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Brief Reports

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Explanation of the apparent T^2 dependence of the surface-induced electrical resistivity in pure metals from measurements on high-purity Au foils

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From previously reported, detailed size-effect measurements in the range $4.2\text{ K} \lesssim T \lesssim 20\text{ K}$ on chlorine annealed, high-purity Au foils of thicknesses $2\ \mu\text{m} \lesssim d \lesssim 25\ \mu\text{m}$, the surface contribution to the electrical resistivity $\rho_S(T)$ has been extracted accurately at several T's, with the use of Soffer's surface-scattering theory. It is shown that this theory, combined with the correct intrinsic T dependence of the metal concerned, consistently predicts the observed behavior of ρ_S against T over the entire T range covered and shows that the relation between ρ_S and T is effectively nowhere a quadratic one, contradicting herewith the apparent general behavior of $\rho_S \propto T^2$ over various pure metals and T ranges as suggested by van der Maas *et al.* It is shown that it is only due to the scatter in experimental size-effect data collected over several temperatures that one can easily select a low-T range (i.e., $T \lesssim 13$ K) where the data seem to fit a T^2 dependence.

I. INTRODUCTION

In recent communications, van der Maas, Huguenin, and Rizzuto[1,2] analyzed the apparent electrical resistivity ρ_S due to the scattering of conduction electrons by the sample surface, from results on various pure metals at low temperatures, typically $1 \lesssim T \lesssim 20$ K. From a plot of $\rho_S(T) \equiv \rho(T) - \rho_\infty(T)$, where $\rho(T)$ and $\rho_\infty(T)$ are, respectively, the measured and bulk resistivities of the metal foils or films under consideration, against temperature, they deduced the empirical relations

$$\rho_S(T) = \rho_S(0) + A_S T^2 \tag{1}$$

and

$$A_S \propto \rho_S(0) \tag{2}$$

for the temperature dependence of ρ_S, where $\rho_S(0)$ is the residual surface resistivity (i.e., $T \rightarrow 0$). However, a large experimental scatter, over all the metals considered, in the data leading to relations (1) and (2) is recognized by these authors and, apart from a large amount of data on Al, limited data on In, Cd, Hg, and Pt lend support to the description represented by (1) and (2). In order to deduce $\rho_S(T)$ for each set of metal foils or films from one study, they used the bulk value $\rho_\infty(T)$ obtained by either extrapolating size-effect data to infinite thickness using Fuchs's[3] theory or, simply, put $\rho_\infty(T)$ equal to ρ of the thickest sample out of the set. Subsequently they argued correctly that the effect described by relation (1), if true, may easily be confused with the intrinsic temperature dependence of the resistivity of a metal, i.e., especially with the resistivity ρ_{ee}, due to electron-electron scattering, if sample dimensions are not sufficiently large, as they rarely are.

Recently, annealing in a chlorine atmosphere was used to purify and increase the conductivity of gold foils of thickness $d \lesssim 25\ \mu\text{m}$. It was optimized with respect to the anneal time t_{an} at $T_{\text{an}} = 870 \pm 20$ °C and several chlorine pressures[4,5] P_{Cl_2}. This treatment gave Au foils with extrapolated residual resistance ratios $\mathcal{R}_\infty$ (where $\mathcal{R} \equiv R_{273.16\text{K}}/R_{4.2\text{K}}$ of 70 000), as deduced from detailed measurements of the influence of size effects on the resistivity, interpreted along the theory of Soffer[6]; the simplest version of Soffer's theory (i.e., neglecting lateral correlations for surface roughnesses) has been applied here. The latter has recently been demonstrated to be able to describe size-effect data accurately, contrary to Fuchs's theory[7–10] which till now has been almost exclusively used to interpret the observed resistivity of thin metal films and foils. From our and other studies of Au foils[4,5,10] it was concluded that Soffer's theory describes the experimetal results very well with a constant value $\rho_\infty \lambda_\infty = (9.6 \pm 0.6) \times 10^{-16}$ Ω m^2, λ_∞ being the bulk mean-free path of the conduction electrons.

II. APPARENT SURFACE-INDUCED T^2 TERM IN Au FOILS: EXPERIMENTAL FACTS

From this interpretation,[4,5] we were able to deduce ρ_∞ at several temperatures in the range $T \lesssim 20$ K. Some of the data are plotted in Fig. 1 as $\log_{10} \rho_i = \log_{10}[\rho_\infty(T) - \rho_\infty(0)]$ vs $\log_{10} T$, where ρ_i is the ideal resistivity for bulk samples. As previously reported[5] and as illustrated in Fig. 1, in the range $10 \lesssim T \lesssim 20$ K, ρ_i is very well described within experimental accuracy by a T^5 power law while the temperature dependence definitely tends to a much weaker power law for temperatures below 10 K, which is in very good agreement with other data.[11]

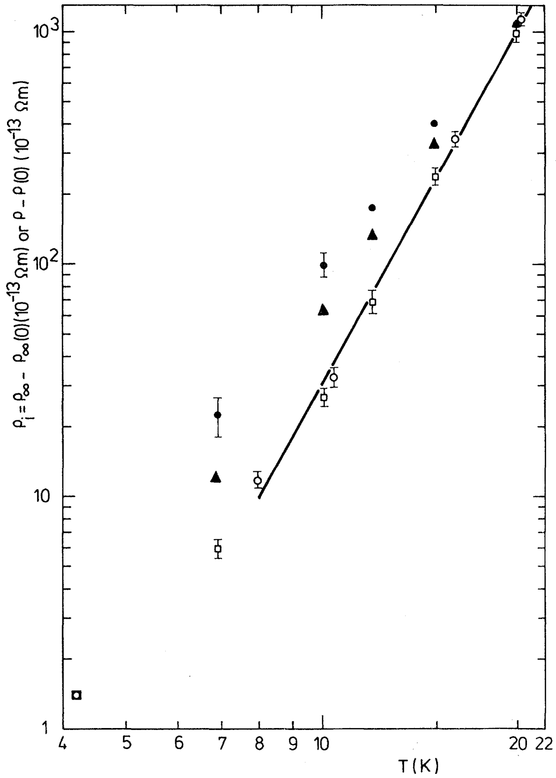

FIG. 1. Open symbols (□, ○) represent plots against temperature of the intrinsic resistivity ρ_i given by the difference between bulk resistivity ρ_∞ and bulk residual resistivity $\rho_\infty(0)$, deduced from detailed size-effect measurements interpreted along Soffer's theory, on chlorine annealed, high-purity gold foils with thicknesses $2 \lesssim d \lesssim 25$ μm, as described in Refs. 4 and 5. □ and ○ stand for data taken on two sets of samples with extrapolated bulk resistance ratio $\mathcal{R}_\infty \simeq 35\,000$ and 15 000, with a surface roughness parameter $r \gg 1$ and $r = 1$, respectively. The solid line indicates a T^5 power law. The full dots and triangles (● and ▲) represent the difference between observed resistivity $\rho(T)$ and $\rho(0)$, against temperature for foils with $d = 10.4$ μm and $d = 14.8$ μm, $\mathcal{R}_\infty \simeq 35\,000$ and $r \gg 1$. This clearly shows the deviations in the observed T dependence of foils, induced by size effects.

Then having available accurate values of $\rho_S = \rho - \rho_\infty$ at several temperatures on these Au foils, the data are plotted as ρ_S vs T^2 in Figs. 2 and 3 in order to check relation (1). Figure 2 contains data from a set of samples (several foils covering the thickness range $2 \lesssim d \lesssim 25$ μm, but identically and simultaneously treated[5]) for which a fit to Soffer's theory yielded $\mathcal{R}_\infty \simeq 35\,000$ and a surface roughness parameter $r \equiv h/\lambda_e \gg 1$, h being the root-mean-square surface roughness and λ_e is the Fermi wavelength of the conduction electrons. For Fig. 3, the corresponding values are $\mathcal{R}_\infty \simeq 15\,000$ and $r = 1$. For clarity we mention here that as is explained in Ref. 5, the difference in $\mathcal{R}_\infty$ between the two sets of samples referred to in Figs. 2 and 3, is only due to the variation in purifying treatment; the possible interference of size of crystallites in this polycrystalline material and the nature of internal grain boundaries has been ruled out. The difference in surface roughness parameter r, however, is due to the kind of final surface treatment (applying chemical etching or not). As found by van der Maas[1,2] *et al.* in other metals, we find here that for Au an apparent T^2 dependence

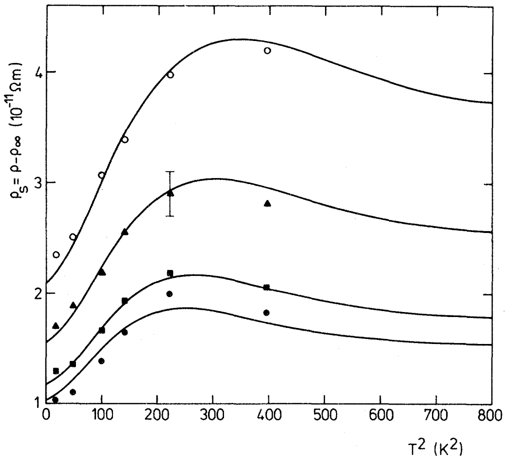

FIG. 2. Deduced surface contribution ρ_S to the electrical resistivity plotted against T^2 for a set of high-purity gold foils, extracted from size-effect data using Soffer's theory; the values $r \gg 1$ and $\mathcal{R}_\infty \simeq 35\,000$ were deduced (see Ref. 5). The symbols ○, ▲, ■, and ● represent data for foils with thicknesses $d = 10.4$, 14.8, 20.7, and 24 μm, respectively. The full curves represent theoretical calculations from Soffer's theory using ρ_∞ values from the solid line shown in Fig. 1, with $r \gg 1$.

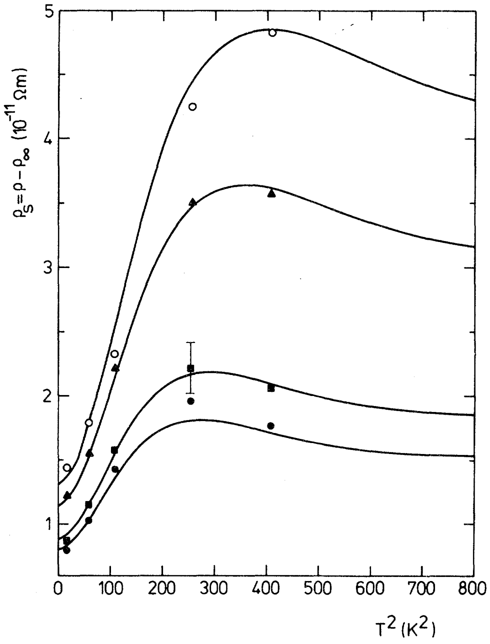

FIG. 3. Plot of observed surface contribution ρ_S to the electrical resistivity against T^2 for a set of high-purity gold foils with $r = 1$ and $\mathcal{R}_\infty \simeq 15\,000$, as deduced from size-effect data using Soffer's theory (see Ref. 5). The symbols ○, ▲, ■, and ● represent foils with thicknesses $d = 9$, 12, 20, and 24.1 μm, respectively. The full curves represent theoretical calculations from Soffer's theory using ρ_∞ values from the solid line shown in Fig. 1, with $r = 1$.

of ρ_S occurs within the experimental scatter, at least for $T \lesssim 13$ K, whereas at higher temperatures deviations occur; the experimental data tend to much lower values than those predicted by the initial "T^2 dependence," a general phenomenon also observed by van der Maas *et al.* (see, e.g., their data on Al).

Since Soffer's theory describes the size-effect influence on resisitivity very well, it is natural to calculate $\rho_S(T)$ from this theory using the correct temperature dependence and realistic values of ρ_∞, and to verify how $\rho_S(T)$ changes with T^2. Using ρ_i values from the solid line of Fig. 1, which represents the mean through experimentally determined ρ_i values, plots of these "theoretical" predictions for $r \gg 1$ and $r = 1$ are also shown in Figs. 2 and 3, respectively. For $T \geqslant 10$ K, the relations

$$\rho_\infty = 4.5 \times 10^{-13} + 3.1 \times 10^{-17} T^5 \ \Omega\,\text{m} \qquad (3)$$

and

$$\rho_\infty = 12.8 \times 10^{-13} + 3.1 \times 10^{-17} T^5 \ \Omega\,\text{m} \qquad (4)$$

have been used in Figs. 2 and 3, respectively.

III. DISCUSSION

Firstly from this comparison it is obvious that Soffer's theory, using the correct temperature dependence of ρ_∞, fits the experimental points very well. This could be expected since the size-effect data are very well described by Soffer's theory.[4,5] Since the above-mentioned comparison is also based on Soffer's theory, one might argue that this comparison adds little to the preceding analysis. That such a comparison is meaningful and supports the consistency of our arguments can be demonstrated by plotting, within one sample set, $\rho_{\text{thin}} - \rho_{\text{thick}}$, where ρ_{thick} is the observed resistivity of the thickest sample out of the set. The same conclusions are arrived at without having to go through the deduction of ρ_∞. However, the preceding analysis may be preferred; indeed, for any given metal with a certain inherent purity and temperature dependence of ρ_∞, that method of presentation used here shows quite clearly how the surface contribution to the resistivity ρ_S evolves as T and d change. It also shows the consistency of the bulk resistivities $\rho_\infty(T)$ that are inferred.

As is clear from the theoretical curves shown in Figs. 2 and 3 , the overall temperature dependence is not T^2. In effect it is the scatter in experimental data that easily makes ρ_s appear to depend quadratically on T in a certain range, i.e., $T \lesssim 13$ K. Similar results are arrived at for size-effect data of other metals, e.g., Al. Moreover, for this temperature range, using the interpretation that $\rho \propto T^2$, it is clear that the slope $A_S \equiv d(\rho_S)/d(T^2)$ increases with increasing $\rho_S(0)$, in agreement with (2). However, further trying to check whether or not there really exists a linear relationship between A_S and $\rho_S(0)$ as indicated by (2) for data below $T \lesssim 13$ K would appear pointless since clearly $\rho \propto T^2$ does not hold.

Also the maximum in the ρ_S vs T^2 plot, beyond which deviations from the T^2 dependence start to show up strongly, moves to lower temperatures for larger d, in agreement with other experimental data (see, e.g. Ref. 1). At this maximum one has $d \simeq \lambda_\infty$.

Finally we have to mention that size effects may mask the intrinsic temperature dependence of ρ if the sample is not sufficiently thick, resulting in apparent strong deviations from Matthiessen's rule.[12] This effect is also observed in all our Au foils, the strength of such deviations being a function of d. Two typical examples are shown in Fig. 1, where $\rho - \rho_0$ is plotted against T for samples with $d = 10.4$ and 14.8 μm, respectively; notice the strong deviation from the bulk temperature dependence.

IV. CONCLUSION

From this interpretation of resistivity data of Au foils it is concluded that Soffer's theory[13] combined with the correct temperature dependence of ρ_∞ fully explains the recent observations of van der Maas[1,2] *et al.* concerning the temperature dependence of ρ_S. Moreover, it shows that there exists no general quadratic relation between ρ_S and T as proposed by these authors, although due to experimental inaccuracies, a T^2 dependence can easily be simulated in a narrow T range on the basis of the preceding discussions.

It has been shown how the observed T dependence and magnitude of the surface resistance evolve as a function of sample thickness and surface quality, and it has been demonstrated what kind of deviations in the bulk intrinsic resistivity ρ_i (deviations from Matthiessen's rule) due to the surface scattering may be expected if the sample dimensions do not meet the condition $d >> \lambda_\infty$.

Despite the semiclassical and still rather simple nature of Soffer's theory, the analysis described above once more illustrates the usefulness of this theory in describing thin-film resistivity data in contrast to the overly simple theory of Fuchs which leads to confusing results.[7] Although Soffer's theory could in principle be improved, e.g., by taking into account inelastic scattering processes, details of the Fermi surface, etc., we feel that, in view of the experimental accuracy and consistency of the data available till now for various sets of thin films and foils, this theory describes the results adequately, eliminating herewith inconsistencies between physical quantities deduced by using other theory.[7,8,14]

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[11] See, e.g., J. F. Kos and R. J. Barton, Can. J. Phys. 57, 1579 (1979); M. Khoshenevisan, P. W. Pratt, P. A. Schroeder, and S. D. Steenwijk, Phys. Rev. B 19, 3873 (1979).

[12] See, e.g., Refs. 7 and 9, and references therein.

[13] It needs to be stated for reasons of completeness that Fuchs's theory and Soffer's theory end up with identical results for $r \rightarrow \infty$ ($p \rightarrow 0$; here p is the specularity parameter, the probability that an electron colliding with the sample surface will be specularly reflected), such that the theoretical curves of Fig. 2 are arrived at by Fuchs's theory also.

[14] See, e.g., J. B. Van Zytveld and J. Bass, Phys. Rev. 117, 1072 (1969).