Electrical Properties of Amorphous Semiconductors

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I. INTRODUCTION

The properties of electrons in a crystalline solid are usually explained on the basis of the band theory of solids. The presence of energy bands of electrons in a solid body is theoretically verified by the quantum-mechanical calculation of the motion of an electron in a periodic, self-consistent field. Thus, the zone energy spectrum usually is associated with the presence of the long-range order in the location of the body atoms. The motion of a charge in a periodic crystal field is mathematically similar to the motion of a free charge in a vacuum with the difference that it is necessary to employ the "effective" mass m^*. This theory has been applied with great success to metals and semiconductors.

Taking into account the above concepts, it is hard to explain that metals retain their metallicity when melted. Experiments on metals and semiconductors have shown that the energy spectrum changes little on the transition from the solid to the liquid state if the short-range order (coordination number and the average distance between atoms) does not change on melting. Furthermore, many substances (see Sec. 3.1) are known to have semiconducting properties in their amorphous state.

Thus, it would appear that the band structure of the energy spectrum is not determined by the long-range order, but is dependent on the short-range order. Gubanov[1,2] has indeed shown this theoretically and has proven that the band structure of the energy spectrum remains correct far beyond the limits imposed by the periodic field from which it was deduced.

Before we discuss the details of Gubanov's theory, a word about the development of the work in this field is in order. Most of the present-day effort in this field has come from the Russian school led by Ioffe,[3,4] Regal,[3,5] Gubanov,[1,2,6–10] Fisher,[11,12] Nagaev,[13] and others. Spear,[14–17] in England, has carried out a fairly extensive study of the properties of amorphous selenium and, more recently, Makinson and Roberts,[18] in Australia, and Lax and Phillips,[19] in the USA, have investigated the formation of bands in a one-dimensional model of liquids and noncrystalline solids. One may point out that the difference between a liquid and an amorphous solid body resides solely in the fact that in the latter the arrangement of the atoms is fixed whereas in the liquid it varies with time; however, the instantaneous potential pattern is quite analogous.

It will be remembered that the conventional band-theory of solids started with the consideration of the one-dimensional periodic structure. Because of its simplicity, we first give an account of the one-dimensional model of liquids and amorphous substances and subsequently extend it to the three-dimensional case.

II. THEORY OF THE ONE-DIMENSIONAL MODEL

It is first assumed that the atoms are distributed periodically and that the spectrum of the electron has a zone structure. Then the long-range order in the distribution of atoms is broken entirely, but in a manner that the distances between the nearest neighbors change only insignificantly. This introduces perturbing terms in the Schrödinger equation. It is proved that these perturbing terms do not eliminate the zone character of the spectrum, but only shift the zones slightly.

Consider a one-dimensional chain of G atoms located at equal distances from each other. Small disturbances of the long-range order, related to thermal lattice oscillations, exist even in this model. The $(N+1)$th atom is at a distance $Na+y$ from the first atom, where $y \ll a$, and so it is for any N. During melting, the distances between each pair of adjacent atoms change slightly and will be equal to

$$a(1+\epsilon\gamma),$$

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[1] A. I. Gubanov, Zh. Eksperim. i. Teor. Fiz. **26**, 139 (1954).

[2] A. I. Gubanov, Zh. Eksperim. i. Teor. Fiz. **28**, 401 (1955) [English transl.: Soviet Phys.—JETP **1**, 364 (1955)].

[3] A. F. Ioffe and A. R. Regel, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 4, p. 237.

[4] A. F. Ioffe, Fiz. Tverd. Tela **1**, 1627 (1959) [English transl.: Soviet Phys.—Solid State **1**, 1487 (1960)].

[5] Yin Shin-tuan and A. R. Regel, Fiz. Tverd. Tela **3**, 3614 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2627 (1962)].

[6] A. I. Gubanov, Zh. Eksperim. i Teor. Fiz. **30**, 862 (1956) [English transl.: Soviet Phys.—JETP **3**, 854 (1957)].

[7] A. I. Gubanov, Zh. Techn. Fiz. **26**, 1651 (1956) [English transl.: Soviet Phys.—Tech. Phys. **1**, 1605 (1956)].

[8] A. I. Gubanov, Zh. Techn. Fiz. **27**, 3 (1957) [English transl.: Soviet Phys.—Tech. Phys. **2**, 1 (1957)].

[9] A. I. Gubanov, Zh. Techn. Fiz. **27**, 2510 (1957) [English transl.: Soviet Phys.—Tech. Phys. **2**, 2335 (1957)].

[10] A. I. Gubanov, Fiz. Tverd. Tela **2**, 651 (1960) [English transl.: Soviet Phys.—Solid State **2**, 605 (1961)].

[11] I. Z. Fisher, Dokl. Akad. Nauk. SSSR **117**, 399 (1957) [English transl.: Doklady **2**, 510 (1957)].

[12] I. Z. Fisher, Fiz. Tverd. Tela **1**, 132 (1958) [English transl.: Soviet Phys.—Solid State **1**, 171 (1959)].

[13] E. L. Nagaev, Fiz. Tverd. Tela **3**, 2567 (1961) [English transl.: Soviet Phys.—Solid State **3**, 1867 (1962)].

[14] W. E. Spear, Proc. Phys. Soc. (London) **B69**, 1139 (1956).

[15] W. E. Spear, Proc. Phys. Soc. (London) **B70**, 669 (1959).

[16] W. E. Spear, Proc. Phys. Soc. (London) **B76**, 826 (1960).

[17] H. P. D. Lanyon and W. E. Spear, Proc. Phys. Soc. (London) **77**, 1157 (1961).

[18] R. Makinson and A. Roberts, Australian J. Phys. **13**, 437 (1960).

[19] M. Lax and J. Phillips, Phys. Rev. **110**, 41 (1958).

where $\epsilon \ll 1$ is a constant parameter that characterizes the degree of slight short-order disturbances. γ has a different value for each pair of adjacent atoms and is accidental and hence statistical in character. Let us assume that there is no expansion or contraction because, theoretically, a uniform chain deformation does not introduce anything new. In this case, $\bar{\gamma}=0$. Probability of the values γ is preset by a normal distribution. Normalize the distribution so that the rms error is equal to unity.

$$\langle \gamma^2 \rangle_{\text{Av}} = 1. \tag{1}$$

The distance of the $(N+1)$th atom from the first atom after melting is equal to $Na+y$, where

$$y = \Gamma_N \epsilon a,$$

where Γ_N is the sum of N γ values. According to Liapunov's[20] theorem, with increasing N, the distribution of Γ_N approaches normal distribution. Considering

$$\bar{\gamma}=0 \quad \text{and} \quad \langle \gamma^2 \rangle_{\text{Av}} = 1$$

the probability density

$$f(\Gamma_N) = [1/(2\pi N)^{\frac{1}{2}} \exp\left(-\Gamma^2{}_N/2N\right)$$

$$(N \to \infty), \quad \langle \Gamma^2{}_N \rangle_{\text{Av}} = N \tag{2}$$

and

$$(\bar{y}^2)^{\frac{1}{2}} = \epsilon a N^{\frac{1}{2}}. \tag{3}$$

If $N > 1/\epsilon^2$, $(\bar{y}^2)^{\frac{1}{2}} > a$, the lattice constant, i.e., the probability of the presence of the $(N+1)$th atom is smeared in a region that exceeds the lattice constant, and the long-range order disappears. Thus, the accumulation of small disturbances of the short-range order leads to a complete disappearance of the long-range order at distances a/ϵ^2. It also follows from Eq. (3) that substantial disturbances of the long-range order take place only under the condition that the number of atoms in the basic region is

$$G \gg 1/\epsilon^2. \tag{4}$$

We here consider G to be a very large, but finite number.

Before melting, the potential energy of the electron in a self-consistent field of the atomic chain was described by some periodic curve $V(x)$ with a period a. During melting, this curve experiences two kinds of distortions. First, all minima and maxima of the curve shift in horizontal directions (along the x axis) according to the displacement of atoms, consequently each point of the potential curve shifts along the x axis by the value y, introduced above. Second, due to the changes in the distances between the nearest atoms, the height of the maxima and minima changes; each point of the curve shifts in the vertical direction (along the axis V) by the value ΔV, which is small due to the smallness of ϵ and is as random in character as γ.

The distortions of the second kind do not nullify the periodicity of the potential, but only introduce small additions of the potential energy to the periodic field, which may easily be taken into account using the ordinary perturbation theory. Therefore, we neglect these distortions and consider only the first of them that actually lead to the elimination of the periodicity $V(x)$. At preassigned values, they cause significant changes of the potential. In some points, the minimum is exchanged for maximum and vice versa.

However, if the coordinate scale is deformed according to the deformation of the atomic chain in melting and horizontal displacements of the points of the potential curve, i.e., if the coordinate ξ is introduced using the relationship

$$d\xi/dx = 1/(1+\epsilon\gamma). \tag{5}$$

Then the potential energy of the electron proves to be a periodic function of ξ.

A. Wave Equation in Deformed Coordinate Scale

We solve the stationary Schrödinger equation in adiabatic approximation, i.e., neglecting the motion of the atoms arising due to thermal vibrations.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi. \tag{6}$$

According to Eq. (5)

$$\frac{d\psi}{dx} = \frac{d\psi}{d\xi}\frac{d\xi}{dx} = \frac{d\psi}{d\xi}\frac{1}{(1+\epsilon\gamma)},$$

$$\frac{d^2\psi}{dx^2} = \frac{d}{d\xi}\left[\frac{d\psi}{d\xi}\frac{1}{(1+\epsilon\gamma)}\right]\frac{d\xi}{dx}$$

$$= \frac{1}{(1+\epsilon\gamma)}\left[\frac{1}{(1+\epsilon\gamma)}\frac{d^2\psi}{d\xi^2} + \frac{d\psi}{d\xi}\frac{(-\epsilon)}{(1+\epsilon\gamma)^2}\frac{d\gamma}{d\xi}\right]$$

$$= \frac{1}{(1+\epsilon\gamma)^2}\frac{d^2\psi}{d\xi^2} - \frac{\epsilon}{(1+\epsilon\gamma)^3}\frac{d\gamma}{d\xi}\frac{d\psi}{d\xi},$$

or

$$\frac{d^2}{dx^2} = \left[1 - 2\epsilon\gamma + \frac{2.3}{2!}\epsilon^2\gamma^2\right]\frac{d^2}{d\xi^2} - \epsilon[1 - 3\epsilon\gamma \cdots]\frac{d\gamma}{d\xi}\frac{d}{d\xi}.$$

Retaining terms up to ϵ^2, we have,

$$\frac{d^2}{dx^2} = \frac{d^2}{d\xi^2} - \epsilon\left[2\gamma\frac{d^2}{d\xi^2} + \frac{d\gamma}{d\xi}\frac{d}{d\xi}\right] + 3\epsilon^2\left[\gamma^2\frac{d^2}{d\xi^2} + \frac{d\gamma}{d\xi}\frac{d}{d\xi}\right] + \epsilon^3 \cdots.$$

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[20] H. Cramer, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, New Jersey, 1946).

Therefore Eq. (6) can be written as $H\psi=E\psi$, where

$$H=H_0+\epsilon W+\epsilon^2 w+\cdots, \tag{7}$$

$$H_0=-(\hbar^2/2m)(d^2/d\xi^2)+V(\xi), \tag{8}$$

$$W=\frac{\hbar^2}{2m}\left[2\gamma\frac{d^2}{d\xi^2}+\frac{d\gamma}{d\xi}\frac{d}{d\xi}\right],$$

and

$$w=-\frac{3\hbar^2}{2m}\left[\gamma^2\frac{d^2}{d\xi^2}+\gamma\frac{d\gamma}{d\xi}\frac{d}{d\xi}\right]. \tag{9}$$

Since $V(\xi)$ is a periodic function, the solution of the unperturbed equation $H_0\psi=E\psi$ is the familiar solution of the problem concerning the electron in the periodic field. The energy spectrum of the unperturbed problem consists of a series of allowed quasicontinuous zones, each of which consists of G levels (depending on the number of atoms in the chain), separated by forbidden zones. Let the energy eigenvalues be denoted by $E_{nk}{}^0$, where the index n refers to the zone number and k is the level number in the zone. The Bloch wave,

$$\psi_{nk}{}^0=U_{nk}\exp(iq_k\xi), \tag{10}$$

corresponds to each eigenvalue. U_{nk} is the modulated function with a lattice spacing $k=1, 2, \cdots, G$; q_k is the wavenumber of the electron.

The solution of the perturbed problem may be looked for in the form of a linear combination of the total system of eigenfunctions of the unperturbed equation.

$$\psi(\xi)=\sum_{n,k} C_{nk}\psi_{nk}{}^0(\xi) \tag{11}$$

and, as is known from the perturbation theory, the expansion coefficients C_{nk} are determined from the system of equations

$$(E_{nk}{}^0+\epsilon W_{nk,nk}+\epsilon^2 w_{nk,nk}-E)C_{nk}+\sum_{n'k'\neq n,k}(\epsilon W_{nk,n'k'}+\epsilon^2 w_{nk,n'k'})C_{n'k'}=0, \tag{12}$$

where n and k run through all possible values; $W_{nk,n'k'}$ and $w_{nk,n'k'}$ are the matrix elements of the respective perturbation operators. Note that till now, we have said nothing about the smallness of the perturbation.

The unperturbed eigenfunctions are normalized to unity, so that

$$\int_0^L |\psi_{nk}{}^0(\xi)|^2 d\xi=1, \tag{13}$$

where $L=Ga$ is the chain length according to the scale ξ.

B. Evaluation of Perturbation Matrix Elements

Since expressions for $W_{nk,n'k'}$ and $w_{nk,n'k'}$ contain the random variable γ, these matrix elements cannot be calculated exactly, but the probability distribution of their values may be determined by using Liapunov's theorem. This leads to

$$\langle W_{nk,n'k'}\rangle_{\text{Av}}=0, \tag{14}$$

$$\langle w_{nk,nk}\rangle_{\text{Av}}=(3\hbar^2/2m)[(1/a^2)+q_k{}^2],$$

$$\langle\{|W_{nk,n'k'}|^2\}\rangle_{\text{Av}}^{\frac{1}{2}}=\frac{\hbar^2}{2mG^{\frac{1}{2}}}\left\{\alpha_{kk'}{}^2\left(\frac{4}{a^4}+4q_{k'}{}^4+\frac{q_{k'}{}^2}{a^2}\right)+\beta_{kk'}{}^2\left(\frac{1}{a^4}+16\frac{q_{k'}{}^2}{a^2}\right)\right\}^{\frac{1}{2}},$$

and

$$\langle\{|w_{nk,n'k'}|^2\}\rangle_{\text{Av}}^{\frac{1}{2}}=\frac{3\hbar^2}{2mG^{\frac{1}{2}}}\left\{\alpha_{kk'}{}^2\left(\frac{1}{a^4}+q_{k'}{}^4+\frac{q_{k'}{}^2}{a^2}\right)+\beta_{kk'}{}^2\left(\frac{1}{a^4}+4\frac{q_{k'}{}^2}{3}\right)\right\}^{\frac{1}{2}},$$

where $\alpha_{kk'}$ and $\beta_{kk'}$ are multipliers less than unity and dependent mainly on the difference in $k-k'$. As $(k-k')$ approaches zero $\alpha_{kk'}\rightarrow 1$, but $\beta_{kk'}\rightarrow 0$; as $(k-k')\rightarrow G$, both $\alpha_{kk'}\rightarrow 0$ and $\beta_{kk'}\rightarrow 0$. Also, we notice that

$$\epsilon^2 w_{nk,nk}\gg\epsilon\langle\{|W_{nk,nk}|^2\}\rangle_{\text{Av}}^{\frac{1}{2}}, \tag{15}$$

i.e., the diagonal matrix elements of the operator $\epsilon^2 w$ are larger than those of the operator ϵW. This necessitates the retention of the term ϵ^2 in the expansion.

The number of unperturbed energy levels in each zone is equal to G, and the width of the zone is of the order of magnitude $\hbar^2/2ma^2$ (because $\Delta p\,\Delta x\simeq\hbar$ but $\Delta x\simeq a$). Therefore

$$\Delta p\simeq\hbar/a$$

or

$$\Delta E=(\Delta p)^2/2m\simeq\hbar^2/2ma^2, \tag{16}$$

consequently, the distance between adjoining levels $E_{nk}{}^0$ in the same zone is of the magnitude $\hbar^2/ma^2G$. Taking into consideration that

$$q_k\leq 1/a \quad\text{and}\quad G\gg 1/\epsilon^2,$$

one finds that the nondiagonal perturbation matrix elements $[\epsilon W_{nk,n'k'}]$ is larger than the distances between the adjacent, unperturbed energy levels. Consequently, the ordinary method of consecutive approximations for a discrete spectrum cannot be applied to the problem discussed.

C. The Relative Degeneration Method[21]

The relative degeneration is a case in which the unperturbed energy spectrum may be divided into groups

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[21] L. Landau and E. Lifshitz, *Non-Relativistic Quantum Mechanics* (Addison Wesley Publishing Company, Inc., Reading, Massachusetts, 1958).

of levels separated by rather wide distances, but the distances between the levels within each group may be small at will. In our case, each such level group is an allowed zone and the distances between them are the forbidden zones. The only criterion for applying this method—the smallness of the nondiagonal perturbation matrix element in comparison with the width of the forbidden zone—obviously, meets demands due to the smallness of $\epsilon/(G)^{\frac{1}{2}}$.

From here on we drop the index n. Since $\epsilon^2 w_{kk} \gg \epsilon W_{kk}$ we may drop $\epsilon W_{kk} w.r.t. \epsilon^2 w_{kk}$. However, since $w_{kk'}$ and $W_{kk'}$ are of the same order of magnitude, let us drop $\epsilon^2 w_{kk'}$ in nondiagonal terms. As a result, the system of the zero approximation equations for each zone has the form

$$(E_k^0+\epsilon^2 w_{kk}-E)C_k+\sum_{k'\neq k}\epsilon W_{kk'}C_{k'}=0. \qquad (17)$$

The solvability of this system depends on a condition that its determinant must approach zero.

$$\Delta(\epsilon)=\begin{vmatrix} E_1'-E & \epsilon W_{12} & \cdots & \epsilon W_{1G} \\ \epsilon W_{21} & E_2'-E & \cdots & \epsilon W_{2G} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \epsilon W_{G1} & & \cdots & E_G'-E \end{vmatrix}=0, \qquad (18)$$

where

$$E_{k'}=E_k^0+\epsilon^2 w_{kk}, \qquad k=1,2,\cdots,G.$$

Expanding the determinant and dividing by the product of diagonal elements, one obtains

$$1-\epsilon^2\sum_{k<k'}\sum\frac{W_{kk'}W_{k'k}}{(E_{k'}'-E)(E_{k'}'-E)}$$
$$+\epsilon^3\sum_{k,k',k''}\sum\sum\frac{W_{kk'}W_{k'k''}W_{k''k}}{(E_k'-E)(E_{k'}'-E)(E_{k''}'-E)}$$
$$+\cdots+(-1)^{r+1}\epsilon^r\sum_{r-\text{terms}}\prod_{j=1}^{r}W_{kk}(j)$$
$$\times\prod_{j=1}^{r}(E_{k'}(j)-E)+\cdots=0. \qquad (19)$$

To evaluate the order of magnitude of different sums in the expression (19), we show in Appendix I that the mean value of the product of symmetrical matrix elements $W_{kk'}W_{k'k}$ is always positive. (This is not obvious since W is not a Hermitian operator.) Using this fact, one can further show that Eq. (19) has a solution if, and only if, E lies within the zone E_k'.

D. Investigation of the Solution Obtained

It was shown above that when the long-range order in the chain is broken, the zone structure of the energy levels is maintained, but all levels shift somewhat. Since

$$E_k'=E_k^0+\epsilon^2(3\hbar^2/2m)[(1/a^2)+q_k^2], \qquad k=1,2,\cdots,G,$$

it follows that the energy change is positive, i.e., all levels increase in proportion to ϵ^2, where ϵ is the degree of the small disarrangement of the short-range order. For the lower edge of each allowed zone $q=0$, for the upper edge $q=\pi/a$, therefore the lower edge of the zone increases by a smaller value than the upper edge, i.e., the allowed zones expand and the forbidden zones contract.

Let us evaluate the order of magnitude of the displacement of the energy levels. If $a=3\times10^{-8}$ cm, then

$$3\hbar^2/2ma^2\simeq5\times10^{-3}\text{ erg}\simeq1\text{ eV}.$$

Since q_k varies between 0 and π/a, $w_{nk,nk}\simeq1$–10 eV. Consequently if $\epsilon=0.1$, then the lower edges of the allowed zones shift by 0.01 eV and the upper edges by 0.1 eV, which may be measured experimentally.

E. Comments on the Zero-Approximation Wavefunction

To obtain some conception of the zero-approximation wavefunctions, let us use Eq. (17) which may be written as

$$(E_k'-E)C_k=-\epsilon\sum_{k'\neq k}W_{kk'}C_{k'}, \qquad k=1,2,\cdots,G.$$

From this, it is easy to show that only a fraction of the coefficients C_k (in fact only $\epsilon^2 G$), markedly differ from zero.

This means that the zero-approximation functions represent wave packets where the expansion coefficients of these wave packets into the unperturbed functions ψ_k^0 are Gaussian functions from $k-k_0$, where k_0 corresponds to the energy value $E_{k_0}'=E$. The width of this Gaussian curve on the scale k is of the order of $\epsilon^2 G$. Thus each wave packet includes functions that correspond to the levels of the zone E_k' in a strip, which is a fraction ϵ^2 of the entire width of the zone and lies around the value E.

F. Criticism of the One-Dimensional Model

Makinson and Roberts[18] have also considered a one-dimensional model in which the potential energy of an electron is nearly periodic over short distances but has no long-range order. The liquid is simulated by a series of δ-type potential wells with an equal power $\hbar^2 K_0/2m$ and the distances between adjacent wells are distributed according to a cutoff parabolic distribution about the mean value. Various values are taken for the rms deviation σ, which corresponds to ϵ in Gubanov's model. The length of the chain, usually 2000 "atoms," was always sufficient to ensure that long-range order was breached many times over within its length.

In agreement with Gubanov's conclusions, the authors find that a definite gap in the energy spectrum exists and that it narrows as σ increases. However, in two important respects, their findings are in disagreement with those of Gubanov's.

In Gubanov's theory, all the energy levels of the periodic model are shifted upward, and the gap narrowing is a consequence simply of a difference in the magnitude of the upward shifts of the levels bounding the gap. However, Makinson and Roberts show that there is, indeed, an upward shift of the lower gap edge, but a downward shift of the upper gap edge which is contrary to Gubanov's conclusions.

Also, while Gubanov gives no criterion for preservation of the gap, an order of magnitude estimate of a representative narrowing is about 0.1 eV for $\sigma=0.1$. In the present model, the gap is totally destroyed for this value of σ.

The neglect of variations in the shape of the potential in different cells is another point open to question in Gubanov's model. Of course, this effect does not influence the results of Makinson and Roberts.

III. EXTENSION TO THE THREE-DIMENSIONAL MODEL

As shown for the one-dimensional case, the result of small deformation in the short-range order is the disappearance of long-range order at distances of the order of a/ϵ^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.

All the results obtained for the one-dimensional case are applicable here. The zone structure of the energy levels is retained except that each level is shifted by an amount $\epsilon^2 w'_{nk,nk}$, where

$$w_{kk}'=(3\hbar^2/2m)(3/a^2+k^2).$$

The wavefunctions in a zero approximation are linear combinations of all G^3 Bloch functions belonging to the given zone. However, as was shown for the one-dimensional case, in each solution only a fraction ϵ^2 of all the functions have coefficients significantly different from zero. This estimate remains valid here. Thus, 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 the order of

$$\Delta p=\hbar\epsilon^2/a$$

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

$$\Delta\xi=a/\epsilon^2,$$

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

A. Scattering of Electrons Due to Violation of Long-Range Order

Although the disappearance of long-range order has an unimportant effect on the energy spectrum of the electrons in the body and on the character of their motion, the disappearance of strict periodicity in the position of the atoms ought to lead to additional scattering of electrons, to a decrease in their mean free path, and to an increase in resistance. The resistance of a liquid with electronic conductivity is determined in part by the disorder of the regular positions of the atoms and in part from the thermal vibrations of the lattice.

The first component of resistance is referred to as the "liquid resistance" and the second component as the "phonon resistance." Mott[22] has already shown that the length of mean free path L_{ph}, due to scattering by phonons, decreases in fusion or on transition to an amorphous state. For $T>\theta$, the Debye temperature, $L_{\mathrm{ph}}\simeq\theta^2$. On fusion, θ decreases (i.e., the frequency of oscillation of the atoms decreases) and so does L_{ph}. Wilson obtained the ratio for the conductivity in the solid and liquid phases close to the melting point for a series of metals and tried to explain the higher resistance upon liquidation by a change only in the Debye temperature θ, assuming that the other quantities do not change appreciably during the melting process. For several metals, the agreement between the ratio of conductivities calculated by such a method and those obtained experimentally were satisfactory. However, for mercury the experimentally measured ratio was 4.1, the computed value, 2.23. Consequently, there is here an appreciable amount of an additional mechanism for the scattering of the electrons—the liquid resistance. It is not accidental that this resistance was specifically observed in mercury; actually, mercury liquifies at a low temperature at which point the lattice vibrations are not very intense. One can assume that in other metals, which liquify at much higher temperatures, the liquid resistance is masked by the phonon resistance.

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[22] N. F. Mott, Proc. Roy. Soc. (London) **A146**, 465 (1934).

Gubanov has established that the mean free path connected with the loss of long-range order is given by $L_d \simeq a/\epsilon^2$. Taking $\epsilon = 0.1$ again, we find $L_d \simeq 10^{-6}$ cm. At high temperature, in the liquid state, it is found that $L_d > L_{\mathrm{ph}}$, and because reverse paths of motion are put together on calculation of the number of scattering centers, the scattering connected with the loss of long-range order may be said to have little effect on the free path. For amorphous semiconductors at low temperatures, L_d may be the determining effect; and the free path will be much less than in a crystal at the same temperature. In fact, since solid amorphous bodies can exist at low temperatures when "liquid scattering" exists, the theoretical laws obtained for the length of the mean free path of electrons are best compared with experimental data for amorphous semiconductors.

There is still another cause of electron scattering in a liquid. When the disturbance of long-range order on fusion of the crystals was examined, it was noted that the maxima and minima of potential of the self-consistent field in which the electron moves are displaced in space; but it was not considered that with the atom displacement the value of these maxima and minima can also change. Further, in a liquid, besides the smooth disturbance in the order of the atom positions, there always occur local, sharper disturbances of structure, cavities and other distortions. The result of all this is that the potential of the self-consistent field does not appear as a strictly periodic function of the deformed coordinates.

The character of these deviations of potential from periodicity agrees completely with the case of impurities and other defects in the crystal. All deviations from periodicity of potential in the coordinate system ξ are referred to as defects, and we consider both defects characteristic for the liquid state (cavities, scatter of maxima and minima potential values) as well as defects peculiar also to crystals (impurity atoms, empty lattice positions, atoms in interstitial positions). It is the presence of these defects which causes additional electron scattering apart from the phonon and liquid scattering.

IV. THE IMPURITY CONDUCTION IN LIQUID AND AMORPHOUS SEMICONDUCTORS

In some conducting crystals both intrinsic and impurity conductions are observed, and the transition between them appears as a break in the curve which gives the temperature dependence of the logarithm of electrical conductivity. Venegal and Kolomiets[23] studied glasses of various composition in a wide range of temperatures, and they found no breaks in the electrical conductivity curves. Introduction into such glasses of impurities which were found to be electrically active in crystals did not affect the electrical conductivity curves. These results suggest that in amorphous semiconductors the mechanism of impurity conduction does not work; this fact should have a theoretical basis.

When an impurity ion is introduced into a crystal, then electrons (holes) move in the vicinity of this ion approximately in the same way as in a Coulomb field which is reduced by the permittivity of the medium. Although the magnitude of the crystal-lattice field may be considerably greater than the field of the impurity ion, it does not materially affect the conditions because of its periodicity. An electron (a hole) may be captured by the ion field and the binding energy of such a state is the activation energy ΔE of a donor or an acceptor. Theoretical considerations lead to a value of the order of 0.1 eV, in agreement with experiment.

We now discuss an amorphous medium. Considering the short-range order, one can imagine a donor or acceptor model of the same type as in a crystal, but the motion of an electron (a hole) is now affected (apart from the Coulomb field of the impurity ion) also by an additional field δU which is due to departure from periodicity in the atomic distribution in an amorphous body. The field δU gives the fluctuations of the interatomic electric field and corresponds approximately to the potential perturbations which give rise to liquid resistance in Gubanov's theory. The possibility of the formation of bound donor- or acceptor-type states depends on the relative values of δU and ΔE. In a hypothetical glass, whose structure differs very little from that of a crystal, $|\delta U| \ll \Delta E$, and donors and acceptors are possible, but the energy of activation is smaller by an amount which is of the order of the mean value of $|\delta U|$. If the fluctuation of field δU in a glass or a liquid is comparable or exceeds the value of ΔE in a corresponding crystal (i.e., if $\delta U > 0.1$ eV) then formation of donors or acceptors in it is impossible.

It follows that the existence of impurity conduction can be settled by an estimate of the fluctuations of the interatomic field in a glass or a liquid, which are related to the fluctuations of the atomic order.

The estimates of Fisher show that $|\delta U| > 1$ eV and hence the impurity conduction in noncrystalline conductors is impossible.

V. AVAILABLE EXPERIMENTAL DATA

Experimental data show that one has to distinguish between two cases on melting.

(1) Coordination number increases, the short-range order radically changes, the density increases, and the electrical conductivity becomes metallic in character. This is observed for semiconductors with a diamond or sphalerite crystal, lattice-type germanium, silicon, gallium antimonide, indium antimonide, and others for which the coordination number in the solid state is 4, in the liquid state 8.

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[23] T. N. Venegal and B. T. Kolomiets, Zh. Techn. Fiz. **27**, 2484 (1957) [English transl.: Soviet Phys.—Tech. Phys. **2**, 2314 (1957)].

TABLE I. Mobility in selenium.

	Hexagonal Se (Plessner)	Single crystal[26] Se (Henkels)	Amorphous Se (Spear)
ϵ (eV)	0.13	0.15	0.14
μ (cm^2 sec^{-1}V^{-1})	0.14	0.13	0.13 −0.14

(2) The coordinate number does not change, the short-range order changes slightly, the density decreases by a few percent and the semiconducting properties are retained. This occurs during melting of oxides and sulfides such as Tl_2S, Cu_2S, Ag_2S, Bi_2O_3, V_2O_5, SbS_3, FeS, and CuS.

There are also intermediate cases and more complex changes of the properties during the transition through the melting point, but the above two cases are most typical. The easiest experimental method to distinguish between these two cases is the determination of density.

According to the calculations of Hund and Mrowka,[24] the energy spectrum of the crystal depends to a great extent on its coordination number z. In particular, in the case of diamond lattice ($z=4$), the position of bands, corresponding to s and p electrons, lead to the formation of the forbidden band, as a result of which, the crystal is an insulator or a semiconductor; in crystals of higher value of z, the forbidden band is not formed and the conductivity is metallic in character. This fully explains why there is a change to metallic conductivity during melting of semiconductors in case one, when z increases from 4 to 8. In this case, the effective mass and other parameters are completely different in the solid and liquid states.

From the point of view of the electron theory of liquids, case two is more interesting because here the only difference between the liquid and the crystalline states is the absence of the long-range order and a small increase of the volume, so that the difference between the energy spectra is very small.

A crude analysis was made above to evaluate the change in the forbidden gap on melting. It was shown that a slight change in short-range order leads to small changes in the forbidden gap. But this calculation neglected the changes due to (1) actual changes in volume, and (2) the change in the magnitude of the potential. Further investigations have shown that the influence of these and other distortions on the energy spectrum has an effect of the same order of magnitude in some cases; for instance, in the case of electrons strongly bonded to atoms. The distortions of potentials due to both origins almost completely cancel each other. The improved calculations show that the widths of the forbidden band can increase as well as decrease; if the expansion of the body during melting is considerable, an increase in the width of the forbidden band is more probable, and, conversely, during small changes in the volume, a contraction of the forbidden band is more probable.

A. Amorphous Selenium

Since amorphous selenium has been the most investigated of the amorphous substances, we will give a brief account of its properties.

Spear finds that mobility in amorphous selenium is controlled by traps (acceptor levels above the valence band) with activation energy $\epsilon = 0.14$ eV and it is almost the same for hexagonal and single crystals forms of selenium. This is shown in Table I.[25,26]

The variation of mobility with temperature shows an anomalous behavior. μ is found to be proportional to $\exp(-\epsilon/kT)$. Normally mobility decreases with increasing temperature due to increased thermal motion and consequently decreased mean free path. This type of variation has also been reported for many other substances with small mobilities, e.g., B, NiO, Fe_2O_3, $n-In_2Te_3$, $n-Ga_2Se_3$, and $n-Ga_2Te_3$.

For thinner specimens, Spear observed a decrease in μ with decreasing thickness (see Fig. 1). No suitable explanation is possible at this stage. The samples are too thick to make an explanation on the basis of surface scattering plausible.

Carrier density is found to be independent of temperature, but the conductivity of hexagonal form is greater than that in the amorphous form. This seems to indicate that carrier density is related to long-range order. In fact, a qualitative explanation of this can be given on the basis of Gubanov's theory.

Hartke[27] has repeated Spear's experiments using purer samples of amorphous selenium. The purity of

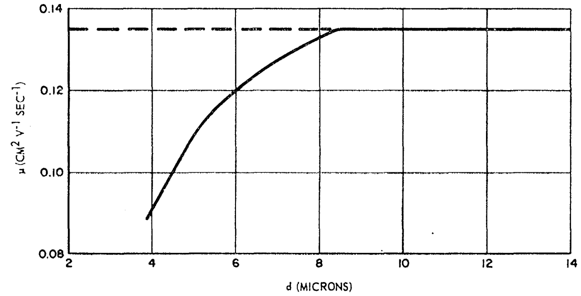

FIG. 1. Graph of mobility vs specimen thickness of selinium films at 20°C (W. E. Spear[16]).

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[24] F. Hund and B. Mrowka, Ber. Sachs. Akad. Wiss. Math. Phys. Ki, **87**, 185, 325 (1935); F. Hund, Z. Physik. **36**, 888 (1935).

[25] K. W. Plessner, Proc. Phys. Soc. (London) **B64**, 671, 681 (1951).

[26] H. W. Henkels, J. Appl. Phys. **22**, 916, 1265 (1951).

[27] J. L. Hartke, Phys. Rev. **125**, 1177 (1962).

the samples is confirmed by a drop in conductivity. Since Hartke's values for activation energy and hole mobility are in excellent agreement with those of Spear, it would seem unlikely that the shallow traps in amorphous selenium are caused by impurities. This is further confirmed by adding arsenic to selenium. Arsenic, which is found to be very active in many crystalline substances, is found to have no noticeable effect on hole mobility and its temperature dependence. These observations would seem to indicate the correctness of Fisher's conclusions about the impossibility of impurity conduction in amorphous substances.

B. Amorphous Boron Films

Work on amorphous boron films has been in progress for approximately a year at Melpar.[28] The work is chiefly concerned with the passage of electrons through thin layers. The boron films were formed by an electron-beam deposition technique, yielding uniform amorphous layers. These layers are deposited between deposited metal electrodes (Al) and the conduction properties are determined.

The salient facts acquired, to date, from this study are as follows: (a) Films are amorphous as determined by x-ray and electron-diffraction studies. (b) Films have a band gap similar to bulk value. (c) Room-temperature resistivity is very high, about 10^{12} Ω-cm measured at 1 V. (d) Conduction through the layer follows a general relation $i=KV^n$, where i and V are the current and voltage, respectively, and n and K are constants. (e) Conduction in the films depends very strongly on the purity. That is, n and K are dependent on purity; n varies between 6 and 8. (f) Films formed, to date, do not seem to be photoconductive, although this has not been closely looked for.

Typical current–voltage characteristics of amorphous films are shown in Fig. 2. A theoretical treatment on the conduction mechanism on the layer has not yet been carried out.

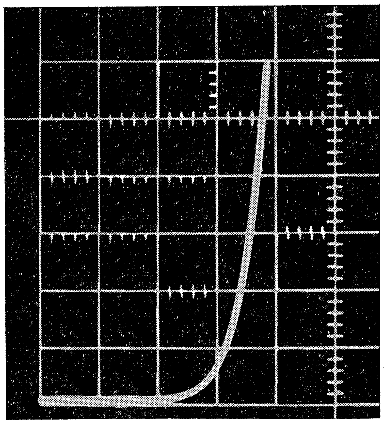

Fig. 2. Current–voltage characteristics through 2700-Å-thick boron film. Scale: horizontal—10V/div., vertical—0.5mA/div.

APPENDIX I

Let us write W as a sum of Hermitian operator W' and anti-Hermitian operator W''.

$$W=W'+W'',$$

$$W'=\frac{\hbar^2}{2m}\left(2\gamma\frac{d^2}{d\xi^2}+2\gamma'\frac{d}{d\xi}+\frac{\gamma''}{2}\right),$$

$$W''=-\frac{\hbar^2}{2m}\left(\gamma'\frac{d}{d\xi}+\frac{\gamma''}{2}\right),$$

$$W_{kk'}W_{k'k}=(W_{kk'}'+W_{kk'}'')(W_{k'k}'+W_{k'k}'');$$

now

$$W_{kk'}'^{*}=W_{k'k}' \quad \text{and} \quad W_{kk'}''^{*}=-W_{k'k}'',$$

$$\begin{aligned}W_{kk'}W_{k'k}&=(W_{kk'}'+W_{kk'}'')(W_{kk'}'^{*}-W_{kk'}''^{*})\\&=|W_{kk'}'|^2-|W_{kk'}''|^2+W_{kk'}''W_{kk'}'^{*}\\&\qquad-W_{kk'}'W_{kk'}''^{*}.\qquad(\text{A1})\end{aligned}$$

The last two addends in expression (A1), on an average, as products of different random values, are equal to zero. It is easy to prove that

$$|W_{kk'}'|^2>|W_{kk'}''|^2.$$

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[28] See Reports 12–14, Bureau, Naval Weapons, Control: NOw 60-0362-c.

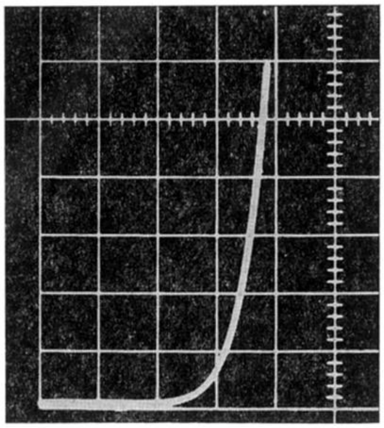

FIG. 2. Current–voltage characteristics through 2700-Å-thick boron film. Scale: horizontal—10V/div., vertical—0.5mA/div.