TEMPERATURE DEPENDENCE OF THE DENSITY OF CONDUCTION ELECTRONS IN METALS

G. P. MOTULEVICH

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

The temperature dependence of the density $N_{opt\,z}$ of conduction electrons in polyvalent metals, determined by an optical method, is considered. It is shown that an increase in the intensity of the thermal vibrations of the lattice with increasing temperature leads to a reduction in the Fourier components of the pseudopotential, which, in turn, diminishes the difference $N_{val} - N_{opt}$ (N_{val} is the density of valence electrons), i.e., an increase in N_{opt}. The dependence of the difference $N_{val} - N_{opt}$ on the temperature is governed by the Debye-Waller factor. The temperature dependence of N_{opt}, obtained by optical and x-ray methods, are compared for aluminum and lead.

IT is widely held that the density of conduction electrons in metals is independent of temperature. This is indeed true of monovalent metals, in which the influence of the periodic lattice potential is weak. The situation is different in polyvalent metals. Measurements of the optical constants of polyvalent metals Pb, Sn, Al, and In, carried out at helium, nitrogen, and room temperatures,[1-4] have shown that the density of conduction electrons N_{opt}, determined by an optical method, increases with increasing temperature. Between helium and room temperatures, this increase amounts to 5—20%. In the present paper, we shall show that the value of N_{opt} depends on the thermal vibrations of the lattice and that this determines the temperature dependence of N_{opt}.

The influence of the periodic lattice potential on the optical properties of metals has been determined in[5]. The following relationship has been obtained for N_{opt} of cubic metals, using the pseudopotential density:

$$\frac{N_{val} - N_{opt}}{N_{val}} = \sum \frac{\pi}{4} \frac{p_g}{p_F^0} \frac{|V_g|}{E_F^0} \left(\frac{1}{2} + \frac{\varphi_g}{\pi}\right), \qquad (1)$$

$$\varphi_g = \tan^{-1} \frac{2(p_g/p_F^0)[1 - p_g/p_F^0]}{|V_g|/E_F^0}. \qquad (1a)$$

Here, N_{val} is the density of valence electrons; N_{opt} is the density of conduction electrons, determined by an optical method, $p_g = (\frac{1}{2}|2\pi\hbar g|)$; g is the reciprocal lattice vector; p_F^0 is the Fermi momentum of free electrons for N_{val}; E_F^0 is the Fermi energy of the same free electrons; V_g is the Fourier component of the pseudopotential. Summa-

tion is carried out over all the reciprocal lattice vectors for which $V_g \neq 0$ and $p_g \leq p_F^0$.

The formulas (1) and (1a) are derived on the assumption of a static lattice potential without any allowance for its vibrations. We shall allow for the thermal vibrations of the lattice. Using the theory of weakly bound electrons, we shall represent the Fourier component of the pseudopotential in the following form:[6-8]

$$V(\mathbf{K}) = F(\mathbf{K})U(\mathbf{K}). \qquad (2)$$

Here, K is the wave number; U(K) is the Fourier component of the self-consistent atomic potential; F(K) is a structure factor, which depends only on the ion positions:[9]

$$F(\mathbf{K}) = \frac{1}{N}\sum_l e^{-i\mathbf{K}l} \qquad (3)$$

(N is the number of unit cells per unit volume; l is the lattice vector corresponding to a site l). For a rigid ideal lattice:

$$F(\mathbf{K}) = \delta_{\mathbf{K}g}, \qquad (4)$$

$$V(\mathbf{K}) = U(\mathbf{K})\delta_{\mathbf{K}g}, \quad V_g = U(g). \qquad (4a)$$

Let us assume that lattice vibrations are excited in a crystal. Allowance for these vibrations gives rise to a temperature factor e^{-W} in F(K), which is known as the Debye—Waller factor. A similar factor governs the intensity of x-ray diffraction maxima.[10-13] The factor can be derived in the usual manner.[9,10] The radius vector corresponding to a site l will be represented in the form

$$R_l = 1 + u_l = 1 + \sum_q (u_q e^{iql} + u_q^* e^{-iql}). \quad (5)$$

Here, u_q is the vector amplitude of the lattice vibration having the wave vector q. Then,

$$e^{-iKR_l} = e^{-iKl} \prod_q \exp\{-i[(Ku_q)e^{iql} + (Ku_q^*)e^{-iql}]\}. \quad (6)$$

The expression (6) contains various products of factors of the type $e^{\pm iq \cdot l}$. Each such factor represents the creation or annihilation of a phonon. The probability of such processes decreases rapidly with increase in the order of the process. We shall be interested in no-phonon processes. In these processes, we have

$$\prod_q \exp\{\ \} = \prod_q \left(1 - \frac{1}{2}|Ku_q|^2\right)$$

$$\cong \exp\left(-\frac{1}{2}\sum_q |Ku_q|^2\right) = e^{-W_K}, \quad (7)$$

$$W_K = \frac{1}{2}\sum_q |Ku_q|^2. \quad (8)$$

Using Eqs. (3), (5), (7), and (8), we obtain

$$F(K) \equiv \frac{1}{N}\sum_l e^{-iKl} = e^{-W_K}\delta_{Kg}. \quad (9)$$

Hence

$$V(K) = e^{-W_K}U(K)\delta_{Kg}, \quad (10a)$$
$$V_g = e^{-W_g}U(g). \quad (10b)$$

We have thus found that the Fourier components of the pseudopotential depend on temperature. This should lead to a temperature dependence of N_{opt}. Using Eqs. (1), (1a), and (10b), we obtain

$$\frac{N_{val} - N_{opt}}{N_{val}} = \sum_g \frac{\pi}{4} \frac{p_g}{p_F^0} \frac{|U_g|}{E_F^0} e^{-W_g(T)}\left(\frac{1}{2} + \frac{\varphi_g}{\pi}\right), \quad (11a)$$

$$\varphi_g = \tan^{-1}\frac{2(p_g/p_F^0)[1 - p_g/p_F^0]}{|U_g|/E_F^0}e^{W_g(T)}. \quad (11b)$$

The Fourier components of the pseudopotential become smaller when the temperature is increased. This gives rise to an increase in $N_{opt}(T)$. In the limit, at very high temperatures, $N_{opt} \to N_{val}$.

For a cubic crystal, W_g is proportional to the mean square value of the atomic displacements $\overline{u^2}$. We shall consider the dependence $W(T)$ and estimate the value of W. For this purpose, we shall use the Debye model in which a solid is regarded as a continuous medium, and a limiting phonon momentum q_D as well as a limiting phonon energy, governed by the Debye temperature Θ, are introduced. In this model

$$W(T) = \frac{3}{2}K^2\frac{\hbar^2}{Mk\Theta}\left(\frac{T}{\Theta}\right)^2\int_0^{\Theta/T}\left(\frac{z}{e^z - 1} + \frac{z}{2}\right)dz. \quad (12)$$

Here, k is Boltzmann constant, M is the atomic mass. At $T \gg \Theta$

$$W(T) \approx \frac{3}{2}K^2\frac{\hbar^2}{Mk\Theta}\left(\frac{T}{\Theta}\right), \quad (12a)$$

but when $T \to 0$

$$W(0) = \frac{3}{8}K^2\frac{\hbar^2}{Mk\Theta}. \quad (12b)$$

We note that we should use the relationship $K\hbar = g\hbar = 2pg$ to go over to the notation employed in Eqs. (1) and (11). Then

$$W(0) = \frac{3}{2}\frac{p_g^2}{M}\frac{1}{k\Theta}. \quad (12c)$$

When $T \to 0$, the value of W tends to a finite limit. This is associated with the zeroth vibrations of the lattice.
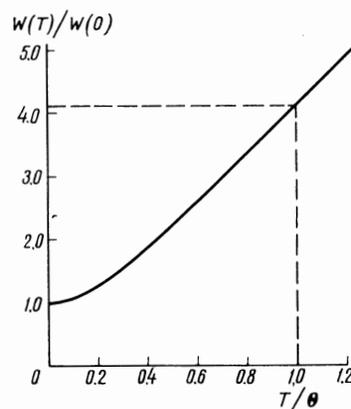
We shall use the notation

$$\varphi(x) = \frac{1}{x}\int_0^x \frac{z\,dz}{e^z - 1} + \frac{x}{4}. \quad (13)$$

The function $\varphi(x)$ differs from the Debye function by an amount $x/4$. The values of the Debye function have been tabulated in many papers, in particular in[10,13]. Using Eqs. (12), (12b) and (13), we obtain

$$W(T) = W(0)\frac{4\varphi(x)}{r}, \qquad x = \frac{\Theta}{T} \quad (14)$$

The figure shows the dependence of $W(T)/W(0)$ on T/Θ.

We shall estimate the variation of N_{opt} associated with the Debye—Waller factor, and we shall compare it with experiment. To determine the value of W, we shall use the results found in the determination of the temperature factor in the x-ray region. X-ray measurements, carried out over a wide range of temperatures, make it possible to determine the

temperature dependence of Θ_{x-ray} for cubic crystals. Using the average value of this parameter in the temperature range 293—78°K and substituting it into Eqs. (12b) and (14), we obtain $W(T_C)$ and $W(T_N)$ ($T_C = 293°K$ and $T_N = 78°K$). Moreover, we take into account that $\varphi_g/\pi \approx \frac{1}{2}$ in Eq. (11a) and introduce the average value $\overline{W}_g(T)$ [the averaging is carried out over all indices g which occur in Eq. (1)]. Since $W_g(T) \ll 1$, we use the relationship $e^{-\overline{W}(T)} \approx 1 - \overline{W}(T)$. Consequently, we have

$$\frac{N_{opt}(T_C)}{N_{opt}(T_N)} - 1 \approx \left(\frac{N_{val}}{N_{opt}(T_N)} - 1 \right)[\overline{W}(T_C) - \overline{W}(T_N)]. \quad (15)$$

To compare the theory with experiment we need to know the temperature factors determined from the x-ray and optical measurements to be obtained for the same metals. At present, such information is available only for Al and Pb.[1,2,14] The results on the dependence of $N_{opt}(T)$, obtained from the x-ray and optical measurements ($T_C = 293°K$, $T_N = 78°K$), are given below:

Metal:	Al	Pb
$\overline{\Theta}_{x-ray}$, °K:	405	89
$N_{val}/N_{opt}(T_N) - 1$	1.26	2.42
$[N_{opt}(T_C)/N_{opt}(T_N) - 1]_{x-ray}$	0.037	0.110
$[N_{opt}(T_C)/N_{opt}(T_N) - 1]_{opt}$	0.038	0.052

In calculations employing Eq. (15), we used the value of $N_{val}/N_{opt}(T_N) - 1$ obtained from the optical experiments. As the average value $\overline{W}_g(T)$, we used the value corresponding to the index g for which the influence of V_g on N_{opt} was strongest. The values of this index were as follows: $\overline{W} \approx W_{200}$ for Al and $\overline{W} \approx W_{111}$ for Pb.

The results reported here show good agreement between the x-ray and optical values for Al, but for Pb the x-ray value is considerably greater than the optical value. The reason for this discrepancy is not yet clear.

Optical measurements show that the temperature dependence of N_{opt} for In and Sn[3,4] is several times stronger than that for Al and Pb. Both In and Sn have the tetragonal structure. Unfortunately, no x-ray-measured values of the temperature factor are available for these metals. Measurements of the optical constants of In, carried out in the visible and near infrared region at room and helium temperatures,[4] have indicated a temperature dependence of the Fourier components of the pseudopotential, which was in agreement with the dependence $N_{opt}(T)$.

The temperature dependence of N_{opt} should be considerably stronger at high temperatures than at low temperatures. The results of a determination of the optical constants of W at high temperatures, reported in[15], are in qualitative agreement with this conclusion. Unfortunately, the optical constants of W were determined only in the near infrared region, in which the contribution of the interband transitions may have been considerable.

In conclusion, the author expresses his gratitude to R. A. Suris and A. G. Khachaturyan for discussing the problems referred to in the present paper.

[1] A. I. Golovashkin, G. P. Motulevich, and A. A. Shubin, JETP 38, 51 (1960), Soviet Phys. JETP 11, 38 (1960).
[2] A. I. Golovashkin and G. P. Motulevich, JETP 44, 398 (1963), Soviet Phys. JETP 17, 263 (1963); A. I. Golovashkin, JETP 48, 825 (1965), Soviet Phys. JETP 21, 548 (1965).
[3] A. I. Golovashkin and G. P. Motulevich, JETP 46, 460 (1964), Soviet Phys. JETP 21, 310 (1964); JETP 47, 64 (1964), Soviet Phys. JETP 20, 44 (1965).
[4] A. I. Golovashkin, I. S. Levchenko, G. P. Motulevich, and A. A. Shubin, JETP 51, (1966), this issue, p. 1093.
[5] R. N. Gurzhi and G. P. Motulevich, JETP 51, 1220 (1966), Soviet Phys. JETP 24, 818 (1967).
[6] J. M. Ziman, Adv. in Phys., 13, 89 (1964).
[7] D. Pines, The Many-Body Problem, Benjamin, New York, 1961 (Russ. Transl., IIL, 1963).
[8] P. Nozières, Le probleme a les Corps, Dunod, Paris, 1963.
[9] J. M. Ziman, Principles of the Theory of Solids, Cambridge, 1965 (Russ. Transl., Mir, 1960).
[10] R. James, Optical Principles of X-ray Diffraction (Russ. Transl., IIL, 1950).
[11] P. Debye, Ann. Physik 43, 49 (1913).
[12] I. Waller, Z. Physik 17, 398 (1923).
[13] L. I. Mirkin, Spravochnik po rentgenostrukturnomu analizu polikristallov (Handbook on X-ray Analysis of Polycrystalline Materials), Fizmatgiz, 1961.
[14] D. R. Chipman, J. Appl. Phys. 31, 2012 (1960).
[15] W. S. Martin, E. M. Duchane, and H. H. Blau, Jr., J. Opt. Soc. Am. 55, 1623 (1965).

Translated by A. Tybulewicz
232