TABLE V. Experimental and theoretical values for the ratio A/A_{mass} obtained by various workers.

	Filling pressure (atm)	Molar Volume (cm^3/mole)	$A_{\mathrm{exp}}/A_{\mathrm{mass}}$	$A^{a}{}_{\mathrm{cal}}/A_{\mathrm{mass}}$ [e]
He^4-rich mixtures	60[a]	...	2.8	10
	90[a]	...	2.0	8.3
	140[a]	...	1.5	5.6
	96[b]	...	~3	...
	...	19.5[c]	21–41	...
	...	20.2[d]	~31	...
He^3-rich mixtures	145[a]	...	1.2	2.8
	...	19.5[c]	9–27	...
	...	20.2[d]	~23	...

[a] Values of Berman *et. al.* (Ref. 3).
[b] Values of Callaway (Ref. 2).
[c] Values of Bertman *et al.* (Ref. 4).
[d] Present values.
[e] Reference 5, 6.

the value observed in the hcp phase of solid He^4. Finally, in Table V, we have summarized all the known experimental and theoretical values of A/A_{mass}.

CONCLUSIONS

The thermal-conductivity curves of isotopic mixtures of solid He^4 have been analyzed at the molar volume 20.2 cm^3/mole. The He^4-rich mixture solids at this molar volume have the hcp crystal structure while the He^3-rich mixtures crystallize in the body-centered-cubic structure. The Debye temperatures are similar in the case of pure He^4 and pure He^3, thus diminishing the possibility of the variation of sound velocity in the mixed solids.

Large values of phonon scattering by point defects are obtained from the analysis. The enhanced scattering is considered to be present because of the distortion of the lattice around the isotopic impurity. The concentration dependence of phonon scattering produced by lattice distortion is found to be the theoretically expected one. These conclusions are different from the earlier conclusions of Bertman *et al.* The magnitudes of the lattice distortion scattering are also higher than the values obtained by Berman *et al.* The estimates of the atomic misfit parameter ϵ are the same in both phases of solid helium.

ACKNOWLEDGMENTS

The author expresses his gratitude and sincere thanks to Professor G. S. Verma for his helpful suggestions and discussion.

PHYSICAL REVIEW VOLUME 162, NUMBER 3 15 OCTOBER 1967

Electronic Structure of the *U* Center. I. Optical Absorption and Lattice Relaxation*

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(Received 7 June 1967)

The electronic structure of the *U* center in KCl, KBr, and KI is calculated for the ground and first excited states using a model in which the interactions with the first-nearest-neighbor ions are taken into account in detail and all other ions are treated as point charges. A second, more refined model, which involves the electronic structure of all ions and polarization effects, is briefly described. It is used for calculations of the electronic structure, optical absorption, and lattice relaxation of the *U* center in KCl.

I. INTRODUCTION

THE *U* center in alkali-halide crystals consists of an H$^-$ ion trapped at a lattice site normally occupied by a negative halogen ion. The center has been studied extensively experimentally, and several interesting properties have been established.[1] It is responsible for a single pronounced characteristic absorption in the ultraviolet (at approximately 5.8 eV in KCl). Other absorption bands are probably associated with the center, but, if so, they are difficult to observe because of masking by the intrinsic absorption of the pure crystals. In contrast to many other defects in alkali-halide crystals, no emission bands have been associated with the *U* center. Instead, a number of photochemical reactions take place, which suggests that in the excited state of the center the neutral hydrogen atom is able to diffuse away from the vacancy into an interstitial position. The result is that the *U* band is bleached and the *F* band is generated. The diffusion process should be aided by lattice relaxation if in the relaxed state the excited electron is in a diffuse orbital, as might be expected from results on the *F* center.[2,3]

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

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Recently, interest in the U center has been restimulated by Shaefer's work[4] on the infrared absorption associated with it. This work coincided with an increasing theoretical interest[5] in the vibrational properties of crystals containing defects, particularly in localized and quasilocalized modes. The U center is an interesting case of a localized mode lying well above the limit of the band of longitudinal optical frequencies of the perfect crystal. We shall go into the problem of calculating the force-constant changes associated with a localized mode of this type in the second paper of this series.

As far as we know, theoretical work on the electronic structure of the U center is limited to the point-ion calculation of Gourary.[6] This work gives transition energies about 20% lower than the observed values.

We have used two different models in the work reported here, both of which involve, in part, extensions beyond the Hartree-Fock (HF) approximation. The first model considers the electronic structure of the first-nearest-neighbor (1nn) ions only, and no attempt is made to calculate any electronic polarization effects associated with the center. In the second model, the electronic structure of the first three shells of neighboring ions is taken into account rather accurately and that of all of the more distant ions somewhat less so. Polarization effects are included in this model by the theory of Toyozawa,[7] and Haken and Schottky[8] (THS). Lattice-distortion effects are included in both models in the ground state, but relaxation of the lattice in the excited state is calculated only with the second model. The calculations with the first model are carried out for KCl, KBr, and KI, whereas with the second model scarcity of some required input data compels us to limit the calculations to KCl. Nevertheless, we shall be able to carry out a limited study of polarization and "further ion" effects with these results.

The Hamiltonian, exclusive of electronic polarization effects, and wave functions of both models are discussed in Sec. II. Section III contains a brief discussion of the inclusion in the second model of polarization effects and of lattice relaxation in both models. Some of the details of the calculations and the results are given in Sec. IV, and in Sec. V these results are discussed.

II. DERIVATION OF EQUATIONS

A. Hamiltonian and Wave Functions

The spin-independent Hamiltonian for the problem of a single U center in an otherwise perfect crystal can be written as

$$H(1,2,3,\cdots,M)=H_U(1,2)+H_{\mathrm{cr}}(3,\cdots,M)+H_{\mathrm{int}}(1,2,3,\cdots,M). \quad (1)$$

H_U is the same as the Hamiltonian for an H$^-$ ion in free space and is given in atomic units by

$$H_U(1,2)=h_1(1)+h_1(2)+r_{12}^{-1}, \quad (2)$$

with

$$h_1(i)=-\tfrac{1}{2}\nabla_i^2-r_i^{-1}, \quad (3)$$

in which r_i^{-1} is the interaction of the ith electron with the proton and r_{12}^{-1} is the mutual interaction of the two electrons.

H_{cr} is the Hamiltonian for the rest of the crystal and the nuclear interactions which we write for completeness even though it is not used explicitly in this paper.

$$H_{\mathrm{cr}}(3,\cdots,M)=\sum_j\{-\tfrac{1}{2}\nabla_j^2-\sum_\nu Z_\nu|\mathbf{r}_j-\mathbf{R}_\nu|^{-1}+\tfrac{1}{2}\sum_k{}'|\mathbf{r}_j-\mathbf{r}_k|^{-1}\}+\tfrac{1}{2}\sum_{\mu,\nu}{}'Z_\mu Z_\nu|\mathbf{R}_\mu-\mathbf{R}_\nu|^{-1}, \quad (4)$$

in which M is the total number of electrons under consideration, $\mathbf{r}_j$ is the position coordinate of the jth electron, and $\mathbf{R}_\nu$ is the coordinate of the νth ion. The primes on the summation signs indicate that the terms in which $i=j$ and $\mu=\nu$ are to be excluded. The summations over μ and ν include the proton. The interaction between the H$^-$ ion and the rest of the crystal is given by

$$H_{\mathrm{int}}(1,2,3,\cdots,M)=V(1,2)+\sum_{i=1}^{2}v(i,3,\cdots,M), \quad (5)$$

in which V, the interaction with the nuclei of the crystal, is given by

$$V(1,2)=-\sum_\nu Z_\nu\{|\mathbf{r}_1-\mathbf{R}_\nu|^{-1}+|\mathbf{r}_2-\mathbf{R}_\nu|^{-1}\}, \quad (6)$$

and the interaction of electron i ($i=1$, 2) with all of the other electrons of the crystal by

$$v_i\equiv v(i,3,\cdots,M)\equiv\sum_{j=3}^{M}v_{ij}=\sum_{j=3}^{M}|\mathbf{r}_i-\mathbf{r}_j|^{-1}. \quad (7)$$

Of course, the entire Hamiltonian is symmetrical with respect to an interchange of any two electrons.

The electronic wave function of a crystal containing a single U center can be written as

$$\Psi(\mathbf{1},\mathbf{2},\cdots,\mathbf{M})=\{M!/2!(M-2)!\}^{1/2}\times A\psi_U(\mathbf{1},\mathbf{2})\psi_c(\mathbf{3},\mathbf{4},\cdots,\mathbf{M}), \quad (8)$$

in which $\psi_U(\mathbf{1},\mathbf{2})$ is a two-electron group wave function for the H$^-$ ion embedded in the crystal and ψ_c is an $(M-2)$-electron group function for the rest of the crystal. The spin coordinates are assumed to be included by the notation **1**, **2**, etc., in boldface type. The same notation in lightface type means that the spin is not included. If ψ_U and ψ_c are considered to be sep-

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[4] G. Schaefer, Phys. Chem. Solids **12**, 233 (1960).

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[6] B. S. Gourary, Phys. Rev. **112**, 337 (1958).

[7] Yutaka Toyozawa, Progr. Theoret. Phys. (Kyoto) **12**, 421 (1954).

[8] H. Haken and W. Schottky, Z. Physik. Chem. Neue Folge **16**, Simon-Gedenkheft, 218 (1958).

arately antisymmetrized, then the operator A is given by

$$A=[M!/2!(M-2)!]^{-1}\sum_P(-1)^pP(U,c)\,, \qquad (9)$$

in which $P(U,c)$ is a permutation operator which exchanges electrons between but not within groups U and c. We also assume that so-called "strong orthogonality" holds, i.e.,

$$\int\psi_U(\mathbf{1},\mathbf{2})\psi_c(\mathbf{3},\cdots,\mathbf{k-1},\mathbf{1},\mathbf{k+1},\cdots,\mathbf{M})d\tau_1=0\,, \quad (10)$$

and that ψ_U and ψ_c are separately normalized to unity.

As it stands in Eq. (8), the wave function Ψ allows for correlation within the two groups but neglects all intergroup correlation effects except those introduced by antisymmetrization. For our purposes, this is probably an acceptable approximation for the ground state of the U center but inadequate for the excited state because of the polarization of the crystal when the defect electrons are described by more extensive functions. We shall return to this problem in the next section.

We now approximate ψ_U by

$$\psi_U(\mathbf{1},\mathbf{2})=N_U[\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)]\theta(s_1,s_2)\,, \quad (11)$$

in which ψ_a and ψ_b are one-electron spatial orbitals and N_U is a normalization factor which is readily seen to be given by

$$N_U=[2(1+S_{ab}{}^2)]^{-1/2}\,, \qquad (12)$$

with $S_{ab}=(\psi_a|\psi_b)$. Here $\theta(s_1,s_2)$ is the normalized singlet spin function given by

$$\theta(s_1,s_2)=[\alpha(s_1)\beta(s_2)-\alpha(s_2)\beta(s_1)]/\sqrt{2}\,. \qquad (13)$$

This type of function, first used for the helium atom, allows for some radial correlation as well as giving a fairly adequate approximation to the HF doubly occupied orbital. In carrying out the quantum-mechanical calculations associated with H_U and H_{int}, we approximate ψ_c by

$$\psi_c=[(M-2)!]^{1/2}A_c a_{1,1}(\mathbf{3})a_{1,2}(\mathbf{4})\cdots \times a_{\nu,j-1}(\mathbf{i-1})a_{\nu,j}(\mathbf{i})\cdots\,, \quad (14)$$

where

$$A_c=[(M-2)!]^{-1}\sum_P(-1)^pP(c) \qquad (15)$$

and $a_{\nu,j}(\mathbf{i})$ is short for $a_j(\mathbf{r}_i-\mathbf{R}_\nu)$ times a one-electron spin function. $P(c)$ means that the permutations considered are all within group c. The spatial parts of the a's are considered to be Wannier functions and $a_j(\mathbf{r}_i-\mathbf{R}_\nu)$ indicates that the ith electron is in the Wannier spin orbital constructed from the jth band and located on the νth ion. In fact, since we do not have the Wannier functions at our disposal, we assume that the free-ion HF functions are fairly good approximations to them. This is undoubtedly true for the energetically low-lying, very narrow bands, but calculations showed it to be inadequate for the valence band functions. We found it necessary to introduce modified orbitals constructed by orthogonalizing the orbitals on the negative ions to those on the neighboring positive ions.

Since the Wannier functions, even on different lattice sites, are orthogonal to each other, we can ensure that the strong orthogonality condition holds by writing, for the spatial part of the orbitals,

$$\psi_a(\mathbf{r})=N_a[\phi_a(\mathbf{r})+\sum_{\nu,j}c_{\nu,j}a_{\nu,j}(\mathbf{r})]\,, \qquad (16)$$

in which

$$\phi_a=(\beta_a{}^3/\pi)^{1/2}\exp(-\beta_a r)\,,\quad c_{\nu,j}=-(a_{\nu,j}|\phi_a)\,, \quad (17)$$

and

$$N_a=(1-\sum_{\nu,j}c_{\nu,j}{}^2)^{-1/2}\,. \qquad (18)$$

The form of ϕ_b in the ground state is taken to be exactly the same as that given by (17). The use of free-ion atomic orbitals may mean that some of the orthogonality properties of Wannier functions are lost, but the modification mentioned above should substantially correct this.

B. Energy Expression

Using Eq. (8) and the orthogonality condition, Eq. (10), we find for the expectation value of H

$$\langle\Psi|H|\Psi\rangle=\langle\psi_U|H_U|\psi_U\rangle+\langle\psi_c|H_{\text{cr}}|\psi_c\rangle +[M!/2!(M-2)!]\langle\psi_U\psi_c|H_{\text{int}}A|\psi_U\psi_c\rangle\,. \quad (19)$$

In writing this expression, we have used the facts that H is symmetric in the electron coordinates and therefore commutes with the antisymmetrizer A and that A itself is a projection operator, i.e., $A^2=A$.

Considering only the spatial part of ψ_U, the first term in Eq. (19) gives

$$\langle\psi_U|H_U|\psi_U\rangle=2N_U{}^2\{(\psi_a(1)\psi_b(2)|H_U|\psi_a(1)\psi_b(2)) +(\psi_a(1)\psi_b(2)|H_U|\psi_a(2)\psi_b(1))\}\,. \quad (20)$$

Considering the first term, we get

$$(\psi_a(1)\psi_b(2)|H_U|\psi_a(1)\psi_b(2)) =(a|h_1|a)+(b|h_1|b)+(ab|ab)\,, \quad (21)$$

in which

$$(a|h_1|a)\equiv(\psi_a|h_1|\psi_a)\equiv\int\psi_a{}^*h_1\psi_a d\tau\,,\quad \text{etc.}\,, \quad (22)$$

and, in general,

$$(ab|cd)\equiv\int\psi_a{}^*(1)\psi_b{}^*(2)r_{12}{}^{-1}\psi_c(1)\psi_d(2)d\tau_1 d\tau_2\,. \quad (23)$$

For the second term, we find

$$(\psi_a(1)\psi_b(2)|H_U|\psi_a(2)\psi_b(1)) =\{2(a|h_1|b)S_{ab}+(ab|ba)\}\,. \quad (24)$$

So finally we have

$$\langle\psi_U|H_U|\psi_U\rangle=2N_U^2\{(a|h_1|a)+(b|h_1|b)+(ab|ab)+2(a|h_1|b)S_{ab}+(ab|ba)\}. \quad (25)$$

The second term in Eq. (19) will be treated by classical ionic crystal theory and will be discussed later. The third term can be reduced further, still retaining the group wave function approximation as follows:

$$\frac{M!}{2!(M-2)!}\langle\psi_U(\mathbf{1,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})|H_{\text{int}}A|\times\psi_U(\mathbf{1,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})\rangle$$
$$=\langle\psi_U(\mathbf{1,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})|H_{\text{int}}|\times\sum_P(-1)^pP(U,c)\psi_U(\mathbf{1,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})\rangle. \quad (26)$$

Using Eqs. (5)–(7), we obtain a term from V, i.e.,

$$\langle\psi_U(\mathbf{1,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})|V(1,2)|\times\sum_P(-1)^pP\psi_U(\mathbf{1,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})\rangle$$
$$=\langle\psi_U(\mathbf{1,2})|V(1,2)|\psi_U(\mathbf{1,2})\rangle$$
$$=-2\sum_\nu Z_\nu\int\psi_U^2(1,2)|\mathbf{r}_1-\mathbf{R}_\nu|^{-1}d\tau_1d\tau_2 \quad (27)$$

and terms from $\sum v_i$ which we shall now consider in more detail. When $i=1$, we obtain two types of terms:

$$\sum_{j=3}^{M}\langle\psi_U(\mathbf{1,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})|v_{1j}|\psi_U(\mathbf{1,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})-\psi_U(\mathbf{j,2})\psi_c(\mathbf{3},\cdots,\mathbf{M})\rangle. \quad (28)$$

The notation in the second term indicates that 1 and j have been exchanged exactly between the U and c groups. Exactly similar terms occur when $i=2$. The reduction to the form in (28) results solely because of Eq. (10). On introducing the one-electron orbital approximation given by Eq. (14), we can commute A_c through v_i, since v_i is symmetric in all variables affected by A_c and through $\psi_U(\mathbf{1,2})$ because A_c does not act on 1 and 2. We then get for the first term of Eq. (28)

$$\sum_{\nu,j}\langle\psi_U(\mathbf{1,2})a_{\nu,j}(\mathbf{3})|v_{13}|\psi_U(\mathbf{1,2})a_{\nu,j}(\mathbf{3})\rangle, \quad (29)$$

and a similar result for v_{23}. This result is obtained by noting that the operator $\sum_P(-1)^pP(c)$ places each electron once in each of the orthogonal Wannier spin orbitals. Similarly, for the second term in Eq. (28), we get

$$-\sum_{\nu,j}\langle\psi_U(\mathbf{1,2})a_{\nu,j}(\mathbf{3})|v_{13}|\psi_U(\mathbf{3,2})a_{\nu,j}(\mathbf{1})\rangle, \quad (30)$$

and a corresponding result with $\mathbf{r}_2$ replacing $\mathbf{r}_1$.

We now introduce that part of the Fock-Dirac density matrix corresponding to ψ_c by writing

$$\rho_c(1;3)=2\sum_{\nu,j}a_j^*(\mathbf{r}_1-\mathbf{R}_\nu)a_j(\mathbf{r}_3-\mathbf{R}_\nu), \quad (31)$$

where the sum runs only once over the spatial Wannier functions, each of which is doubly occupied.

Inserting the approximation to ψ_U given by Eq. (11), we obtain, for the sum of the two terms of the form given in (29),

$$2N_U^2\int d\tau_1d\tau_3\{\psi_a^2(1)+\psi_b^2(1)+2S_{ab}\psi_a(1)\psi_b(1)\}v_{13}\rho_c(3;3). \quad (32)$$

For the sum of the two terms of the form given in (30), we find

$$-N_U^2\int d\tau_1d\tau_3\{\psi_a(1)v_{13}\rho_c(1;3)\psi_a(3)+\psi_b(1)v_{13}\rho_c(1;3)\psi_b(3)+2S_{ab}\psi_a(1)v_{13}\rho_c(1;3)\psi_b(3)\}. \quad (33)$$

We retain 3 as the integration variable for the c group for clarity. Combining these results with those for $\langle\Psi|H_U|\Psi\rangle$, we get

$$\langle\Psi|H_U+H_{\text{int}}|\Psi\rangle=2N_U^2\{(a|h|a)+(b|h|b)+2S_{ab}(a|h|b)+(ab|ab)+(ab|ba)\}, \quad (34)$$

in which

$$h=h_1-\sum_\nu Z_\nu|\mathbf{r}_1-\mathbf{R}_\nu|^{-1}+\int v_{13}(\rho_c(3;3)-2^{-1}\rho_c(1;3)P_{13})d\tau_3 \quad (35)$$

is an effective one-electron Hamiltonian.

Substituting ψ_a from Eq. (16) into the first term of Eq. (36) gives

$$(a|h|a)=N_a^2\{\langle\phi_a|h|\phi_a\rangle+2\sum_{\nu,j}c_{\nu,j}(\phi_a|h|a_{\nu,j})+\sum_{\nu,j}c_{\nu,j}^2(a_{\nu,j}|h|a_{\nu,j})\}. \quad (36)$$

From the first term, one obtains the kinetic, point-ion, Coulomb, and exchange energies for the trial function ϕ_a. The second and third terms combined give the effects of orthogonalization to the ion-core Wannier functions. The reduction of Eq. (36) is covered rather thoroughly in Ref. 3, although here we have treated one of the integrals more rigorously. This is the integral

$$(\phi_a|r^{-1}|a_{\nu,j})\equiv\int d\tau\phi_a(\mathbf{r})r^{-1}a_{\nu,j}(\mathbf{r}-\mathbf{R}_\nu), \quad (37)$$

which gives the energy of the overlap charge distribution of the trial and core functions in the field of a charge at the defect site. It is a two-center integral and can be easily calculated exactly, although in Ref. 3 it was approximated by

$$(\phi_a|r^{-1}|a_{\nu,j})\simeq[\phi_a(\mathbf{r})|a_{\nu,j}(\mathbf{r}-\mathbf{R}_\nu)]/R_\nu. \quad (38)$$

This is probably a good approximation when $a_{\nu,j}$ is very compact, as we expect it to be for low-lying core states. For more extended core functions such as the outer orbitals of K^+, Cl^-, Br^-, etc., the approximation is less adequate and we have therefore calculated the integral exactly. We obtain for the second and third matrix elements in Eq. (36)

$$(\phi_a|h|a_{\nu,j})=(\epsilon_{\nu,j}\pm a_M R^{-1})c_{\nu,j}-2(\phi_a|r^{-1}|a_{\nu,j}) \quad (39)$$

and

$$(a_{\nu,j}|h|a_{\nu,j})=\epsilon_{\nu,j}\pm a_M R^{-1}-2(a_{\nu,j}|r^{-1}|a_{\nu,j}). \quad (40)$$

R is the nearest-neighbor distance and a_M is the Madelung constant. The plus (minus) sign is taken if the νth ion is positive (negative). The factor of 2 occurs in the third term because of the proton and because the interaction with the other electron is taken into account in the two-electron terms, so that a second positive effective charge must be included in the one-body part of the Hamiltonian of the core states. $\epsilon_{\nu,j}$ is either a free-ion HF energy or such an energy modified slightly to take into account the effects of overlap with other ions (and polarization contributions when they are included).

C. Two Hartree-Fock Models

We have employed the energy expressions derived above with two different sets of approximations which, together with the differences in calculational methods, constitute essentially two distinct models. In the first model, the sums in Eqs. (16) and (31) run over the 1nn ions only and no polarization effects are included. All other ions are treated as point ions. Free-ion HF orbitals are employed for *all* of the core electrons, and the two-center two-electron integrals are evaluated very accurately by the elliptical coordinate method. This model follows very closely the work in Ref. 3. We expect it to give reasonably accurate results as long as both U-center electrons have a high probability of being within the 1nn distance. The validity of the model is questionable when one of the electrons is in an excited state and is almost certainly inadequate after lattice relaxation, when the excited electron is likely to be in a quite diffuse orbital. The computational problems associated with the extension of the sums in Eqs. (16) and (31) to more neighbors within the framework of the first model are formidable, and the time required on even a large computer would be prohibitive. We have therefore developed a second model which we shall describe briefly here and in more detail in another paper, to be published later.

In this second model, we extend the sum in Eq. (31) to explicitly include the first three shells of ions. However, the Coulomb and exchange integrals are calculated by first deriving an effective potential including l-dependent exchange for a single electron moving in the field of the free HF ions. This has been discussed elsewhere.[9] We then evaluate the required integrals by a method, also described briefly in Ref. 9, which involves expanding the trial functions ϕ in Eq. (36) in spherical harmonics about the ions. This method turns out to be sufficiently accurate for most purposes and much quicker than the elliptic coordinate method.

For ions more distant than the 3nn, the overlap integrals appearing in Eq. (16) are evaluated by an approximate method which turns out to be quite accurate for slowly varying trial functions. In this outer region, we abandon the attempt to calculate the energy of interaction with the ions exactly and instead approximate it by χ_{HF}, the bottom of the conduction band in the HF approximation, i.e., minus the electron affinity in that approximation. In this way the sum in (31) is extended well beyond 3nn, albeit not very rigorously. We shall estimate χ_{HF} in a manner to be given later. Thus, we now approximate h of the previous section by

$$\begin{aligned} h_{\mathrm{HF}}&=h \quad \text{from Eq. (35)}, & r&<R_a \\ h_{\mathrm{HF}}&=-(1/2m_e{}^*)\nabla^2+\chi_{\mathrm{HF}}-r^{-1}, & r&>R_a \end{aligned} \quad (41)$$

in which $m_e{}^*$ is the effective mass, and the impurity potential for $r>R_a$ is approximated by r^{-1}. The quantity R_a is a suitably chosen radius, here taken between the 3nn and 4nn. An integral part of the second model is the inclusion of polarization effects, which we shall consider in the following section.

III. INCLUSION OF POLARIZATION AND LATTICE-RELAXATION EFFECTS

Since the "size" of the H^- ion will not be exactly the same as that of the negative ion it replaces, we expect some lattice distortion or relaxation to occur in the ground state. In the excited state, where the probability that the electron will be outside of the 1nn distance may be appreciable, lattice distortion effects may be even more pronounced. Also, under these circumstances it is expected that electronic and ionic polarization effects will become more important. In fact, it appears that in many instances in ionic crystals polarization and relaxation effects act cooperatively to increase enormously the effective radius of the wave function of the excited electron. Here we shall first discuss the polarization effects.

A. Polarization Effects

If one or both of the electrons of the U center have a significant probability of being outside of the lattice volume of the ion the defect replaces, as we expect to occur in the excited state, polarization of the lattice will occur. In principle, this effect can be taken into account through configuration interaction by writing the wave function as

$$\Psi(1,2,\cdots,M)=\sum_i C_i\Psi_i(1,2,\cdots,M), \quad (42)$$

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[9] U. Öpik and R. F. Wood, in Proceedings of the Skyland Conference on the Properties of Vacancies and Interstitials (to be published).

in which Ψ_i is of the form of Eq. (8) but with either or both of $\psi_{U,i}$ and $\psi_{c,i}$ representing excited configurations of the two groups. An equivalent but more convenient, direct, and elegant method is to use second-quantization and Green's-functions techniques of modern many-body theory to suggest an effective one-electron Hamiltonian which includes polarization effects.

For a system with a Hamiltonian such as Eq. (1), which contains only one- and two-body interactions, all physical quantities of interest to us are determined exactly by one- and two-particle Green's functions G and G_2. These are defined by

$$G(1;1')=-i\langle 0|T(\psi(1)\psi^\dagger(1'))|0\rangle \tag{43}$$

and

$$G_2(1,2;1',2')=i^{-2}\langle 0|T(\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1'))|0\rangle . \tag{44}$$

$\psi^\dagger(1)$ and $\psi(1)$ are creation and annihilation operators (Heisenberg representation), respectively, for a particle at the space-time point $\mathbf{r}_1 t_1$ (spin is neglected here and boldface numbers indicate instead that time is included) and $|0\rangle$ is the exact ground-state wave function in the occupation number representation. T is Wicks's chronological operator. The first-order density matrix $\rho(\mathbf{r};\mathbf{r}')$, of which $\rho_c(1;3)$ of the previous section is a special case, is related to G for equal times by

$$\rho(\mathbf{r};\mathbf{r}')=G(\mathbf{r}t;\mathbf{r}'t). \tag{45}$$

Furthermore, G and G_2 are related by the equation[10]

$$(i\partial/\partial t_1-h_1(\mathbf{r}_1))G(1;1') +i\int d\mathbf{r}_2 v(\mathbf{r}_1-\mathbf{r}_2)G_2(1,2;1',2^+)|_{t_2=t_1} =\delta(1-1'), \tag{46}$$

in which $v(\mathbf{r}_1-\mathbf{r}_2)$ contains all two-body interaction terms and h_1 contains all single-particle operators. The total energy of the crystal can be written in terms of G and G_2, but here we wish to determine an effective single-particle Hamiltonian, for which we need have only G. We note that G_2 can be formally eliminated from the problem by defining the self-energy operator M through the relationship

$$-\int d\mathbf{r}_2 M(1,2)G(2,1') \equiv i\int d\mathbf{r}_2 v(\mathbf{r}_2-\mathbf{r}_1)G_2(1,2;1',2^+)|_{t_2=t_1}. \tag{47}$$

This transforms Eq. (46) to

$$(i\partial/\partial t-h_1(\mathbf{r}_1))G(1,1')-\int d\mathbf{r}_2 M(1,2)G(2,1') =\delta(1-1'), \tag{48}$$

which can be Fourier-inverted with respect to time to give

$$(\epsilon+h_1(\mathbf{r}_1))G(\mathbf{r}_1;\mathbf{r}_1',\epsilon)-\int d\mathbf{r}_2 M(\mathbf{r}_1;\mathbf{r}_2,\epsilon)G(\mathbf{r}_2;\mathbf{r}_1',\epsilon) =\delta(\mathbf{r}_1-\mathbf{r}_1'), \tag{49}$$

or more simply in operator form

$$(\epsilon+h_1-M(\epsilon))G=1. \tag{50}$$

Also, we can write $G_0\equiv(\epsilon+h_1)^{-1}$ and obtain the Dyson equation

$$G=G_0+G_0MG, \tag{51}$$

which is itself sometimes used as the starting point for defining $M(\epsilon)$. Let us assume that a complete set of orthonormalized eigenfunctions of $h_1-M(\epsilon)$ exists, i.e.,

$$(h_1-M(\epsilon))\psi_k=\epsilon_k\psi_k. \tag{52}$$

We can then expand G in terms of them,

$$G(r_1;r_1')=\sum_k \frac{\psi_k(\mathbf{r}_1)\psi_k^*(\mathbf{r}_1')}{\epsilon-\epsilon_k} \tag{53}$$

and introduce it into Eq. (49) to obtain

$$\sum_k \psi_k(\mathbf{r}_1)\psi_k^*(\mathbf{r}_1')=\delta(\mathbf{r}_1-\mathbf{r}_1'). \tag{54}$$

This is just the closure relationship which we expect to hold for a complete set of basis functions. Although we have not established that Eq. (52) will in general generate a complete set of linearly independent one-electron functions of physical significance, we know that in the Hartree and HF approximations such sets are obtained and that the one-electron energies have some relevance (Koopmans's theorem). The Hartree result is obtained by approximating G_2 by

$$G_2(1,2;1',2')=G(1;1')G(2;2') \tag{55}$$

and the HF approximation by

$$G_2(1,2;1',2')=G(1;1')G(2;2') -G(1;2')G(2;1'), \tag{56}$$

with corresponding approximations for the M operator.

The energy dependence of the self-energy operator is already apparent in the HF approximation where nonlocal potentials are introduced by the exchange effect. Here we shall approximate M by

$$M=M_{\mathrm{HF}}+M_{\mathrm{pol}}, \tag{57}$$

where M_{pol} is a polarization contribution whose energy dependence we simply ignore.

Kohn[11] has shown that the effect of the M_{pol} operator beyond the HF approximation is to screen the impurity potential at large distances with the high-frequency dielectric constant, that is, $1/r \rightarrow 1/\kappa_\infty r$. More recently,

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[10] A full discussion of the derivation of this equation and of the significance of the plus sign superscript on the 2 in G_2 is given in L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

[11] W. Kohn, Phys. Rev. **110**, 857 (1958).

Morita *et al.*[12] have derived the same result and given several forms for the total Hamiltonian of the crystal plus defect which in principle are valid for small values of r as well. Practical difficulties associated with the solution of the problem are still formidable.

The most complete treatment of polarization effects in defect and exciton problems leading to a practical result from the computational side is that given by Toyozawa[7] and by Haken and Schottky.[8] The latter authors started from the quantum-field theoretic Hamiltonian

$$\int \psi^\dagger(\mathbf{r})h_1(\mathbf{r})\psi(\mathbf{r})d\tau + \frac{1}{2}\int\int \psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}\psi(\mathbf{r}')\psi(\mathbf{r})d\tau\, d\tau' \quad (58)$$

and expanded the one-particle creation and annihilation operators in a set of appropriately chosen functions. This set was selected so that the electronic polarization of the lattice produced by an electron or a hole is described in terms of tightly bound electron-hole states or excitons. Following closely the formalism developed for polaron theory, they arrived at a two-particle Schrödinger equation of the form

$$\left(-\frac{1}{2m_e^*}\nabla_e^2-\frac{1}{2m_h^*}\nabla_h^2-r^{-1}+U(r)\right)\psi(\mathbf{r}_e,\mathbf{r}_h) = E\psi(\mathbf{r}_e,\mathbf{r}_h)\,, \quad (59)$$

$$U(r)=(1-\kappa_\infty^{-1})r^{-1}\{1-\tfrac{1}{2}[\exp(-\rho_e r) + \exp(-\rho_h r)]\}+\text{const}\,, \quad (60)$$

in which ρ_e and ρ_h are constants proportional to the square root of the band gap and r is the electron-hole separation. We note that

$$-1/r+U(r)\to -1/\kappa_\infty r+\text{const} \quad \text{at large } r\,, \quad (61)$$

$$-1/r+U(r)\to -1/r+\tfrac{1}{2}(1-1/\kappa_\infty)(\rho_e+\rho_h) + \text{const} \quad \text{at small } r. \quad (62)$$

Since it is to be expected that polarization effects vanish when $r\to 0$, the above form suggests we choose the constant in Eq. (60) as

$$\text{const}=-\tfrac{1}{2}(1-1/\kappa_\infty)(\rho_e+\rho_h)\,. \quad (63)$$

This form is just the classical result for the polarization energy of two point charges well separated in a dielectric medium in which the polarization is "turned on" at a radius of ρ^{-1} from the point charge.

The assumptions under which Eq. (59) was derived make it doubtful that the form of $V_{\text{eff}}\equiv r^{-1}+U(r)$ is valid for small r. Nevertheless, it is the only simple form developed thus far which takes into account the interaction of the polarization clouds of the electron and hole at intermediate values of r and their mutual cancellation at small r's. Furthermore, the form is easily extended to include the effects of ionic polarization, for which one obtains

$$\begin{aligned}U'(r)=(1-\kappa_\infty^{-1})\{-(\rho_e+\rho_h)/2+r^{-1}-(2r)^{-1} &\\ \times[\exp(-\rho_e r)+\exp(-\rho_h r)]\}+(\kappa_\infty^{-1}-\kappa_{\text{st}}^{-1}) &\\ \times\{-(v_e+v_h)/2+r^{-1}-(2r)^{-1}[\exp(-v_e r) &\\ +\exp(-v_h r)]\}\,, &\quad (64)\end{aligned}$$

where $v_e=(2m_e^*\omega_{\text{LO}})^{1/2}$, κ_{st} is the static dielectric constant, and ω_{LO} is the longitudinal optical phonon frequency.

For a lattice defect such as the U center or F center, m_h^* can be assumed to be infinite, thus eliminating the kinetic-energy term in Eq. (59). Note, however, that polarization effects due to the hole remain. Fowler[2] has used the THS theory in a semicontinuum calculation of the F center and has shown that the effective interaction can give a radius of the relaxed excited state which apparently accounts nicely for the long lifetime measured by Swank and Brown.[13]

We incorporate polarization effects into our second model simply by adding $U'(r)$ defined above to the HF Hamiltonian defined in Eq. (41). Corresponding to Eq. (57), we make the very loose association

$$M_{\text{HF}}=\int v_{13}[\rho(3,3)-2^{-1}\rho(1,3)]P_{13}d\tau_3\,, \quad r<R_a \quad (65)$$

and

$$M_{\text{pol}}=U'(1)\,, \quad \text{all } r. \quad (66)$$

B. Lattice Relaxation

We turn now to the term $E_{\text{cr}}\equiv\langle\psi_c|H_{\text{cr}}|\psi_c\rangle$ in Eq. (19) of the previous section. It gives the remaining energy of the crystal with which we shall be concerned and includes the self-energies and interaction energies of all of the other ions in the crystal. We shall calculate these energies entirely from classical ionic crystal theory. We write

$$E_{\text{cr}}=E_{\text{cr}}(R^0)+\Delta E_{\text{cr}}(R)\,, \quad (67)$$

where $E_{\text{cr}}(R^0)$ is the energy at the equilibrium positions of the ions in the perfect crystal (denoted collectively by R^0) and $\Delta E_{\text{cr}}(R)$ is the change in E_{cr} as a function of the cubic relaxation. A Born-Mayer-Verwey form is used for the repulsive potential $V_{\mu\nu}$ between ions μ and ν at a distance $R_{\mu\nu}$ apart. $\Delta E_{\text{cr}}(R)$ can be divided into a Coulomb part ΔE_{coul} and a repulsive part ΔE_{rep}. The details of the calculation of these quantities are given in a recent paper[14] [Eq. (28) of which is for ΔE_{rep} rather than E_{rep} as shown], and will not be repeated here.

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[12] A. Morita, M. Azuma, and H. Nava, J. Phys. Soc. Japan **17**, 1570 (1962).

[13] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).

[14] R. F. Wood, Phys. Rev. **151**, 629 (1966).

Finally, we have corresponding to the terms in Eq. (1)

$$E_{\mathrm{tot}}(R)=E_U(\beta_a,\beta_b,R)+E_{\mathrm{int}}(\beta_a,\beta_b,R)+E_{\mathrm{cr}}(R)\,, \quad (68)$$

where the notation is intended to show that E_U and E_{int} depend explicitly on the variation parameters β_a and β_b as well as the nearest-neighbor distance, whereas E_{cr} depends only on the variable 1nn distance.

IV. DETAILS AND RESULTS OF THE CALCULATIONS

The input data for the calculations associated with the classical ionic crystal part of the energy ΔE_{cr} are gathered together in Table I. The quantity R_0 is the interionic distance; R_+ and R_- are the effective radii defined by Fumi and Tosi[15] and used in determining the constants B and C appearing in the expressions for ΔE_{rep} in Ref. 14. ρ is the compressibility, which also is needed for the calculations.

The HF free-ion orbitals and energies were taken from work by Bagus.[16] We have used his so-called minimal-basis set. In most of the calculations with the first model, the K$^+$ 1s orbitals were included as well as the 2s, 2p, and 3s, 3p, even though they have very small effects on the energies. In the second model, the 1s orbital is neglected altogether. Although we shall not go into the details here, we perhaps should mention that as a result of the construction of l-dependent exchange potentials we actually work with core orbitals somewhat modified from the free-ion HF orbitals.

The calculations of E_U and E_{int} with the first model were done for the ground state for several different positions of the 1nn ions and combined with E_{cr} to obtain new equilibrium positions of the ions. The minima of the curves were so flat that, considering other sources of error, the values of the displacements obtained were rounded off to the nearest half of a percent. We assume the Franck-Condon principle to hold and take the same values for the excited state when calculating the optical transition energies. The first row in Table II shows the results of these calculations. The other figures in the table have the following meaning: β_a and β_b are the values of the variation parameters in Eq. (17) and its analog for which the energy E_U+E_{int} is a minimum. The unprimed quantities are for the ground state and the primed quantities for the excited state; ΔE_{th} is the theoretical transition energy and ΔE_{exp} is the corresponding experimental value. For the first model, the radial part of ϕ_b in the excited state is given by a single function $r\exp(-\beta_b r)$. A few test cases on KCl showed that the optimum values of β_a differed so little in the ground- and excited-state calculations that it was unnecessary to vary it in the latter. Of course, the second term in Eq. (12) and the third term in Eq. (34) vanish in the excited state because of symmetry.

TABLE I. Input data for the calculations. The meaning of the quantities is given in the text. Units are indicated in the KCl column.

	Crystal		
	KCl	KBr	KI
R_0	3.14 Å	3.30	3.53
R_+	1.554 Å	1.554	1.554
R_-	1.678 Å	1.814	2.013
ρ	0.324 Å^{-1}	0.333	0.346

TABLE II. Some results for various quantities obtained from the calculations. "1st" and "2nd" after KCl refer to the models discussed in text. $(1+\delta_c)R_0$ is the new equilibrium distance of the 1nn ions. The other quantities are defined in the text. Units are given in the first column.

	Crystal			
	KCl (1st)	KCl (2nd)	KBr	KI
δ_c	−0.020	−0.020	−0.025	−0.030
E_g	−1.0712 a.u.	−1.1428	−1.0647	−1.0490
β_a	1.0213	1.0213	1.0250	1.0284
β_b	0.5106	0.5106	0.4920	0.4649
E_e	−0.8666 a.u.	−0.9242	−0.8632	−0.8576
β_a'	1.0213	1.0213	1.0250	1.0284
β_b'	0.2801	see text	0.3160	0.3410
ΔE_{th}	5.57 eV	5.95	5.48	5.21
ΔE_{exp}	5.79 eV	5.79	5.44	5.08

It was not possible for us to carry out exactly comparable calculations with the first and second models because of difficulties with the terms $(ab|ab)$ and $(ab|ba)$ in Eq. (34). When ψ_a of Eq. (16) and ψ_b are substituted into these integrals, terms up to the fourth order in $c_{\nu,j}$ appear just as they do to the second order in Eq. (36). We treated these terms by making what we believe to be reasonably accurate approximations in the first model where only 1nn ions are included. In the second model, no attempt was made to treat them. We did find, however, that the effects of the normalization factors N_a and N_b and the effects due to these orthogonalization terms tended to compensate one another. Therefore, in the second model we calculate $(ab|ba)$ and $(ab|ab)$ using only ϕ_a of Eq. (17) and ϕ_b. In all other respects (except, of course, for the numerical methods already mentioned in the last part of Sec. II), the calculations can be made essentially equivalent.

The constants appearing in Eqs. (59)–(64) were chosen as follows. The effective mass which is supposed to include polarization effects was taken as 0.6. We took $\kappa_\infty=2.13$ and $\kappa_{\mathrm{st}}=4.68$. ρ_e and ρ_h were taken equal, so that it is assumed, in effect, that a static hole or vacancy and the moving electron are equally effective in polarizing the crystal. Instead of relating ρ_e and ρ_h to the square root of the band gap, the results of Mott and Littleton[17] on the polarization around a vacancy were used to determine them via Eq. (63). v_e and v_h were

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

[16] P. S. Bagus, Phys. Rev. **139**, A619 (1965).

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

TABLE III. Intermediate results for S_{olap} and the polarization energy for ϕ_b, the more extended of the two functions in Eq. (11).

Model	S_{olap} (b,b) 1nn ions	 all ions	E_{pol} (b,b)
		Ground	
1st	0.0775	0.0775	0.0000
2nd	0.0773	0.1112	−0.0248 a.u.
		Excited	
1st	0.1015	0.1015	0.0000
2nd	0.0950	0.4409	−0.0505 a.u.

assumed equal and their value was determined as indicated after Eq. (64) with $\omega_{\text{LO}}=3.96\times10^{13}$ rad/sec. We found $\rho_e=\rho_h=0.1969$ and $v_e=v_h=0.0339$. χ_{HF} in Eq. (41) was given a value of +0.82 eV, which is the difference between $\frac{1}{2}(1-\kappa_\infty^{-1})\rho_e$ and the experimental electron affinity $-\chi_{\text{exp}}(0.6\text{ eV})$. This assumes that χ_{exp} does not include ionic polarization effects, but this assumption may not be entirely correct.

In order to give an indication of the importance of the electronic structure of ions more distant than the 1nn and of polarization effects, we show in Table III a comparison of some of the intermediate quantities entering into the calculations with the two models. The quantity S_{olap} is the sum of the squares of the overlap integrals of the more diffuse trial function ϕ_b with the orbitals on the neighboring ions. It corresponds to the second term in Eq. (18). S_{olap} gives an indication of the spatial extent of the wave function and of the importance of overlap effects. $E_{\text{pol}}(b,b)$ is the expectation value of $U'(r)$ from Eq. (64) with respect to ϕ_b. Unfortunately, E_{pol} does not give the entire effect of polarization because the core energies entering into Eqs. (39) and (40) are also modified by $U(r)$ in a manner which is not easily separated out in our calculations. Here again, however, normalization effects tend to cancel the overlap effects and E_{pol} alone should give at least a fairly good idea of the importance of polarization effects in this model. For the excited state with the second model, S_{olap} and E_{pol} are given for the first trial function only in Eq. (69) below.

In the excited-state calculations with the second model, we chose the radial part of the p function to be

$$\phi_b=\sum_{i=1}^{4}B_i\phi_{bi}. \tag{69}$$

Here ϕ_{b1} and ϕ_{b2} were chosen to be $2p$ and $3p$ Slater orbitals, respectively

$$[\sim r\exp(-\beta_{b1}r)\quad\text{and}\quad\sim r^2\exp(-\beta_{b2}r)].$$

β_a and β_{b1} were set at the values determined for the first model and β_{b2} was chosen to be somewhat more compact than the outer part of an effective-mass $n=2$ hydrogenic function. Two more Slater p orbitals were added to ϕ_b, and these were again chosen to be $2p$ and $3p$ functions with exponents selected so as to duplicate closely the outer portions of the $n=2$ and $n=3$ effective-mass hydrogenic functions. We used $\beta_1=0.3$, $\beta_2=0.26$, $\beta_3=0.14$, and $\beta_4=0.9$. With the number of terms in Eq. (69) and with the choice of parameters, we expect also to obtain a fairly good approximation to the second excited state of the p-like symmetry. We included an f term in some of the trial calculations, but this contributed very little, so we subsequently dropped it. The ionic polarization terms in Eq. (64) (those containing v_e and v_h) were neglected when calculating the excited levels reached by an optical transition. As the lattice relaxes, though, the ionic motion can begin to follow the electron, and we therefore included these terms in $U(r)$ for all values of the relaxation parameter other than the one corresponding to ground-state equilibrium.

TABLE IV. Results of the relaxation calculation. E_1 and E_2 are the lowest energy levels of p-like symmetry and E_{cond} gives the bottom of the conduction band. All of these quantities are in eV and contain the contribution from ΔE_{cr} in Eq. (67). The B's are the coefficients in Eq. (69) for E_1. The first row shows the results when only electronic polarization is allowed. All other rows include the effects of ionic motion as well. δ is the percentage change in the new 1nn distance.

δ	E_1	E_2	E_{cond}	B_1	B_2	B_3	B_4
−2	−2.310	−1.864	−1.612	0.7312	0.2071	0.1136	0.0046
−2	−2.342	−1.966	−1.848	0.7021	0.1944	0.1534	0.0083
0	−2.615	−2.362	−2.254	0.4914	0.2501	0.3179	0.0365
+2	−2.851	−2.673	−2.579	0.2906	0.1762	0.5355	0.1196
+4	−3.025	−2.881	−2.807	0.1359	0.0496	0.6744	0.2699
+6	−3.112	−2.974	−2.922	0.0444	−0.0507	0.6963	0.4223
+8	−3.072	−2.929	−2.897	−0.0023	−0.1121	0.6678	0.5318

Table IV shows the energies of the first two excited states of Γ_4^- symmetry and the bottom of the conduction band as a function of the relaxation parameter δ. The coefficients of the functions in Eq. (69) for the first excited state are also shown. The energies include the contribution from lattice relaxation, i.e., ΔE_{cr} of Eq. (67). It should be kept in mind that, from the formulation of the second model, the energy of the bottom of the conduction band includes the contribution from the polarization associated with the hole as well as that from the electron. It is given by χ_{exp} plus the constant part of Eq. (60) if ionic polarization is not included and by χ_{exp} plus the constant part of Eq. (64) if ionic polarization is included.

V. DISCUSSION

The results presented in Table II show that both models give fairly good values of the transition energies. They are significantly better than the point-ion results of Gourary, who obtained transition energies about 20% lower than the experimental values. Nevertheless, since the two models are rather different, it can be seen once again that the ability of a model to predict a single transition energy is not a very satisfactory criterion for the validity of the model.

In the ground state, the values of S_{olap} shown in Table III for the 1nn ions are virtually the same in the two models. Inclusion of the electronic structure on all of the other ions in the second model changes the result somewhat, primarily because of the 2nn, but S_{olap} is still small in value, thus indicating a rather compact function. The situation is different in the excited state, where for the first model S_{olap} is still small but for the second model it has become large. In the latter case about 25% of S_{olap} comes from the 1nn ions, 50% from the 2nn ions, and 25% from all other ions. As we shall see below, even in the excited state the wave functions in the two models are fairly similar in their degree of localization. We therefore conclude that the neglect of the structure of ions further out than the 1nn, as is done in the first model, would be an approximation of dubious validity unless there were effects which compensated for the overlap contributions to the energy.

The results obtained with the second model indicate that polarization effects are significant even in the ground state. Although not shown in Table III, even the most compact $1s$ function has a few tenths of an eV of polarization energy associated with it, whereas one tends to think that polarization effects should be negligible for such a function. Also, the value of -0.0248 a.u. for the polarization energy of the more diffuse function ϕ_b in the ground state seems rather large. We therefore suspect that the THS theory overestimates somewhat the polarization energy for compact functions. It would not be particularly surprising if it did, since the theory is not expected to be valid at small electron-hole separation. On the other hand, in the ground state of a perfect crystal, where polarization effects presumably vanish because the electron and hole have recombined, there are still correlation effects between electrons on different ions as well as between those on the same ion. Perhaps the THS theory can be considered as taking some of this correlation energy into account as well.

As one might surmise from the foregoing discussion together with the fact that the first and second models both give fairly good results for the transition energies in KCl, there is a tendency for electronic structure and polarization effects to cancel each other. This tendency is particularly pronounced for wave functions of intermediate degrees of diffuseness.

Table IV shows the effects of lattice relaxation, and we can see quite clearly the pronounced spreading of the wave function as the lattice relaxes. This is indicated by the increasing values of the coefficients of the diffuse functions ϕ_{b3} and ϕ_{b4}. As was to be expected, the situation here is quite similar to that in the F center. In fact, the core of the H^- ion in the excited state, consisting of a proton and a tightly bound electron (neutral hydrogen), has very little effect on the energy and wave function of the excited electron after relaxation and in turn is very little affected by the excited electron. This may allow the neutral core to diffuse readily into the lattice or perhaps to form a molecular complex with a negative ion and thus help explain the absence of an easily identifiable luminescence in contrast to the F-center results. In general, the excited states of the U center are so similar to those of the F center that it seems likely K and L bands are associated with the former as well as with the latter.[18]

It is interesting to compare our results for the excited state with the second model with those obtained from effective-mass theory, where the energy levels are given relative to the bottom of the conduction band by

$$\epsilon_n = \epsilon_{\text{cond}} - m^* 13.605/mn^2\kappa^2 , \qquad (70)$$

in which n is the principal quantum number and κ is the dielectric constant. With $\kappa=\kappa_\infty$ we find $\epsilon_2=-2.468$ eV and $\epsilon_3=-2.218$ eV, whereas the corresponding quantities calculated here are $\epsilon_2=-2.716$ eV and $\epsilon_3=-2.270$ eV. Thus the $n=3$ level appears to be energetically close to the effective-mass state and this is borne out by the very large value of B_4 which we obtained for this state. B_4 is the coefficient of a $3p$ term which, as stated earlier, was chosen to duplicate closely the outer portion of an effective-mass function for $\kappa=\kappa_\infty$. The energy of the $n=2$ level, on the other hand, differs markedly from the effective-mass result and its wave function is considerably more compact, as indicated by the large value of B_1 and the small value of B_3. In fact, the data in Table IV show that for this state it does not matter greatly whether or not the ionic part of $U'(r)$ is omitted. The effect on the second excited state whose orbital is already quite effective-mass-like is more pronounced, as might be expected from the form of $U'(r)$. The large value of B_1 also indicates that the first excited state wave function is not a great deal more diffuse in the second model than it is in the first.

ACKNOWLEDGMENT

We wish to thank J. F. Cooke for useful discussions.

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[18] See discussion and references in D. Y. Smith and G. Spinolo, Phys. Rev. 140, A2121 (1965).