from our calculations with 2nn effects included in column 6.

The results in the tables and curves more or less speak for themselves and we shall not spend a great deal of time in discussing them. It is obvious that polarization of the H$^-$ ion is an important effect. Not quite so obvious, but a point which was revealed by some of the early calculations and which is clear physically, is the following. Stated rather loosely, the larger the force constants calculated without polarization, the greater will be the polarization effects. Thus, if we are to believe that our calculations give a correct picture of the size of the polarization effect, we must first be certain that the calculation without polarization is valid. We are reasonably confident of this for those reasons already stated in the Introduction. One might legitimately ask, however, if our neglect of certain correlation effects is justified. The form of the U-center wave function allows for considerable radial correlation of the two H$^-$ electrons with each other but the electrons on the 1nn ions have been treated strictly in the HF approximation and all interion correlations have been neglected. The energy associated with these effects is not necessarily small, but since we deal only with energy changes, we would not expect their inclusion (even if we could do it) to affect the results greatly.

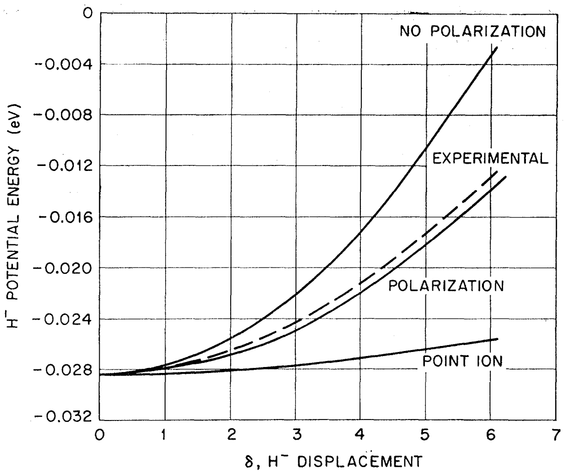

FIG. 2. Potential-energy curves for the displacement of the H$^-$ ion in KCl in various approximations. The curves are adjusted to have the same values at zero displacement. Here δ is given as a percent of the nearest-neighbor distance in the crystal distorted by the presence of the U center.

Another point which shows up somewhat in the figures for α_m and even more clearly in some of the other parameters not shown here is that the H$^-$ ion cannot be assigned a definite radius or polarizability valid for all crystals. The corresponding point for the perfect crystal has been emphasized recently in calculations of Tosi and Fumi[11] and of Ruffa.[12]

We assume that the results obtained for the 2nn interactions have no more than qualitative significance. They do suggest that such effects are more important in KI than in KCl, which would seem to be quite correct intuitively.

We want to mention briefly a few points in connection with some of the problems encountered in carrying out these calculations. These problems were caused chiefly by the complexity of the programming and the

---

[12] A. R. Ruffa, Phys. Rev. **130**, 1412 (1963).

need to cut down on computer time. For both of these reasons, we first did the calculations by approximating the $3s$ and $3p$ K^+ ion orbitals by single Slater functions with parameters chosen according to the usual prescription. This calculation gave not unreasonable results, but the approximation was too gross to be very satisfactory. Had we continued using it, the extent of the H^- polarization would most likely have been misleadingly small. The calculations were useful, though, in that they provided good starting values for the parameters β_a and β_b in the trial functions of the more exact calculations with HF ion orbitals. In connection with H^- polarization effects, we did a limited number of calculations to ascertain if it would be a good approximation to neglect the electronic structure on the four 1nn ions at right angles to the displacement of the H^- ion. We soon found out that these ions are quite important, especially to the polarization effect.

We hope to extend these calculations soon to the sodium halides and thus obtain further insight into the validity of some of the approximations.

ACKNOWLEDGMENT

We wish to thank R. Tseng for numerous, useful discussions.

PHYSICAL REVIEW VOLUME 162, NUMBER 3 15 OCTOBER 1967

Anisotropy Effects in the Excitonic Insulator*

Johannes Zittartz†
University of California, San Diego, La Jolla, California
(Received 10 April 1967)

A new insulating phase in semiconductors and semimetals has been discussed recently in the literature. This paper extends the analysis of this excitonic phase to the more general case of an anisotropic band structure of the underlying two-band model. The thermodynamic properties of the excitonic phase are worked out. Whereas the anisotropy does not lead to qualitativly new features in the case of a positive band gap (semiconductor region), important changes occur in the case of a negative band gap (semimetallic region). The latter situation is discussed in detail. Finally, the phase diagram of the excitonic phase is calculated for a particular anisotropic band model.

I. INTRODUCTION

Recently a new kind of insulating phase has been discussed in the literature. The idea is based on observations by Mott[1] and Knox[2] that in semimetals and semiconductors with small energy gaps the electrons and holes will under certain conditions form bound pairs of the exciton type. The properties of the new phase which has been called the "excitonic insulator"[3] have been investigated theoretically in several papers.[3–8] While most of these papers deal with the simple case of an isotropic band structure, Kopaev[7] has pointed out the importance of anisotropy in the description of the new phase.

In this article we investigate in detail the excitonic phase in the more realistic case of anisotropic energy bands. In Sec. II we derive the thermodynamic properties of the new phase quite generally. The influence of the anisotropy is discussed in detail in Secs. III and IV. For a positive band gap we find essentially the same results as in the isotropic case[3,5,6] apart from quantitative corrections. In the semimetallic region (band overlap), however, the description differs qualitatively from the corresponding isotropic case. The electron system condenses only partly in electron-hole pairs, whereas parts of the system remain in the normal state. It follows especially that the normal semimetallic state is stable against pair formation, if the anisotropy is large enough as has been shown first by Kopaev.[7]

We consider the familiar two-band picture of valence and conduction electrons and assume that Coulomb interactions of electrons within one band have been taken into account in the calculation of the energy bands. The dynamics of the system are then governed

---

* Supported in part by the Office of Naval Research and the National Science Foundation.

† On leave from Institute for Theoretical Physics, University of Cologne, Cologne, Germany until Oct. 1, 1967.

[1] N. F. Mott, Phil. Mag. 6, 287 (1961).

[2] R. S. Knox, in *Theory of Excitons, Solid-State Physics* (Academic Press Inc., New York, 1963), Suppl. 5, p. 100.

[3] D. Jerome, T. M. Rice, and W. Kohn, Phys. Rev. 158, 248 (1967).

[4] J. Des Cloizeaux, J. Phys. Chem. Solids 26, 259 (1965).

[5] L. V. Keldysh and Yu. V. Kopaev, Fiz. Tverd. Tela 6, 2791 (1964) [English transl.: Soviet State 6, 2219 (1965)].

[6] A. N. Kozlov and L. A. Maksimov, Zh. Eksperim. i Teor. Fiz. 48, 1184 (1965); 49, 1284 (1965) [English transls.: Soviet Phys.—JETP 21, 790 (1965); 22, 889 (1966)].

[7] Yu. V. Kopaev, Fiz. Tverd. Tela 8, 223 (1966) [English transl.: Soviet Phys.—Solid State 8, 175 (1966)]. In fact Kopaev shows from an analysis of the electron-hole vertex part that the instability of the normal state does not occur, if the anisotropy is large enough. However, his "gap equation" is in error as may be compared with our corresponding Eq. (32).

[8] E. V. Baklanov and A. V. Chaplik, Fiz. Tverd. Tela 7, 2768 (1965) [English transl.: Soviet Phys.—Solid State 7, 2240 (1966)].