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Surface Scattering of Electrons on Copper Whiskers and Its Influence on the Electrical Resistivity at 4.2 K

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Abstract. The effect of specimen size on the electrical resistivity at 4.2 K of copper whiskers having transverse dimensions in the order of the electron mean-free path was measured. The experimental data are interpreted by means of a modified Nordheim formula adapted to the exact theory of Dingle. Assuming for copper the value of the product $\varrho_0 \cdot \lambda$ obtained from the free electron model a specularity parameter p for the surface scattering of conduction electrons is deduced from the diameter dependence of the sample resistivity. Values of $p=0.45$ (up to 0.66 in an individual case) and $p=0.18$ are calculated exhibiting that significant specular reflection is present. Differences in the amount of specular reflection appear to arise from differences in the microscopically observed surface conditions of the whiskers.

Index Headings: Electrical conductivity – Size effect

In thin samples of high purity metals the mean-free path of conduction electrons at very low temperatures may be of the order of the smallest transverse specimen dimension. The scattering of electrons at the metal surface increases the electrical resistivity by an amount depending on the specimen size and the character of surface scattering. In this case the measured specific resistance of thin samples is not a constant of the given material. The observed size effect is weaker when the surface scattering is not totally diffuse, but partial specular reflection occurs, i.e., the tangential component of electron momentum is not lost completely after collision with the surface. The conditions under which diffuse or specular reflection takes place have not yet been thoroughly clarified.

In the present work we have investigated the size effect in the dc resistance of copper whiskers. Since one expects that the degree of specular reflection corresponds to the smoothness of the surface [1], we have taken into account the surface conditions of our samples as far as microscopically observable. Copper whiskers are filamentary grown single crystals of copper which can be produced with optical smooth surfaces and have a natural crystallographic faceting. Therefore they are suitable objects for the investigation of surface scattering of conduction electrons.

1. Theory

A simple description of the size dependence of the electrical resistivity of wires with circular cross section was given by Nordheim [2]. Assuming that Matthiessen's rule is valid for that portion of resistivity due to surface scattering one obtains for a circular wire with diffuse scattering of the surface

$$\varrho = \varrho_0(1 + \lambda/d). \qquad (1)$$

Here ϱ is the resistivity of the thin wire. ϱ_0 the bulk resistivity, λ the corresponding bulk mean-free path according to the free electron model, and d the specimen diameter. The rigorous theoretical treatments of the problem are based on the solution of the Boltzmann equation for different sample geometries in the relaxation time approximation. The first analysis of size effects by this method was given by Fuchs [3] for a thin film geometry. The Fuchs treatment has been applied to the calculation of the electrical resistivity of thin wires of circular cross section by Dingle [4], of square cross section by Mac Donald and Sarginson [5], and of rectangular cross section by Ditlefsen and Lothe [6].

Most of our investigated copper whiskers had hexagonal, in some cases (2%) square cross section. The theory of Dingle can also be used for this geometries to interprete the experimental data (see below). The case of partial specular reflection is described in this theory by a specularity parameter p, which had been introduced first by Fuchs [3]. The parameter p is the fraction of electrons, which suffer specular reflection at the surface ($0 \leqq p \leqq 1$). The assumption of a constant specularity parameter independent of the electron de Broglie-wavelength and the angle of incidence at the surface is quite a simplification of the nature of surface scattering.

In the usual theoretical models of surface scattering of electrons the problem is treated analogously to optical reflection at rough surfaces. This leads to a higher degree of specular reflection for longer electron wavelength and greater angle of incidence relative to the surface normal [1, 7]. Contrary to this theoretical predictions all experimental results of the size dependence of the electrical resistivity could be explained in terms of a constant specularity parameter. So hereafter we shall follow the assumption of constant p. Evidence for increasing p with greater angle of incidence has been obtained from the observation of magnetic surface states [8]. A new summary of the experimental results in size effect studies has recently been given by Larson [9].

For diffuse scattering ($p=0$) the calculations of Dingle [4] for circular wires yield

$$\varrho_0/\varrho = K \cdot \psi^{-1}(K)\,, \tag{2}$$

where $K = d/\lambda$, and $\psi(K)$ is an integral function, explicitly given by Dingle [4], values of which can only be obtained by numerical integration. The diameter dependence of resistivity for partial specular reflection ($p>0$) can be derived from the case $p=0$ by means of a power series

$$(\varrho_0/\varrho)_{p,K} = (1-p)^2 \sum_{\nu=1}^{\infty} \nu \cdot p^{\nu-1} \cdot (\varrho_0/\varrho)_{p=0,\nu\cdot K}\,. \tag{3}$$

The ratio ϱ_0/ϱ for some K-values has been tabulated by Dingle [4] for $p=0$ and $p=0.5$. An extensive numerical evaluation of Dingle's calculations have been given by Dworschak *et al.* [10] for $p=0$ in the range $3.5 \cdot 10^{-3} \leqq K \leqq 18.8$ and published in form of tables. Since not enough resistivity values for $p \neq 0$ were available in the K-range, which is of interest in our measurements, we have calculated $(\varrho_0/\varrho)_{p,K}$ by a computer program using (3). The values $(\varrho_0/\varrho)_{p=0,\nu\cdot K}$ required for the summation were found by interpolation from the tables of Dworschak *et al.* [10]. The calculated values ϱ/ϱ_0 as a function of K^{-1} for different values of the specularity parameter are shown in Fig. 1. The dashed straight line is plotted with respect to Nordheim's formula (1), which intersects the exact curve for $p=0$ at $K^{-1} \approx 0.7$. The resistivity values for diffuse scattering obtained from Dingle's theory agree with those from the simple Nordheim formula within 5% in the whole K-range [9]. It is seen from the figure that also in the case of $p \neq 0$ the computed curves deviate only slightly from straight lines in the shown range of K^{-1}-

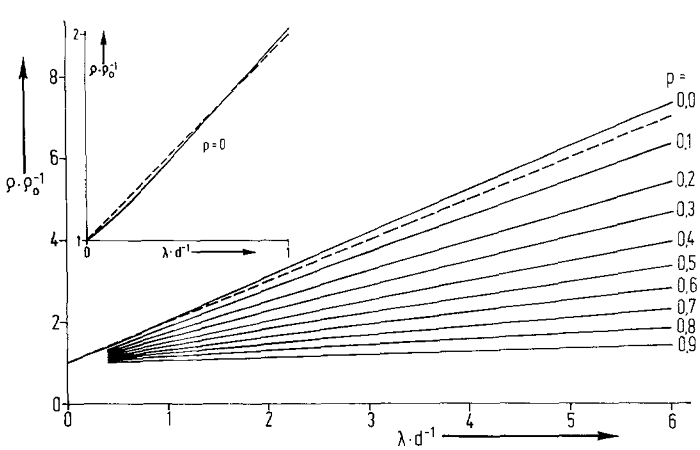

Fig. 1. Calculated resistivity ϱ/ϱ_0 of circular wires vs. $K^{-1} = \lambda/d$ for various values of the specularity parameter p. The dashed line is plotted for $p=0$ according to the simple Nordheim formula (1)

values except small values of K^{-1}. So it seems obvious to describe the K- and p-dependence of resistivity by a modified Nordheim formula

$$\varrho = \varrho_0[1 + C(K, p) \cdot (1 - p) \cdot K^{-1}], \tag{4}$$

where $C(K, p)$ is a fitting parameter. For the range of K-values, in which our experimental data lie ($K \approx 1$), C depends only weakly on K and therefore can be treated as a constant without introducing a greater error. For the limits of $K \gg 1$ and $K \ll 1$ it is found that $C = 0.75$ and $C = (1 + p)^{-1}$, respectively, so that (4) is in agreement with the approximate expressions for limiting K-values given by Sondheimer [11].

The hexagonal or square cross sections of the copper whiskers are taken into account by introducing an effective diameter as follows: Comparison between the size dependence of resistivity of a square wire (K being in this case the ratio of the side of the wire to the mean-free path) according to the calculations of Ditlefsen and Lothe [6] and a cylindrical wire with the same cross sectional area as the square wire shows good agreement of the curves except for the smallest K-values ($K \leqq 0.05$). From the agreement of the curves in the interesting range of K-values ($K \approx 1$) one may conclude that differences in the ratios of perimeter and area of cross sections within the limiting cases of circular and square shapes do not appreciably affect the size dependence of resistivity of specimens with equal cross sectional areas. So for not too small values of K Dingle's theory may be applied to the case of hexagonal cross section. The effective diameter to be used in the above equations is then found by comparing the cross section A of the whisker to the area of a circle

$$d_{\text{eff}} = (4A/\pi)^{1/2} . \tag{5}$$

In the following $d := (A)^{1/2}$ will be called the diameter of a whisker by convention.

2. Experimental Techniques

The copper whiskers were grown by the reduction of copper iodide in a hydrogen stream at 650° C according to the method described by Brenner [12]. For the measurements straight, well-grown whiskers of uniform cross section and a minimum length of about 15 mm were selected, using a stereo microscope. Besides whiskers with optical smooth surfaces also whiskers, which showed microscopic surface roughness were retained and the surface condition noted. In this context we will call a surface to be "smooth" if no surface irregularities are visible up to a magnification of 1000 x, otherwise the surface is termed as "rough". The whiskers found in this way had hexagonal, in some cases square cross sections. X-ray analysis yielded ⟨111⟩-orientation of the whisker axis for the hexagonal and ⟨100⟩-orientation for the square cross section. Nittono *et al.* [13] determined the faces of copper whiskers to be {110}-planes in both cases of orientation. The same results were obtained by own investigations about the angle of slip lines with the surface of whiskers which were slight plastically deformed.

The sample resistance was determined at 293.2 K and 4.2 K by measuring the voltage drop across the specimen due to a current passing through it. The cross sectional areas of the whiskers were obtained from the resonance frequency of transverse vibrations [14]; the sample length between the potential contacts was measured with a dial gauge in combination with a microscope and a micromanipulator.

3. Results and Discussion

During the course of measurements a considerable dispersion of the residual resistivity values, i.e. $\varrho_{4.2\text{K}}$ in practice, of the copper whiskers was observed depending on the growth conditions. No essential influence of the purity of copper iodide and gases used for growing the whiskers on the residual resistivity could be determined. But it was found that the residual resistivity values of the copper whiskers were greatly affected by traces of oxygen in the growth apparatus, which obviously cause the scatter of experimental values between different growth charges. The influence of oxygen upon residual resistivity and surface scattering in copper whiskers will be reported elsewhere [15]. For a quantity evaluation of the diameter dependence of resistivitative one must be assured that the bulk resistivity $\varrho_{04.2\text{K}}$ is the same for all samples of different diameter. So we only compared, with one another, the experimental data of whiskers from the same growth charge or from charges grown under identical conditions. In addition, the microscopically observed surface conditions are taken into account, since different surface qualities might lead to different values of the specularity parameter and consequently to a scatter of experimental data.

Figure 2 shows the reciprocal resistivity ratio $\varrho_{4.2\text{K}}/\varrho_{293.2\text{K}}$ as a function of inverse sample dia-

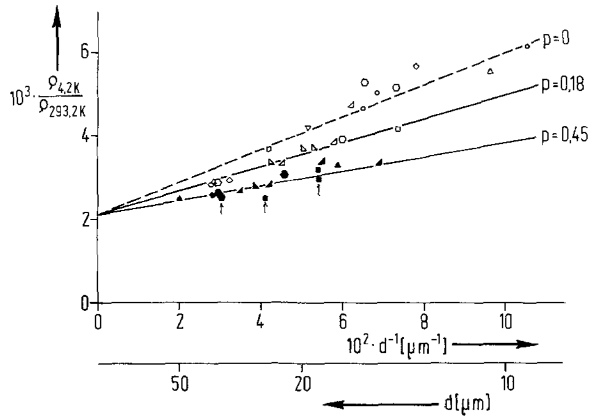

Fig. 2. Reciprocal resistivity ratio $\varrho_{4.2K}/\varrho_{293.2K}$ of copper whiskers as a function of the inverse diameter d^{-1}. Equal symbols correspond to whiskers taken from the same growth charge. Solid symbols imply "smooth" surfaces and open symbols "rough" surfaces. The solid lines are fits to the experimental data. The dashed line is calculated for $p=0$ with respect to (6)

meter, d^{-1}. Equally marked data points represent whiskers prepared from the same charge. The data are interpreted according to (4) by the relation

$$(\varrho_{4.2K}/\varrho_{293.2K}) = (\varrho_{04.2K}/\varrho_{0293.2K}) + [C \cdot (1-p)\varrho_{04.2K} \cdot \lambda_{4.2K}]/(\varrho_{0293.2K} \cdot 1.128 \cdot d) . \quad (6)$$

Thereby it is presumed that $\varrho_{293.2K} = \varrho_{0293.2K}$, which is reasonably because of the small mean-free path at room temperature ($\lambda_{293.2K}(\text{Cu}) \approx 400$ Å). The coefficient 1.128 makes allowance for the effective diameter [see (5)].

The measured room temperature resistivity was $\varrho_{293.2K} = 1.59 \cdot 10^{-6}\,\Omega\,\text{cm}$ ($\pm 5\%$). The magnitude of the specularity parameter can be determined by (6) provided the value of the product $\varrho_0 \cdot \lambda$ is known. According to the Sommerfeld model of free electrons $\varrho_0 \cdot \lambda$ is a temperature independent constant for a given metal

$$\varrho_0 \cdot \lambda = 1.27 \cdot 10^{-4}\,\Omega \cdot n^{-2/3} , \quad (7)$$

where n is the number of free electrons per unit volume. From this a theoretical value of

$$\varrho_0 \cdot \lambda = 0.66 \cdot 10^{-11}\,\Omega\,\text{cm}^2 \quad (8)$$

results for copper assuming one free electron per copper atom. A value of $\varrho_0 \cdot \lambda = 0.65 \cdot 10^{-11}\,\Omega\,\text{cm}^2$ was found by Chambers [16] from measurements of the anomalous skin effect. Mende and Neitz [17] determined a value of $0.69 \cdot 10^{-11}\,\Omega\,\text{cm}^2$ from the thickness dependence of resistivity of thin pure copper wires under the assumption of $p=0$. Other investigations of size effects in copper samples yielded higher values of $\varrho_0 \cdot \lambda$ (see, e.g. [17]). To interpret our data we use the free electron value, which is in good agreement with the values of [16, 17].

At first a relative large scatter of the experimental data will be noted, but there is great evidence that the observed differences in surface conditions are responsible for the dispersion of points. From the intersection with the ordinate of the lower solid line in Fig. 2 a bulk resistivity of

$$\varrho_{04.2K} = 3.34 \cdot 10^{-9}\,\Omega\,\text{cm} \quad (9)$$

is obtained and hence

$$\lambda_{4.2K} = 19.8\ \mu\text{m} . \quad (10)$$

The slope of the lower line yields

$$C(1-p) = 0.47_6 . \quad (11)$$

The data points lie within the range of $0.4 \leqq K^{-1} \leqq 1.4$. For an average value of $K^{-1} \simeq 1$ we have from our calculations with respect to (3), (4) $C = 0.86_2$ – the maximum deviation of C from this value is not more than 2% in the above K^{-1}-range – and

$$p = 0.45 , \quad (12)$$

i.e. 45% of conduction electrons incident at the surface are reflected specularly.

The whiskers with points on this line showed microscopically smooth, optically high reflecting surfaces.

Another group of points in Fig. 2 can be fit by a second straight line with the same indicated bulk resistivity as the $p=0.45$ curve. The specularity parameter for this line is

$$p = 0.18 . \quad (13)$$

Contrary to the whiskers with $p=0.45$ the whiskers with points on this line as well as all upper points were classified as slightly rough by microscopic observation.

In addition the figure shows the calculated line for diffuse ($p=0$) scattering, which is with the exception of a few points the upper limit for the data.

Three points, marked by ↑, are situated below the $p=0.45$ line. These whiskers had hexagonal cross sections broadened into a blade. The broad sides of such whiskers always showed an extremely smooth surface. Under the assumption of the same bulk resistivity a specularity parameter of $p=0.66$ is obtained for the lowest of that points.

It is seen from the experimental results that the surfaces of copper whiskers show an appreciable fraction of specular reflection. Thereby a relation is turned out between the microscopically observed surface condition and the value of the specularity surfaces have $p=0.45$ ($p=0.66$ in an individual case). Whiskers with microscopically rough, but otherwise clean surfaces show smaller values $p=0.18$ to $p=0$.

Theoretically the high values of the specularity parameter in a metal like copper are difficult to understand, since it is hard to believe that metal surfaces are smooth on an atomic scale. Surface roughness in the order of the Fermi wavelength, i.e., 4.6 Å for Cu, should be responsible for a diffuse surface scattering of conduction electrons.

According to Soffer [18] correlation in roughness between different points at the surface, which is to be expected in the case of copper whiskers due to their natural crystallographic faceting, might be an important factor in explaining the partial specular reflection, which has been experimentally observed, predominantly in single crystal samples. Other measurements on copper whiskers reported by Isaeva [19] yielded a value of $p=0.6$ without consideration of the effective diameter. For zinc whiskers Gaidukov and Kadlecova [20, 21] found that most of the experimental points lay within the region of $0.5 \leqq p \leqq 0.6$.

Surface oxidation can give rise to a decrease in specular reflection [15]. In our measurements the specimes were in contact with air for a short time during preparation, which may lead to a slight surface oxidation. As Isaeva [19] has pointed out, possibly this is the reason why partially diffuse scattering is observed in smooth copper whiskers. Another effect, which can give an upper limitation for the magnitude of the specularity parameter, is umklapp surface scattering, as recently suggested by More [22]. In the case of copper, due to the topology of the Fermi surface, umklapp processes should occur by scattering at {110}-planes, which are found to be the boundaries of our copper whiskers.

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