Low-temperature electrical resistivity of noble metals*

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We have accomplished a study of the low-temperature electrical resistivity for the noble metals silver and copper. We have described the Fermi surface of the noble metals by the simple eight-cone model and have taken into account two-orthogonalized-plane-wave corrections which are very important at the lowest temperatures. The use of the standard trial function in the variational formula for the resistivity makes the calculation more applicable to the temperature-dependent resistivity of impure samples. This interpretation is supported by comparison with the available experimental data. Our results evidence the preponderance of the "umklapp" contribution to the low-temperature resistivity over the normal one. Moreover, they show that the resistivity as a function of temperature does not follow a well-defined power law, but, if one assumes the validity of a simple relation $\rho \sim T^n$, the exponent n varies continuously ranging from a value of nearly 6 to a value of nearly 4 in the region $T = 1$–15 K.

I. INTRODUCTION

Recent accurate measurements of the electrical resistivity at low temperature have frequently shown substantial deviations from the Bloch-Grüneisen T^5 law, and have motivated more detailed calculations of the electrical resistivity due to the electron-phonon interaction. These calculations, on the other hand, have evidenced the essential role of the umklapp scattering contribution to the electrical resistivity, in particular, when the Fermi surface lies outside the first Brillouin zone or just touches the zone boundary. Moreover these calculations showed that to obtain a reliable result, one, in general, must overcome several difficulties which arise from the necessity of taking into account the effective shape of the Fermi surface of the metal (which seldon can be considered as nearly spherical), the phonon spectrum, and the matrix element for the electron-phonon scattering. Although all these are computational difficulties, only the first represents a hard task to be taken into account, as it is possible, at present, to evaluate the phonon spectrum by standard, even if sophisticated, numerical methods, and to take into account the electron-phonon matrix element in the framework of the well-established pseudopotential formalism.

As we well know, the first complete calculation of the electrical resistivity of metals with distorted Fermi surface was due to Pytte, [1] who evaluated the aluminum electrical resistivity in the temperature range from nearly 10 K to about 100 K. Along the same lines, one can consider the recent work by Lawrence and Wilkins, [2] who accomplished an enlightening and detailed study of the effects of umklapp electron-phonon scattering on the electrical resistivity of polyvalent metals. The only, but not negligible, limit in the Lawrence and Wilkins calculation is in the fact that, since their work has been chiefly directed to showing that the umklapp scattering is the major source of the observed deviations from the T^5 Bloch-Grüneisen law in the low-temperature range, it gives, on the other hand, only the qualitative behavior of the resistivity as a function of temperature. However Lawrence and Wilkins were able to show that, besides the importance of the umklapp processes, the theoretical values of the resistivity are, at low temperatures, very sensitive to the way in which the distortions of the Fermi surface are taken into account, and that two-orthogonalized-plane-waves (OPW) corrections play a fundamental role in the same temperature region. The predominant role of the umklapp processes and the fact that the one-OPW model did not give accurate results in the low-temperature region were also discussed by the present authors in their work on the resistivity of hexagonal metals Be, Mg, Zn. [3]

Once the previously discussed difficulties have been taken into account, one is then faced with another problem which has received particular emphasis in recent works. The probelm is to extract from the linearized Boltzmann equation the form of the deviation (from equilibrium) function $\Psi(\vec{k})$ of the electron Fermi distribution.

As it is quite impossible to solve the linearized Boltzmann equation in the general case, most of the calculations of the electrical resistivity have been usually accomplished by inserting a standard-deviation function $\Psi_0(\vec{k}) = \vec{v}(\vec{k}) \cdot \vec{E}$ into the variational (Köhler) expression for the resistivity constructed from the linearized Boltzmann equation. On the other hand, several works[4–6] made evident that, owing to the strong orientational dependence of the electron-phonon umklapp interaction, the simple Ψ_0 form of the deviation function cannot produce reliable results if the umklapp scattering predominates over the normal and impurity contributions to the resistivity.

More recently, the complicated task of deter-

mining a reliable expression for the trial function $\Psi(\vec{k})$ has been attacked by Ekin and Bringer[7] and by Black and Mills.[8] Black and Mills start from constructing a trial function (for a simple fcc metal) by expanding its angular dependence as a linear combination of cubic harmonics; the appropriate linear combination is then determined through the use of the variational principle. They are able to show that many terms in the expansion of the trial function are generally necessary in order to obtain convergence in the theoretical calculation of the resistivity at low temperatures. Moreover Black and Mills show that greater corrections, with respect to the standard trial function, are necessary when the Fermi surface lies outside the Brillouin zone or just touches the zone boundary. The same conclusions were essentially reached by Ekin and Bringer, who used a number of different trial functions to test the dependence of the results on the particular form chosen for Ψ. Ekin and Bringer[7] specifically examine the potassium metal. In this case, the Fermi surface is well inside the first Brillouin zone so that comparable amounts of normal and umklapp scattering are found. Owing to the moderate importance of the umklapp contributions, minor corrections are obtained, with respect to the standard trial function, than in the case of a Fermi surface which approaches or lies outside the zone boundary. In conclusion, the previous discussion shows that a reliable calculation of the low-temperature electrical resistivity must take into account, in addition to a correct evaluation of the phonon spectrum and electron-phonon matrix element, the distortions of the Fermi surface from sphericity, two-OPW corrections when the Fermi surface approaches, or lies outside, the zone boundary, and lastly, the anisotropic relaxation of the electron distribution. This being the situation, an acceptable description of the electrical resistivity in a real metal would bring up great computational difficulties. On the other hand, if one limits himself to considering only the low-temperature region, which has received great attention in recent years in connection with the problem of the deviations from Matthiessen's rule, it is possible to allow for a considerable simplification of the calculations. In fact, it has been shown by several authors[2,7,8] that in the case where impurity scattering dominates, such as in dilute alloys or at sufficiently low temperatures, the deviation function $\Psi(\vec{k})$ may be closely approximated by the standard form $\Psi_0(\vec{k}) = \vec{v}(\vec{k}) \cdot \vec{E}$. In this case it is then possible to overcome the difficulties arising from the anisotropy of the electron-phonon interaction.

In this work we will then examine, using the standard trial function Ψ_0, the low-temperature behavior of the electrical resistivity of the noble metals Cu and Ag. Though our analysis is in many respects related to the Lawrence and Wilkins approach, it is on the other hand more realistic. Indeed our calculations are performed without approximations, apart from the use of a simple but reliable model of the Fermi surface, the "eight-cone" model,[9] which already in the past produced results for the magnetic susceptibility[10] and the hyperfine properties[11] in close agreement with experiments.

In our calculations electron-phonon matrix element have been considered within a pseudopotential formalism,[12,13] and the phonon dispersion curves have been take into account on the basis of the experimental results. Previous calculations of noble metals resistivity have been performed by several authors (see, e.g., Refs. 14 and 15); however, no one is able to produce reliable results at very-low temperatures as plausible shape of the Fermi surface and two-OPW corrections are not taken into account.

In Sec. II we present the relevant expressions of our calculations of the electrical resistivity of noble metals. The results of the calculations are given in Sec. III and compared with available experimental data. Summary and conclusions follow in Sec. IV.

II. GENERAL FORMULATION

The general variational expression for the electrical resistivity has been reported in several places[2,16] so that here we limit ourselves to simply give the final results

$$\rho = \frac{\pi}{6\hbar}\left(\frac{1}{4\pi^3\hbar}\right)^2 \int \frac{dS_{\vec{k}}}{|\vec{v}(\vec{k})|} \frac{dS_{\vec{k}'}}{|\vec{v}(\vec{k}')|} \times |\vec{v}(\vec{k}) - \vec{v}(\vec{k}')|^2 \sum_\lambda |g_\lambda(\vec{k}, \vec{k}')|^2 \frac{f_s(\hbar\omega_{\vec{q}\lambda}/k_B T)}{(\Psi_0, X)^2} \tag{2.1}$$

In this expression the double integral is on the effective Fermi surface, $\vec{v}(\vec{k})$ is the electron group velocity on the Fermi surface and $g_\lambda(\vec{k}, \vec{k}')$ is the matrix element for the scattering of an electron from $\vec{k}$ to $\vec{k}'$ through the emission or absorption of a phonon with wave vector $\vec{q}$, polarization $\hat{\epsilon}_{\vec{q}\lambda}$, and energy $\hbar\omega_{\vec{q}\lambda}$:

$$|g_\lambda(\vec{k}, \vec{k}')|^2 = (\hbar/MN\omega_{\vec{q}\lambda})|(m_\lambda(\vec{k}, \vec{k}')|^2, \tag{2.2}$$

where

$$m_\lambda(\vec{k}, \vec{k}') = \langle \vec{k} | \hat{\epsilon}_{\vec{q}\lambda} \cdot \vec{\nabla} V | \vec{k}' \rangle \tag{2.3}$$

is the reduced matrix element, N is the density of unit cells, and M is the ionic mass. In Eq. (2.1), $f_s(\hbar\omega_{\vec{q}\lambda}/k_B T)$ is the statistical factor given by

$$f_s(x) = x/[(e^x - 1)(1 - e^{-x})]. \tag{2.4}$$

The denominator of (2.1) is given, in general, by

$$(\Psi_0, X) = \frac{e}{12\pi^3\hbar} \int dS_{\vec{k}} \left| \vec{v}(\vec{k}) \right| = en/m_{opt}, \qquad (2.5)$$

where there are n electrons per unit volume and m_{opt} is the optical effective mass. In the expression (2.1), we have used for the trial function the standard form

$$\Psi_0(\vec{k}) = \vec{v}(\vec{k}) \cdot \vec{E}. \qquad (2.6)$$

We have previously remarked that, though this form is strictly suited only to a spherical Fermi surface, it may be considered valid also for distorted Fermi surfaces when the contribution to the electrical resistivity from impurity scattering is greater than that from electron-phonon scattering. In Eq. (2.1), the contributions both from normal and umklapp processes are to be included in a convenient way.

As it appears evident from Eq. (2.1), a reliable calculation of the electron-phonon resistivity requires a detailed knowledge of the lattice dynamics, for evaluating the eigenfrequencies $\omega_{\vec{q}\lambda}$ and eigenvectors $\hat{\epsilon}_{\vec{q}\lambda}$, and a suitable pseudopotential for evaluating electron-phonon matrix element $g_\lambda(\vec{k}, \vec{k}')$. In fact, in many calculations of the electrical resistivity the authors have directed their attention mainly toward the form of the phonon spectrum and pseudopotential, completely disregarding the role of the distortions in the Fermi surface and of two-OPW corrections. These calculations have been seen to give reliable results only at high temperatures, as a correct determination of the electrical resistivity requires that, in the low-temperature region, the effective shape of the Fermi surface and two-OPW corrections be taken into account. On this basis, deferring the discussion on the phonon spectrum and pseudopotential to Sec. III, here we will first consider in some detail a plausible model for the Fermi surface of the noble metals. As is well known, the Fermi surface of the solid noble metals is so much distorted from a spherical shape as to contact the (111) faces of the Brillouin zone. For this reason it is not possible, even allowing for some approximations in the results, to treat the Fermi surface as a sphere when calculating the electrical resistivity or other properties of the noble metals. On the other hand, for the noble metals a simple eight-cone model was proposed several years ago by Ziman.[9] In the eight-cone model the shape of the energy surfaces is made dependent on a single parameter which can be interpreted as the pseudopotential form factor, or one-half the s-p band gap at L, the center of the nearest (111) zone face. The first Brillouin zone is supposed to be made of eight circular cones pointing into the center along the diagonals of a cube. Each cone subtends the solid angle $\frac{1}{2}\pi$, so that its vertex angle is $\cos^{-1}(\frac{3}{4})$. The axis of the cone is a vector $\vec{p} = \frac{1}{2}\vec{G}$, where $\vec{G}$ is the vector of the reciprocal lattice corresponding to the nearest hexagonal (111) zone face. The free Fermi surface would have a radius $k_F = 0.902p$.

Taking the local z axis in the $\vec{p}$ direction and introducing, as in Ziman's paper, dimensionless variables $x = k_x/p$, $y = k_y/p$, $z = k_z/p$, $\epsilon = E_{\vec{k}}/\hbar^2p^2$, and $u = V_G/(\hbar^2G^2/4m)$ (where V_G is the Fourier component of the lattice pseudopotential), the energy surfaces are conveniently written

$$\epsilon = \tfrac{1}{2}(x^2 + y^2) + f(z), \qquad (2.7)$$

where

$$f(z) = \tfrac{1}{2} + \tfrac{1}{2}(1 - z)^2 - [u^2 + (1 - z)^2]^{1/2}. \qquad (2.8)$$

The Fermi surface cuts the side surface of the cone at an ordinate z_1. This same energy surface meets the zone boundary at $z_2 = 1$. By knowing the pseudopotential form factor u, the values of z_1 and ϵ_F (the Fermi energy) are obtained along the same line as reported in Ref. 9.

Owing to the distortions of the Fermi surface of noble metals, a convenient way of describing the electronic states near the Bragg planes is to use two plane-wave electronic functions. In the framework of the eight-cone model the electronic wave function near the (111) zone face is then written

$$\Psi_{\vec{k}}(\vec{r}) = C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + C_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}}, \qquad (2.9)$$

where

$$C_{\vec{k}} = \tfrac{1}{2}\sqrt{2}[1 + t/(1 + t^2)^{1/2}]^{1/2} \qquad (2.10)$$

and

$$C_{\vec{k}-\vec{G}} = -\tfrac{1}{2}\sqrt{2}[1 - t/(1 + t^2)^{1/2}]^{1/2}, \qquad (2.11)$$

with

$$t = |z - 1|/u.$$

As in the Lawrence and Wilkins calculations,[2] we will work in the extended-reduced zone scheme and adopt the same convention to classify normal and umklapp processes. Moreover, as we work at very-low temperatures, so that we are concerned with very-small phonon wave vectors, we may classify the polarization vectors as corresponding, one, to longitudinal mode ($\hat{\epsilon}_{\vec{q}L} \cdot \vec{q} = q$) and, two, to transverse modes ($\hat{\epsilon}_{\vec{q}T} \cdot \vec{q} = 0$).

In the eight-cone model the relevant quantities of Eq. (2.1) are then expressed

$$\vec{v}(\vec{k}) = (\hbar/m)p(x\hat{i} + y\hat{j} + \{z - [1 - t/(1 + t^2)^{1/2}]\}\hat{k}), \qquad (2.12)$$

$$|\vec{v}(\vec{k}) - \vec{v}(\vec{k}')|^2 = (\hbar^2p^2/m^2)[q^2/p^2 + F(z, z')], \qquad (2.13)$$

where

$$F(z,z')=[z+t/(1+t^2)^{1/2}-z'-t'/(1+t'^2)^{1/2}]^2-(z-z')^2,$$

$$-im_L(\vec{k},\vec{k}')=\tfrac{1}{2}qV(q)(\{[1+t/(1+t^2)^{1/2}][1+t'/(1+t'^2)^{1/2}]\}^{1/2}+\{[1-t/(1+t^2)^{1/2}][1-t'/(1+t'^2)^{1/2}]\}^{1/2}) \quad (2.14)$$
$$-\tfrac{1}{2}(q-\hat{\epsilon}_{\vec{q}L}\cdot\vec{G})V(\vec{q}-\vec{G})\{[1+t/(1+t^2)^{1/2}][1-t'/(1+t'^2)^{1/2}]\}^{1/2}-\tfrac{1}{2}(q+\hat{\epsilon}_{\vec{q}L}\cdot\vec{G})V(\vec{q}+\vec{G})$$
$$\times\{[1-t/(1+t^2)^{1/2}][1+t'/(1+t'^2)^{1/2}]\}^{1/2},$$

and

$$\sum_T|m_T(\vec{k},\vec{k}')|^2=\tfrac{1}{4}[G^2-(\hat{\epsilon}_{qL}\cdot\vec{G})^2](V(\vec{q}-\vec{G})\{[1+t/(1+t^2)^{1/2}][1-t'/(1+t'^2)^{1/2}]\}^{1/2}-V(\vec{q}+\vec{G})^{1/2}$$
$$\times\{[1-t/(1+t^2)^{1/2}][1+t'/(1+t'^2)^{1/2}]\}^{1/2})^2. \quad (2.15)$$

Now the calculation of the electrical resistivity by means of the Eq. (2.1) depends on the evaluation of a double surface integral. This is accomplished in the appendix to which we refer for the details. The resulting expression for ρ is

$$\rho=(\pi/6\hbar)(1/4\pi^3\hbar)^2(m_{\rm opt}^2/e^2n^2)S, \quad (2.16)$$

where

$$S=32\pi\int_{z_1}^{2-z_1}dz'\int_{z_1}^{1}dz\int_{q_m(z,z')}^{q_M(z,z')}q\,dq \times\frac{M(z,z',q)}{[(q^2-q_m^2)(q_M^2-q^2)]^{1/2}}, \quad (2.17)$$

again referring to the Appendix for the signification of the symbols.

III. RESISTIVITY OF SILVER AND COPPER

By using formulas (2.16) and (2.17) a numerical evaluation of the electrical resistivity for silver and copper may be accomplished. In order to complete the calculation the knowledge of an electron-ion pseudopotential form factor, which enters in the calculation through Eqs. (2.14) and (2.15), and of a reliable phonon spectrum is necessary.

As far as the pseudopotential form factor is concerned, we have first used a semiempirical model potential recently proposed by the present authors,[12] and which has already been used in previous works giving good agreement with experiments (see, e.g., Refs. 17–19). Then, in order to determine how much changes in the potential affect the temperature dependence and the magnitude of the resistivity, the Harrison-Moriarty "first-principles" pseudopotential[13] has also been used.

With regards to the phonon spectrum, in principle, it would only be a matter of numerical computations to obtain it through an accurate description of lattice dynamics.[20] However, a rigorous treatment of the phonon spectrum would require a great amount of further computational work so that, in order to make more tractable the computational difficulties, we have assumed a phonon frequency proportional to its wave vector $\omega_{\vec{q}\lambda}\sim q$. This assumption appears to be quite reasonable since our treatment starts from considering an isotropic trial function and then has a range of validity limited to very-low temperatures. Moreover we allow the transverse frequencies $\omega_{\vec{q}T}$ to differ from the longitudinal one $\omega_{\vec{q}L}$, but take the two transverse frequencies as equal to each other. The positions $\omega_{\vec{q}L}=v_Lq$ and $\omega_{\vec{q}T}=v_Tq$ are in close agreement with the experimental dispersion curves for low q values.[18,21,22] The v_L and v_T values have been obtained by averaging over the various symmetry directions of the Brillouin zone. We have obtained

$$\left.\begin{aligned}v_L&=4.08\times10^5\ \text{cm/sec}\\ v_T&=1.96\times10^5\ \text{cm/sec}\end{aligned}\right\}\ \text{for silver,}$$

and

$$\left.\begin{aligned}v_L&=4.90\times10^5\ \text{cm/sec}\\ v_T&=2.56\times10^5\ \text{cm/sec}\end{aligned}\right\}\ \text{for copper.}$$

Finally, in order to complete the calculation it is essential to have a knowledge of the Fermi-surface parameters. In the eight-cone model the Fermi surface is made dependent on the only parameter r/p, i.e., the neck radius relative to the axis of the cone.[23] The simplicity of the model, on the other hand, should hardly affect the reliability of the resistivity calculations because, as we will see, owing to the predominance of the umklapp scattering, nearly the total contribution to the electrical resistivity in the low-temperature range arises from a very-small region near the necks. In our calculations we have used for the r/p quantities the values quoted by Ziman[9]

$$r/p=0.126\ (\text{Ag}),\quad r/p=0.180\ (\text{Cu}).$$

To conclude we simply mention that for the values of the optical mass we have adopted the experimental results by Schulz[24]

$$m_{\rm opt}^{\rm Cu}=1.45\ m,\quad m_{\rm opt}^{\rm Ag}=0.97\ m,$$

where m is the free-electron mass.

Using the previous entries the integration in Eq. (2.17) was performed by means of the Gauss method with the help of a CII-10070 computer.

TABLE I. Electron-phonon contributions to the electrical resistivity of silver (Ω m). [a]

Temperature (°K)	Umklapp longitudinal	Umklapp transverse	Normal	Total
1	0.131×10^{-17}	0.162×10^{-16}	0.137×10^{-19}	0.175×10^{-16}
2	0.657×10^{-16}	0.771×10^{-15}	0.455×10^{-18}	0.837×10^{-15}
3	0.596×10^{-15}	0.641×10^{-14}	0.356×10^{-17}	0.701×10^{-14}
4	0.271×10^{-14}	0.271×10^{-13}	0.146×10^{-16}	0.298×10^{-13}
5	0.847×10^{-14}	0.802×10^{-13}	0.422×10^{-16}	0.887×10^{-13}
6	0.210×10^{-13}	0.190×10^{-12}	0.957×10^{-16}	0.211×10^{-12}
7	0.447×10^{-13}	0.389×10^{-12}	0.188×10^{-15}	0.433×10^{-12}
8	0.856×10^{-13}	0.713×10^{-12}	0.339×10^{-15}	0.799×10^{-12}
9	0.151×10^{-12}	0.120×10^{-11}	0.578×10^{-15}	0.135×10^{-11}
10	0.252×10^{-12}	0.190×10^{-11}	0.929×10^{-15}	0.215×10^{-11}
11	0.401×10^{-12}	0.285×10^{-11}	0.145×10^{-14}	0.325×10^{-11}
12	0.610×10^{-12}	0.408×10^{-11}	0.217×10^{-14}	0.469×10^{-11}
13	0.896×10^{-12}	0.564×10^{-11}	0.316×10^{-14}	0.654×10^{-11}
14	0.127×10^{-11}	0.755×10^{-11}	0.449×10^{-14}	0.882×10^{-11}
15	0.176×10^{-11}	0.982×10^{-11}	0.621×10^{-14}	0.116×10^{-10}

[a]These values are obtained by using the semiempirical pseudopotential (Ref. 12).

In the calculation the normal and umklapp processes have been evaluated separately. Furthermore, for the umklapp processes, the longitudinal- and transverse-components contribution have been considered apart. In Table I and II the results of the calculations, obtained by using the semiempirical pseudopotential, [12] have been reported. The calculations have been limited to the temperature region between 1 and 15 K, as only in this region the residual resistivity of the experimental samples[25,26] overcomes the electron-phonon resistivity, so that our starting hypothesis is justified.

As can be seen in Tables I and II, the umklapp contribution exceeds the normal one by about three orders of magnitude; moreover, with respect to the umklapp scattering, the transverse contribution dominates over the longitudinal one. Searching for a simple power law in the temperature behavior of the resistivity, we note that (if one assumes $\rho \sim T^n$) the exponent n decreases continuously starting from a value $n = 5.5$ (Ag)–6 (Cu) for $T \simeq 1$ K and reaching a value $n = 4$ (Ag)–4.5 (Cu) for $T \simeq 15$ K.

In particular, we observe for the resistivity of silver a temperature decrease which is quicker

TABLE II. Electron-phonon contribution to the electrical resistivity of copper (Ω m). [a]

Temperature (°K)	Umklapp longitudinal	Umklapp transverse	Normal	Total
1	0.196×10^{-18}	0.112×10^{-17}	0.776×10^{-20}	0.132×10^{-17}
2	0.116×10^{-16}	0.702×10^{-16}	0.225×10^{-18}	0.821×10^{-16}
3	0.120×10^{-15}	0.715×10^{-15}	0.185×10^{-17}	0.837×10^{-15}
4	0.606×10^{-15}	0.347×10^{-14}	0.795×10^{-17}	0.408×10^{-14}
5	0.207×10^{-14}	0.113×10^{-13}	0.237×10^{-16}	0.134×10^{-13}
6	0.548×10^{-14}	0.289×10^{-13}	0.576×10^{-16}	0.344×10^{-13}
7	0.123×10^{-13}	0.625×10^{-13}	0.118×10^{-15}	0.749×10^{-13}
8	0.243×10^{-13}	0.120×10^{-12}	0.214×10^{-15}	0.144×10^{-12}
9	0.441×10^{-13}	0.212×10^{-12}	0.359×10^{-15}	0.256×10^{-12}
10	0.747×10^{-13}	0.347×10^{-12}	0.567×10^{-15}	0.423×10^{-12}
11	0.120×10^{-12}	0.541×10^{-12}	0.865×10^{-15}	0.662×10^{-12}
12	0.186×10^{-12}	0.805×10^{-12}	0.128×10^{-14}	0.991×10^{-12}
13	0.277×10^{-12}	0.115×10^{-11}	0.182×10^{-14}	0.143×10^{-11}
14	0.401×10^{-12}	0.160×10^{-11}	0.255×10^{-14}	0.200×10^{-11}
15	0.566×10^{-12}	0.216×10^{-11}	0.349×10^{-14}	0.272×10^{-11}

[a]These values are obtained by using the semiempirical pseudopotential (Ref. 12).

than T^5 and slower than T^6 in the temperature region $T \lesssim 3$ K. For $T > 3$ K, we obtain a temperature behavior which is between T^5 and T^4 in close agreement with the experimental data by Kos.[25]

For copper, on the other hand, we observe nearly the same behavior, but the two regions are separated by a temperature value $T \simeq 7$ K. However our theoretical results give no evidence of the strong T^3 dependence which is observed in the Rumbo experimental data for copper.[26]

The same results, as far as the predominance of the transverse umklapp scattering is concerned, are obtained with the use of the Moriarty pseudopotentials,[27] which only affect the magnitude of the resistivity, enhancing the values of the copper resistivity by about a factor of 1.65 and lowering the values of the silver resistivity by about a factor of 1.4.

On the other hand, the temperature dependence of the resistivity is practically unchanged as the exponent n now ranges from

$$n = 5.5 \text{ (Ag)} - 6 \text{ (Cu)} \quad (T = 1 \text{ K})$$

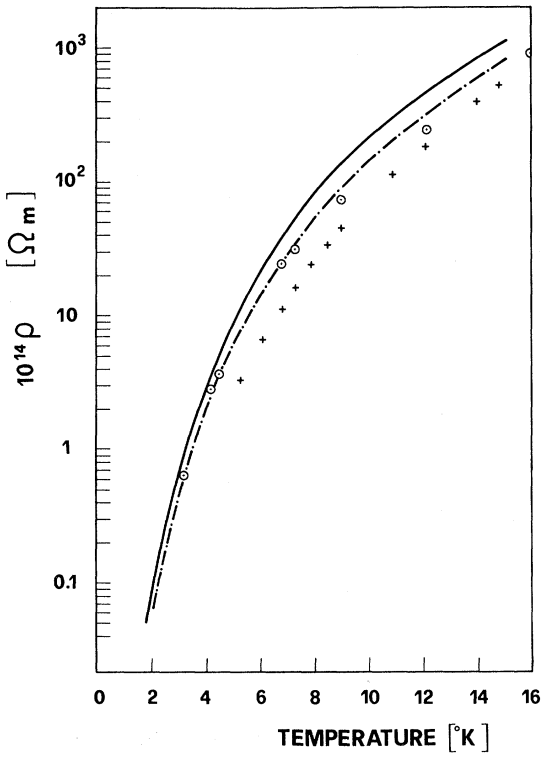

FIG. 1. Electrical resistivity vs temperature for Ag. Continuous and dot-dashed curves give the predictions of the theory obtained by using, respectively, the semiempirical pseudopotential (Ref. 12) and the first-principles pseudopotential (Ref. 13). Extrapolated "ideal resistivity" by Kos (Ref. 25) (o) and the ultrapure experimental data by Ehrlich and Schriempf (Ref. 28) (+) are also reported.

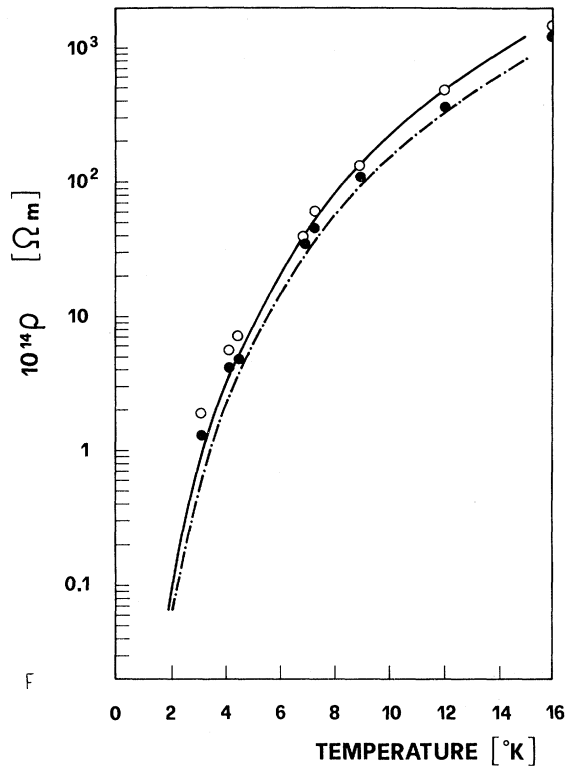

FIG. 2. Electrical resistivity vs temperature for Ag. Continuous and dot-dashed curves give the predictions of the theory obtained by using, respectively, the semiempirical pseudopotential (Ref. 12) and the first-principles pseudopotential (Ref. 13). Experimental $(\rho_T - \rho_0)$ data of impure samples U_1 (white circles) and A_4 (black circles) by Kos (Ref. 25) are also reported.

to

$$n = 4.05 \text{ (Ag)} - 4.6 \text{ (Cu)} \quad (T = 15 \text{ K}).$$

In Figs. 1 and 2 we compare our calculated values for the Ag resistivity, obtained with the use of both the semiempirical and the "first-principles" pseudopotentials, with the experimental data by Kos[25] and by Ehrlich and Schriempf[28] (ES). In the Kos experimental work particularly relevant is the attempt to obtain, by means of a linear extrapolation to zero residual resistivity, the precise determination of the ideal resistivity and the deviation from Matthiessen's rule (MR) ρ_M, where

$$\rho_M = \rho_T - \rho_0 - \rho_i . \tag{3.1}$$

Here ρ_T is the measured resistivity of a sample with residual resistivity ρ_0 and ideal resistivity ρ_i (defined as the resistivity of a specimen having no imperfections and hence $\rho_0 = \rho_M = 0$). Really the Kos experimental data do not permit the determination of the ideal resistivity. In fact, it has to be taken into account that the measurements by ES on a ultrapure sample give values of the electrical re-

sistivity which lie (in this range of temperatures) well below the extrapolated "ideal resistivity" data by Kos. Regarding this subject, it has recently been claimed that it is impossible to estimate the ideal resistivity of Ag from the available experiments.[29] Then the only definite conclusion, as far as the ideal-resistivity values of Ag are concerned, is that they must lie below the ultrapure experimental data by ES.

In Fig. 1 it appears evident that the theoretical values, obtained by the use of the semiempirical potential, are of constantly higher magnitude than both the extrapolated ρ_i values by Kos and the ultrapure experimental values by ES. The same result can be *a fortiori* claimed for the effective ideal resistivity. This fact however is not excessively striking as even in previous works a similar behavior was observed. For this reason it was suggested[2,7] that, owing to the isotropization of the umklapp scattering from the impurities content, the use of the standard trial function Ψ_0 makes the calculation more applicable to the temperature-dependent resistivity $(\rho_T - \rho_0)$ of impure samples, where $\rho_0 \gg \rho_i$ and remarkable deviations from MR are present.

As a result, we have next considered in Fig. 2 a comparison of our theoretical values with the experimental $(\rho_T - \rho_0)$ data of impure samples U_1 $(\rho_0 = 4.714 \times 10^{-9}\ \Omega$ cm) and A_4 $(\rho_0 = 2.273 \times 10^{-9}\ \Omega$ cm) by Kos. Now both the quantitative and the qualitative agreement between the calculation and experiments is very good, particularly if one considers the simplifying assumptions on the phonon spectrum, the use of a simple model for the Fermi surface, and that we have not adjusted any parameter to fit the data. From our analysis it appears clear that a substantial part of the deviation from MR can be ascribed to the isotropization of the umklapp scattering. However we must note that it is not possible to consider the isotropization as the only cause of deviations because this would imply a saturation of ρ_M for $\rho_0 > 4.714 \times 10^{-9}\ \Omega$ cm. Since this saturation is not shown by the experimental data, it is necessary to admit that there are other mechanisms which contribute to the deviations from MR. Apart from the isotropization of the umklapp scattering, many mechanisms have been proposed which certainly contribute to the deviations from MR.[30,31] Since we do not take into account any of these mechanisms we cannot consider our analysis as complete. On the other hand, we think that at present no completely reliable theory of the deviations from MR exists since the proposed mechanisms either have been shown to be incorrect, or give only qualitative explanations, or at most can be adjusted to provide an order-of-magnitude estimate of the deviations. As far as the theoretical results obtained with the use of the Moriarty pseudopotential are concerned, substantially the same conclusions can be reached by inspection of Figs. 1 and 2.

Next, in Fig. 3 we compare our results for copper with the very recent data from Rumbo.[26] Rumbo's measurements were made on copper of high purity $(\rho_0 = 1.131 \times 10^{-10}\ \Omega$ cm) and show a strong T^3 dependence of the resistivity up to $T \sim 7$–8 K. The quantitative agreement between the theoretical values and the significant experimental data is quite respectable, particularly when comparing with another recent calculation on copper-metal resistivity which starts off considering a spherical Fermi surface.[8] In fact, our calculations produce values of the electrical resistivity which, in general, differ by no more than a factor of two from the values measured experimentally. However at this point it is the qualitative agreement which is completely lacking, as in our calculations we have obtained a resistivity-vs-T behavior which shows no trace of a T^3 variation of the resistivity

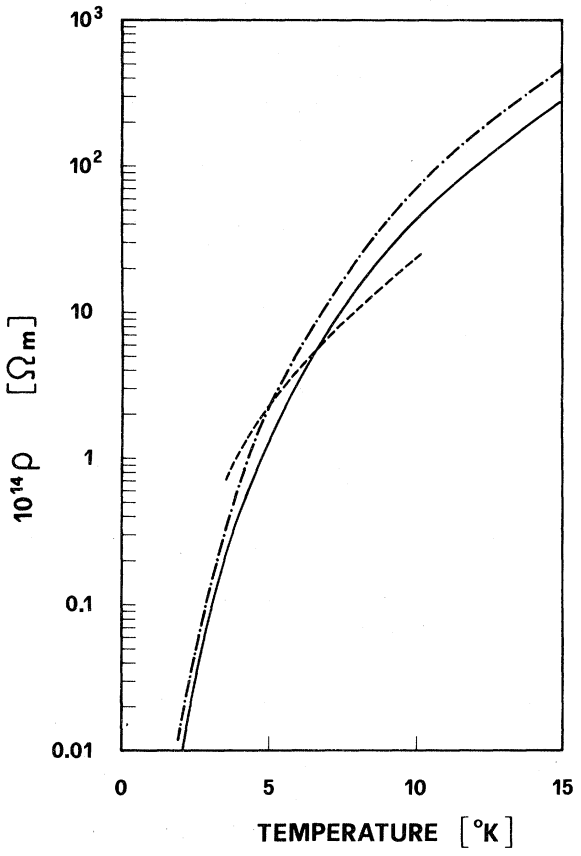

FIG. 3. Electrical resistivity vs temperature for Cu. Continuous and dot-dashed curves give the predictions of the theory obtained by using, respectively, the semiempirical pseudopotential (Ref. 12) and the first-principles pseudopotential (Ref. 13). Dashed line reports on the $(\rho_T - \rho_0)$ behavior as obtained by Rumbo (Ref. 26) from his experimental data.

at low temperature. Indeed our model clearly produces the same features both for Ag and Cu resistivity, and this fact cannot be reconciled with two so very different experimental behaviors. On the other hand, the discrepancies between the Ag and Cu measured values of the resistivity are somewhat surprising, especially if we consider that the noble metals are generally similar in many respects. Therefore our present work cannot shed light on the mechanism which produce the experimental behavior of copper resistivity as observed by Rumbo. A simple empirical rule was proposed several years ago to account for a T^3 dependence of the resistivity in the low-temperature region,[32] but, as we are aware, all the theoretical mechanisms which have been then proposed to explain the T^3 term have been shown to be incorrect.[33-38]

To conclude we have to discuss briefly two other points:

(i) the first point is that, by averaging the phonon velocities over the various symmetry directions, we have completely disregarded the possibility that phonons in certain directions are more important than those in other directions. To test if this simplification significantly affects the results we have then subjected the transverse velocity v_T (the transverse umklapp scattering gives the predominant contribution) to a $\pm 10\%$ variation. The subsequent changes, on either the temperature dependence or the magnitude of the resistivity, should represent a useful, and probably pessimistic, estimate of the changes which would be produced by using a more realistic phonon spectrum in the calculations. We do not observe substantial changes for that concerns the temperature dependence of the resistivity; e.g., a $+10\%$ variation in the value of v_T gives values of the exponent n which ranges from

$$n = 5.6\ (\mathrm{Ag}) - 6\ (\mathrm{Cu}) \quad \text{for } T \simeq 1\ \mathrm{K}$$

to

$$n = 4.1\ (\mathrm{Ag}) - 4.6\ (\mathrm{Cu}) \quad \text{for } T \simeq 15\ \mathrm{K}.$$

On the other hand, changes in the magnitude of the resistivity are observed. These changes are of the same amount as those produced from the uncertainties in the pseudopotentials (i.e., by a factor of 1.5–1.7). It is reasonable to hope that inserting a more realistic phonon spectrum in the calculations should not change the conclusions of the work in any essential way.

(ii) As several other measurements of the neck radius, besides those quoted by Ziman,[9] are available,[39] we have repeated our calculations of the electrical resistivity by using the new values

$$r/p = 0.130\ (\mathrm{Ag}), \qquad r/p = 0.170\ (\mathrm{Cu}),$$

which, among all the experimental neck-radius values, differ the most from the previous reported ones. This new calculation should represent a useful test to see how sensitive the resistivity calculations are with respect to the fine details of the Fermi surface. Again no substantial variation in the temperature dependence of the resistivity is observed as the exponent n now ranges from $n = 5.6$ to $n = 4$ (Ag) and from $n = 5.95$ to $n = 4.45$ (Cu). Also the magnitude of the resistivity is slightly affected by this variation of the neck radius as changes of only a few percentage points (about 3% for Ag and 6% for Cu) are observed.

From all these results we may deduce that the temperature dependence of the resistivity is essentially due to the qualitative shape of the Fermi surface. On the other hand, reasonable variations of the other quantities which enter into the calculation, i.e., of the phonon frequencies, of the pseudopotential form factor and, within the framework of a well-defined shape, of the parameters of the Fermi surface, significantly affect the magnitude of the resistivity.

IV. SUMMARY AND CONCLUSIONS

In this paper we have evaluated the low-temperature resistivity of the noble metals copper and silver, taking into account the distortions of the Fermi surface from the simple free-electron sphere and using two OPW when calculating the matrix elements. Our results evidence the preponderance of the umklapp contribution to the electrical resistivity over the normal one.

As nearly the total umklapp scattering arises from a small region near the necks, this lends support to the reliability of the simple eight-cone model for low-temperature resistivity calculations of the noble metals. Moreover our results show that the temperature dependence of the resistivity is, at low temperatures, largely due to the qualitative shape of the Fermi surface, while it is scarcely sensitive to small changes in the Fermi-surface parameters and to variations of the pseudopotential form factor.

On the other hand, the choice of the pseudopotential form factor significantly affects the magnitude of the resistivity, which is also slightly influenced by small changes in the Fermi-surface parameters. In our calculations we have inserted into the variational expression for ρ the standard trial function Ψ_0, which is a good approach in the case when the ideal electron-phonon resistivity ρ_i is less than the contribution ρ_0 from impurity scattering. This is confirmed by the fact that our calculated values of ρ for Ag are in close agreement with the resistivity experimental data of impure samples. If on the other hand, our calculations for Ag are compared with the extrapolated "ideal resistivity" data by Kos or with the experimental data by Ehrlich and Schriempf, which are obtained

on a ultrapure sample, the agreement appears not to be completely satisfactory. It is clear in fact that in this case the anisotropy of the electron-phonon scattering must be taken into account in a proper manner, and the strong angular distortions of the electron distribution must be considered.[7-8] The difference between the resistivity of impure samples and the ideal resistivity, or the deviations from MR, can be then ascribed, at least partially, to the dependence of the anisotropy on the impurity concentration. However it is plausible that many other causes of deviations from MR are to be considered for a complete explanation of the experimental data.

Finally we remark that the calculated resistivity does not follow, as a function of temperature, a well-defined power law $\rho \sim T^5$, but, if one assumes the validity of a simple relation $\rho \sim T^n$, the exponent n varies continuously ranging (in the region of $T = 1-15$ K) from a value of nearly 5.5 to a value of nearly 4 for Ag and from a value of nearly 6 to a value of nearly 4.5 for Cu.

APPENDIX

By using the equations (2.1) and (2.5), the expression for the electrical resistivity ρ results

$$\rho = \frac{\pi}{6\hbar}\left(\frac{1}{4\pi^3\hbar}\right)^2 \frac{m_{\text{opt}}^2}{n^2e^2} \int \frac{dS_{\vec{k}}}{|\vec{v}(\vec{k})|} \frac{dS_{\vec{k}'}}{|\vec{v}(\vec{k}')|} M(\vec{k}, \vec{k}'), \qquad \text{(A1)}$$

where $M(\vec{k}, \vec{k}')$ is given by

$$M(\vec{k}, \vec{k}') = |\vec{v}(\vec{k}) - \vec{v}(\vec{k}')|^2 \sum_\lambda \frac{\hbar}{MN\omega_{\vec{q}\lambda}} \times |m_\lambda(\vec{k}, \vec{k}')|^2 f_s(\hbar\omega_{\vec{q}\lambda}/k_B T). \qquad \text{(A2)}$$

We evaluate the contribution to the electrical resistivity when $\vec{k}$ is on the eight-cone model surface defined by

$$\epsilon_F = [\tfrac{1}{2}(x^2 + y^2) + f(z)], \qquad z_1 < z < 1, \qquad \text{(A3)}$$

where the local z axis is parallel to the reciprocal vector $\vec{G}$ corresponding to the nearest (111) Bragg plane. As we work at very-low temperatures so that q is very small, we will consider only two types of electron scattering processes: (a) the scattering process in which $\vec{k}'$ lies on the same eight-cone model surface as $\vec{k}$; (b) the scattering process in which $\vec{k}'$ lies on the eight-cone model surface corresponding to the opposite (111) Bragg plane. Moreover we neglect the contribution of the electron scattering from a cone surface to an adjacent cone surface. Then it may easily be seen that, in the extended-reduced zone scheme, $\vec{k}'$ ranges over the surface given by

$$\epsilon_F = [\tfrac{1}{2}(x'^2 + y'^2) + f(z')], \qquad z_1 < z' < 2 - z_1. \qquad \text{(A4)}$$

At this point, introducing the cylindrical coordinates $\rho(z)$, θ, and z, we write

$$x = \rho(z)\cos\theta, \qquad y = \rho(z)\sin\theta, \qquad 0 < \theta \leq 2\pi$$

and

$$\rho(z)^2 = 2[\epsilon_F - f(z)],$$

so that, after a simple calculation, we obtain

$$dS_{\vec{k}}/|\vec{v}(\vec{k})| = dx\,dy/|f'(z)| = d\theta\,dz. \qquad \text{(A5)}$$

An analogous result can be obtained for the primed variables. By using Eq. (A5), Eq. (A1) then becomes

$$\rho = \frac{\pi}{6\hbar}\left(\frac{1}{4\pi^3\hbar}\right)^2 \frac{m_{\text{opt}}^2}{n^2e^2} S,$$

where

$$S = 8\int d\theta \int d\theta' \int dz \int dz' M(\vec{k}, \vec{k}'). \qquad \text{(A6)}$$

In Eq. (A6) the integrals are extended to the cone surfaces given by Eqs. (A3) and (A4), and the result is multiplied by eight to get the total contribution to the electrical resistivity.

By means of the cylindrical coordinates we may write

$$q^2/p^2 = \rho(z)^2 + \rho(z')^2 + (z - z')^2 - 2\rho(z)\rho(z')\cos(\theta - \theta'), \qquad \text{(A7)}$$

so that q is a function of z, z' and $\varphi = \theta - \theta'$. Now we observe that, as it results from Eqs. (2.13), (2.14), and (2.15), $M(\vec{k}, \vec{k}')$ is a function of q, z, z' only. Then by using the new variables z, z', φ and θ', after integrating on θ' we have from Eq. (A6)

$$S = 16\pi \int dz \int dz' \int d\varphi\, M(\vec{k}, \vec{k}'). \qquad \text{(A8)}$$

Finally, by allowing for the change of variables $\varphi \to q$, we obtain after some algebraical calculations

$$\frac{\partial\varphi}{\partial q} = \frac{2q}{[(q^2 - q_m^2)(q_M^2 - q^2)]^{1/2}}, \qquad \text{(A9)}$$

where

$$q_M = p\{[\rho(z) + \rho(z')]^2 + (z - z')^2\}^{1/2}, \qquad \text{(A10)}$$

$$q_m = p\{[\rho(z) - \rho(z')]^2 + (z - z')^2\}^{1/2}, \qquad \text{(A11)}$$

so that Eq. (A8) may be written

$$S = 32\pi \int_{z_1}^{2-z_1} dz' \int_{z_1}^{1} dz \int_{q_m}^{q_M} q\,dq \times \frac{M(z, z', q)}{[(q^2 - q_m^2)(q_M^2 - q^2)]^{1/2}}. \qquad \text{(A12)}$$

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