SOVIET PHYSICS JETP VOLUME 4, NUMBER 6 JULY,1957

Many Electron Treatment of Motion of an Electron (Hole) in a Deformed Crystal. II.

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(Submitted to JETP editor September 26,1956)
J. Exptl. Theoret. Phys. (U.S.S.R.) 31, 1002–1011 (1956)

A many electron treatment of the motion of an electron (hole) is given for an ionic crystal for the case of unfixed nuclei and the presence of vacancies of any ion. The theory is developed in the close coupling approximation using antisymmetrized wave functions and can be used also for the states of small radius. A method of calculation of the deformation of crystal and the energy of local self consistent state are described.

IN a previous work[1] we described a technique of calculation of the local state of an electron (hole) in a perturbed crystal on the assumption that the external field does not lead to displacements of the nuclei while deforming the electron shells of the ions. This means that only the polarization of the lattice by the field of the electron (hole) was considered. Since the Hartree approximation was used, it was not possible to describe correctly the motion of the hole and to take into account the exchange forces between ions which provide for the equilibrium of the lattice together with the Coulomb forces.

For a step-by-step calculation of the deformation of the lattice, which certainly exists near the local level of the electron and substantially influences its energy, a many electron formulation of the problem should allow calculation of the exchange forces. Therefore such a formulation should be based on an antisymmetrized lattice function, i.e., the Fock approximation. The present work is devoted to this generalized problem.

1. BASIC SIMPLIFYING ASSUMPTIONS

We shall consider a binary cubic ionic lattice with one vacancy at the origin of the coordinates. Let us assume that an extra electron (hole) is present in the lattice if a negatively charged (positively charged) ion is removed from the lattice. We shall denote by $\mathbf{r}_s^l$ and $\mathbf{R}_s^l = \mathbf{r}_s^l + \mathbf{u}_s^l$ the equilibrium and the displaced positions of the nucleus of the s th ion in the lth cell (s=1, 2 for + and – ion). By $\rho_s^{l\lambda}$ we shall denote the totality of the $3N_s$ coordinates of the N_s electrons of the ion s, l (λ is an index of the permutation of the electrons of the lattice), and by $\rho_{sn_s}^l$ we shall denote the radius vector of the n_s electron ($n_s = 1,2, \ldots, N_s$).

The lattice function is taken in the form of a linear combination of antisymmetrized products Ψ_s^l of the wave functions of individual ions. Let $\psi_s^l(\rho_s^{l\lambda})$ denote a wave function of the normal ion and $\varphi_s^l(\rho_s^{l\lambda})$ the wave function of an anomalous ion on which an electron (s =1) or a hole (s=2) is localized. We shall consider an electron to be moving about the positively charged ions and a hole about the negatively charged ions. Then

$$\Psi_s^l = (N!)^{-1/2} \sum_\lambda (-1)^\lambda \varphi_s^l(\boldsymbol{\rho}_s^{l\lambda}) \prod_{s'l'}{}' \psi_{s'}^{l'}(\boldsymbol{\rho}_{s'}^{l'\lambda}). \quad (1)$$

The wave functions of the individual ions will be considered to be orthogonal in the sense that

$$\int \varphi_s^{*l}(\rho_s^{l\lambda}) \prod{}' \psi_{s''}^{l''}(\boldsymbol{\rho}_{s''}^{l''\lambda}) \varphi_{s'}^{l'}(\boldsymbol{\rho}_{s'}^{l'\lambda'}) \prod{}' \psi_{s''}^{l''}(\boldsymbol{\rho}_{s''}^{l''\lambda'})\, d\tau = \delta_{\lambda\lambda'}; \quad (2)$$

where $\delta_{\lambda\lambda'} = 0$ if λ and λ' differ by an interchange of only one pair of electrons between different ions or by an interchange of only one electron between ions s, l and s', l' so that

$$\int \Psi_s^{l*} \Psi_{s'}^{l'}\, d\tau = \delta_{ss'}. \quad (3)$$

It is evident that the wave functions of ions may always be orthogonalized without a change in the antisymmetrized product. In doing so we shall neglect the interchange of ψ_s^l and φ_s^l in displacing ions by $\mathbf{u}_s^l$.

In distinction to the works of Pekar[2] and Heisenberg[3] we shall include the effect of the electron (hole) on the wave function of the remaining ions. For a freely moving electron this effect is apparent mainly in polarization of the environment; it causes a slight change in the periodic potential and consequently a lowering of the depth of the conduction band.[4] The interaction of the electron with the dipoles introduced by the same defect results in a change in the potential of the defect (in the macroscopic approximation it decreases it by n_0^2 times, where n_0 is the optical index of refraction). We shall include this effect only as polarization of the surrounding ions, neglecting the non-uniformity of the field of the electron and the defect within the boundaries of each ion, and we shall assume that the polarization follows adiabatically the motion of the electron from one lattice point s, l to another. This is true if the kinetic energy of the electron (hole) is small compared to the lattice excitation energy.

2. THE WAVE FUNCTION OF THE SYSTEM IN THE ADIABATIC APPROXIMATION

The Hamiltonian of the lattice, $\hat{H}$, is equal to the sum of the Hamiltonians of the individual ions $\hat{H}_s^l$, of the interaction energy of the different ions $\hat{H}_{ss'}^{ll'}$ and the energy of all ions in the external field $\mathbf{E}^0$ with the potential v $(\mathbf{r})$:

$$\hat{H}^0 = \sum_{s,l} H_s^{0l} = \sum_{s,l} e\left[z_s v\,(\mathbf{R}_s^l) - \sum_{n_s=1}^{N_s} v\,(\rho_{sn_s}^l)\right], \tag{4}$$

where z_s is the nuclear charge of the sth ion.

Following the adiabatic approximation, we shall determine the wave function of all ions for an arbitrary position of the anomalous site s,l. One can use the variation principal by minimizing the average Hamiltonian, $\hat{H}$, constructed from the trial functions Ψ_s^l:

$$H\,\binom{ll}{ss} = \int \Psi_s^{l*}\hat{H}\Psi_s^l\,d\tau \tag{5}$$

$$= \sum_{s'l'}\Bigl\{\int \psi_{s'}^{l'*}\,[\hat{H}_{s'}^{l} + \hat{H}_{s'}^{0l'}]\,\psi_{s'}^{l'}\,d\tau_{s'}'$$

$$+ {}^1/_2 \sum_{s''l''}{}' \iint \psi_{s'}^{l'*}\psi_{s''}^{l''*}\,H_{s's''}^{l'l''}\,\psi_{s''}^{l''}\psi_{s'}^{l'}\,d\tau_{s'}^{l'}\,d\tau_{s''}^{l''}$$

$$- \frac{e^2}{4}\sum_{s''l''}^{(n)}{}' N_{s'}N_{s''} \iint \psi_{s'}^{l'*}\,(\ldots\boldsymbol{\rho}'\ldots)$$

$$\times\,\psi_{s''}^{l''*}(\ldots\boldsymbol{\rho}''\ldots)\frac{1}{|\boldsymbol{\rho}'-\boldsymbol{\rho}''|}\psi_{s''}^{l''}(\ldots\boldsymbol{\rho}''\ldots)\psi_{s'}^{l'}(\ldots\boldsymbol{\rho}''\ldots)d\tau'\,d\tau''\Bigr\}.$$

In view of the orthogonality condition of Eq. (2), it is sufficient to retain in the product $\Psi_s^{l*}\,\Psi_s^l$ only the identical rearrangments and rearrangements which differ by one transposition. In the latter case it is necessary to retain only those terms of the Hamiltonian which contain the coordinates of the transposed electrons ρ' and ρ''. The exchange integrals will be retained only for the closest neighbors, whose number we shall denote by n. The sums denoted by primes are carried out over all terms except those where s', $l' = s''$, l''. For s', $l' = l, s$ or $s''l'' = s$, l it is necessary to change ψ_s^l by φ_s^l.

We shall assume that the difference between $\psi_{s'}^{l'}$ and the wave function of the ground state of the isolated ions $\underline{\bar{\psi}}_{s'0}^{l'}$ is small. In the expansion

$$\psi_{s'}^{l'} = \sum_{i=0}^{\infty} c_{s'i}^{l'}\psi_{s'i}^{l'}, \quad \sum_{i=0}^{\infty} |c_{s'i}^{l'}|^2 = 1, \tag{6}$$

where $\psi_{si}^{l'}$ are the wave functions of the excited states, we shall assume that the first term $c_{s'0}^{l'} \approx 1$ plays the most important role. The coefficients c_{si}^{l}, $i \geq 1$ will also serve as parameters of the approximation. Inserting the expansion of Eq. (6) into Eq. (5) we shall retain only the terms to the second order in $c_{si}^{l'}$ in the integrals for $\hat{H}_{s}^{l'}$ and in the Coulomb integrals. For those states which give a contribution for the dipole moment of the ions

$$P_{s'x}^{l'} = -eN_{s'} \times \sum_{i=1}^{\infty}[(0\,|\,x\,|\,i)\,c_{s'i}^{l'} + (0\,|\,x\,|\,i)^*\,c_{s'i}^{l'*}], \tag{7}$$

where

$$(0\,|\,x\,|\,i) = \int \psi_{s'0}^{l'*}\,\rho\psi_{s'i}^{l'}\,d\tau_{s'}^{l'}.$$

Thus the dipole-dipole interaction between ions is taken into account. In the exchange integrals and in the integrals of $\hat{H}_s^{0l'}$, we shall retain only the first order terms. In Eq. (7) it is sufficient to retain the terms linear in $c_{si}^{l'}$ since only the product of $\mathrm{P}_{s'}^{l'}$ and vacancy fields of the excess electron and $\mathbf{E}^0$ (all considered small) enter into the energy. If this condition of small fields is not met it is not possible to consider the difference between ${}_{s'}^{l'}$ and $\psi_{s0}^{l'}$ small. Then Eq. (5) takes the form

$$H\binom{ll}{ss} = (M-1)(E_{10}+E_{20}) + \bar{E}_{s0} \qquad (8)$$

$$+ \sum_{s'l'} \Big\{ \sum_{i=1}^{\infty} |c_{s'i}^{l'}|^2 (E_{s'i} - E_{s'0})$$

$$+ {}^1/_2 \sum_{s''l''}{}' [e_{s'} e_{s''} / R - 2e_{s''} \mathbf{P}_{s'}^{l'} \mathbf{R} / R^3$$

$$+ \mathbf{P}_{s'}^{l'} \mathbf{P}_{s''}^{l''} / R^3 - 3 (\mathbf{P}_{s'}^{l'} \mathbf{R}) (\mathbf{P}_{s''}^{l''} \mathbf{R}) / R^5]$$

$$+ e_{s'} v (\mathbf{R}_{s'}^{l'}) - \mathbf{P}_{s'}^{l'} \mathbf{E}^0 (\mathbf{R}_{s'}^{l'}) - \sum_{s''l''}^{(n)}{}' [\omega_{s'0} (\mathbf{R})$$

$$+ \sum_{i=1}^{\infty}{}' (c_{s'i}^{l'} \omega_{s'i} (\mathbf{R}) + c_{s'i}^{l'*} \overset{*}{\omega}_{s'i} (\mathbf{R}))] \Big\}$$

where for thesake of brevity we write the radius vector $R_{s\,s}^{l',l''}$ simply as R. $E_{s'i}$ is the ith energy level of the s'thion, $e_{s'} = e\,(z_{s'} - N_{s'})$ is its charge, M is the numberof cells in thelattice, E_{s0} is the energy of the anomalous ion in its ground state;

$$\omega_{s'i} = \frac{e^2}{2} N_{s'} N_{s''} \iint \psi_{s'0}^{l'*}(\ldots \boldsymbol{\rho}' \ldots)\, \psi_{s''0}^{*\,l''} (\ldots \boldsymbol{\rho}'' \ldots) \qquad (9)$$

$$\frac{1}{|\boldsymbol{\rho}' - \boldsymbol{\rho}''|} \psi_{s'i}^{l'}(\ldots \boldsymbol{\rho}'' \ldots) \psi_{s''0}^{l''}(\ldots \rho' \ldots) d\tau' d\tau''.$$

and $\omega_{s'0}$ has an analogous value but contains only the zero order functions and is multiplied by a factor of 1/2. In particular, the sums over s', l', s'', l'' contain terms for the anomalous ion for which the charge e_s, the dipole moment, and the coefficients ω_{s0}, ω_{si} have different values:

$$\bar{e}_s, \; \bar{\mathbf{P}}_s^l, \; \bar{\omega}_{s0}, \; \bar{\omega}_{si}.$$

It is convenient to find the minimum of Eq. (8) in $c_{s'i}^{l'}$, by the method described by one of the authors,[5] in two steps: first, one finds therelative minimum of $H\binom{ll}{ss}$ for arbitrary fixed $P_{s'}^{l'}$, i.e., under the conditions of Eq. (7), and then one minimizes $H\binom{ll}{ss}$ over $P_{s'}^{l'}$. In the first step,

$$H_{ss}^{ll} = \sum_{s'l'} \Big\{ \frac{1}{2\alpha_{s'}} (\mathbf{P}_{s'}^{l'})^2 \qquad (10)$$

$$+ \sum_{s''l''}^{(n)}{}' \mathbf{P}_{s'}^{l'} \beta_{s's''}^{l'l''} (\mathbf{R}) + U (\ldots \mathbf{R} \ldots) \Big\}$$

$$+ (M-1)(E_{10}+E_{20}) + \bar{E}_{s0} + \sum_{s'l'}{}' \{ e_{s'} v (\mathbf{R}_{s'}^{l'})$$

$$- \mathbf{P}_{s'}^{l'} [\mathbf{E}^0 (R_{s'}^{l'}) + {}^1/_2 \mathbf{E}' (R_{s'}^{l'})]$$

$$+ {}^1/_2 \sum_{s''l''}{}' [e_{s'} e_{s''} / R - 2e_{s''} \mathbf{P}_{s'}^{l'} \mathbf{R} / R^3] \},$$

where

$$\alpha_{s'} = 2e^2 N_{s'}^2 \operatorname{Re} \sum_{i=1}^{\infty} |(0|x|i)|^2 / (E_{s'i} - E_{s'0})$$

where the coefficient of polarizability of the s' th ion

$$\beta_{s's''x} = \frac{2e}{\alpha_{s'}} \operatorname{Re} \sum_{i=1}^{\infty} (0|x|i)\, \omega_{s'i} (\mathbf{R}) / (E_{s'i} - E_{s'0});$$

where $U(\ldots R \ldots)$ is a function depending on the separation R of the ion s', l' from its n closest neighbors and is approximately equal to the sum of the central pair interactions $U \approx \sum_{s''l''}^{(n)}{}' u_j(R)$. Since normal ions have spherical symmetry, then $\alpha_{s'}$ is a scalar and $\beta_{s's''}$ has the direction of R and depends only on its modulus, while β_{12} and β_{21} are different (for anomalous ions $\bar{\beta}_{12}$ and $\bar{\beta}_{21}$).

$$\mathbf{E}' (\mathbf{R}_{s'}^{l'}) = \sum_{s''l''}{}' [3 (\mathbf{P}_{s''}^{l''} \mathbf{R}) \mathbf{R} / R^5 - \mathbf{P}_{s''}^{l''} / R^3] \qquad (11)$$

determines the field of all dipoles $P_{s''}^{l''}$ at the point $R_{s'}^{l'}$.

Thus the problemof finding the function $\psi_{s'}^{l'}$ results in theproblem of determining the dipole moment $P_{s'}^{l'}$, which may be solved by a method pointed outpreviously [1] and already carried out in the work of one of the authors[6] for the particular case of the absence of vacancies and displacements.

3. EVALUATION OF THE IONIC DIPOLE MOMENTS

We shall expand $H\binom{ll}{ss}$ in orders of the displacements of the ions $\mathbf{u}_{s'}^{l'}$, retaining the quadratic form relative to the dipole moments of the displacements $\mathbf{p}_{s'}^{l'} = e_{s'} \mathbf{u}_{s'}^{l'}$ and the electron shells $P_{s'}^{l'}$. Completing Eq. (7) for the energy of an ideal crystal, and taking into account that

$$\sum_{s''l''}{}' \mathbf{r} / r^3 = 0, \qquad (12)$$

$$\sum_{s''l''}{}' [3 (\mathbf{r}, \mathbf{u}_{s'}^{l'}) \mathbf{r} / r^5 - \mathbf{u}_{s'}^{l'} / r^3] = 0,$$

$$\sum_{s''l''}^{(n)}{}' \boldsymbol{\beta}_{s's''} (\mathbf{r}) = \sum_{s''l''}^{(n)}{}' \beta_{s's''} \mathbf{r} / r = 0, \;\; \mathbf{r} \equiv \mathbf{r}_{s's''}^{l'l''},$$

we introduce a displacement field E″ expressed by means of $p_s^{l''}$ analogously to the formula of Eq. (11) for E′. Then using the condition $\partial H\binom{ll}{ss}/\delta P_s^{l'} = 0$ we obtain

$$\mathbf{P}_{s'}^{l'} = \alpha_{s'}\{(\mathbf{E}' + \mathbf{E}'')_{\mathbf{R}_{s'}^{l'}} - \sum_{s''l''}^{(n)} (\mathbf{u}_{s'}^{l'} - \mathbf{u}_{s''}^{l''})\, \nabla \boldsymbol{\beta}_{s's''}|_{\mathbf{r}} + \mathbf{G}_{s'}^{l'}\}, \tag{13}$$

where

$$\mathbf{G}_{s'}^{l'} = \mathbf{E}^0(\mathbf{r}_{s'}^{l'}) + (\bar{e}_s - e_s)\,\mathbf{r}_{s's}^{l'l}/|\mathbf{r}_{s's}^{l'l}|^3 - e_\sigma \mathbf{r}_{s'}^{l'}/|\mathbf{r}_{s'}^{l'}|^3 + \boldsymbol{\beta}_{s'\sigma'}\gamma_{s'\sigma'}^{l'0} - (\bar{\boldsymbol{\beta}}_{\sigma s} - \boldsymbol{\beta}_{\sigma s})\,\gamma_{s's}^{l'l}. \tag{14}$$

Here we neglect the small change of the field $G_s^{l'}$ which is due to the displacement of the ion s', l' by $u_s^{l'}$. The type of ionic vacancy is designated by σ and the symbols $\gamma_{s's}^{l'l}$ and $\gamma_{s'\sigma}^{l'0}$ are equal to unity if the ion $s'l'$ is the nearest neighbor of the corresponding ion s, l and of a vacant lattice site, and equal to zero in the opposite case.

For an ideal lattice, where $G_s^{l'} = 0$, Eqs. (13) are solved by expanding the quantities $P_s^{l'}$ and $p_s^{l'}$ and the fields E′, E″ in plane waves. The presence of a vacant lattice site and also of ion s, l with a different polarizability and a different $\beta_{ss'}$ disturbs the translation symmetry. It is evident that in the first approximation one may write the system of Eqs. (13) in the same way for all lattice sites, express it in the form of a Fourier expansion $G_s^{l'}$ and find all $P_s^{l'}$, then specify P_s^l and set $P_\sigma^0 = 0$. It is convenient to transform to new variables $q_{\alpha\mathbf{k}}$, $R_s^{\mathbf{k}}$ instead of $p_s^{l'}$ and $P_s^{l'}$:

$$\mathbf{p}_{s'}^{l'} = \frac{ea}{M} \sum_{\mathbf{k},\alpha} \mathbf{p}_{s'}^{\alpha,\mathbf{k}} q_{\alpha\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\}; \tag{15}$$

$$\mathbf{P}_{s'}^{l'} = \frac{ea}{M} \sum_{\mathbf{k}} \Big[\sum_{\alpha} \mathbf{P}_{s'}^{\alpha,\mathbf{k}} q_{\alpha\mathbf{k}} + \mathbf{R}_{s'}^{\mathbf{k}}\Big] \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\},$$

where $q_{\alpha\mathbf{k}}$ are the normal coordinates of crystal, $p_{s'}^{\alpha,\mathbf{k}}$, $P_{s'}^{\alpha,\mathbf{k}}$ are the amplitudes of the lattice vibration of an ideal lattice normalized so that

$$\sum_s \mu_s \mathbf{p}_s^{\alpha,\mathbf{k}} \mathbf{p}_s^{\alpha',-\mathbf{k}} = \delta_{\alpha,\alpha'},$$

where $\mu_s = m_s/\mu$; $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass of an ion pair, α is the index of the branch of oscillations. Similarly the fields acting on the dipole $P_s^{l'}$ are expanded in Fourier series:

$$\mathbf{E}^0(\mathbf{r}_{s'}^{l'}) = -\frac{2ie}{Ma^2} \sum_{\mathbf{k}} \mathbf{E}_{s'}^{0\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\};\quad \mathbf{r}_{s's}^{l'l}/|\mathbf{r}_{s's}^{l'l}|^3 = -\frac{2ie}{Ma^3} \sum_{\mathbf{k}} \vec{\boldsymbol{\Psi}}_{m\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s's}^{l'l}\}; \tag{16}$$

$m = 1$ for $s' = s$

and $m = 2$ for $s' \neq s$;

$$\boldsymbol{\beta}_{s'\sigma}\gamma_{s'\sigma}^{l'0} = -\frac{2ie}{Ma^2} h_{s'\sigma} \sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\};$$

$$(\bar{\boldsymbol{\beta}}_{\sigma s} - \boldsymbol{\beta}_{\sigma s})\,\gamma_{s's}^{l'l} = -\frac{2ie}{Ma^2} \Delta h_{\sigma s} \sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\}.$$

Here

$$\mathbf{G}_{s'}^{l'} = -\frac{2ie}{Ma^2} \sum_{\mathbf{k}} \mathbf{G}_{s'}^{\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\};\quad h_{s'\sigma} = \frac{a^2}{e} \beta_{s'\sigma}|_{r=a},$$

$$\mathbf{G}_{s'}^{\mathbf{k}} = \mathbf{E}_s^{0\mathbf{k}} + \frac{\bar{e}_s - e_s}{e} \vec{\boldsymbol{\Psi}}_{m\mathbf{k}} \exp\{-i\mathbf{k}\mathbf{r}_s^l\} - \frac{e_\sigma}{e} \vec{\boldsymbol{\Psi}}_{m\mathbf{k}} + h_{s'\sigma}\mathbf{A}_{\mathbf{k}} - \Delta h_{\sigma s} \exp\{-i\mathbf{k}\mathbf{r}_s^l\}\, \mathbf{A}_{\mathbf{k}}. \tag{17}$$

$$(E_x' + E_x'')_{\mathbf{r}_{s'}^{l'}} = \frac{e}{Ma^2} \sum_{\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\} \times \sum_{s''y} \varphi_{s's''xy}^{\mathbf{k}} \Big[\sum_{\alpha} (p_{s''y}^{\alpha,\mathbf{k}} + P_{s''y}^{\alpha,\mathbf{k}})\, q_{\alpha\mathbf{k}} + R_{s''y}^{\mathbf{k}}\Big], \tag{18}$$

$$\sum_{s''l''}^{(n)} (\mathbf{u}_{s'}^{l'} - \mathbf{u}_{s''}^{l''})\, \nabla \boldsymbol{\beta}_{s's''x} = \frac{e}{Ma^2} \sum_{\alpha\mathbf{k}x} (p_{s'x}^{\alpha\mathbf{k}} g_{s'1x}^{\mathbf{k}} + p_{s''x}^{\alpha,\mathbf{k}} g_{s'2x}^{\mathbf{k}})\, q_{\alpha\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\}.$$

For a lattice of the NaCl type the quantities $\Psi_{m\mathbf{k}}$ and $\varphi_{ss'xy}$ were calculated by us previously[6,8] over 1/8 of the reciprocal lattice cell for all oblique-angled components of the wave vector k.

For this lattice a direct calculation yields

$$\mathbf{A}_{\mathbf{k}} = \mathbf{e}_x \sin ak_x + \mathbf{e}_y \sin ak_y + \mathbf{e}_z \sin ak_z;$$

$$g_{s'1x}^{\mathbf{k}} = \frac{e}{e_{s'}}\Big[4h_{s's''} + \frac{2a^3}{e}\frac{d\beta_{s's''}}{\partial r}\Big]; \tag{19}$$

$$g_{s'2x}^{\mathbf{k}} = \frac{e}{e_{s'}} 2h_{s's''} (\cos ak_x + \cos ak_y + \cos ak_z) + \frac{e}{e_{s'}}\Big[-2h_{s's''} + \frac{2a^3}{e}\frac{d\beta_{s's''}}{\partial r}\Big] \cos ak_x.$$

As was shown previously,[5] a fairly good agreement with experiment may be obtained for a series of alkali halide crystals if one neglects the quantity β_{12} compared with β_{21}. Then

$$g^{\mathbf{k}}_{11x} = 0; \qquad (19')$$

$$g^{\mathbf{k}}_{21x} = g = -4h_{21} - (2a^3/e)\, d\beta_{21}/dr;$$

$$g^{\mathbf{k}}_{12x} = 0;$$

$$g^{\mathbf{k}}_{22x} = [-2h_{21}(\cos ak_x + \cos ak_y + \cos ak_z) + (g + 6h_{21})\cos ak_x].$$

In the notation of Eqs. (17) and (18), the expressions for the dipole moments in the Fourier components can be written in the form:

$$\sum_{\alpha} P^{\alpha,\,\mathbf{k}}_{s'x} q_{\alpha\mathbf{k}} + R^{\mathbf{k}}_{s'x} = A_{s'}\Big\{\sum_{s''y} \varphi^{\mathbf{k}}_{s's''xy}\Big[\sum_{\alpha}(p^{\alpha,\,\mathbf{k}}_{s'y} + P^{\alpha,\,\mathbf{k}}_{s'y})\, q_{\alpha\mathbf{k}} + R^{\mathbf{k}}_{s''y}\Big] - (p^{\alpha,\,\mathbf{k}}_{s'x} g^{\mathbf{k}}_{s'1x} + p^{\alpha,\,\mathbf{k}}_{sx} g^{\mathbf{k}}_{s'2x})\, q_{\alpha\mathbf{k}} - 2iG^{\mathbf{k}}_{s'x}\Big\}; \qquad (20)$$

$$A_{s'} = \alpha_{s'}/a^3.$$

In the absence of the field $\mathbf{G}_s^{\mathbf{k}}$, Eqs. (20) give the expressions for dipole moments of electron shells for free lattice vibrations and are satisfied exactly for any $q_{\alpha\mathbf{k}}$. The solution of the remaining equations for the ionic polarizability component

$$\sum_{s''y} C^{\mathbf{k}}_{s's''xy} R_{s''y} = -2iG^{\mathbf{k}}_{s'x},$$

where $C^{\mathbf{k}}_{s's''xy} = \delta_{xy}\delta_{s's''}/A_{s'} - \varphi^{\mathbf{k}}_{s's''xy}$

has the form

$$R^{\mathbf{k}}_{s'x} = -2i\sum_{s''y} C^{-1\mathbf{k}}_{s's''xy} G^{\mathbf{k}}_{s''y}. \qquad (21)$$

In the same way in the dipole approximation, the effect of the position of the anomalous lattice site on the form of the ψ wave function of the remaining ions is taken into account.

4. EVALUATION OF THE POTENTIAL AND KINETIC ENERGY OF THE EXCESS CHARGE

If we add the expression for the mean Hamiltonian of Eq. (10) taken for the wave functions Ψ_s^l to the energy of ideal lattice we obtain

$$H\binom{ll}{ss} = \overline{H}_{\mathrm{id}} - \sum_{s'l'}(\mathbf{P}^{l'}_{s'}\mathbf{G}^{l'}_{s'} + \mathbf{p}^{l'}_{s'}\mathbf{F}^{l'}_{s'}) + V\binom{l}{s} + H_1, \qquad (22)$$

$$\mathbf{F}^{l'}_{s'} = \mathbf{E}^0(r^{l'}_{s'}) + \frac{\overline{e}_s - e_s}{|\mathbf{r}^{l'l}_{s's}|^3}\mathbf{r}^{l'l}_{s's} - \frac{e_\sigma}{|\mathbf{r}^{l'}_{s'}|^3}\mathbf{r}^{l'}_{s'} - \frac{1}{e_{s'}r}\frac{\partial\Delta u(r)}{\partial r}\Big|_{r=a}\mathbf{r}^{l'l}_{s's} + \frac{1}{e_{s'}r}\frac{\partial u(r)}{\partial r}\Big|_{r=a}\mathbf{r}^{l'}_{s'} + \frac{\delta_{s's}\delta_{l'l}}{e_{s'}}\Big[(\overline{e}_s - e_s)\,\mathbf{E}^0(\mathbf{r}^l_s) + \overline{e}_\sigma(e_s - e_s)\frac{\mathbf{r}^l_s}{|\mathbf{r}^l_s|^3} + \frac{1}{a}\frac{\partial\Delta u}{\partial r}\Big|_{r=a}\mathbf{r}^l_s\Big]. \qquad (23)$$

$$V\binom{l}{s} = -E_{\sigma 0} + \Delta E_{s0} + \frac{e^2_\sigma \alpha_m}{a} - \frac{(\overline{e}_s - e_s)\;{}_s\alpha_m}{a} - nu(a) + n\Delta u(a) - \frac{e_\sigma(\overline{e}_s - e_s)}{r^l_s} + (\overline{e}_s - e_s)\, v(\mathbf{r}^l_s) - e_\sigma v(0) + \Delta u\gamma^{l0}_{s\sigma'}. \qquad (24)$$

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where H_1 denotes all terms of the second order in $\mathbf{p}_s^{l'}$, $\mathbf{P}_s^{l'}$ which are due to the formation of a defect and an anomalous ion and which will be neglected in the further calculation. The presence of these terms destroys the translation symmetry and makes a solution of the problem very difficult.

Substituting Eq. (15), and using the fact that the amplitudes of $\mathbf{p}_s^{\alpha,\mathbf{k}}$, $\mathbf{P}_s^{\alpha,\mathbf{k}}$ are the solutions of the system

$$-(m_s/e_s^2)\,\omega^2_{\alpha\mathbf{k}} p^{\alpha,\,\mathbf{k}}_s = -\partial\overline{H}_{\mathrm{id}}/\partial\mathbf{p}^{\alpha,\,\mathbf{k}}_s;$$

$$0 = -\partial\overline{H}_{\mathrm{id}}/\partial\mathbf{P}^{\alpha,\,\mathbf{k}}_{s'};$$

Eq. (22) can be written in the form

$$H\binom{ll}{ss} = \frac{e^2}{2aM}\sum_k\Big\{\sum_\alpha[\Omega^2_{\alpha,\mathbf{k}} q_{\alpha,\,\mathbf{k}} q_{\alpha,\,-\mathbf{k}} + 4i(\mathbf{p}^{\alpha,\,\mathbf{k}}_{s'}\mathbf{F}^{-\mathbf{k}}_{\prime} + \mathbf{P}^{\alpha,\mathbf{k}}_{s'}\mathbf{G}^{-\mathbf{k}}_{s'})\, q_{\alpha\mathbf{k}}] + 4i\sum_{s'}\mathbf{R}^{\mathbf{k}}_{s'}\mathbf{G}^{-\mathbf{k}}_{s'}\Big\} + V\binom{l}{s} + H_1 + \text{const}, \qquad (25)$$

where $\mathbf{F}_s^{\mathbf{k}'}$ is the Fourier component of the expansion of $\mathbf{F}_s^{l'}$

$$\mathbf{F}_{s'}^{l'} = -\frac{2ie}{Ma^2}\sum_{\mathbf{k}} \mathbf{F}_{s'}^{\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}_{s'}^{l'}\}, \tag{26}$$

$$\mathbf{F}_{s'}^{\mathbf{k}} = \mathbf{E}_{s'}^{0k} + \frac{\bar{e}_s - e_s}{e}\boldsymbol{\Psi}_{m\mathbf{k}} \exp\{-i\mathbf{k}\mathbf{r}_s^l\} - \frac{e_\sigma}{e}\boldsymbol{\Psi}_{m\mathbf{k}}$$
$$+ \left[\frac{e_{s'}}{e}(1-\delta_{ss'})\,\Delta H \exp\{-i\,\mathbf{k}\mathbf{r}_s^l\} - H\frac{e_{s'}}{e}(1-\delta_{\sigma s'})\right]\mathbf{A}_{\mathbf{k}}$$
$$- \frac{\delta_{ss'}}{2ie}\left[a^2\frac{\bar{e}_s - e_s}{e_s}e_\sigma \frac{\mathbf{r}_s^l}{|r_s^l|^3}\exp\{-i\mathbf{k}\mathbf{r}_s^l\} + \frac{e_s}{a}\Delta H \mathbf{r}_s^l \exp\{-i\mathbf{k}\mathbf{r}_s^l\}\right.$$
$$\left. + \frac{a^2(\bar{e}_s - e_s)}{e_s}\mathbf{E}^0(\mathbf{r}_s^l)\exp\{-i\mathbf{k}\mathbf{r}_s^l\}\right]; \quad H = -\frac{a^2}{e^2}\frac{\partial u(r)}{\partial r}\bigg|_{r=a};$$

where ΔH denotes the change in H if only one ion is anomalous.

The expression (25) plays the role of the potential energy of the excess charge which is present at the lattice site s,l.

The wave function of the moving charge is sought in the form of the linear combination

$$\Psi_s = \sum b_s^l \Psi_s^l, \tag{27}$$

where the coefficients $b_s^{\,l}$ will be evaluated from the variational principle—the minimum of $\bar{H}$:

$$\bar{H} = \int \Psi_s^* \hat{H} \Psi_s d\tau = \sum_{ll'} b^{l*} b_s^{l'} H\binom{ll'}{ss}, \tag{28}$$
$$H\binom{ll'}{ss} = \int \Psi_s^{l*} \hat{H} \Psi_s^{l'} d\tau, \qquad \sum_l |b_s^l|^2 = 1.$$

The matrix elements $H\binom{ll}{ss}$ $l' \neq l$ play the role of the kinetic energy since they depend on two positions of the charge near the lattice sites s, l and s,l' analogously to the operator $\Delta\psi$. In view of the orthogonality condition of Eq. (3) and the small overlaps of the wave functions of the remote ions, it is sufficient to retain only the subdiagonal matrix elements $H\binom{ll}{ss}$ when the sites s, l and s,l' are the nearest neighbors of the same kind. Furthermore, we neglect in them the dependence of the wave function of ions ψ on the position of the anomalous site and we shall consider them equal to ψ_{s0}' and retain in the integrals of Eq. (20) only those terms in which the permutation in $\Psi_s^{\,l'}$ differs from the permutation in $\Psi_s^{\,l}$ by the transposition of one electron from the anomalous site s,l' to the site s,l (or conversely in the case of a hole). Then the Hamiltonian $\hat{H}$ retains only those terms which contain the coordinates of the transposed electron $\boldsymbol{\rho}$. This is the kinetic energy $-(\hbar^2/2m)\Delta\rho$ and the energy of its interaction with all electrons and charges of the surrounding ions. The potential of the external field can be neglected in view of its uniformity and the condition of Eq. (3). Integration over the coordinates of electrons of the remaining ions gives the sum of their potentials at the point ρ:

$$\sum_{s''\,l''}{}'' V_{s''}(\boldsymbol{\rho} - \mathbf{R}_{s''}^{l''}).$$

The result is

$$H\binom{li'}{ss} = \int \psi_s^{l'*} \varphi_s^{l*} \left\{ -\frac{\hbar^2}{2m}\Delta_\rho \right.$$
$$- e\sum_{s''l''}{}'' V_{s''}(\boldsymbol{\rho} - \mathbf{R}_{s''}^{l''}) + \sum_{n_s}\frac{e^2}{|\boldsymbol{\rho} - \boldsymbol{\rho}_{sn_s}^l|} \tag{29}$$
$$+ \sum_{n_{s'}}\frac{e^2}{|\boldsymbol{\rho} - \boldsymbol{\rho}_{sn_s}^{l'}|} - \frac{e^2 z_s}{|\boldsymbol{\rho} - \mathbf{R}_s^l|}$$
$$\left. - \frac{e^2 z_{s'}}{|\boldsymbol{\rho} - \mathbf{R}_s^{l'}|}\right\} \psi_s^l \varphi_s^{l'} d\tau.$$

For the case of an extra electron in a lattice constructed of ions with closed shells (for example, NaCl), one may set $\varphi_s^l = \psi_s^l \chi_s(\rho - \mathbf{R}_s^l)$. Then the integration over the coordinates $\rho_{sn_s}^l$, $\rho_{sn_s}^{l'}$ gives the sum of potentials of these ions

$$V_s(\boldsymbol{\rho} - \mathbf{R}_s^l) + V_s(\boldsymbol{\rho} - \mathbf{R}_s^{l'}).$$

Since in the integrals over ρ the main role is played by the terms with $\rho \approx 1/2\,(\mathbf{R}_s^l + \mathbf{R}_s^{l'})$, i.e., members sufficiently remote from the remaining ions, one may set

$$\sum_{s''l''}{}'' V_{s''}(\boldsymbol{\rho} - \mathbf{R}_{s''}^{l''}) \approx \sum{}'' - ee_{s''}/|\boldsymbol{\rho} - \mathbf{R}_{s''}^{l''}|.$$

We shall add this sum to the potential of all ions. If one neglects its weak dependence on the displacement of ions, then one may neglect it entirely in view of the fact that this potential has a plateau near

$$\boldsymbol{\rho} = {}^1/_2(\mathbf{r}_s^l + \mathbf{r}_s^{l'})$$

and is equal to zero at its center because of the symmetry of the lattice. Then

$$H\binom{ll'}{ss}=\int\chi_s^*(\boldsymbol{\rho}-\mathbf{R}_s^l)\Big\{-\frac{h^2}{2m}\Delta_\rho -eV_s(\boldsymbol{\rho}-\mathbf{R}_s^l)-eV_s(\boldsymbol{\rho}-\mathbf{R}_s^{l'}) +\frac{ee_s}{|\boldsymbol{\rho}-\mathbf{r}_s^l|}+\frac{ee_\sigma}{|\boldsymbol{\rho}|}+\frac{ee_s}{|\boldsymbol{\rho}-\mathbf{r}_s^{l'}|}\Big\}\chi_s(\boldsymbol{\rho}-\mathbf{R}_s^{l'})\,d\tau. \tag{30}$$

For the case of a hole one uses Eq. (29). As a rough approximation one may suppose that

$$\psi_s^l=\varphi_s^l\chi_s^l(\boldsymbol{\rho}-\mathbf{R}_s^l).$$

Then an expression similar to Eq. (30) is obtained, only it is necessary to move the star from

$$\chi_s(\boldsymbol{\rho}-\mathbf{R}_s^l)\quad\text{to}\quad\chi_s(\boldsymbol{\rho}-\mathbf{R}_s^{l'}),$$

and the potential V_s replaced by the potential of ions deficient in electrons:

$$\bar{V}_s(\boldsymbol{\rho}-\mathbf{R}_s^l)=V_s(\boldsymbol{\rho}-\mathbf{R}_s^l)+e\int\frac{|\chi_s(\boldsymbol{\rho}'-\mathbf{R}_s^l)|^2}{|\boldsymbol{\rho}-\boldsymbol{\rho}'|}d\tau'. \tag{31}$$

Since the product

$$\chi^*(\boldsymbol{\rho}-\mathbf{R}_s^l)\chi(\boldsymbol{\rho}-\mathbf{R}_s^{l'}),$$

is sensitive to the change in the separation between the ions R_{ss}^{ll}, we shall expand $H\binom{ll'}{ss}$ in the powers of the displacements of these ions. Transforming to normal coordinates we obtain, using Eq. (15) in a linear approximation [sufficiently good in view of the small value of $H\binom{ll'}{ss}$]:

$$H\binom{ll'}{ss}=I_{ss}^{ll'}+\frac{2ie^2}{aM}\sum_{\alpha,\mathbf{k}}I_{ss\alpha\mathbf{k}}^{ll'}q_{\alpha\mathbf{k}};$$

$$I_{ss\alpha\mathbf{k}}^{ll'}=\frac{a^2}{2iee_s|\mathbf{r}_{ss}^{ll'}|}\frac{dH\binom{ll'}{ss}}{dR_{ss}^{ll'}} \tag{32}$$

$$\times\,\mathbf{p}_s^{\alpha\mathbf{k}}\mathbf{r}_{ss}^{ll'}(\exp\{i\mathbf{k}\mathbf{r}_s^l\}-\exp\{i\mathbf{k}\mathbf{r}_s^{l'}\}),$$

$$I_{ss}^{ll'}=H\binom{ll'}{ss}_{\mathbf{R}_{ss}^{ll'}=\mathbf{r}_{ss}^{ll'}}. \tag{33}$$

5. EVALUATION OF THE SELF CONSISTENT ELECTRON (HOLE) STATES

In evaluation of the energy of the local state we shall assume with Pekar[4] that the displacement of ions corresponds to the minimum of the average energy $\bar{H}$, i.e., we shall seek the self-consistent state. For states of small radius, it is not sufficient to limit oneself to the calculation of the interaction only with the longitudinal optical branch of vibrations and neglect the dispersion, as was done by Pekar.[4] Our expressions allow us to calculate the states of any arbitrary radius. We must minimize the average energy $\bar{H}$ of Eq. (28) both over b_s^l and over $q_{\alpha\mathbf{k}}$. The latter may be carried out in a general way. Substituting Eqs. (25) and (32) into Eq. (28) we obtain the equilibrium displacement from the condition $\partial\bar{H}/\partial q_{\alpha,-\mathbf{k}}=0$:

$$q_{\alpha,\mathbf{k}}=q_{\alpha,\mathbf{k}}^0=-2i\Omega_{\alpha,\mathbf{k}}^{-2}\Big[\sum_l|b_s^l|^2(\mathbf{p}_{s'}^{\alpha,-\mathbf{k}}\mathbf{F}_{s'}^{\mathbf{k}}+\mathbf{P}_{s'}^{\alpha,-\mathbf{k}}\mathbf{G}_{s'}^{\mathbf{k}})+\sum_{ll'}b_s^{l*}b_s^{l'}I_{ss\alpha,-\mathbf{k}}^{ll'}\Big]. \tag{34}$$

It is necessary to keep in mind that $q^0_{\alpha,\mathbf{k}}$ is determined not by the instantaneous but the quantum-mechanical average of the position of the anomalous site l,s and thus the quantity

$$\Omega_{\alpha\mathbf{k}}^2q_{\alpha\mathbf{k}}q_{\alpha,-\mathbf{k}}$$

in Eq. (28) may be taken out of the summation over l. Using Eqs. (34), (25) and (32) we obtain from Eq. (28):

$$\begin{aligned}\bar{H}&=(2e^2/aM) \qquad (35)\\ &\times\sum_{\mathbf{k},\alpha}\Omega_{\alpha\mathbf{k}}^{-2}\Big\{\sum_l|b_s^l|^2(\mathbf{p}_{s'}^{\alpha,-\mathbf{k}}\mathbf{F}_{s'}^{\mathbf{k}}+\mathbf{P}_{s'}^{\alpha,-\mathbf{k}}\mathbf{G}_{s'}^{\mathbf{k}}) +\sum_{ll'}{}'b_s^{l*}b_s^{l'}I_{ss'\alpha,-\mathbf{k}}^{ll'}\Big\}\Big\{\sum_l|b_s^l|^2(\mathbf{p}_{s'}^{\alpha,\mathbf{k}}\mathbf{F}_{s'}^{-\mathbf{k}}\\ &+\mathbf{P}_{s'}^{\alpha,\mathbf{k}}\mathbf{G}_{s'}^{-\mathbf{k}})+\sum{}'b_s^{l*}b_s^{l'}I_{ss\alpha\mathbf{k}}^{ll'}\Big\}\\ &+\sum_l|b_s^l|^2\Big\{\frac{4e^2}{aM}\sum_{\substack{hs's''\\xy}}G_{s'x}^{-\mathbf{k}}C_{s's''xy}^{-1\mathbf{k}}G_{x''y}^{\mathbf{k}}+V\binom{l}{s}\Big\}\\ &+\sum_{ll'}{}'b_s^{l*}b_s^{l'}I_{ss}^{ll'}.\end{aligned}$$

Minimizing Eq. (35) over b_s^1, it is not possible to obtain the minimum of Eq. (35) over b_s^l for a general case. It is necessary to carry out minimizing for each particular case by numerical method since $\partial\bar{H}/\partial b_s^l=0$ gives a system of cubical equations for b_s^l. In order to solve these equations one must know all

$$\Omega_{\alpha,\mathbf{k}},\ \mathbf{p}_s^{\alpha,\mathbf{k}},\ \mathbf{P}_s^{\alpha,\mathbf{k}},\ I_{ss}^{ll'},\ I_{ss\alpha,\mathbf{k}}^{ll'},$$

and also the parameters

$$h_{s's},\ \Delta h,\ H,\ \Delta H.$$

The problem may be simplified by making use of the symmetry of the lattice and thus reducing the number of independent coefficients b_s^l. For example, for the ground state of an F—center b_s^l are identical for all ions equidistant from the vacant site σ and it is sufficient to limit b_s^l to the first and the third configuration spheres. Thanks to the normalization condition

$$\sum_l |b_s^l|^2 = 1$$

only one approximation parameter remains.

The proposed method is useful also for the calculation of hole states of small radii for which a theory is lacking at present.

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Translated by M. J. Stevenson
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