# Electron-electron scattering in the low-temperature resistivity of the noble metals*

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Recently observed behavior in the electrical resistivity of copper at temperatures below 8 K and of silver below 5 K is interpreted as arising from electron-electron scattering. Similar behavior is predicted for gold below about 4 K, where data are not yet available. An estimate of the electron-phonon contribution shows that its $T^5$ asymptote is approached in the regime where electron-electron scattering is important.

## I. INTRODUCTION

The electrical resistivity of transition metals clearly exhibits the effect of electron-electron scattering[1] (typically below about 20 K), although there is no strong evidence of it in the simple metals.[2] It is suggested here that the behavior recently observed by Rumbo[3] in the resistivity of copper below 8 K (silver below 5 K) is consistent with electron-electron ($e-e$) scattering, and that similar behavior would be expected in gold below about 4 K.

The data reported by Rumbo[3] are plotted in Fig. 1, for comparison with the calculated $e-e$ terms in Cu and Ag. Examples of data reported by other workers[4–6] are also plotted. These are from samples covering a range of lesser purity, and generally do not extend to as low temperatures. In the case of Au the data do not approach the $e-e$ regime closely enough to test it. In Ag the Barber-Caplin[5] data extend into the $e-e$ regime and seem less suggestive than do Rumbo's data, although there is good agreement in the overall magnitudes of the resistivities. Rumbo's are the purest samples measured; the data labeled 0, due to Barber and Caplin, are generated by extrapolating their actual data to $\rho_{\text{imp}}=0$. It should perhaps be mentioned that an earlier interpretation of Rumbo's data in terms of phonon drag (see second paper of Refs. 3 and 7) has been abandoned; Sheard[8] has reconsidered this mechanism and concluded on general grounds that a previously predicted[9] $T^3$ contribution does not occur.

The theoretical results presented in Fig. 1 make use of the standard trial solution of the Boltzmann equation (i.e., relaxation-time approximation) and

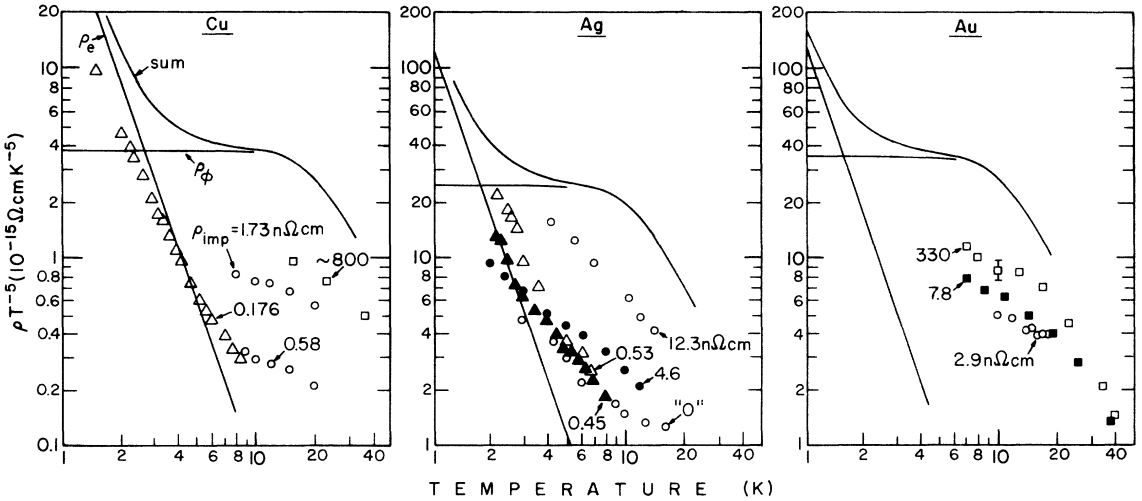


FIG. 1. Shown for each metal is the calculated electron-electron contribution $\rho_e$, electron-phonon contribution $\rho_\phi$, and their sum, which represents the temperature-dependent resistivity of the impure metal. Data from samples of widely varying purity are labeled by their residual resistivities; if the $e$-$e$ contribution is not very sensitive to purity, the crossover temperatures may apparently be larger than the indicated ones by up to a factor of 2, in pure samples. Data on Cu are from Refs. 3 and 4 (△, Rumbo; ○, Schriempf; and □, Lengeler *et al.*), Ag from Refs. 3 and 5 (△, Rumbo; ○, Barber and Caplin, with 0 determined by extrapolation), and Au from Ref. 6 (○, Whall *et al.*; □, Damon *et al.*).

therefore they apply to impure samples, where at sufficiently low temperatures the contributions from different mechanisms are distinct,

$$\rho = \rho_{\text{imp}} + \rho_e + \rho_\phi \quad (\rho_{\text{imp}} \text{ large}), \tag{1}$$

and exhibit power laws $\rho_e \sim T^2$ and $\lim_{T\to 0} \rho_\phi \sim T^5$ for the $e-e$ and $e-\phi$ (electron-phonon) contributions, respectively, with impurity resistivity $\rho_{\text{imp}}$ constant. It is well known[10] that $\rho_\phi$ is very sensitive to purity, as exhibited by the data shown.[4-6] Presumably $\rho_e$ is relatively insensitive to purity; if this is assumed, then the crossover temperatures $T_0$ between the $e-\phi$ and $e-e$ regimes are increased with purity. In particular the $T_0$ values for the pure metals are roughly double those indicated by the theoretical curves (based on the extrapolation of the pure Au data to lower temperatures). It should be noted that in pure samples such as Rumbo's, $\rho_e$ and $\rho_\phi$ are not additive, and consequently the resistivity is not simply the sum of powers as in (1). Specifically, the crossover from $T^2$ to $T^5$ behavior is "smoothened," and this may cause the apparent exponent "$m$" in a fitting formula such as

$$\rho = \rho_0 + aT^m + bT^5, \tag{2}$$

used in Ref. 3 (second paper), to appear greater than two, *near* the crossover.

Another question in the general nonadditivity problem is that of the "saturation" of $\rho_\phi$ as $\rho_{\text{imp}}$ is increased, or in other words, the existence of a "dirty limit" of $\rho_\phi$. If relaxation-time anisotropy is the only important source of nonadditivity, then a dirty limit certainly exists. It is this theoretical dirty limit which is shown in Fig. 1. It is possible of course that some additional mechanism, not yet understood, becomes active at large values of $\rho_{\text{imp}}$, so that $\rho_\phi$ does not saturate at the values predicted by the present theory. To determine whether or not such a mechanism is active, it would be helpful to know for what values of $\rho_{\text{imp}}$ saturation should be "expected". Only in the alkali metals is the theory of relaxation-time anisotropy sufficiently complete to answer this question. In potassium at $T = 3$ K, for example, 90% saturation is predicted[11,12] when $\rho_{\text{imp}}/\rho_\phi \approx 30$. (See Fig. 9 of Ref. 12.) There is very little experimental data in this regime, but what there is shows no evidence of saturation, and other mechanisms of nonadditivity in the large-$\rho_{\text{imp}}$ regime have in fact been suggested.[11] In copper, the regime $\rho_{\text{imp}}/\rho_\phi \approx 10^3$ has been approached without evidence of saturation.[10] Although there is no theory of this effect in Cu, it is certain that its relaxation time is much more anisotropic than potassium's, and plausible that much larger values of $\rho_{\text{imp}}/\rho_\phi$ may be required for saturation. It is difficult to say more at this point; the nonadditivity problem is the subject of ongoing investigation whose results will be reported later elsewhere.

## II. CALCULATIONS

The remainder of this paper describes the calculations, which utilize the 2-OPW (orthogonalized-plane wave) formalism developed in Refs. 2 and 13 for the simple metals. In the noble metals this formalism is essentially an application of Ziman's eight-cone model.[14] The 2-OPW model is used because the 1-OPW model fails, qualitatively, for both mechanisms at low temperatures. In the case of $e-e$ scattering, the lattice effect is essential for nonvanishing electrical resistivity. Two models which include it are Baber scattering[15] (a two-band model) and the 2-OPW model; the latter seems appropriate for the single-sheeted noble metal Fermi surfaces. Also, Ziman[14] has provided their 2-OPW parametrizations. In the case of $e-\phi$ scattering, the $T^5$ dependence at low $T$ follows from the small-$q$ linearity of the scattering probability in the crystal-momentum transfer $q$, and from the continuity of the velocity field $\vec{v}(\vec{k})$. The 2-OPW model satisfies these properties where 1-OPW fails. While the latter may provide reasonable results at higher temperatures,[16] it spuriously produces a $T^2$ dependence (provided the Fermi surface intersects zone boundaries) at low $T$, as shown in Ref. 13. Incidentally, the small-$q$ linearity of the scattering probability is evident from the quasiparticle scattering rate (e.g., in Cu), which is cubic in $T$, at low $T$.[17] The two mechanisms are now discussed in detail.

## III. ELECTRON-ELECTRON SCATTERING

The $e-e$ contribution is calculated using the formalism of Ref. 2. Its starting point is to factor $\rho_e$ into one term representing the essential effect of the ionic medium (called the "fractional umklapp scattering" $\Delta$) and into other terms which may be regarded approximately as characteristic of the translationally invariant electron gas (with density, Fermi energy, and wave vector related by $3\pi^2 n = k_F^3$ and $2mE_F = \hbar^2 k_F^2$) to give

$$\rho_e = (m/ne^2)\{[\pi(\pi k_B T)^2/12\hbar E_F]\Gamma\}\Delta. \tag{3}$$

$\Delta$ is a measure of the effectiveness of scattering events $(\vec{k}_1, \vec{k}_2) \to (\vec{k}_3, \vec{k}_4)$ in degrading the current;

$$\Delta = \langle |\vec{v}_1 + \vec{v}_2 - \vec{v}_3 - \vec{v}_4|^2 W\rangle \langle |2\vec{v}|^2 W\rangle^{-1}, \tag{4}$$

where $\vec{v}_i$ is the velocity in the state $\vec{k}_i$. The angular brackets denote the Fermi-surface integrals over all quartets of crystal-momentum-conserving states $\vec{k}_i$, with scattering probability $W$. The 2-OPW model is used to calculate both $W$ and the

$\vec{v}_i$. The rather involved method of estimating $\Delta$ from these integrals is described in Ref. 2. (Secs. III, IV, and Appendix B). Typical values estimated there for the simple metals range from about $\frac{2}{5}$ to $\frac{3}{5}$. I estimate conservatively that $\Delta \sim \frac{3}{4}$ for all the noble metals (Cu slightly greater, Ag slightly less); the main point is that $\Delta$ is about the same for all of them, and of order unity.

The quantity in curly brackets in (3) is a basic electron-electron scattering rate; $\Gamma$ is a dimensionless number which represents the Fermi-surface average of the scattering probability. If, as in Ref. 2, $W$ is calculated in the Born approximation from the Thomas-Fermi screened Coulomb interaction, then

$$\Gamma(x) \equiv \frac{\langle W \rangle}{\langle W(0) \rangle} = \frac{\tan^{-1} x}{x} + \frac{1}{x^2+1} - \frac{\tan^{-1} x(2+x^2)^{1/2}}{x(2+x^2)^{1/2}}, \tag{5a}$$

where

$$x = 2k_F/k_s = (3\pi^5 a_0^3 n)^{1/6} \tag{5b}$$

exhibits the weak dependence of $\Gamma$ on density $n$. ($k_s$ is the Thomas-Fermi screening wave vector.) The third term in (5a) is the effect of exchange. The numerical values from (5a) are $\Gamma = 0.57$ for Cu, and 0.55 for Au and Ag. The sameness of $\Gamma$ for the different noble metals is independent of the scattering model chosen (for any reasonable choice) even though the actual values of $\Gamma$ are not. The principal density dependence in $\rho_e$ has been factored out of $\Gamma$ and appears in (3) explicitly $\rho_e \sim n^{-1} E_F^{-1} \sim n^{-5/3}$, which accounts for the difference between Cu and the others listed in Table I.

Improvements to the scattering model, which have been considered in the context of thermal resistivity calculations,[18] do not improve the overall agreement with measured values in the noble metals, which is within about a factor of two. Incidentally, lattice effects are ignored in the thermal resistivity calculations since they are not essential there; it seems justified to ignore them here as well, except of course in $\Delta$.

## IV. ELECTRON-PHONON SCATTERING

For the $e-\phi$ contribution $\rho_\phi$, I quote the general result for the low-temperature limit, which is derived in Ref. 13 using a 2-OPW Debye model; the 2-OPW electron states are used both for the $e-\phi$ matrix elements and Fermi-surface shape, and the usual Debye model is modified as described in Ref. 13 to allow for the almost complete (order-of-magnitude) predominance of transverse phonons at low temperatures. The result is

$$\lim_{T\to 0} \rho_\phi = \frac{9\pi}{4}\left(\frac{m}{ne^2}\right)\frac{m}{ZM}\left(\frac{T}{\Theta_D}\right)^5 J_5(\infty) \times \sum_G \frac{G}{k_F}\nu_G\left(\frac{E^3(\frac{1}{2}G)}{\hbar k_B \Theta_D V(G)}\right) I(a_G), \tag{6a}$$

where

$$I(a_G) = \int_{-\infty}^{\infty} dy\,(y^2+1)^{-7/2}(a_G y^2+1)^{-5/2} \times [y^2(1-\tfrac{5}{6}a_G^2)+\tfrac{1}{6}]. \tag{6b}$$

The summation is over all pairs of zone boundaries ($G$) which intersect the Fermi surface, and $\nu_G$ is the number of sheets intersected by ($G$). $V(G)$ is the usual Fermi-surface distortion parameter (or band gap) and $E(\frac{1}{2}G)$ is the free-electron energy at $\frac{1}{2}\vec{G}$, the center of the neck. $M$ is the ionic mass, $Z$ is the number of electrons per atom, and $J_5(\infty) = 124.4$ is the usual low-temperature limit of a Debye integral $J_5(x) = \int_0^x t^5 dt (e^t-1)^{-1}(1-e^{-t})^{-1}$, except that here the upper limit $x = \Theta_G/T$ is determined by a characteristic temperature associated with the scale of Fermi-surface distortion[13]

$$\Theta_G \sim \Theta_D V(G)/E(\tfrac{1}{2}G), \tag{7}$$

rather than by the usual Debye temperature $\Theta_D$. Accordingly, deviations from the $T^5$ asymptote occur at lower temperatures than expected on the basis of the usual Blöch-Grüneisen formula. The integrand in (6b) represents the relative contribution from a Fermi surface point $\vec{k}$ near the plane ($G$), and it falls off rapidly with the dimensionless "distance" $a_G y = \hbar^2(\vec{k}-\vec{G}/2)\cdot\vec{G}[2mV(G)]^{-1}$ between them. Because of the sharp peaking at the zone boundary ($y=0$), the extension of integration limits to $\pm\infty$ is inconsequential. The geometrical parameter $a_G$ is the ratio of the Fermi-surface neck diameter to $|\vec{G}|$.

Almost the entire dependence of (6a) on the neck

TABLE I. Numerical values for the calculated resistivity contributions [Eqs. (3) and (8)] are given, together with the necessary material parameters. Entries in the last two columns are from Ref. 14. Values of $\Theta_D$ are the averages of those listed, which vary over a (10–15)% range [±(5–8)%]. The consequent uncertainties in $\rho_\phi$ are ±30% for Cu and Ag, and ±50% for Au.

| | $n(10^{22}\ \mathrm{cm}^{-3})$ | $\Delta(\pm 30\%)$ | $\rho_e T^{-2}(10^{-14}\ \Omega\ \mathrm{cm\,K}^{-2})$ | $\rho_\phi T^{-5}(10^{-15}\ \Omega\ \mathrm{cm\,K}^{-5})$ | $E(\frac{1}{2}G)(\mathrm{eV})$ | $V(G)/E(\frac{1}{2}G)$ | $\Theta_D(\mathrm{K})$ |
|---|---|---|---|---|---|---|---|
| Cu | 8.52 | 0.79 | 7.6 | 3.8 | 8.66 | 0.40 | 320 |
| Au | 5.92 | 0.77 | 14 | 35 | 6.78 | 0.376 | 180 |
| Ag | 5.88 | 0.73 | 14 | 24 | 6.76 | 0.336 | 215 |

size occurs through the relationship

$$\lim_{T\to 0} \rho_\phi \sim V^{-1}(G) .$$

Additional dependence which occurs through $I(a_G)$ is very minor. For example, as the neck contracts, $I(a_G)$ approaches a finite limit: $I(a_G) \to \frac{4}{9}$ as $a_G \to 0$. The neck diameters of Cu, Au, and Ag are given by $a_G = 0.18$, 0.162, and 0.126 respectively,[14] and $I(a_G) = 0.41$, 0.42, and 0.43. Taking the average of these, substituting $Z = \nu_G = 1$, and noting that there are four pairs of zone boundaries $G = (111)$, one finds for the noble metals that

$$\lim_{T\to 0} \rho_\phi \approx 26\left(\frac{m}{ne^2}\right)\frac{m}{M}\left(\frac{T}{\Theta_D}\right)^5 J_5(\infty)\left(\frac{E^3(\frac{1}{2}G)}{\hbar k_B \Theta_D V(G)}\right) , \tag{8}$$

in the low-temperature limit. Numerical values of the coefficients of $T^5$ are tabulated. Deviations from this asymptotic form evident in Fig. 1 are calculated by means of the method described in Ref. 13. They are not of interest here except to illustrate that the $T^5$ regime is approached for temperatures below about one-fifth of $\Theta_G$ [Eq. (7) and Table I].

In conclusion we may understand, within the framework presented here, why the noble metals should present greater possibility for the observation of electron-electron scattering than do the simple metals. The first point is that $\rho_e$ is *not* much greater for the noble metals than for typical simple metals. In fact (according to Table I of Ref. 2) potassium has a larger $\rho_e$ than Cu, Au, or Ag. The main reason then is that $\rho_\phi$ is small for the noble metals (compare potassium, for example[19]), and this follows (8) from the combination of large band gaps $V(G)$ and fairly large Debye temperatures. Except for the alkalis, simple metals (by definition) have small $V(G)$. Moreover, if a metal has several $V(G)$, then the *smallest* (6a) is most important, both for the magnitude of $\rho_\phi$ at low temperatures, and the regime $T < \frac{1}{5}\Theta_G$ over which $\rho_\phi \sim T^5$ holds. The smallest band gap of a simple metal is typically an order of magnitude smaller than those of the noble metals.

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