

Zone Theory of the Three-Dimensional Model of a Liquid

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The zone theory of a one-dimensional liquid model¹ proposed earlier by the author is extended to a three-dimensional model. By solving the Schrödinger equation in a deformed coordinate system, it is shown that during melting of a crystal, the electron energy spectrum retains its zone structure, in accordance with the experimental facts.

1. INTRODUCTION

As is well known, the energy spectrum of electrons in solids possesses a zone structure. On this basis we are able correctly to explain the electrical conductivity of metals and semiconductors and a whole series of other phenomena. Theoretically, the occurrence of a zone structure is demonstrated for motion of the electron in a strictly periodic field, i.e., for the case of long range order. On the other hand, the electrical conductivity of metals and semi-conductors does not change during melting, despite the disappearance of long range order. This leads one to the idea that the zone structure of the energy spectrum is related, not to the long range, but rather to the short range, order of location of atoms in a body.

In paper 1* we showed theoretically, for the simplest model of a one-dimensional chain of atoms, that for small disturbance of short range order and complete disappearance of long range order, the energy spectrum retains the zone character. In the present paper, the theory is extended to the more realistic case of a three-dimensional model. All the assumptions and the method of calculation are the same as for the one-dimensional model, so we shall repeat the discussion only very briefly, noting special features of the three-dimensional case.

Let us suppose that initially we have a crystal with a regular arrangement of atoms, so that the potential energy of an electron in the self-consistent field of the crystal is a periodic function $V(x_1, x_2, x_3)$ of Cartesian coordinates x_1, x_2, x_3 fixed in the crystal. This periodicity is meant in the sense that the potential is periodic along certain crystallographic directions, which either

coincide with the axes x_1, x_2, x_3 , or, in the case of crystals of lower symmetry, are described by linear equations in the x_1, x_2, x_3 coordinate system.

X-ray and electron diffraction studies show that liquids possess short range order. Upon melting it may turn out that the short range order is practically kept unchanged, or it may change abruptly if, as in the case of water, the number of nearest neighbors changes. We shall suppose that short range order always changes very little during melting. If the real crystal has essentially different short range order than the liquid, then we shall consider the melting of a certain hypothetical crystal with the same short range order as the liquid. In this connection, we suppose that each unit cell of the crystal suffers only a small deformation during melting, leading to slight changes in the lengths of the cell edges and the angles between them. The percentage deformation of the cell is of the order of a small quantity ϵ , and is a random variable. For simplicity, we shall assume that during melting there occurs no macroscopic deformation of the crystal, in particular, no change in its volume. In this case all deformations can have either sign with equal probability.

As shown in reference 1, the result of the superposition of small deformations of cells, according to the law of addition of random variables with varying sign, is the disappearance of long range order at distances of the order of $1/\epsilon^2$ from unit cells. In the three-dimensional case, this means not only that the probability of location of a particular atom is smeared over a region larger than the unit cell, but also that distant cells are turned relative to one another through arbitrarily large angles.

During melting, as a result of the deformation of the lattice, the potential field $V(x_1, x_2, x_3)$ undergoes two types of changes. First, all the maxima and minima of V are shifted in space parallel to

¹ A. I. Gubanov, J. Exper. Theoret. Phys. USSR **26**, 139 (1954)

* The formulas of paper 1 will be cited as Roman I.

the displacement of the atoms. Secondly, because of the small disturbance of the short range order, the value of V changes by a small amount ΔV . As in the one-dimensional case, changes of the second type do not destroy the periodicity of the potential, but lead only to small corrections to the periodic field which can easily be taken into account by ordinary perturbation theory. We shall therefore not consider these changes at all, and shall suppose that the entire change of the potential field during melting is just the result of a shift in space of points with given potential parallel to the displacement of the atoms. This assumption is equivalent to the hypothesis of deformable ions which gives a good approximation for the calculation of the interaction of lattice waves and electrons in the theory of metals.

We introduce a distorted coordinate system ξ^1, ξ^2, ξ^3 in such a way that the coordinate curves in the liquid pass through points with the same values of the potential as do the corresponding coordinate lines x_1, x_2, x_3 in the crystal. By suitably selecting the variable scale for the coordinates ξ , we can arrange for the potential to be periodic in the coordinate system ξ , in the sense that the potential will be periodic along certain crystallographic lines (curves) which either coincide with the coordinate curves ξ or are described in this system of coordinates by linear equations. The coordinates ξ are slightly non-orthogonal.

Since corresponding elements of the coordinate lines x_α and ξ^α ($\alpha = 1, 2, 3$) can be turned through large angles relative to one another, we cannot in the three-dimensional case introduce ratios of dx_α and $d\xi^\alpha$ of the type of equation I - (5). However, for what follows it is not necessary to know completely the transformation from the coordinates x to the coordinates ξ ; it is sufficient to give the metric tensor in the ξ coordinate system. Since, during melting, each element of the crystal undergoes a small random deformation, the diagonal and non-diagonal elements of the metric tensor must have the form:

$$g_{\alpha\alpha} = 1 + \varepsilon\gamma_{\alpha\alpha}; \quad (g_{\alpha\beta})_{\alpha \neq \beta} = \varepsilon\gamma_{\alpha\beta}; \quad (1)$$

$$\alpha, \beta = 1, 2, 3.$$

Here the $\gamma_{\alpha\beta}$ are random functions of the coordinates, of order of magnitude unity. (Some of them may be of lower order, or be equal to zero.) Unlike the one-dimensional case, we cannot here normalize the $\gamma_{\alpha\beta}$ exactly, since their ratios depend on the liquid structure.

We note that the functions $\gamma_{\alpha\beta}$ are defined somewhat differently from the function γ for the one-dimensional case; on the basis of Eq. (1) we would write in place of Eq. I - (5):

$$d\xi/dx = 1/\sqrt{1 + \varepsilon\gamma}. \quad (2)$$

Consequently, if we make the transition from the formulas derived in the present paper to the one-dimensional case, we obtain results differing from the corresponding formulas of reference 1 by the numerical factor $1/2$ for the first approximation, and $1/3$ for the second approximation.

2. WAVE EQUATION IN THE DISTORTED COORDINATE SYSTEM

The method of calculation consists in solving the Schrödinger equation for the electron in the distorted coordinate system ξ , in which the potential energy of the electron is a periodic function. As in the one-dimensional case, the problem is solved in the adiabatic approximation -- for pre-assigned instantaneous positions of the atoms. We use the time-independent Schrödinger equation

$$-\left(\hbar^2/2m\right)\nabla^2\psi + V\psi = E\psi, \quad (3)$$

with the usual symbols.

The Laplace operator in curvilinear non-orthogonal coordinates has the form

$$\nabla^2\psi = \frac{1}{Vg} \sum_{\alpha, \beta} \frac{\partial}{\partial \xi^\alpha} \left(g^{\alpha\beta} \sqrt{g} \frac{\partial \psi}{\partial \xi^\beta} \right), \quad (4)$$

where g is the determinant formed from the covariant components of the metric tensor, whose contravariant components are

$$g^{\alpha\beta} = G_{\beta\alpha}/g; \quad (5)$$

$G_{\beta\alpha}$ is the algebraic complement of the element $g_{\beta\alpha}$ in the determinant, i.e., the corresponding minor multiplied by $(-1)^{\alpha+\beta}$.

Substitution of Eq. (5) in Eq. (4) and of Eq. (4) in Eq. (3), and expansion in powers of ε brings the Schrödinger equation to the form

$$\hat{H}\psi = E\psi; \quad \hat{H} = \hat{H}_0 + \varepsilon\hat{W} + \varepsilon^2\hat{w} + \dots; \quad (6)$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \sum_{\alpha=1}^3 \frac{\partial^2 \psi}{\partial \xi^{\alpha^2}} + V(\xi^1, \xi^2, \xi^3); \quad (7)$$

$$\hat{W} = \frac{\hbar^2}{2m} \sum_{\alpha=1}^3 \left[\gamma_{\alpha\alpha} \frac{\partial^2}{\partial \xi^{\alpha^2}} - \frac{1}{2} \frac{\partial}{\partial \xi^\alpha} (\gamma_{\beta\beta} + \gamma_{\gamma\gamma}) \right] \quad (8)$$

$$-\gamma_{\alpha\alpha}) \frac{\partial}{\partial \xi^\alpha} - (-1)^{\beta+\gamma} \left(\gamma_{\beta\gamma} \frac{\partial^2}{\partial \xi^\beta \partial \xi^\gamma} + \frac{\partial \gamma_{\beta\gamma}}{\partial \xi^\beta} \frac{\partial}{\partial \xi^\gamma} + \frac{\partial \gamma_{\beta\gamma}}{\partial \xi^\gamma} \frac{\partial}{\partial \xi^\beta} \right)].$$

Here α, β, γ are a cyclic permutation of the indices 1, 2, 3. The operator \hat{W} contains only terms variable in sign, of first order in the random functions $\gamma_{\alpha\beta}$.

The operator \hat{w} can be separated into two parts

$$\hat{w} = \hat{w}' + \hat{w}'' \quad (9)$$

\hat{w}' consists of terms of fixed sign, quadratic in the functions $\gamma_{\alpha\beta}$ and is equal to

$$\hat{w}' = -\frac{\hbar^2}{2m} \sum_{\alpha=1}^3 (\gamma_{\alpha\alpha}^2 + \gamma_{\alpha\beta}^2 + \gamma_{\alpha\gamma}^2) \frac{\partial^2}{\partial \xi^{\alpha^2}}; \quad (10)$$

\hat{w}'' contains only terms variable in sign. The expression for it is rather complicated and has no practical value since \hat{w}'' is of the same order of magnitude as \hat{W} , is also variable in sign, and is multiplied by ϵ^2 rather than by ϵ .

The operators $\epsilon \hat{W}$ and $\epsilon^2 \hat{w}$ or $\epsilon^2 \hat{w}'$ are considered as perturbations. As in the one-dimensional case, they are not self-adjoint.

Since $V(\xi^1, \xi^2, \xi^3)$ is a periodic function, the solution of the unperturbed equation $\hat{H}_0 \psi = E \psi$ is the familiar solution of the problem of an electron in a periodic field. Let the fundamental volume contain G^3 unit cells as is usually done in the theory of metals. In order to have a significant disturbance of the long-range order, we must impose the condition

$$G \gg 1/\epsilon^2 \quad (11)$$

The energy spectrum of the unperturbed problem consists of a series of separated zones, in each of which the electron wave vector \mathbf{k} can take on G^3 values. To each value there corresponds a Bloch wave function:

$$\psi_{n\mathbf{k}}^0 = u_{n\mathbf{k}} \exp \left(i \sum_{\alpha=1}^3 k_\alpha \xi^\alpha \right). \quad (12)$$

Here n gives the zone number, the k_α are coefficients giving the state within a zone, $u_{n\mathbf{k}}$ is a modulating function which has the period of the lattice.

We look for a solution of the perturbed problem in the form of a linear combination of Eq. (12)

$$\psi(\xi^1, \xi^2, \xi^3) = \sum_{n, \mathbf{k}} c_{n\mathbf{k}} \psi_{n\mathbf{k}}^0, \quad (13)$$

where the coefficients in the expansion are determined from the system of equations:

$$(E_{n\mathbf{k}}^0 + \epsilon W_{n\mathbf{k}n\mathbf{k}} + \epsilon^2 w'_{n\mathbf{k}n\mathbf{k}} - E) c_{n\mathbf{k}} \quad (14)$$

$$+ \sum_{n', \mathbf{k}' \neq n, \mathbf{k}} (\epsilon W_{n\mathbf{k}n'\mathbf{k}'} + \epsilon^2 w'_{n\mathbf{k}n'\mathbf{k}'}) c_{n'\mathbf{k}'} = 0.$$

Summation over \mathbf{k} means summation over all G^3 values of the three coefficients k_1, k_2, k_3 .

The matrix elements $W_{n\mathbf{k}n'\mathbf{k}'}$ and $w_{n\mathbf{k}n'\mathbf{k}'}$ are calculated with weight functions equal to the factor of orthogonality of the zeroth order functions, i.e., to unity. The functions $\psi_{n\mathbf{k}}^0$ are normalized to unity, i.e.,

$$\int |\psi_{n\mathbf{k}}^0|^2 d\xi^1 d\xi^2 d\xi^3 = 1, \quad (15)$$

where the integration extends over the whole fundamental domain, i.e., over G^3 elementary cells.

3. EVALUATION OF THE MATRIX ELEMENTS OF THE PERTURBATION

According to Eqs. (8) and (12), the matrix element of the operator \hat{W} has the form

$$W_{n\mathbf{k}n'\mathbf{k}'} = \frac{\hbar^2}{2m} \int u_{n\mathbf{k}}^* B_{n'\mathbf{k}'} \quad (16)$$

$$\times \exp \left[i \sum_{\alpha=1}^3 (k'_\alpha - k_\alpha) \xi^\alpha \right] d\xi^1 d\xi^2 d\xi^3.$$

Explicit expressions for the functions $B_{n'\mathbf{k}'}$ are rather complicated, but for determining the order of magnitude of the quantity $W_{n\mathbf{k}n'\mathbf{k}'}$ it is sufficient to note that $B_{n'\mathbf{k}'}$ consists of terms of the type

$$\gamma_{\alpha\beta} u_{n'\mathbf{k}'} k'_\alpha k'_\beta, \quad \gamma_{\alpha\beta} \frac{\partial u_{n'\mathbf{k}'}}{\partial \xi^\alpha} k'_\beta, \quad \gamma_{\alpha\beta} \frac{\partial^2 u_{n'\mathbf{k}'}}{\partial \xi^\alpha \partial \xi^\beta},$$

$$\frac{\partial \gamma_{\alpha\beta}}{\partial \xi^\alpha} \frac{\partial u_{n'\mathbf{k}'}}{\partial \xi^\beta} \quad \text{and} \quad \frac{\partial \gamma_{\alpha\beta}}{\partial \xi^\alpha} u_{n'\mathbf{k}'} k'_\beta.$$

The functions $u_{n'\mathbf{k}'}$ have the periodicity of the lattice, while the functions $\gamma_{\alpha\beta}$ which are of order of magnitude unity, change substantially from cell to cell. Therefore, differentiating $u_{n'\mathbf{k}'}$ and $\gamma_{\alpha\beta}$ with respect to ξ^α gives a factor of order $1/a$, where a is the lattice constant. The mean value of k'_α is also of order $1/a$. From the normalization condition of Eq. (15) we have $u_{n'\mathbf{k}'} \approx 1/G^{3/2} a^{3/2}$. Consequently, each of the terms which make up $B_{n'\mathbf{k}'}$ is of order of magnitude $(1/a^2) u_{n\mathbf{k}} \approx 1/G^{3/2} a^{7/2}$. The functions $B_{n'\mathbf{k}'}$, which consist of a finite number

of terms, are of this same order of magnitude.

To evaluate the integral in Eq. (16), we separate it into a sum of integrals over the G^3 elementary cells. Within the confines of a single unit cell, the functions $\gamma_{\alpha\beta}$ and their derivatives have more or less definite values. Therefore, if $u_{n\mathbf{k}}$ and $u_{n'\mathbf{k}'}$ are close to one another, and the factor $\exp[i \sum_{\alpha=1}^3 (k'_{\alpha} - k_{\alpha}) \xi^{\alpha}]$ is close to unity, integration over the unit cell reduces to multiplication by a factor of order a^3 , so that the integral I_l over the l 'th unit cell is of order

$$|I_l| \approx \frac{1}{G^3 a^5} a^3 = \frac{1}{G^3 a^2}. \quad (17)$$

Actually, because of the factor

$$\exp \left[i \sum_{\alpha=1}^3 (k'_{\alpha} - k_{\alpha}) \xi^{\alpha} \right]$$

and the non-equality of the functions $u_{n\mathbf{k}}$ and $u_{n'\mathbf{k}'}$, the quantity I_l will be somewhat smaller -- the smaller, the larger the difference $k_{\alpha} - k'_{\alpha}$. All the I_l are random quantities of variable sign. As discussed in detail in reference 1, on the basis of Liapounoff's theorem, the sum of random quantities of varying sign conforms to a Gaussian distribution, with average value zero and root mean square proportional to the square root of the number of terms. Therefore, carrying out the summation over the G^3 unit cells, we find that the root mean square of the matrix element $W'_{n\mathbf{k}n'\mathbf{k}'}$ is of order

$$\sqrt{\overline{W'^2_{n\mathbf{k}n'\mathbf{k}'}}} = \sqrt{G^3} \frac{\hbar^2}{2m G^3 a^2} = \frac{\hbar^2}{2m G^{3/2} a^2} \quad (18)$$

and decreases with increasing difference $k_{\alpha} - k'_{\alpha}$.

In precisely the same way one can evaluate the matrix elements of the operator \hat{w}' . Equation (17) is still valid for the order of magnitude of the integral over a unit cell. The integral over a unit cell, which enters into a non-diagonal matrix element $W'_{n\mathbf{k}n'\mathbf{k}'}$ is variable in sign because of the presence of the factor

$$\exp \left[i \sum_{\alpha=1}^3 (k'_{\alpha} - k_{\alpha}) \xi^{\alpha} \right],$$

which means that its mean square value is also given, in order of magnitude, by Eq. (18).

On the other hand, the integrals which enter into the diagonal matrix element $w'_{n\mathbf{k}n\mathbf{k}}$ are fixed in sign. Taking the quantities $\gamma_{\alpha\beta}^2$ out from under the integral sign for a given unit cell, and considering that

$$\int |u_{n\mathbf{k}}|^2 d\xi^1 d\xi^2 d\xi^3 = \frac{1}{G^3}, \quad (19)$$

$$\int u_{n\mathbf{k}}^* \frac{\partial u_{n\mathbf{k}}}{\partial \xi^{\alpha}} d\xi^1 d\xi^2 d\xi^3 \approx 0,$$

$$\int u_{n\mathbf{k}}^* \frac{\partial^2 u_{n\mathbf{k}}}{\partial \xi^{\alpha^2}} d\xi^1 d\xi^2 d\xi^3 \approx -\frac{1}{G^3 a^2},$$

where the integrals go over a unit cell (cf the similar evaluations in reference 1), we obtain

$$w'_{n\mathbf{k}n\mathbf{k}} \quad (20)$$

$$\approx \frac{\hbar^2}{2m} \frac{1}{G^3} \sum_{\alpha=1}^3 \sum_{l=1}^{G^3} (\gamma_{\alpha\alpha}^2 + \gamma_{\alpha\beta}^2 + \gamma_{\alpha\gamma}^2)_l \left(\frac{1}{a^2} + k_{\alpha}^2 \right),$$

where the values of the functions $\gamma_{\alpha\beta}$ are taken for the l 'th cell. Carrying out the summation over l we have

$$w'_{n\mathbf{k}n\mathbf{k}} \approx \frac{\hbar^2}{2m} \sum_{\alpha=1}^3 (\overline{\gamma_{\alpha\alpha}^2} + \overline{\gamma_{\alpha\beta}^2} + \overline{\gamma_{\alpha\gamma}^2}) \left(\frac{1}{a^2} + k_{\alpha}^2 \right). \quad (21)$$

The dash denotes an average over all cells. In the case of a cubic lattice, clearly $\overline{\gamma_{11}^2} = \overline{\gamma_{22}^2} = \overline{\gamma_{33}^2}$, $\overline{\gamma_{12}^2} = \overline{\gamma_{13}^2} = \overline{\gamma_{23}^2}$, consequently

$$w'_{n\mathbf{k}n\mathbf{k}} \approx \frac{\hbar^2}{2m} (\overline{\gamma_{\alpha\alpha}^2} + 2\overline{\gamma_{\alpha\beta}^2}) \left(\frac{3}{a^2} + k^2 \right). \quad (22)$$

Finally, if we set $\overline{\gamma_{\alpha\alpha}^2} = \overline{\gamma_{\alpha\beta}^2} = 1$,

$$w'_{n\mathbf{k}n\mathbf{k}} \approx \frac{3\hbar^2}{2m} \left(\frac{3}{a^2} + k^2 \right). \quad (23)$$

Comparing Eqs. (18) and (21) - (23), and noting the inequality (11), we see that in Eq. (14) we can neglect the diagonal element $\epsilon W'_{n\mathbf{k}n\mathbf{k}}$ compared to $\epsilon^2 w'_{n\mathbf{k}n\mathbf{k}}$; on the other hand, the non-diagonal element $\epsilon^2 w'_{n\mathbf{k}n'\mathbf{k}'}$ is negligible compared to $\epsilon W'_{n\mathbf{k}n'\mathbf{k}'}$.

4. SOLUTION BY THE METHOD OF RELATIVE DEGENERACY

If the unperturbed energy of the electron in a given zone, measured from the lower edge of the zone, is proportional to $\sum k_{\alpha}^2$ (isotropic approximation), it is easy to show that the minimum distance between neighboring levels in the zone is

$$\Delta E_{\min} = 2\pi^2 \hbar^2 / a^2 G^2. \quad (24)$$

In fact, if we fix k_1 and k_2 , and give k_3 neighboring values -- zero and $\pm 2\pi/aG$, we get two energy values differing by the amount given in Eq. (24). The levels are highly degenerate, since their number does not exceed G^2 in order of magnitude, while the total number of electron states in the

zone is G^3 . If we take account of the anisotropy, this degeneracy is partially removed, so that we get even closer spacing of energy levels.

Comparing Eqs. (18) and (24), and noting Eq. (11), we see that the non-diagonal matrix elements of the perturbation are larger than the distance between neighboring levels in zeroth approximation, so that we cannot use ordinary perturbation theory, but must, as in the one-dimensional case, carry out the calculation by the method of relative degeneracy. The system of equations for the zeroth approximation, completely analogous to I - (23) will have the form

$$(E'_k - E)c_k + \varepsilon \sum_{k' \neq k} W_{kk'} c_{k'} = 0, \quad (25)$$

where we have dropped the index n and introduced the notation

$$E'_k = E_k^0 + \varepsilon^2 \omega'_{kk}. \quad (26)$$

Setting the determinant of the system (25) equal to zero, and expanding according to the Laplace formula, we obtain an equation differing from I - (26) only in that the summation is taken over a vector index running through G^3 values:

$$\begin{aligned} 1 - \varepsilon^2 \sum_k \sum_{k'} \frac{W_{kk'} W_{k'k}}{(E'_k - E)(E'_{k'} - E)} & \quad (27) \\ + \varepsilon^3 \sum_k \sum_{k'} \sum_{k''} \frac{W_{kk'} W_{k'k''} W_{k''k}}{(E'_k - E)(E'_{k'} - E)(E'_{k''} - E)} - \dots \\ \dots + (-1)^{r+1} \varepsilon^r \sum_k \sum_{k'} & \\ \dots \sum_{k^{(r)}} \frac{\prod_{j=1}^r W_{kk^{(j)}}}{\prod_{j=1}^r (E'_{k^{(j)}} - E)} + \dots = 0 \end{aligned}$$

So long as $r \ll G^3$, the number of terms in the sum appearing as a factor after ε^r is of order G^{3r} .

As in the one-dimensional case, we can show that $\overline{W_{kk'} W_{k'k}} > 0$. To do this, we separate the operator \widehat{W} into a Hermitian part \widehat{W}' and a skew-Hermitian part \widehat{W}''

$$\begin{aligned} \widehat{W}' = \frac{\hbar^2}{2m} \sum_{\alpha=1}^3 \left[\gamma_{\alpha\alpha} \frac{\partial^2}{\partial \xi^{\alpha^2}} + \frac{\partial \gamma_{\alpha\alpha}}{\partial \xi^\alpha} \frac{\partial}{\partial \xi^\alpha} \right. & \quad (28) \\ \left. + \frac{1}{4} \frac{\partial^2 (\gamma_{\alpha\alpha} + \gamma_{\beta\beta} + \gamma_{\gamma\gamma})}{\partial \xi^{\alpha^2}} \right. \\ \left. - (-1)^{\beta+\gamma} \left(\gamma_{\beta\gamma} \frac{\partial^2}{\partial \xi^\beta \partial \xi^\gamma} - \frac{1}{2} \frac{\partial^2 \gamma_{\beta\gamma}}{\partial \xi^\beta \partial \xi^\gamma} \right) \right]; \end{aligned}$$

$$\begin{aligned} \widehat{W}'' = \frac{\hbar^2}{2m} \sum_{\alpha=1}^3 \left[-\frac{1}{2} \frac{\partial (\gamma_{\alpha\alpha} + \gamma_{\beta\beta} + \gamma_{\gamma\gamma})}{\partial \xi^\alpha} \frac{\partial}{\partial \xi^\alpha} \right. & \quad (29) \\ \left. - \frac{1}{4} \frac{\partial^2 (\gamma_{\alpha\alpha} + \gamma_{\beta\beta} + \gamma_{\gamma\gamma})}{\partial \xi^{\alpha^2}} \right. \\ \left. - (-1)^{\beta+\gamma} \frac{1}{2} \left(\frac{\partial^2 \gamma_{\beta\gamma}}{\partial \xi^\beta \partial \xi^\gamma} + \frac{\partial \gamma_{\beta\gamma}}{\partial \xi^\beta} \frac{\partial}{\partial \xi^\gamma} + \frac{\partial \gamma_{\beta\gamma}}{\partial \xi^\gamma} \frac{\partial}{\partial \xi^\beta} \right) \right]. \end{aligned}$$

In summing random quantities, their squares accumulate. Therefore, since the terms in Eq. (29) are similar to those in Eq. (28), and some of them have the coefficient $1/2$, we can conclude that

$$|\overline{W'_{kk'}}|^2 > |\overline{W''_{kk'}}|^2, \quad (30)$$

which means that

$$\overline{W_{kk'} W_{k'k}} = |\overline{W'_{kk'}}|^2 - |\overline{W''_{kk'}}|^2 > 0. \quad (31)$$

Consequently we can repeat here the whole argument used in reference 1. If the energy E lies outside the band of values E'_k , then, according to Eq. (18), each term in the sum for ε^r in Eq. (27) is of order $G^{-3r/2}$. For odd powers of ε , all these sums are variable in sign, and the root mean square value of the sum including the factor ε^r is of order ε^r ($r > 2$); which means that these sums can be neglected. On the other hand, the sums for even values of ε have a number of terms of order G^{3r} and are fixed in sign; so these sums form a series of the type $1 - \varepsilon^2 G^3 - \varepsilon^4 G^6 - \dots$. This means that Eq. (27) cannot be satisfied for a value of E lying outside the zone E'_k .

Thus during melting of the crystal, the zone structure of the energy levels is retained, except that each level is shifted by an amount $\varepsilon^2 \omega'_{nk} \mathbf{k}$.

The wave functions in zeroth approximation are linear combinations of all G^3 Bloch functions belonging to the given zone. However, it was shown in reference 1, on the basis of Eq. (25), that in each solution only a fraction ε^2 of all the functions have coefficients significantly different from zero. This estimate remains valid here. Consequently each wave function in zeroth approximation represents a packet of approximately $\varepsilon^2 G^3$ Bloch functions, all corresponding to energy values E'_k close to E , but with various values of the coefficients k_α . However, as we pointed out earlier, the perturbation matrix element $W_{kk'}$ decreases with increase in the difference $k_\alpha - k'_\alpha$; thus in each wave packet, functions grouped around particular values of k_1, k_2, k_3 will predominate. Because of this the electrons in the liquid are not described by standing waves, but rather by wave packets moving

in definite directions, i.e., the medium is a conductor.

The uncertainty in the momentum component in the direction of the resultant motion of the packet is of order

$$\Delta p = (\hbar / a) \varepsilon^2, \quad (32)$$

if we note that the packet is built up from $\varepsilon^2 G$ neighboring values of this momentum component; from the uncertainty relations it then follows that the packet is localized within a region of dimension

$$\Delta \xi = a / \varepsilon^2, \quad (33)$$

i.e., precisely the same interval within which the long range order shows a noticeable breakdown.

We could carry the calculation to the next approximation and take account of the interaction between zones, but nothing new would be gotten compared to the one-dimensional theory [formulas I - (32) - (34)].

In conclusion I take the opportunity to express my sincere thanks to A. I. Ansel'm and I. M. Shmushkevich for discussion of the work.

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