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The Interaction of an Electron Hole with the Lattice Vibrations in a Homopolar Crystal

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The motion of a hole in a homopolar crystal of the diamond type is examined on the basis of the many-electron equations of Schrödinger. The presence of a hole is represented by the substitution of one paired bond by a monoelectronic one, which leads to the appearance of an additional force tending to deform the crystal. The corresponding term in the Hamiltonian is considered as the interaction of the hole with the deformations of the lattice. The meaning of the force obtained in the way for the problem of autolocalization of the hole, the scattering of current carriers by the lattice vibrations, and the theories of mobility, thermal emf and Nernst effect, is discussed.

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1. INTRODUCTION

THE experimental study of the temperature dependence of the mobility, thermal emf and galvanomagnetic effects in Ge, and in particular in Si, indicates the insufficiency of the elementary theory of scattering of electron waves on the acoustic oscillations of the lattice[1], leading in particular to a temperature behavior of the mobility $u \sim T^{-3/2}$. For Ge of p-type the mobility more closely follows the formula $u \sim T^{-2.3}$[2]. There are known to be anomalies in the dependence of the latter. The value of the effective mass of a hole in Ge is found to be different in different experiments (in particular, cyclotron resonance gives $m_{\text{eff}}/m \sim 0.04$[3]).

These anomalies are usually connected with the complex structure of the valence band at its upper edge (the triple degeneracy, whereby the surface of constant energy in k-space for small k differs from the spherical shape and the maximum energy corresponds to $\mathbf{k} \neq 0$[4]). The corresponding calculations of the energy bands in Si, Ge and diamond[5-7], in general support this conclusion. However, in examining such detailed effects as the temperature dependence of mobility, the anisotropy of the resistivity in a magnetic field, etc., it is hardly possible completely to trust the one-electron approximation and the entire band scheme.

It is expedient to examine the motion of a hole on the basis of the many-electron problem and to find the energy of the crystal as a function of its wave vector, taking into account that the valence electrons of a homopolar crystal bring about bonding forces between the atoms therein. The formation of a hole must therefore produce the breaking of a bond and the appearance of forces tending to deform the crystal. There is no reason to expect that the corresponding potential energy will have the usual form $\mathbf{u}\nabla V$ ($\mathbf{u}$ is the displacement of a point of the crystal, V is the periodic potential). The destruction of the bond must lead to a strong interaction of the hole, particularly with the optical vibrations, which obliges us to examine the mobility anew. In the work of Kontorova[8], who studied the scattering of the conduction electrons by the acoustic vibrations of the lattice, using the dispersion law $\omega = \omega_0$ in place of the usually assumed law $\omega = ck$ (c is the velocity of sound), the mobility turned out to be proportional to $T^{-5/2}$, in better agreement with experiment than the usual theory gives[1]. In fact, the dispersion law $\omega = \omega_0$ can take place in the optical modes. However, the term $\mathbf{u}\nabla V$ assumed by all authors (among them Kontorova also) for the interaction with the vibrations cannot guarantee any strong scattering by the optical modes. Furthermore, the concept of a periodic potential V for the hole is devoid of meaning. In this case the interactions are more correctly considered as the alterations of the bonds between the atoms.

Finally, the mean free path of the current carriers is usually (except in Ge) of the order of or smaller than the de Broglie wavelength[9]. In each case the criterion for applicability of the perturbation theory, $uM/m \gg 500\ \text{cm}^2/\text{sec/v}$ (M is the mass of a current carrier, m is the electron mass, u is the mobility), shown by Pekar, is very seldom satisfied[10]. Therefore, the possibility is not excluded that the current carriers in a homopolar crystal, as in a polar one, are so-called "condensons" considered by Pekar and Deigen[11]. It is clear that the success of the computation of the "condensons" depends essentially on the correct choice for the forces of interaction between electron and lattice.

One of us (A.M.F.) has carried out a calculation of the wave functions and energy of the crystal with an electron missing from one of the bonds (hole)[12], taking into account a possible small deformation of the crystal. The results of this calculation and consideration of the consequences of the interaction found for a hole with the lattice vibrations are presented below.

2. THE WAVE FUNCTION AND ENERGY ON AN IDEAL CRYSTAL

We consider a diamond crystal, having in view that for Si, Ge and α-Sn, the structure of the lattice and the configurations of the valence electrons and bonds are quite similar.

In the union of C atoms into a crystal the wave functions of the valence electrons of each atom are deformed, with the formation of σ-bonds with each of the four nearest neighbors. The functions of the σ-bonds, considering the symmetry of the crystal, are approximately represented by the formula[13]

$$\psi_a(\mathbf{r}) = c_1 S(r) + 3c_2 P(r)\cos\vartheta, \tag{1}$$

where ϑ is the angle between the radius vector of the electron **r** and the radius vector of the nucleus nearest to the given electron, $S(r)$ and $P(r)$ are radial parts of the *s*- and *p*-functions, c_1, c_2 are approximation parameters.

We seek the wave-function of the crystal in the form of an antisymmetrized product of wave functions of the bonds of each pair of atoms *a*, *b*:

$$\Psi_{ab}(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = [\alpha_a(\sigma_1)\beta_b(\sigma_2) - \alpha_a(\sigma_2)\beta_b(\sigma_1)]\,[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)], \tag{2}$$

α, β are spin functions equal to 1 or 0 for $\sigma = \pm 1/2$. In what follows we shall number the atoms with a cell-index *l*, the index of the atom in the cell $s = 1,2$, and we shall also introduce for each function the number of the bond $\alpha = 1, 2, 3, 4$.

Besides interchanges of the electrons inside the bond (2) we consider also interchanges between the wave functions belonging to the same atom. In Fig. 1 this corresponds to the interchange of electrons between Ψ_{ab} and Ψ_{ac} only in the terms $\psi_a(r_1)$ and $\psi_a(r_3)$. We neglect the exchange and the exchange energy of electrons found on different atoms but not on the same bond. The potential energy excludes the mutual interaction of all the valence electrons and the nuclei, screened by the internal electrons. The wave functions of the electrons on different nuclei we consider approximately orthogonal. The functions of the electrons of one atom but of different bonds are orthogonal on account of the angular parts [see Eq. (1)]. With these assumptions the energy of the system will be

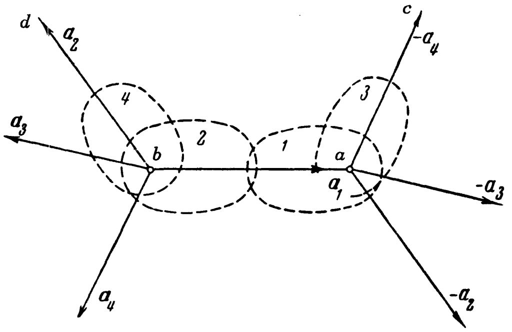

FIG. 1. Schematic representation of the bonds in a crystal of the diamond type. The dotted ovals *1, 2, 3, 4* represent the form of the ψ-cloud of electrons $\psi_a(1)$, $\psi_b(2)$, $\psi_a(3)$, $\psi_b(4)$. The vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{a}_4$ (or what is the same thing, a_{si}, since $a_{1i} = -a_{2i}$) represent the directions of the bonds.

$$\overline{\mathscr{H}} = \int\cdots\int \sum_P \varepsilon(P)\, P \prod_{ls\alpha} \Psi_{ls\alpha}(\mathbf{r}_{ls\alpha 1}\sigma_{ls\alpha 1}\mathbf{r}_{ls\alpha 2}\sigma_{ls\alpha 2})\, \mathscr{H} \times \prod_{ls\alpha} \Psi_{ls\alpha}(\mathbf{r}_{ls\alpha 1}\sigma_{ls\alpha 1}\mathbf{r}_{ls\alpha 2}\sigma_{ls\alpha 2})\, d\tau; \tag{3}$$

P is the exchange operator for electrons, $\epsilon(P) = \pm 1$. In computing the average potential energy of an electron located on the bond *ab* of Fig. 1, atom *c* can be considered neutral. In the indicated approximation Eq. (3) breaks up into the sum of the average energies of the separate bonds; in this the energies of the interactions of the electrons on the bonds *ab* and *ac* are conveniently divided equally between these bonds. In atomic units,

$$\begin{aligned}\overline{\mathcal{H}} = \sum_{ls\alpha}\mathcal{H}_{ls\alpha}(\mathbf{R}_a,\ \mathbf{R}_b) = \sum_{ls\alpha}\Big\{3\,(1+S^2)^{-2}\int\frac{1}{r_{13}}\,[\rho_a(1)+S\rho_{ab}(1)]\,[\rho_a(3)\\ + S\rho_{ac}(3)]\,d\tau_1 d\tau_3 + 6\,(1+S^2)^{-2}\int\frac{1}{r_{23}}\,[\rho_b(2)+S\rho_{ba}(2)]\,[\rho_a(3)\\ + S\rho_{ac}(3)]\,d\tau_2 d\tau_3 + \frac{Z^2}{a} - \frac{2Z}{1+S^2}\int\frac{1}{r_{a1}}\,[\rho_a(1)+\rho_b(1)+2S\rho_{ab}(1)]\,d\tau_1\\ - \frac{6Z}{1+S^2}\int\frac{1}{r_{1c}}\,[\rho_a(1)+S\rho_{ab}(1)]\,d\tau_1 + (1+S^2)^{-2}\sum^{(9)}\int\frac{1}{r_{34}}\,[\rho_a(3)\\ + S\rho_{ac}(3)]\,[\rho_b(4)+S\rho_{bd}(4)]\,d\tau_3 d\tau_4\\ + \frac{1}{2\,(1+S^2)}\int\frac{1}{r_{12}}\,[\psi_a(1)\,\psi_b(2)+\psi_a(2)\,\psi_b(1)]\,d\tau_1\,d\tau_2\\ - \frac{1}{1+S^2}\Big[\int\psi_a\Delta\psi_a d\tau + 2S\int\psi_a\Delta\psi_b d\tau\Big]\Big\}.\end{aligned} \tag{4}$$

Here the first two terms give the interaction of the electrons on bond *ab* with electrons found on the bonds of atom *a* with atoms of type *c*; the third term gives the interaction of the nuclei *a*, *b*; the fourth and fifth terms, the interaction of the electrons on bond *ab* with their own and also with neighboring nuclei; the sixth term, the interaction of electrons on bonds *bd* with electrons on the bonds *ac*. The last two terms represent the exchange and kinetic energy of the electrons of the bond *ab* (see Fig. 1).

3. THE WAVE FUNCTION AND ENERGY OF THE CRYSTAL WITH ONE ELECTRON REMOVED

In the presence of a hole it is necessary to find the wave function of the system in the form of a linear combination of functions $\Psi_{ls\alpha}$ of the type (2), in each of which one of the bond functions Ψ_{ab} is replaced with a function of one electron with indeterminate direction of spin

$$\varphi_b(r_{ls\alpha})\,[\alpha_l(\sigma_{ls\alpha})+\beta_l(\sigma_{ls\alpha})], \tag{5}$$

that is,

$$\Psi' = \sum_{ls\alpha} A_{ls\alpha}\Psi'_{ls\alpha}. \tag{6}$$

If all the atoms are at rest at the lattic sites, then

$$A_{ls\alpha} = N^{-1/2}A_{s\alpha}(\mathbf{k})\exp\,\{i\mathbf{k}\mathbf{R}_s^l\}. \tag{7}$$

Substitution of Eqs. (5)-(7) into $\overline{\mathcal{H}}$ gives

$$\begin{aligned}\overline{\mathcal{H}}' = \sum_{s\alpha}\Big\{\,|A_{s\alpha}|^2\mathcal{H}_{s\alpha,\,s\alpha} + \sum_{\alpha'}\overset{*}{A}_{s\alpha}A_{s\alpha'}\mathcal{H}_{s\alpha,\,s\alpha'}\\ + \sum_{\alpha' l}\overset{*}{A}_{s\alpha}A_{s'\alpha'}\mathcal{H}^{l-l'}_{s\alpha,\,s'\alpha'}\exp\,\{i\mathbf{k}\,(\mathbf{R}^{l'}_{s'}-\mathbf{R}^{l}_{s})\},\end{aligned} \tag{8}$$

where $\overline{\mathcal{H}}_{s\alpha,s\alpha}$ is the average value of the Hamiltonian $\overline{\mathcal{H}}$ over the functions $\Psi_{ls\alpha}$, which does not depend on the index *l* and which is obtained by striking out of the expression (4) the terms corresponding to the missing electron. $\overline{\mathcal{H}}_{sd,sd'}$ and $\overline{\mathcal{H}}^{l-l'}_{s\alpha,s'\alpha'}$ are matrix elements for the transition of a hole from the bond *ab* to the bond *ac* and correspongingly, from atom *a* to atom *b* on the same bond *ab*. Only these off-diagonal matrix elements are considered which correspond to the transition of an electron from one atom to the neighboring one on the same bond, or to the transition of an electron on a single atom from one bond to another.

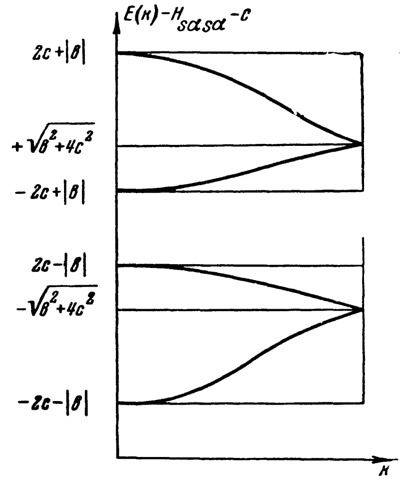

FIG. 2. Relative locations of the hole bands in the crystal of the diamond type. The energy levels (9)-(10) coincide, respectively, with the lower edge of the first and the upper edge of the second band.

Figure 1 gives the notation for the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{a}_4$ characterizing the directions of the bonds 1, 2, 3, 4. The coefficient A_{12} designates that the hole is found on atom 1 and bond 2, etc.

Applying a variational principle, we obtain a system of linear equations for the eight coefficients $A_{s\alpha}$; setting the determinant of this system equal to zero, we obtain the eigenvalues of the energy:

$$E = \mathscr{H}_{s\alpha,\, s\alpha} + c \pm [b^2 + 4c^2 \pm 2bc\sqrt{\varphi(\mathbf{k})}]^{1/2}, \tag{9}$$

$$E = \mathscr{H}_{s\alpha,\, s\alpha} \pm b - c, \tag{10}$$

$$\varphi(\mathbf{k}) = 1 + \cos(k_x d/2)\cos(k_y d/2) + \cos(k_x d/2)\cos(k_z d/2) + \cos(k_y d/2)\cos(k_z d/2) \tag{11}$$

$$a = \mathscr{H}_{s\alpha,s\alpha} - E;\ c = \mathscr{H}_{s\alpha,s\alpha'};\ b = \mathscr{H}^{l-l'}_{s\alpha,s'\alpha'}$$

(d is the edge of the lattice cube); the roots (10) are double-valued. In analogy with the results of calculations for molecules, one can expect that $c > 0$ and $b < 0$ [13].

Figure 2 shows the arrangement of the bands. For hole conduction only the lowest band (signs –, +) is significant. The states in this band are nondegenerate and the energy for small k can be written as

$$E - \mathscr{H}_{s\alpha,s\alpha} - c = -2c - |b| + (\hbar^2/2\mu)k^2; \tag{12}$$
$$\hbar^2/2\mu = (d^2/16)|b|c/(2|c| + |b|).$$

In this way in our approximation it is impossible to explain the peculiarities observed in hole Ge (the presence of two effective masses, the selective infra-red absorption, the anisotropy of magnetoresistivity, etc.). Obviously, for this it is necessary to keep the exchange integrals for more weakly overlapping wave functions, which leads to a splitting of the levels (10) into four bands.

4. INVESTIGATION OF LOCAL HOLE COMPOUNDS OF LARGE RADIUS

If the atoms of the crystal are deformed, the coefficients $\mathscr{H}_{s\alpha,s\alpha}$, etc. depend on the coordinates of all the atoms, and the solution (7) will not obtain. However, it is possible to use the more general formula (6) with arbitrary constants $A_{ls\alpha}$, or their Fourier expansions:

$$A_{sl\alpha} = \frac{1}{N^{1/2}}\int A(\beta, \mathbf{k})\, A_{s\alpha}(\mathbf{k}) \exp\{i\mathbf{k}\,\mathbf{R}^l_s\}\, d\mathbf{k}. \tag{13}$$

The $A(\beta, \mathbf{k})$ are functions of $\mathbf{k}$ to be determined; they contain certain approximation parameters β. We assume that the "radius of the state" of our hole is large enough and that in the expansion (14) there enter only values of $\mathbf{k}$ small compared with the inverse lattice constant. Then it is possible to use Eq. (12) for the energy and assume approximately $A_{s\alpha}(k) \approx A_{s\alpha}(0)$. For the lowest bands:

$$A_{11} = A_{21} = A_{12} = A_{22} = 1/\sqrt{8};$$

$$A_{13} = A_{23} = A_{14} = A_{24} = -1/\sqrt{8}.$$

The average value of the Hamiltonian over the functions (6) will be :

$$\overline{\mathscr{H}'} = \frac{\hbar^2}{2\mu}\int A^*(\beta, \mathbf{k})\, \mathbf{k}^2 A(\beta, \mathbf{k})\, d\mathbf{k} + \iint A^*(\beta, \mathbf{k}')\, W[u^l_s]_{\mathbf{k}'\mathbf{k}}\, A(\beta, \mathbf{k})\, d\mathbf{k}\, d\mathbf{k}'; \tag{14}$$

$$W[\mathbf{u}^l_s]_{\mathbf{k}\mathbf{k}'} = \frac{1}{N}\sum_{\substack{sl\alpha\\ s'l'\alpha'}} A_{s\alpha} A_{s'\alpha'} \exp\{-i\mathbf{k}\mathbf{R}^{l'}_{s'} + i\mathbf{k}'\,\mathbf{R}^l_s\}\int \Psi_{l's'\alpha'}\, \hat{\mathscr{H}}\, \Psi_{ls\alpha}\, d\tau. \tag{15}$$

On account of the axial symmetry of the wave functions with $\mathbf{R}^l_s \neq \mathbf{R}^{l'}_s$, the basic dependence of the integral (15) will be a dependence on the distances of the atoms occurring in the bond ll', ss'; $\mathbf{a}_{si} = \mathbf{R}^l_s - \mathbf{R}^{l'}_s$. But if $\mathbf{R}^l_s = \mathbf{R}^{l'}_s$, then the principal role in the dependence of the deformation will be played by the term for the interaction of an atom lacking an electron with the neighboring atom. We designate the corresponding terms

$$\mathscr{H}^{l-l'}_{s\alpha,s'\alpha'} + F_2(\mathbf{u}^l_s - \mathbf{u}^{l'}_{s'})\,\mathbf{a}_{si}/|\mathbf{a}_{si}| \text{ and } \mathscr{H}_{s\alpha,s\alpha} + F_1(\mathbf{u}^l_s - \mathbf{u}^{l'}_{s'})\,\mathbf{a}_{si}/|\mathbf{a}_{si}|. \tag{16}$$

The first components in (16) [after the summation in (15) over l and l'] are retained only for $\mathbf{k}' = \mathbf{k}$, and will give a constant contribution to $\overline{\mathscr{H}}$. In summing the second components, we shall change from the deformations $\mathbf{u}^l_s$ to the normal coordinates of the crystal $q_{\mathbf{f}\gamma}$ by the formula:

$$\mathbf{u}^l_s = \sum_{\mathbf{f}\gamma} \mathbf{u}^\gamma_s(\mathbf{f}) \exp\{i\mathbf{f}\mathbf{R}^l_s\}\, q_{\mathbf{f}\gamma}; \tag{17}$$

f is the wave vector, $\mathbf{u}_s^{\gamma}$ and γ are the amplitude and branch number of the eigenfrequencies. Substitution of (16) and (17) into (15) gives

$$W\,[\mathbf{u}_s^l]_{\mathbf{kk}'} = \sum_{\mathbf{f}\gamma} (\mathbf{u}_s^{\gamma} - \mathbf{u}_{s'}^{\gamma} e^{i\mathbf{fa}_{si}})\, q_{\mathbf{f}\gamma} \tag{18}$$

$$\times \left[F_1 \mathbf{a}_{si} + \frac{1}{2} (e^{i\mathbf{ka}_{si}} + e^{-i\,(\mathbf{k}+\mathbf{f})\,\mathbf{a}_{si}})\, F_2 \mathbf{a}_{si}\right]$$

$$\times\, \delta_{\mathbf{k}+\mathbf{f},\,\mathbf{k}'} / |\,\mathbf{a}_{si}\,|.$$

The local states of the hole will be stable if $\mathfrak{H}' + U^0$ has a minimum and lies lower than the bottom of the band. Here U^0 is the work of deformation of the crystal, equal to

$$U^0 = {}^1\!/_2 N \sum \omega_{\mathbf{f}\gamma}^2\, q_{\mathbf{f}\gamma}^* q_{\mathbf{f}\gamma}. \tag{19}$$

Adding (14) and (19) and minimizing the sum over $q_{\mathrm{f}\gamma}$ we find the equilibrium deformations of the atoms of the crystal, $\bar{q}_{\mathrm{f}\gamma}$. We take as an approximation

$$A\,(\beta,\, k) = (2\pi\beta^2)^{-3/4}\, e^{-k^2/4\beta^2} \tag{20}$$

and limit ourselves to only the interactions with the longitudinal vibrations of the lattice, whereby the optical and acoustic frequencies are $\omega_{\mathrm{opt}} = \omega_0$, $\omega_{\mathrm{ac}} = cf$. As the result of a moderatley long computation[12] we obtain:

$$\bar{\mathscr{H}} + U^0\,(\bar{q}_{\mathrm{f}\gamma}) \tag{21}$$

$$= (4F_1^2 / 3\,(2\pi)^{3/2}\, \omega_0^2\, |\,a_{si}\,|^2)\,[(B\hbar^2 x^2 / 2\mu) - J\,(x)],$$

$$B = 9\rho\,(a_{si}\,(2\pi)^{3/2}\, \omega_0^2 / 4F_1^2, \quad x = \beta\,|\,\mathbf{a}_{si}\,|;$$

$$J\,(x) = x^3 \Bigl\{1 - e^{-8x^2/3} + e^{-4x^2} \tag{22}$$

$$+ e^{-4x^2/3} + 4\frac{F_2}{F_1} e^{-x^2/2} (e^{-x^2/4} - e^{-19x^2/12}$$

$$+ e^{-9x^2/4} - e^{-11x^2/12})$$

$$+ 4\frac{F_2^2}{F_1^2}\, e^{-x^2} (1 - e^{2x^2/3} + e^{-x^2} + e^{-x^2/3}) \Bigr\}$$

$$+ \frac{\sqrt{\pi}\,|\,a_{si}\,|^2 \omega_0^2}{4c^2} \Bigl\{ \frac{2}{\sqrt{\pi}} x - \sqrt{\frac{3}{8}}\, \Phi \Bigl(\sqrt{\frac{8}{3}} x\Bigr)$$

$$- \frac{1}{2} \Phi\,(2x) + \sqrt{\frac{3}{4}}\, \Phi \Bigl(\sqrt{\frac{4}{3}} x\Bigr)$$

$$+ \frac{4F_2}{F_1} \Bigl[2\Phi \Bigl(\frac{x}{2}\Bigr) - \sqrt{\frac{12}{19}}\, \Phi \Bigl(\sqrt{\frac{19}{12}} x\Bigr)$$

$$- \frac{2}{3} \Phi \Bigl(\frac{3}{2} x\Bigr) + \sqrt{\frac{22}{11}}\, \Phi \Bigl(\sqrt{\frac{11}{12}} x\Bigr)\Bigr]$$

$$+ 4\frac{F_2^2}{F_1^2} e^{-x^2} \Bigl[\frac{2}{\sqrt{\pi}} x - \sqrt{\frac{3}{2}}\, \Phi \Bigl(\sqrt{\frac{2}{3}} x\Bigr)$$

$$- \Phi\,(x) + \sqrt{3}\,\Phi \Bigl(\frac{x}{\sqrt{3}}\Bigr)\Bigr]\Bigr\},$$

$$\Phi\,(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2}\, dx.$$

The quantity $J\,(x)$ for $x \ll 1$ behaves like

$$(a_{si}^2\, \omega_0^2 / c^2)\, x^3\, ({}^{11}\!/_9 + 13F_2 / 36\, F_1 + 7F_2^2 / 9F_1^2),$$

and for $x \gg 1$ like

$$(a_{si}^2\, \omega_0^2\, x / 2c^2) + x^3.$$

The true order of magnitude of B can be obtained by considering that $F_1 \sim e^2/a_{si}^2$. Then $Bh^2/\mu \sim 50$. Consequently, the minimum of Eq. (21) is attained for $x \sim 30$, i.e., for very small radii of the state, when the effective-mass approximation is insufficient. Thus the existence in a homopolar crystal of states of large radius, similar to those in a polar crystal, appears hardly likely.

5. INVESTIGATION OF LOCAL HOLE STATES OF SMALL RADIUS

For local states of small radius it is convenient to use an expansion of the form (6), into which will enter only a small number of terms. From the form of the symmetries one can expect that the lowest local states of the hole will be of two types:

a) Coefficients $A_{ls\alpha}$ for a certain central atom are all equal to A, but on the four nearest neighbors to it only those $A_{ls\alpha}$ which refer to the bonds of these atoms with the central one are equal to $B \neq 0$;

b) The coefficients $A_{ls\alpha}$ for two neighboring atoms are equal to A, if α is their common bond, and to B if α denotes their bonds with neighbors. The normalization conditions will be

$$\text{a) } 4\,(A^2 + B^2) = 1, \quad \text{b) } 2A^2 + 6B^2 = 1. \tag{23}$$

The average value of the Hamiltonian $\mathfrak{H}$ over the functions (5) is equal to

$$\text{a) } \bar{\mathscr{H}}' = 6A^2 c + 4ABb + 4\,(A^2 + B^2)\, \mathscr{H}_{s\alpha,s\alpha}, \tag{24}$$

b) (25)'

$$\overline{\mathscr{H}}' = A^2b + 6ABc + 6B^2c + (2A^2 + 6B^2)\,\mathscr{H}_{s\alpha,s\alpha}.$$

Finding the minimum $\overline{\mathscr{H}}'$ and the coefficients A and B in both cases, we obtain

$$\text{a)}\ E = \mathscr{H}_{s\alpha,s\alpha} + {}^3/_4\, c \pm {}^1/_4 \sqrt{9c^2 + 4b^2}; \tag{26}$$

$$B/A = -4b/[-6c \mp \sqrt{36c^2 + 16b^2}],$$

$$\text{b)}\ E = \mathscr{H}_{s\alpha,s\alpha} + {}^1/_2 c + {}^1/_4 b \pm {}^1/_4 \sqrt{(4c-b)^2 + 4bc}; \tag{27}$$

$$B/A = -c/[c - {}^1/_2 b \mp {}^1/_2 \sqrt{(4c-b)^2 + 4bc}].$$

Comparison with Eqs. (12) shows that the autolocalization of the holes is energetically disadvantageous with respect to the bottom of the lowest hole band. It is easy to imagine that a calucation of the deformation of the lattice leads to a small change in the coefficients b and c and cannot change these results significantly. It is possible to interpret them thus: local states are not satisfactory since the short-range forces and the interactions of the holes with the deformations of a small number of atoms cannot compenstae for the increase of kinetic energy occurring upon localization of a hole.

6. INVESTIGATION OF THE INTERACTION OF A HOLE WITH THE LATTICE BY THE PERTURBATION METHOD

For the deformed crystal the wave function in the general case can be represented in the form (13), but the equations for the coefficients $A(\beta, k)$ are found from the variational principle by minimizing $\overline{\mathscr{H}}'$ (14). The average Hamiltonian of the crystal will be

$$\overline{\mathscr{H}}' = \int A(\mathbf{k})\,\frac{\hbar^2k^2}{2\mu}\,A(\mathbf{k})\,d\mathbf{k} \tag{28}$$

$$+ \iint A(\mathbf{k})\,A(\mathbf{k}')\sum_{\mathbf{f}\gamma si}(\mathbf{u}^{\gamma}_{s\mathbf{f}} - \mathbf{u}^{\gamma}_{s'\mathbf{f}}e^{i\mathbf{f}\mathbf{a}_{si}})$$

$$\times \left[F_1\mathbf{a}_{si} + \frac{1}{2}(e^{i\mathbf{k}\mathbf{a}_{si}} + e^{-i(\mathbf{k}+\mathbf{f})\mathbf{a}_{si}})\,F_2\mathbf{a}_{si}\right]$$

$$\times \frac{\delta_{\mathbf{k}+\mathbf{f},\,\mathbf{k}'}}{|a_{si}|}\,d_{\mathbf{k}}d_{\mathbf{k}'} + \frac{N}{2}\sum \omega^2_{\mathbf{f}\gamma}q^*_{\mathbf{f}\gamma}q_{\mathbf{f}\gamma}.$$

We consider the second term in Eq. (28) a small perturbation and determine the scattering of holes by the vibrations by the methods of perturbation theory. In the zero-order approximation the wave function and the energy of the system are equal to

$$A(\mathbf{k}_1)\,\delta(\mathbf{k}-\mathbf{k}_1)\,\Phi_{\ldots n_{\mathbf{f}\gamma}\ldots}(\ldots q_{\mathbf{f}\gamma}\ldots); \tag{29}$$

$$E = (h^2k^2/2\mu) + \sum \hbar\omega_{\mathbf{f}\gamma}(n_{\mathbf{f}\gamma} + {}^1/_2).$$

Φ is an oscillator wave function, $n_{\mathbf{f}\gamma}$ the quantum numbers of the oscillators. We find the mixed matrix elements:

$$(\ldots n'_{\mathbf{f}\gamma\ldots}\,\mathbf{k}'\,|\,W\,|\mathbf{k}\ldots n_{\mathbf{f}\gamma\ldots}) \tag{30}$$

$$= \sum_{si}(\mathbf{u}^{\gamma}_{s,\,\mathbf{k}'-\mathbf{k}} - \mathbf{u}^{\gamma}_{s',\,\mathbf{k}'-\mathbf{k}}\,e^{i(\mathbf{k}'-\mathbf{k})\mathbf{a}_{si}})$$

$$\times \left[F_1\mathbf{a}_{si} + \frac{1}{2}(e^{i\mathbf{k}\mathbf{a}_{si}} + e^{-i\mathbf{k}'\mathbf{a}_{si}})\,F_2\mathbf{a}_{si}\right]$$

$$\times \frac{1}{|\mathbf{a}_{si}|}\begin{Bmatrix}\sqrt{(\hbar/2N\omega_{\mathbf{f}\gamma})(n_{\mathbf{k}'-\mathbf{k},\,\gamma}+1)}\\ \sqrt{(\hbar/2N\omega_{\mathbf{f}\gamma})\,n_{\mathbf{k}'-\mathbf{k},\,\gamma}}\end{Bmatrix},$$

where all numbers $n_{\mathbf{f}\gamma}$ on the right and left are assumed equal, except for that one $n_{\mathbf{f}\gamma}$ for which $\mathbf{f} = \mathbf{k}' - \mathbf{k}$.

The probability of scattering of a wave with vector k into the solid angle $d\Omega$ is

$$W_{\mathbf{k}\mathbf{k}'} = (2\pi/\hbar)\,|(\ldots n_{\mathbf{f}\gamma} \tag{31}$$

$$\mp 1\ldots\mathbf{k}\pm\mathbf{f}\,|\,W\,|\,\mathbf{k}\ldots n_{\mathbf{f}\gamma\ldots})|^2\,(V/8\pi^3)\,(\mu k'/\hbar^2)\,d\Omega$$

in applying the conservation conditions

$$\mathbf{k}' = \mathbf{k} \pm \mathbf{f}; \quad (\hbar^2/2\mu)(k'^2 - k^2) = \pm\hbar\omega_{\mathbf{f}\gamma}. \tag{32}$$

For the thermal electrons k is much smaller than a vector of the reciprocal lattice; therefore, there will be emitted and absorbed only phonons with $f \sim k$, but for them it is possible to take $|\mathbf{f}\mathbf{a}_{si}| \ll 1$ and expand the matrix element (30) into powers of $\mathbf{f}\mathbf{a}_{si}$:

$$(\ldots n_{\mathbf{f}\gamma}\mp 1\ldots\mathbf{k}\pm\mathbf{f}\,|\,W\,|\,\mathbf{k}\ldots n_{\mathbf{f}\gamma}\ldots) \tag{33}$$

$$= \sqrt{\frac{\hbar}{2N\omega_{\mathbf{f}\gamma}}}\left\{\sum_{si}\pm i\,(\mathbf{f}\mathbf{a}_{si})\,(\mathbf{a}_{si}\,\mathbf{u}^{\gamma}_{s'\mathbf{f}})\,(F_1+F_2)\right.$$

$$\left.\mp i\,(\mathbf{f}\mathbf{a}_{si})\,\mathbf{a}_{si}\,(\mathbf{u}^{\gamma}_{sf} - \mathbf{u}^{\gamma}_{s'f})\,F_2\right\}\frac{1}{|\mathbf{a}_{si}|}\begin{Bmatrix}\sqrt{n_{\mathbf{f}\gamma}+1}\\ \sqrt{n_{\mathbf{f}\gamma}}\end{Bmatrix}.$$

As a simplification we assume that for the limit of long waves, for the longitudinal acoustic vibrations, $\mathbf{u}^{\gamma}_{sf} \parallel \mathbf{f}$ and it does not depend on the index s, but $\omega_{f\gamma} = cf$; for the optical vibrations $\mathbf{u}^{\gamma}_{1f} = -\mathbf{u}^{\gamma}_{2f} \parallel \mathbf{f}$, and $\omega_{f\gamma} = \text{const}$. We neglect the interaction with the transverse vibrations. Then

$$\sum_i (\mathbf{f}\mathbf{a}_{si})(\mathbf{u}^{\gamma}_{sf}\,\mathbf{a}_{si}) = (2M)^{-1/2} f a_{si}^2 \sum_{i=1}^{4} \cos^2(\widehat{\mathbf{f}\mathbf{a}_{si}}) = 4a_{si}^2 f / 3\sqrt{2M}$$

and our matrix element is equal for the acoustic vibrations to

$$\pm\sqrt{\frac{\hbar}{2Nfc}}\,\frac{4f\,|\mathbf{a}_{si}|}{3\sqrt{2M}}\,(F_1+F_2)\cdot\begin{Bmatrix}\sqrt{n_{f\gamma}+1}\\ \sqrt{n_{f\gamma}}\end{Bmatrix}, \quad (34a)$$

and for the optical ones to

$$\pm\sqrt{\frac{\hbar}{2N\omega_{\gamma}}}\,\frac{4f\,|\mathbf{a}_{si}|}{3\sqrt{2M}}\,(F_1+3F_2)\begin{Bmatrix}\sqrt{n_{f\gamma}+1}\\ \sqrt{n_{f\gamma}}\end{Bmatrix}. \quad (34b)$$

Thus for the probability of scattering by the acoustic and optical vibrations we find, respectively,

$$W_{\mathbf{kk}'} = \frac{\mu k'\,\Delta a_{si}^2 f\,(F_1+F_2)^2}{9\pi^2 Mc\hbar^2}\begin{Bmatrix}n_{f\gamma}+1\\ n_{f\gamma}\end{Bmatrix}, \quad (35a)$$

$$W_{\mathbf{kk}'} = \frac{\mu k'\Delta\,|a_{si}|^2 f^2\,(F_1+3F_2)^2}{9\pi^2 M\omega_{\gamma}\hbar^2}\begin{Bmatrix}n_{f\gamma}+1\\ n_{f\gamma}\end{Bmatrix}, \quad (35b)$$

$\Delta = V/N$ is the volume of an elementary cell.

In calculating the mobility we assume that (1) the velocity of sound c is much smaller than the velocity of an electron, and the change of its energy in emitting or absorbing a phonon can be neglected; $k' \approx k$, $f = 2k\sin(\theta/2)$, θ is the scattering angle; (2) the temperature is not too low and for acoustic phonons $\hbar\omega \ll \varkappa T$ ($\varkappa$ = Boltzmann's constant). For the change of the energy-distribution functions as a result of collisions Eq. (35a) gives the usual quantity $(v/l)\chi\mathbf{v}$, where $\chi\mathbf{v}$ is the nonsymmetrical part of the distribution and l is the mean free path:

$$l = 9\pi Mc^2\hbar^4 / 8\mu^2\Delta\,|a_{si}|^2 (F_1+F_2)^2\varkappa T. \quad (36)$$

This gives the usual dependence of mobility with temperature: $u \sim T^{-3/2}$. The interaction of a hole with the optical vibrations of the lattice is conveniently considered in two limiting cases: $\hbar\omega_{\text{opt}} \gg \varkappa T$ and $\hbar\omega_{\text{opt}} \ll \varkappa T$. In the former case only transitions with absorption are possible, and $k'^2 = 2\mu\omega_{\gamma}/\hbar \approx f^2$. Then the change of the distribution functions on account of scattering of the type (35b) gives the quantity $\chi\mathbf{v}/\tau$, where

$$\tau = 9\pi M\hbar^3\omega_{\gamma}\left(e^{\hbar\omega_{\gamma}/\varkappa T} - 1\right)/\mu\,(2\mu\omega_{\gamma}/\hbar)^{1/2} \quad (37)$$

$$\times\,\Delta\,|a_{si}|^2\,2\mu\omega_{\gamma}\,(F_1+3F_2)^2.$$

The time of free path does not depend on the velocity of the hole. This gives a mobility proportional to $e^{\hbar\omega_{\gamma}/\varkappa T} - 1$.

For high temperatures, computation with Eq. (35b) leads to the approximations $k' = k$, $f = 2k\sin(\theta/2)$; $\overline{2n+1} = 2\varkappa T/\hbar\omega_{\gamma}$. This leads to the formula $(v/l)\chi\mathbf{v}$, with

$$l = 27\pi M\hbar^4\omega_{\gamma}^2 / 64\mu^2\Delta\,|a_{si}|^2 (F_1+3F_2)^2\varkappa Tk^2. \quad (38)$$

The free path length is inversely proportional to the square of the velocity and to the temperature. This gives a dependence of mobility on temperature of the form $u \sim T^{-5/2}$. If the exchange forces are more sensitive to the distance, then $|F_2| \gg |F_1|$ and the numerical factor of the probability of scattering by optical vibrations differs by a factor $9fc/\omega_{\gamma}$ from the probability of scattering by the acoustic vibrations.

Therefore, at high temperatures, the scattering by optical vibrations can prove to be dominating. This also leads to a different temperature dependence of the mobility: $u \sim T^{-5/2}$. At low temperatures, $\bar{n}_{\text{ac}} \gg \bar{n}_{\text{opt}}$ and $fc \ll \omega_{\gamma}$, and one must obtain the previous formula $u \sim T^{-3/2}$.

It is of interest to examine the thermo- and galvanoelectrical and magnetic effects, the coefficients of which are determined from the dependence of the free-path length on the velocity. In the case of a power-law $l \sim v^n$ the corresponding formulas were obtained in the work of one of the authors[14]. As is obvious from Eqs. (36)-(38), essentially new results can be obtained only at high temperatures: $\varkappa T \gg \hbar\omega_{\gamma}$, if the scattering by optical vibrations dominates. Thus, in the formula for the thermal emf

$$\alpha = \frac{\varkappa}{e}\left\{\frac{n}{2} + 2 + \ln\frac{2\,(2\pi\mu\varkappa T)^{3/2}}{h^3}\right\}$$

the constant component is equal here to 1 instead of 3, according to the theory of Davydov and Shmushkevich. Since at low temperatures the results coincide, the temperature dependence of α must also change correspondingly.

For the transverse Nernst-Ettingshausen effect:

$$\text{emf} = {}^1\!/_2 (n - 1)(\varkappa T / e) R\sigma H dT / dx$$

(H is the magnetic field, R is the Hall constant, σ is the electrical conductivity) one must expect an increase of the coefficient ($n - 1$) by a factor of three.

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[1] B. I. Davydov and I. M. Shmushkevich, Usp. Fiz. Nauk **24**, 19 (1940).

[2] W. C. Dunlap, Phys. Rev. **79**, 286 (1950).

[3] Dresselhaus, Kip and Kittel, Phys. Rev. **92**, 827 (1953).

[4] F. G. Morin, Phys. Rev. **93**, 62 (1954).

[5] F. Herman, Phys. Rev. **88**, 1210 (1952).

[6] D. K. Holmes, Phys. Rev. **87**, 782 (1952).

[7] F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953).

[8] T. A. Kontorova, J. Tech. Phys. (U.S.S.R.) **24**, 2217 (1955).

[9] K. B. Tolpygo, J. Exptl. Theoret. Phys. (U.S.S.R.) **22**, 378 (1952).

[10] S. I. Pekar, J. Tech. Phys. (U.S.S.R.) **25**, 2030 (1955).

[11] S. I. Pekar and M. F. Deigen, J. Exptl. Theoret. Phys. (U.S.S.R.) **18**, 481 (1948).

[12] A, M. Fedorchenko, Thesis, Kiev State University, 1954.

[13] G. Gell-Mann, *Quantum Chemistry*, ONTI, Moscow-Leningrad, 1937.

[14] K. B. Tolpygo, Trudy Inst. Fiz., Akad. Nauk SSSR **3**, 52 (1952).

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On the Theory of the Stability of a Layer Located at a Superadiabatic Temperature Gradient in a Gravitational Field

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The stability of a layer of liquid or gas in the presence of a superadiabatic temperature gradient is investigated for cases in which the upper and lower boundaries of the layer are not fixed, and convection arising in it may spread into stable regions bordering it.

1. INTRODUCTION

IT is known that the equilibrium of a layer located in a gravitational field is stable if its entropy S increases with ehight[1]. A series of authors[2-4] have investigated the stability of a layer bounded by horizontal planes on which the temperature is given and the vertical component of the velocity $v_z = 0$. However, in a whole series of cases, the layer in which instability arises, causing an increase of convection, is bordered on one or both sides by stable layers in which the temperature gradient is less than adiabatic, but in which the motion is propagated, occupying a region considerably exceeding the region of instability. The propagation of convection beyond the limits of the unstable layer may be understood in the following way.

With a random rise of a separate convective element, a lifting force is developed proportional to the difference between the temperature ϑ of this element and that of the surrounding medium, and increases monotonically up to the upper boundary of the unstable layer. Therefore, the convective element arrives at the upper boundary with maximum acceleration. Above the boundary, the temperature difference, and consequently the acceleration,