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## Grain size-dependent Hall coefficient in polycrystalline copper films

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**Abstract.** The Hall coefficients reported for polycrystalline copper films show a rather puzzling behaviour. This paper discusses systematic investigations of the temperature-dependent Hall coefficient for Cu films with *known* grain size. Grain boundary scattering will be shown to be dominant as soon as the grain size becomes smaller than the electronic mean free path due to scattering by phonons.

### 1. Introduction

The low-field ( $\omega_c \tau < 1$  where  $\omega_c$  is the cyclotron frequency and  $\tau$  the relaxation time) Hall coefficient ( $R_H$ ) of a metal depends very sensitively on its particular Fermi surface, i.e. on the symmetry of the conduction electrons [1].

For noble metals, a Hall factor ( $r$ ) is introduced in order to describe the deviation of the real Hall coefficient ( $R_H$ ) from the corresponding standard Hall constant ( $R_{fe}$ ) of free electrons

$$r = R_H/R_{fe} \quad R_{fe} = -1/ne. \quad (1)$$

The Hall factor of Cu can be described semi-empirically in a 'two-band model' [2–6]. The Fermi surface of copper is divided into two regions (bands, groups): (i) (100) and (110) regions, corresponding to belly electrons (s symmetry) with isotropic scattering time  $\tau_b$ , (ii) (111) regions, corresponding to neck electrons (p symmetry) with isotropic scattering time  $\tau_n$ .

According to Dugdale and Firth [6], the Hall factor ( $r$ ) of Cu ( $R_{fe} = -7.45 \times 10^{-11} \text{ m}^3 \text{ C}^{-1}$ ) is given by

$$r = 4\pi(A + Bx^2)/(C + Dx)^2 = (4.6 + 0.1x^2)/(7.3 + 1.85x)^2 \quad x = \tau_n/\tau_b. \quad (2)$$

The constants  $A$ ,  $B$ ,  $C$ ,  $D$  in equation (2) have been calculated from the Fermi surface of copper. Equation (2) describes the main feature of the low-field Hall coefficient of copper: its value is only influenced by qualitative changes in the scattering mechanisms themselves, i.e. depends only on the ratio of the scattering times  $x = \tau_n/\tau_b$ .

The temperature dependence of the Hall coefficient in bulk material can be well explained by the model discussed above (2). Scattering of electrons by phonons at 300 K is isotropic [7], i.e.  $x = 1$ . For temperatures below 100 K, the phonon scattering will be

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highly anisotropic because the umklapp scattering processes for bellies are 'frozen out' [8], i.e.  $x \ll 1$ . According to (2) the Hall factor ( $r$ ) changes with temperature from  $r = 0.72$  at 300 K to  $r = 1.085$  at 4.2 K. These values are in good agreement with experimental data on bulk Cu [9, 10]. The temperature dependence of  $r$  produced by phonon scattering will be changed as soon as new scattering mechanisms become effective. The scattering at defects (vacancies, dislocations, etc) is anisotropic, since neck electrons (p symmetry) are scattered much more strongly by lattice distortions than belly electrons (s symmetry). The defect scattering (temperature independent) can be described by the ratio  $x_0 = (\tau_n/\tau_b)_0 < 1$  characteristic of each type of defect. At low temperatures defect scattering will be dominant, i.e. the value of  $r$  at 4.2 K is given by equation (2) for  $x = x_0$  (Matthiessen rule).

Experimentally,  $x_0 \approx 0.8$  for vacancies [11] and 0.11–0.25 for dislocations [11, 12] have been found for bulk copper. At room temperature, the Hall factor reflects the enhanced contribution from defect scattering mechanisms, showing a monotonic change in its value with increasing density of scattering centres. If defect scattering becomes completely dominant, a saturation (temperature-independent) value of  $r$  can be obtained.

The interpretation of the Hall effect data for polycrystalline copper films in particular seems to be more difficult. During their deposition on the substrate, a high density of defects (point, line defects, etc.) will be created.

A considerable amount of experimental data for copper films related to the thickness dependence and annealing behaviour of the Hall coefficient has been reported in the literature.

Generally 'thin' films ( $d < 20$ – $30$  nm where  $d$  is the film thickness) show values of  $r_{300\text{K}} \approx 1.0$ – $1.4$ , whereas for epitaxial and polycrystalline 'thick' films ( $d > 30$  nm), values of  $r_{300\text{K}} \approx 0.7$ – $0.8$  have been reported [13–19]. After annealing the films usually exhibit values of  $r$  comparable to the bulk value ( $r \approx 0.72$ ). An increase of the grain size after annealing was reported by Chopra and co-workers [15]. Unfortunately these data are not directly related with the measured Hall coefficients.

The influence of the grain size on the Hall coefficient was discussed within a two band model by Koepke [20] and Wedler and Wiebauer [17]. The grain size of their films, however, was an unknown parameter. The concentration of dislocations present in the grain boundaries was assumed to increase with decreasing grain size, leading to an anisotropic scattering time. This interpretation, however, presumes a homogeneous distribution of defects in the entire volume of the film. This is certainly not true for the dislocations located in the grain boundaries.

The grain sizes in polycrystalline metal films are often comparable with the mean free path of the conduction electrons [21]. Therefore it can be suspected, that grain boundary scattering completely dominates the low-field Hall coefficient of polycrystalline Cu films. Thus the puzzling behaviour of the Hall coefficient can be simply produced by different grain sizes and their variation with film thickness.

This paper reports a systematic investigation concerning the contribution of grain boundary scattering to the Hall factor ( $r$ ) of polycrystalline Cu films. For this purpose, the temperature dependence of  $r$  for Cu films of known crystallite size has been investigated.

## 2. Experimental details

Cu (Balzers, 99.9%) was deposited by evaporation or RF sputtering on Corning glass and NaCl substrates. The substrate temperature ranged between 300 K and 650 K. The

residual gas pressure was varied between  $10^{-6}$  and  $10^{-9}$  mbar while the Ar pressure during sputtering was kept at  $10^{-3}$  mbar. Additionally some films deposited at 300 K have been post-annealed at 600 K in UHV in order to enhance the crystallite size.

During evaporation the film thickness was monitored with a quartz oscillator balance. The absolute film thickness was determined using a stylus profilometer with an accuracy of about 5%. The purity of the films was controlled by Auger electron spectroscopy (AES). Within the accuracy of this method (1%) no impurities have been detected, except the common contamination at the film surfaces. The film structure was investigated by transmission electron microscopy (TEM). All films were continuous even after heat treatment. The diffraction patterns reveal the FCC rings of polycrystalline Cu; no evidence for a preferential orientation of the crystallites has been found.

The mean grain size ( $\bar{D}$ ) was determined from electron transmission micrographs. The distribution of the grain sizes reveals a single log-normal distribution typical for random oriented polycrystalline films [23, 24, 27]. The values of  $\bar{D}$  determined from these distributions have an accuracy of about  $\pm 8\%$ . A variation of the grain size in the range 5–300 nm has been obtained. The film thickness ranged from 50 nm for fine-grained up to 300 nm for coarse-grained films. Consequently size effects are excluded during our investigations.

The problem of a thickness dependent Hall factor for polycrystalline Cu films has been discussed in detail elsewhere [22]. After deposition the films were transferred to a He cryostat with a 6 T superconducting coil. The Hall voltage was measured in lock-in technique with 32 Hz sample current modulation and ranged from  $5 \mu\text{V}$  to  $40 \mu\text{V}$ . The offset compensation of the Hall voltage was temperature independent. For all films and temperatures only a linear dependence of the Hall voltage on magnetic field has been observed. The temperature dependence of the Hall voltage was measured with an accuracy of at least 0.5%. The Hall factor  $r$  was calculated by

$$r = (U_{\text{H}}d/IB)/R_{\text{fe}} \quad (3)$$

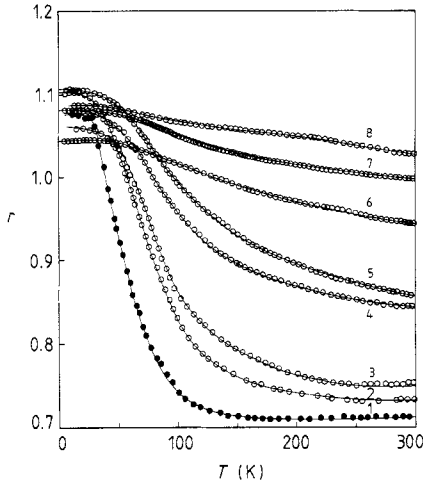
where  $I$  is the sample current and  $B$  the magnetic induction.

The film geometry was  $2 \text{ mm} \times 8 \text{ mm}$  in order to avoid geometric corrections in (3) [25]. Equation (3) finally shows that the accuracy of Hall coefficient data is limited by the accuracy of the film thickness value, i.e. about 5% in our case.

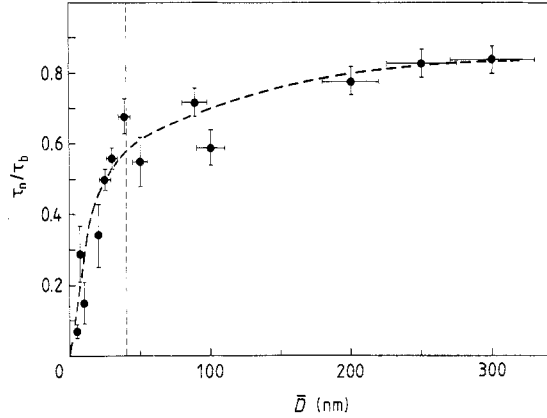
### 3. Results

The temperature dependence of the Hall factor ( $r$ ) for several Cu films with different grain sizes is given in figure 1. The other data corresponding to these films are given in table 1. Additionally the results of Alderson and co-workers [10] for massive (not annealed) polycrystalline Cu are plotted in figure 1 (sample 1).

Figure 1 reveals a dependence of the Hall factor on the grain size. Coarse-grained films (samples 2 and 3) show roughly the same behaviour as the bulk material. At 300 K  $r$  monotonically increases with decreasing grain size. For fine grained films (sample 8) a saturation value of  $r$  is achieved, i.e.  $r$  becomes nearly independent of temperature. Regardless of grain sizes, all values of  $r$  at low temperature converge approximately to the value of the polycrystalline bulk material. The observed scattering of these values at low temperature is smaller than 5% and is attributed to the limited accuracy of the film thickness. If the data for all measured (30) films are taken into account, a mean value of  $r_{4.2\text{K}} = 1.04 \pm 0.04$  can be estimated.



**Figure 1.** The temperature dependence of the Hall factor  $r$  for copper films with different grain sizes. The numbers correspond to the samples in table 1.



**Figure 2.** The anisotropy factor  $x = \tau_n/\tau_b$  at 300 K estimated from equation (2) versus grain sizes determined by TEM.

**Table 1.** Thickness and grain size data of the films discussed in figure 1.  $d$  is the film thickness,  $\bar{D}$  the mean grain size,  $\rho_{4.2K}$  the residual resistivity.

Sample	$d$ (nm)	$\bar{D}$ (nm)	$\rho_{4.2K}$ ( $\mu\Omega$ cm)	Comments
1	$9 \times 10^5$			Massive polycrystalline Cu [10]
2	300	$250 \pm 21$	0.12	Substrate: NaCl, kept at 650 K
3	200	$200 \pm 17$	0.2	Condensed on Corning glass at 300 K; postannealed at 600 K
4	230	$100 \pm 8$	0.42	
5	50	$50 \pm 4$	1.2	
6	50	$20 \pm 2$	2.5	Condensed on Corning glass at 300 K
7	50	$20 \pm 2$	3.1	
8	50	$5 \pm 1$	6.8	Sputtered onto Corning glass kept at 300 K

An increase in the Hall factor ( $r$ ) with decreasing temperature could be produced by a transition from  $\omega_c\tau < 1$  to  $\omega_c\tau > 1$  (high-field effects) at low temperatures. The residual resistivity ( $\rho_{4.2K}$ ) decreases with increasing grain size (see table 1). Its lowest value of  $0.12 \mu\Omega$  cm (sample 2) leads to a  $\tau_{\max} \approx 3 \times 10^{-13}$  s (Drude relation [26]). With  $\omega_c \approx 10^{12} \text{ s}^{-1}$  estimated for  $B \approx 6$  T, a maximum value of  $\omega_c\tau \approx 0.3$  has been achieved at 4.2 K during the measurements. High field effects therefore do not contribute to the observed temperature dependence of the Hall factor ( $r$ ) given in figure 1.

Therefore, figure 1 clearly shows that grain boundary scattering is the dominant process determining the Hall factor and its temperature dependence in polycrystalline Cu films.

#### 4. Discussion

The temperature dependence of  $r$  in Cu films of various grain sizes given in figure 1 can be discussed in terms of the two-band model presented in § 1. Equation (2) allows an estimation of the anisotropy factor  $x = \tau_n/\tau_b$  and its correlation with the crystallite size.

At 4.2 K a constant value of  $r$  independent on grain size was observed within the experimental accuracy. In terms of the two-band model grain boundary scattering thus is the dominant defect scattering mechanism in polycrystalline Cu films. The value of  $r$  should therefore correlate with the anisotropy factor  $x_0 = (\tau_n/\tau_b)_0$  of dislocations, which are the typical defects in grain boundaries. If the mean value of  $r_{4.2K} = 1.04 \pm 0.04$  is introduced into equation (2), one obtains:  $x_0 = (\tau_n/\tau_b)_0 \approx 0.09 \pm 0.07$ . This value is still inaccurate, mainly due to the 5% error in the determination of film thickness. In any case, however, this is smaller than  $x_0 = 0.11$ – $0.25$  determined for scattering at dislocations in bulk copper [11, 12].

At 300 K  $r$  clearly depends on the grain size. Figure 2 shows the dependence of  $x$  at 300 K on the grain size  $\bar{D}$ . The estimation of  $x$  was done using the simple relation (2). As shown in figure 2, coarse grained films ( $\bar{D} \geq 200$  nm) are characterised by  $x \approx 0.8$ – $0.9$ . According to the commonly accepted interpretation given in § 1, the Hall factor of coarse-grained films can be mainly explained by isotropic scattering ( $x = 1$ ) of electrons by phonons. For grain sizes smaller than 40 nm, a steep decrease of  $x = \tau_n/\tau_b$  can be observed in figure 2.

A kind of 'cut-off crystallite size' seems to be responsible for the enhanced anisotropic scattering at room temperature in fine grained Cu films. Therefore the simple argumentation of an enhanced anisotropic scattering due to increasing concentration of dislocations at smaller crystallite sizes [17, 20] cannot explain the dependence of  $x$  on  $\bar{D}$  ( $\bar{D} \leq 40$  nm) given in figure 2. As discussed in § 1, this simple argumentation assumes that all scattering centres (phonons, vacancies, dislocations, etc.) are homogeneously distributed throughout the entire volume of the film. This is true for phonons and vacancies within the grains, but certainly not for the dislocations located in grain boundaries.

The observed dependence of  $x$  on the crystallite size  $\bar{D}$  in polycrystalline Cu films can be explained within a simple geometrical model. The grains are separated by narrow distorted regions (small or large angle grain boundaries) containing a large concentration of dislocation networks; in addition the periodicity of the lattice is broken in these regions. Conduction electrons therefore are strongly scattered by the grain boundaries. This scattering mechanism will be more effective for neck than for belly electrons.

Figure 2 shows a strong decrease in  $x$  for grain sizes below 40 nm. The mean free path of the conduction electrons limited only by phonon scattering ( $l_{ph}$ ) in bulk copper can be estimated to  $l_{ph,300K} \approx 39$  nm [21]. The origin of the small values of  $x$  at 300 K seems to be evident: relative to scattering at grain boundaries, the scattering of the neck electrons (p symmetry) by phonons decreases rapidly for  $\bar{D} < l_{ph}$  because they are strongly scattered by the dislocation networks of the grain boundaries. To a first approximation the mean free path of the neck electrons will be limited by the grain size. Consequently the anisotropy of the scattering time changes strongly, i.e. the Hall factor increases according to equation (2) as soon as  $\bar{D} \leq l_{ph}$ .

Belly electrons (s symmetry), however, have a larger mean free path, i.e. they are scattered at defects less than neck electrons. Therefore a certain probability exists that electrons with s-symmetry cross one or more grain boundaries. For fine-grained films, this is important only for the electrical conductivity [27–29] but not for the Hall effect,

since the anisotropy of the scattering time will be mainly determined by the neck electrons scattered at grain boundaries. Moreover in this case the temperature dependence of the Hall factor saturates, i.e. it does not depend on temperature.

In summary, the Hall factor  $r$  of polycrystalline Cu films shows a strong dependence on the grain size. For  $\bar{D} < l_{\text{ph}}$  (electron-phonon scattering length), the neck electrons becomes 'confined' within the grains, whereas the belly electrons can cross more than one crystallite. The resulting asymmetry of the scattering time strongly influences the Hall factor obtained for microcrystalline materials. A correct interpretation of the Hall factor of polycrystalline materials or thin films thus requires in any case a detailed structural analysis. The discussion above gives clear evidence for the decisive contribution of crystallite sizes to the measured Hall coefficient and its temperature dependence in polycrystalline Cu films.

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