SOVIET PHYSICS JETP VOLUME 16, NUMBER 5 MAY, 1963

# CALCULATION OF THE ELECTRONIC PARAMETERS OF METALS FROM THE RESULTS OF MEASUREMENTS OF THEIR OPTICAL CONSTANTS

K. P. GUROV, I. E. LEKSINA, and N. V. PENKINA

A. A. Baĭkov Institute of Metallurgy

Submitted to JETP editor June 25, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **43**, 1957-1963 (November, 1962)

A method is given for calculating the electronic microparameters of metals (average velocity at the Fermi level, effective electron mass, and frequency of electron-phonon collisions) from the results of optical measurements. The microparameters of $\alpha$-Fe, Pd, Al, and Cu are calculated using this method.

THE present paper describes the method and results of calculations of the electronic microparameters for several pure metals using measurements of the optical constants (refractive index and absorption coefficient) of these metals[1-4] and theoretical calculations of their electronic structure.

All the calculations are based on a fully established model: it is assumed that the electronic structure is such that the isotropic effective mass approximation is a valid description of the effects involving excitation of the electron system of the metal (absorption of heat, thermal conductivity, electrical conductivity, excitation with radiation, etc.).

This model implies that we are considering a system of free quasiparticles which are not bound by an internal potential field. The number of such particles in unit volume is given by

$$N^* = \int_0^\infty g(E) f_0(E)\, dE, \tag{1}$$

where g(E) is the density of levels with energies E; $f_0(E)$ is the equilibrium Fermi distribution; and the zero level of the energy E is in each case different. In the Bloch one-electron representation of the energy spectrum of a metal the integral is taken in practice from the bottom (or the ceiling) of the appropriate energy band and integration is carried out only within that band.

For a system described by the effective mass approximation, g(E), and consequently also N*, depend, in general, on T but if temperatures are not too high (T less or comparable with the Debye temperature of the metal) the dependence of g(E) on T is negligible and therefore, in complete analogy with the theory of free electrons, we can assume that

$$N^* = \int_0^{E_F} g(E)\, dE, \tag{2}$$

where $E_F$ is the Fermi level energy.

In the free-electron theory the number of electrons per unit volume is

$$N = \tfrac{8}{3}\pi\,(2mE_F)^{3/2}(2\pi\hbar)^{-3}, \tag{3}$$

$$g(E) = 4\pi\,(2m)^{3/2}E^{1/2}\,(2\pi\hbar)^{-3}. \tag{4}$$

Hence we have

$$N = \tfrac{2}{3}g(E_F)\,E_F = \tfrac{1}{3}g(E_F)\,mv_F^2, \tag{5}$$

where $v_F$ is the velocity on the Fermi surface.

In exactly the same way, for a system described by the effective mass approximation, we have

$$N^* = \tfrac{1}{3}g(E_F)\,m^*v_F^2. \tag{6}$$

In experiments on the excitation of the electron system the results are always interpreted (in the effective mass approximation) using relationships of the type

$$B = \Phi\,(N^*/m^*), \tag{7}$$

where B is the measured quantity and $\Phi$ is a certain known function of N*/m* and several other microscopic parameters. It is therefore convenient to introduce instead of N* a new "effective number of electrons," equal, by definition, to

$$N_{\text{eff}} = N^*m/m^*. \tag{8}$$

Then from Eq. (6) we find

$$N_{\text{eff}} = \tfrac{1}{3}g(E_F)\,mv_F^2. \tag{9}$$

$N_{\text{eff}}$ defined by Eq. (9) can be calculated independently from the results of optical measurements on metals (see [5,6]). Thus using the results of optical measurements we can employ Eq. (9) to determine $g(E_F)$, provided we know $v_F$, or to determine $v_F$ if we know $g(E_F)$.

Golovashkin et al[3] measured the optical constants as well as the electrical conductivity of the same metal samples, and calculated $N_{\rm eff}$ and $v_F$, using Eq. (9) to determine $g(E_F)$ (see also [6]).

In the present paper $v_F$ is determined from the data on $g(E_F)$, obtained from theoretical calculations of the electron structures. Such calculations have recently been carried out for several metals.[7-12]

We should note an important assumption made in the derivation and use of Eq. (9). The assumption of the isotropy of the electron structure implies an assumption that the Fermi surfaces are spherical and therefore the velocities $v_F$ on these surfaces are constant. In fact, the electron structure of almost all metals (single crystals) is anisotropic. Consequently in experiments of this type the samples are always polycrystals with fine-grained structure. It is assumed that due to the random orientation of the single-crystal grains in the sample we can use the isotropic parameters representing averaging on the Fermi surface. Equation (9) now has the form

$$\overline{N}_{\rm eff} = \frac{1}{3}\, m\, \overline{g(E_F)\, v_F^2}, \qquad (10)$$

where the bar over $N_{\rm eff}$ denotes averaging over the Fermi surface. Using the above formula to determine $v_F$ [or $g(E_F)$] from the data on $N_{\rm eff}$ and $g(E_F)$ (or $v_F$), we implicitly make an important assumption that $\overline{g(E_F)v_F^2}$ is approximately equal to $\overline{g(E_F)}\,\overline{v_F^2}$, and we naturally understand the velocity at the Fermi level $v_F$ to be the root-mean-square velocity $(\overline{v_F^2})^{1/2}$.

With these assumptions the velocity on the Fermi surface is given by the formula

$$v_F = \sqrt{3N_{\rm eff}/mg(E_F)} = 10^{-14}\sqrt{N_{\rm eff}/3g(E_F)} \qquad (11)$$

(since $m = 9 \times 10^{-28}$ g). We note that in Eq. (11) the quantities $N_{\rm eff}$ and $g(E_F)$ can be taken not only per unit volume, but also per atom, which may be more convenient in calculations.

Using $E = \frac{1}{2}m^*v^2$ we find from Eqs. (4) and (9)

$$m^* = \pi\sqrt{\hbar^3 g(E_F)/v_F} = 6.18\cdot 10^{-27}\sqrt{N_{\rm eff}/v_F^3}. \qquad (12)$$

For the majority of metals the Fermi level lies in the region of overlap of the energy bands of several zones. For example in transition metals the Fermi level lies in the region of the s-band, as well as five d-sub-bands. In principle, the electrons (or holes) of all these bands should contribute to the effects considered. It is not possible to allow for the contribution of each band separately. Consequently, instead of microparameters of the conduction electrons belonging to one band, we have to introduce some "weighted average" microparameters.

Let there be, for example, n bands which can in principle contribute to the effects considered and assume that the effective mass approximation is valid for all these bands:

$$E_i = E_{0i} + p^2/2m^* \; (i = 1, 2, \ldots, n). \qquad (13)$$

Each band has its own effective mass $m_i^*$ and its own energy scale with a zero at $E_{0i}$. Because of these assumptions we have for each band

$$N_{i\,\rm eff} = \frac{1}{3} g_i(E_{iF}) m v_{iF}^2. \qquad (14)$$

The value of $N_{\rm eff}$ found experimentally is then obviously equal to

$$N_{\rm eff} = \sum_{i=1}^{n} N_{i\,\rm eff} = \frac{m}{3}\sum_{i=1}^{n} g_i(E_{iF})\, v_{iF}^2. \qquad (15)$$

We shall define the weighted-average square of the velocity on the Fermi surface as

$$\overline{v_F^2} = \sum_{i=1}^{n} g_i(E_{iF}) v_{iF}^2 \Big/ \sum_{i=1}^{n} g_i(E_{iF}) = \sum_{i=1}^{n} g_i(E_{iF})\, v_{iF}^2 / g(E_F), \qquad (16)$$

where $g(E_F)$ is the total density of states at the Fermi level. Substituting Eq. (16) into Eq. (15) we obtain

$$N_{\rm eff} = \frac{1}{3} g(E_F)\, m \overline{v_F^2}. \qquad (17)$$

Thus if we know $N_{\rm eff}$ and the total $g(E_F)$, we can determine $\overline{v_F} = (\overline{v_F^2})^{1/2}$ from Eq. (17).

For this weighted-average velocity on the Fermi surface we can introduce the corresponding "average effective mass," defined by

$$m^* = 6.18\cdot 10^{-27}(N_{\rm eff}/\overline{v_F^3})^{1/2}, \qquad (18)$$

and the "average Fermi level energy," defined by

$$\overline{E}_F = \frac{1}{2}\overline{m^*}\,\overline{v_F^2}. \qquad (19)$$

Apart from the microparameters listed above, our model can be used to estimate approximately (without allowance for the quantum corrections of Gurzhi 1) [13]) the frequency of electron-phonon

---

[1] The quantum correction of Gurzhi can easily be included.[6,13] However, for room temperatures which are considered in this paper, it amounts to ≈10-15%, i.e., it does not exceed the error of the calculation method.

collisions $\nu_{ef}$. As is known, the formula for estimating $\nu_{ef}$ can be obtained from the appropriate transport equation

$$\frac{\partial f(t,\mathbf{p})}{\partial t} = A \int\limits^{|\mathbf{q}|\leqslant q_{max}} \Big\{ q\,d\mathbf{q}\,\delta\,(E\,(\mathbf{p}+\mathbf{q}) - E\,(\mathbf{p}) - h\nu_q)\,[f\,(t,\mathbf{p}+\mathbf{q})\,(1-f\,(t,\mathbf{p})) \times (\overline{N}_q+1) - f\,(t,\mathbf{p})\,(1-f\,(t,\mathbf{p}+\mathbf{q}))\,\overline{N}_q] + \delta\,(E\,(\mathbf{p}-\mathbf{q}) - E\,(\mathbf{p}) + h\nu_q)\,[f(t,\mathbf{p}-\mathbf{q})\,(1-f\,(t,\mathbf{p}))\,\overline{N}_q - f\,(t,\mathbf{p})\,(1-f\,(t,\mathbf{p}-\mathbf{q}))\,(\overline{N}_q+1)]\Big\}, \tag{20}$$

where $\mathbf{q}$ is the phonon momentum, $h\nu_q$ is the phonon energy; for the phonon system we assume the simplest dispersion relation:

$$h\nu = qu. \tag{21}$$

Here $h\nu_{max} = k\Theta$, $q_{max} = k\Theta/u$, $u$ is the velocity of sound, $\Theta$ is the Debye temperature, $k$ is the Boltzmann constant, and $\overline{N_q}$ is the equilibrium distribution of phonons (the Bose distribution).

The constant $A$ in Eq. (20) is approximately equal[14] to

$$A = \pi\Delta C^2\,/\,(2\pi\hbar)^3\,\hbar M u = 0.36\,\pi a^3 E_F^2\,/\,(2\pi\hbar)^3\,\hbar M u, \tag{22}$$

where $\Delta$ is the volume of a unit cell in the crystal lattice (for cubic structures $\Delta = a^3$), $a$ is the lattice constant, $C$ is the average energy of electrons ($C \approx 0.6E_F$), $M$ is the mass of an atom in the crystal.

Assuming that the deviation of $f(t,\mathbf{p})$ from the equilibrium Fermi distribution $f_0(\mathbf{p})$ is small, we find that the right-hand part of Eq. (20) defines the quantity $1/\tau_p$, where $\tau_p$ is the relaxation time for particles with a momentum $\mathbf{p}$. The required electron-phonon collision frequency $\nu_{ef}$ is equal to the value of $1/\tau_p$ averaged over all momenta:

$$\nu_{ef} = \overline{\frac{1}{\tau_p}} = \frac{\Delta}{(2\pi\hbar)^3}\int \frac{1}{\tau_p} f_0(\mathbf{p})\,d\mathbf{p} = \frac{a^3}{(2\pi\hbar)^3}\int \frac{1}{\tau_p} f_0(\mathbf{p})\,d\mathbf{p}. \tag{23}$$

After simple transformations Eq. (20) becomes

$$\frac{1}{\tau_p} = A \int\limits^{|\mathbf{q}|\leqslant q_{max}} q\,d\mathbf{q}\,\{\delta\,(E\,(\mathbf{p}+\mathbf{q}) - E\,(\mathbf{p}) - qu)\,[\overline{N}_q + f_0\,(\mathbf{p}+\mathbf{q})] + \delta\,(E\,(\mathbf{p}-\mathbf{q}) - E\,(\mathbf{p}) + qu)\,[\overline{N}_q + 1 - f_0\,(\mathbf{p}-\mathbf{q})]\}. \tag{24}$$

In integration with respect to $\mathbf{q}$ we shall use spherical coordinates

$$d\mathbf{q} = -\,q^2 dq\,d\varphi\,d\xi, \tag{25}$$

where $\xi = \cos\vartheta$ and the orientation of the spherical system is selected so that $\vartheta$ is the angle between the vector $\mathbf{q}$ and the vector (fixed during integration) $\mathbf{p}$. Then

$$E\,(\mathbf{p}\pm\mathbf{q}) = p^2/2m^* + q^2/2m^* \pm pq\xi/m^*, \tag{26}$$

$$f_0\,(\mathbf{p}\pm\mathbf{q}) = \left[\left(\frac{p^2}{2m^*} + \frac{q^2}{2m^*} \pm \frac{pq\xi}{m^*} - E_F\right)/kT + 1\right]^{-1}. \tag{27}$$

Substituting Eqs. (26) and (27) into Eq. (24) and integrating with respect to $\varphi$ and $\xi$ we obtain

$$\frac{1}{\tau_p} = 2\pi A\,\frac{m^*}{p}\int\limits_0^{q_{max}} q^2 dq\,\{2\overline{N}_q + 1 + f_0\,(E+qu) - f_0\,(E-qu)\} \approx 2\pi A\,\frac{m^*}{p}\int\limits_0^{q_{max}} q^2 dq\left\{2\overline{N}_q + 1 + 2qu\,\frac{\partial f_0(E)}{\partial E}\right\}. \tag{28}$$

After laborious but uncomplicated calculations of the integrals with respect to q we obtain

$$\frac{1}{\tau_p} = 2\pi A\,\frac{m^* k^3 T\Theta}{pu^3}\left\{1 + \frac{1}{24}\left(\frac{\Theta}{T}\right)^2 + \frac{kT}{2}\left(\frac{\Theta}{T}\right)^2\frac{\partial f_0(E)}{\partial E}\right\}. \tag{29}$$

We shall now average $1/\tau_p$ using Eq. (23):

$$\nu_{ef} = \frac{a^3}{(2\pi\hbar)^3}\int\frac{1}{\tau_p} f_0(\mathbf{p})\,d\mathbf{p} = \frac{2\pi a^3 m^* A k^3 \Theta^2 T}{(2\pi\hbar)^3 u^3} \times \int\frac{1}{p}\,d\mathbf{p} f_0(\mathbf{p})\left\{1 + \frac{1}{24}\left(\frac{\Theta}{T}\right)^2 + \frac{kT}{2}\left(\frac{\Theta}{T}\right)^2\frac{\partial f_0(E)}{\partial E}\right\} = \frac{8\pi^2 a^3 (m^*)^2 A k^3 T \Theta^2}{(2\pi\hbar)^3 u^3}\int dE f_0(E)\left\{1 + \frac{1}{24}\left(\frac{\Theta}{T}\right)^2 + \frac{kT}{2}\left(\frac{\Theta}{T}\right)^2\frac{\partial f_0(E)}{\partial E}\right\}. \tag{30}$$

We note that $\int f_0(E)\,dE = E_F$ and the function $\partial f_0(E)/\partial E$ can be approximated by the $\delta$-function

$$\partial f_0(E)\,/\,\partial E \approx -\,\delta\,(E - E_F). \tag{31}$$

Then

$$\int f_0(E)\,\frac{\partial f_0(E)}{\partial E}\,dE = -\,f_0(E_F) = -\,\frac{1}{2}. \tag{32}$$

Thus, using Eq. (22) for A we find

$$\nu_{ef} = \frac{0.36\cdot 8\pi^3 a^6 E_F^3 (m^*)^2 k^3 T \Theta^2}{(2\pi\hbar)^6\,\hbar M u^4} \times \left\{1 + \frac{1}{24}\left(\frac{\Theta}{T}\right)^2 - \frac{kT}{4E_F}\left(\frac{\Theta}{T}\right)^2\right\}. \tag{33}$$

In metals we always have $kT \ll E_F$, and therefore we can neglect the third term in the braces of Eq. (33). Finally we obtain

$$\nu_{ef} = \frac{0.045 a^6 (m^*)^2 k^3 E_F^3 T \Theta^2}{\pi^3 \hbar^7 M u^4}\left\{1 + \frac{1}{24}\left(\frac{\Theta}{T}\right)^2\right\} \tag{34}$$

$$= \frac{2{,}72\cdot 10^{138} a^6 (m^*)^2\, T\Theta^2 E_F^3}{Mu^4}\left\{1+\frac{1}{24}\left(\frac{\Theta}{T}\right)^2\right\}. \tag{35}$$

For convenience in calculations we should substitute into Eq. (35) the energy $E_F$, expressed in eV, the lattice constant a, in angstroms, and the mass ratio $\alpha = m^*/m$. Then we find

$$\nu_{ef} = \frac{9.0 a^6 \alpha^2 T\Theta^2 (E_F)^3}{Mu^4}\left\{1+\frac{1}{24}\left(\frac{\Theta}{T}\right)^2\right\}. \tag{36}$$

Using Eqs. (11), (12), and (36) we have calculated the microparameters of $\alpha$-Fe, Pd, Al, and Cu. For $N_{eff}$ we used the optical constants data, and for $g(E_F)$ we employed the published theoretical calculations. The table lists values of $N_{eff}$, $g(E_F)$ and the results of our calculations. For $g(E_F)$ we used the published total values corresponding to all the energy bands overlapping in the region of the Fermi level. The results for this case are given in the third column of the table. Similar calculations were repeated with $g(E_F)$ determined from measurements of the electronic specific heat[15] (fifth column of the table). For a more reliable analysis of the results, calculations were also carried out for values of $g(E_F)$ solely for the conduction band (fourth column of the table). All the results in the table are given for room temperature.

An analysis of the tabulated results indicates that in Pd and Fe the d-sub-bands undoubtedly make a large contribution to the effects considered; large effective quasiparticle masses corresponding to these sub-bands dominate the weighted-average values. There is good agreement between the results obtained from specific heat measurements and the calculations carried out by the method described here. For aluminum the hypothesis of Matyass[10] is obviously confirmed, i.e., that in the effects considered one 3p-band predominates.

Simultaneous measurements of the optical constants and the static electrical conductivity were carried out by Golovashkin et al[3] for aluminum and by Padalka and Shklyarevskiĭ[4] for copper (evaporation-deposited samples with porous structure). Their results for $v_F$ and $\nu_{ef}$ (without allowance for the Gurzhi corrections) are listed in the sixth column of the table. For Al their results agree satisfactorily with ours, if we allow for the complex electronic structure of Al for which the effective mass method is a very rough approximation. For Cu the table indicates excellent agreement between our results and those in the sixth column.

Thus an analysis of the tabulated results leads to the conclusion that our method, employing experimental results of optical measurements and theoretical calculations of electronic structures,

| Metal | Quantity | Values | | | |
|---|---|---|---|---|---|
| | | for overlapping bands | for conduction band | from electronic specific-heat data | from measurements of optical constants and electric conductivity |
| $\alpha$-Fe<br>($N_{\text{eff}} = 7.7\cdot 10^{22}$ cm$^{-3}$ [1]) | $g(E_F)$, eV$^{-1}$ (per atom) | 2.4 [7] | 0.2 [7] | 2.2 | |
| | $v_F\cdot 10^{-8}$, cm/sec | 0.45 | 1.5 | 0.47 | |
| | $m^*/m$ | 6.3 | 1.0 | 6.0 | |
| | $\nu_{ef}\cdot 10^{-14}$, sec$^{-1}$ | $0{,}8_5$ | $1{,}2_5$ | 0.8 | |
| Pd<br>($N_{\text{eff}} = 6{,}5\cdot 10^{22}$ cm$^{-3}$ [2]) | $g(E_F)$, eV$^{-1}$ (per atom) | 2.0 [8,9] | 0.2 [8,9] | 4.6 | |
| | $v_F\cdot 10^{-8}$, cm/sec | 0.5 | 1.5 | 0.3 | |
| | $m^*/m$ | 5.5 | $0.9_5$ | 9.2 | |
| | $\nu_{ef}\cdot 10^{-14}$, sec$^{-1}$ | 5.0 | 0.94 | 8.8 | |
| Al<br>($N_{\text{eff}} = 7.4\cdot 10^{22}$ cm$^{-3}$ [3]) | $g(E_F)$, eV$^{-1}$ (per atom) | 0.9 [10,11] | 0.4 [10,11] | 0.5 | |
| | $v_F\cdot 10^{-8}$, cm/sec | 0.9 | 1.3 | 1.2 | 2.8 [3] |
| | $m^*/m$ | 2.2 | 1.1 | 1.4 | |
| | $\nu_{ef}\cdot 10^{-14}$, sec$^{-1}$ | 3.9 | 1.5 | 2.5 | 0.63 [3] |
| Cu<br>($N_{\text{eff}} = 4.95\cdot 10^{22}$ cm$^{-3}$ [4]) | $g(E_F)$, eV$^{-1}$ (per atom) | 0.26 [12] | | 0.32 | |
| | $v_F\cdot 10^{-8}$, cm/sec | 1.1 | | 1.0 | 1.4 [4] |
| | $m^*/m$ | 1.3 | | 1.5 | |
| | $\nu_{ef}\cdot 10^{-14}$, sec$^{-1}$ | 0.17 | | 0.25 | 0.19 [4] |

can, in spite of the very approximate nature of the latter, be used to estimate the electronic microparameters of metals. The usefulness of such estimates lies in the fact that they allow us to compare the microparameters of various metals and analyze the variation of these parameters in dilute solid solutions with variation of the concentration of the impurity component.

Concluding, the authors express their gratitude to I. B. Borovskiĭ and G. P. Motulevich for reading this paper and making several comments.

---

[1] I. B. Borovskiĭ and O. V. Neklyudova, Trudy, Metallurgy Inst, **6** (1960).

[2] I. E. Leksina and N. V. Penkina, FMM **11**, 470 (1961).

[3] Golovashkin, Motulevich, and Shubin, JETP **38**, 51 (1960), Soviet Phys. JETP **11**, 51 (1960).

[4] V. G. Padalka and I. N. Shklyarevskiĭ, Optika i spektroskopiya, **12**, 291 (1962).

[5] V. L. Ginzburg and G. P. Motulevich, UFN **55**, 469 (1955).

[6] G. P. Motulevich, JETP **37**, 1770 (1959), Soviet Phys. JETP **10**, 1249 (1960).

[7] J. B. Greene and M. F. Manning, Phys. Rev. **63**, 203 (1943).

[8] F. E. Hoare and B. Yates, Proc. Roy. Soc. (London) **A240**, 42 (1957).

[9] J. A. Rayne, Phys. Rev. **118**, 1545 (1960).

[10] Z. Matyass, Phil. Mag. **39**, 429 (1948).

[11] G. V. Raynor, Reports on Progress in Physics **15**, 173 (1952).

[12] H. M. Krutter, Phys. Rev. **48**, 664 (1935).

[13] R. I. Gurzhi, JETP **35**, 965 (1958), Soviet Phys. JETP **8**, 673 (1959).

[14] R. I. Gurzhi, JETP **33**, 451 (1958), Soviet Phys. JETP **6**, 352 (1958).

[15] P. H. Keesom and N. Pearlman, in: Low Temperature Physics, Handbuch der Physik, vol. XIV-XV, Springer, 1956.

Translated by A. Tybulewicz
328