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# Determination of Charge-Transport Parameters for the Group IV Metals

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Measuring the electrical resistivity and Hall constant of vacuum-deposited thin films and cold-rolled thick foils of Sn, Pb, Ti, Zr and Hf and introducing the results so obtained into suitable relations corresponding to limiting forms of the well-known Sondheimer size-effect equations, an estimate was made of the liquid-helium-temperature and room-temperature values of the parameters involved in the laws ruling the electron transfer in bulk metal and the carrier-surface interactions in thin films.

Medindo a resistividade elétrica e a constante de Hall de filmes finos obtidos por deposição em vácuo e de folhas espessas de Sn, Pb, Ti, Zr e Hf obtidas por folheamento a frio e introduzindo os resultados assim obtidos em expressões adequadas correspondentes às formas limites das bem conhecidas equações de Sondheimer para os efeitos de volume, uma estimativa é feita dos parâmetros envolvidos nas leis que descrevem o transporte dos elétrons no volume do metal bem como as interações dos carregadores (de corrente) com a superfície em filmes frios. Tais parâmetros foram obtidos a temperatura ambiente, bem como a temperatura do Hélio liquido.

## 1. Introduction

To interpret the charge-transport processes occurring in a macroscopic metal sample in all three dimensions, one must take into accourit that the carriers contributing to the conductivity can be scattered by the thermal vibration of the lattice (electron-phonon collisions) and by structural defects such as interstitials, vacancies, impurity atoms, etc., which disturb the periodicity of the crystal. But if one of the dimensions of the specimen becomes rather small, as in the case of films whose thickness is so reduced as to be comparable with the mean free path of the electrons in the bulk metal (or less than it), then another interaction mechanism must be considered, the one consisting in the diffuse reflection of the carriers from the sample surfaces, which may be thought of as a sort of structural imperfection imposing a geometrical limitation on the movement of the charges

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Hence, the electrical and galvanomagnetic behaviours'of a thin layer depend on a size effect that can be studied by introducing, in the ordinary equations for bulk metals, the boundary conditions at the film surfaces.

The aim of the present investigation is to utilize the above concepts for determining the values of various transport parameters such as the concentration and mean free path of the conduction electrons, and the probability of their elastic scattering from the specimen surfaces, in the case of the fourth group metals (tin, lead and transition elements of the titanium family) at both liquid-helium and room temperatures. Before describing the theoretical treatment, some information is given about the method employed in preparing the samples and the techniques used for controlling their properties.

## 2. Experimental Procedure

Polycrystalline tin, lead, titanium, zirconium and hafnium films 100-250 Å thick were vacuum deposited onto very smooth, optically polished, square-shaped alkalizinc borosilicate substrates held at room temperature: prior to the film condensation, the substrates had been degassed by baking in vacuo at 350°C for 6 hours and cleaned afterwards by both ultrasonic agitation at 50 kHz and ionic bombardment using a glow discharge of 5 kV. Tin and lead were evaporated from molybdenum boat heaters coated with alumina layers; the other metals from copper liquid-nitrogen-cooled crucibles employing a 270" beam deflection electron gun. The pressure during deposition was of the order of $10^{-10}$ torr for zirconium and hafnium, $3 \times 10^{-10}$ torr for titanium, $10^{-9}$ torr for tin and $5 \times 10^{-9}$ torr for lead. Both the film thickness and the condensation rate were accurately controlled with a piezoelectric quartz crystal monitor maintained at the substrate temperature.

After deposition, the films were annealed for 3 hours at 120" C (Sn), 150" C (Pb) and 300" C (Ti, Zr and Hf) to remove frozen-in structural defects and subsequently cooled down to 4.2° K (Ti, Zr, Hf and Sn, which keeps the tetragonal crystal structure characteristic of the $\beta$ phase as shown by electron-diffraction analysis) or 8° K (Pb, which must be held above 7.2" K, to avoid the occurrence of superconductivity) using liquid helium as the refrigerant: during all these treatments, the specimens were always kept under vacuum at the condensation pressure; moreover, to minimize the deformation arising from differential thermal expansion between metal and glass, both heating and cooling took place very slowly, at rates lower than

1°C/sec. After the annealing process, *in situ* measurements, at both room and liquid-helium temperatures, of the sheet resistivity and Hall voltage of the films were carried out by employing the method due to van der Pauw[1]: the four ohmic contacts required for connecting the film with the Wheatstone bridge circuit were formed by sealing copper terminals in the substrate corners, that had been covered with chromium electrodes vacuum deposited by electron bombardment before film condensation. The Hall effect was produced by using a low magnetic field applied perpendicular to the plane of the film. To avoid the tests being affected by a chemical contamination of the samples due to oxidation or adsorption of some other gases, all the experiments were performed in the vacuum conditions utilized for film preparation. To compare the results so obtained with the values of the sheet resistivity and Hall voltage in the absence of dimensional restrictions, measurements of both these quantities were performed also on bulk specimens consisting of Sn, Pb, Ti, Zr and Hf coldrolled thick foils subject to the same treatments and hence having the same lattice-defect structure as the films.

## 3. Calculations

Measurements were made of the values of both the film thickness $t$ and the ratios $\rho_f/\rho_b$ and $R_f/R_b$ of the resistivity and Hall coefficient of the film to that of a bulk sample of the same material. These quantities are now introduced into the known size-effect relations derived by Sondheimer[2] from the Boltzmann equation for the distribution function of the conduction electrons.

a) Liquid-helium temperature – Writing the Sondheimer expressions in the asymptotic form, valid in the limiting case where $t$ is much less than the bulk-metal electron mean free path, $L_b$, and the magnetic field producing the Hall effect is small, modifying them according to Mayer[3] suggestions and considering that at low temperatures the small-angle electron-phonon scattering becomes very effective in deflecting the carriers toward the film boundaries for further reflection (which entails replacing $L_b$ by a shorter mean free path $L_e$ in the logarithmic term of the formulae, as proposed by Azbel' and Gurzhi[4]), the following equations are obtained:

$$\frac{\rho_b R_f}{\rho_f R_b} = \frac{\mu_f}{\mu_b} = \frac{1}{\log(L_e/t) + 0.4228} \tag{1}$$

$$\frac{\rho_f^2 R_b}{\rho_b R_f} = \frac{4L_b(1-p)}{3t(1+p)}. \tag{2}$$

Here $\mu_f$ and $\mu_b$ are the electron mobilities in the film and bulk, respectively, and $p$ is the proportion of carriers striking the film surfaces which are elastically scattered.

b) Room temperature – In this case, where $t/L_b > 1$, the Sondheimer relations for $\rho_f/\rho_b$ and $R_f/R_b$ can be approximated by

$$\frac{\rho_f}{\rho_b} = 1 + \frac{3L_b}{8t}(1-p), \tag{3}$$

$$\frac{R_f}{R_b} = 1. \tag{4}$$

The lack of thickness dependence of the Hall effect predicted by Eq. (4) is fully confirmed by the experimental data.

c) Details of the theoretical treatment – To solve Eqs. (2) and (3), a knowledge of *L,* is required. The value of this quantity may be calculated using the formula

$$L_b = \frac{h}{2e^2\,\rho_b}\left(\frac{3}{\pi N_b^2}\right)^{1/3}, \tag{5}$$

where h is Planck's constant, e the electronic charge and $N_b$ is the carrier density in the bulk metal, that can be represented as a function of *R,* by the expression

$$N_b = \frac{1}{eR_b}, \tag{6}$$

and does not depend on the temperature.

The results obtained for $N_b$ and *L,* from Eqs. (6) and (5), respectively, and those obtained for *L,* and $p$ inserting Eq. (5) into Eqs. (2) and (3), and fitting then Eqs. (1), (2) and (3) to the observed variation of $\rho_f/\rho_b$ and $R_f/R_b$ with $t$, are listed in Table 1 along with the values of the ratio $r_b$ of the bulk resistivity at 293° K to that at 4.2" K. As for lead, the low temperature data were derived by extrapolation on the assumption that it does not become superconducting.

Let us emphasize that the above considerations refer to isotropic conductors, whereas of the five metals taken into account only lead has cubic symmetry. Therefore, the parameters involved in charge-transport processes in the other four elements must exhibit crystallographic anisotropy and should then be expressed in tensor notation. However, since the films contain a large number of randomly oriented crystallites (as evidenced

| Element | $N_b$ (electrons/atom) | 4.2" K | | | 293° K | | $r_b$ |
|---|---|---|---|---|---|---|---|
| | | $L_b$(Å) | $L_\rho$(Å) | $p$ | $L_b$(Å) | $p$ | |
| Sn* | 1.14 | $5.08 \times 10^6$ | 1.45 x 10" | 0.09 | 95 | 0.05 | $53.5 \times 10^3$ |
| **Pb**** | 0.69 | $1.12 \times 10^6$ | $1.03 \times 10^5$ | 0.06 | 77 | 0.04 | $14.5 \times 10^3$ |
| Ti | 0.38 | $2.51 \times 10^3$ | $1.83 \times 10^3$ | 0.11 | 39 | 0.08 | 64.4 |
| Zr | 0.40 | $2.36 \times 10^3$ | $1.61 \times 10^3$ | 0.14 | 48 | 0.10 | 49.2 |
| Hf | 0.44 | $1.92 \times 10^3$ | $1.31 \times 10^3$ | 0.15 | 50 | 0.10 | 38.4 |

*Tin remains in the $\beta$ phase even at 4.2° K. **The low-temperature lead data were got by extrapolating from the normal state as if superconductivity did not set in.

**Table** 1 - Values of parameters involved in charge-transport phenomena deduced from measurements of both resistivity and Hall constant of bulk samples and thin films.

by transmission-electron-diffraction patterns, which consist of sharp rings of uniform intensity), and the bulk specimens have a structure similar to that of the films (as results from surface examinations carried out using the glancing-angle reflection-electron-diffraction technique), then by averaging the components along the crystal axes the tensors reduce to scalars, and thus the same mathematical procedure can be used as for electron transfer in isotropic materials.

## 4. Discussion of Results and Conclusions

The data given in Table 1 agree rather satisfactorily with the results published by several authors, as shown by the following comparisons:

### a) Bulk-Metal Transport Parameters

I) Tin – The number of carriers is in good accord with those deduced by Meissner[5], Aleksandrov and Kaganov[6], and Aleksandrov[7] from low-temperature studies of the size dependence of the resistivity of high-purity single-crystal wires and by Chambers[8] from anomalous skin effect measurements in bulk samples, yielding 1.30, 1.18, 1.26 and 1.15 electrons/atom, respectively. It stands midway between those which can be calculated from the values of $\rho_b L_b$ obtained by Andrew[9] for rolled foils and by Kunzler and Renton[10], Aleksandrov and Verkin[11], Reich and Montariol[12] and Reich and Forsvoll[13] for thin wires and those derivable from the anomalous skin effect results reported by Fawcett[14]. Moreover, both the resistivity ratio $r_b$ and the bulk mean free path at 4.2° K are of the same order

of magnitude as the findings of all the above investigators, though the fit is not perfect: for instante, our value for $L_b$ is very close to both the prediction of Aleksandrov and that of Kunzler and Renton, giving 600 and 450$\mu$ respectively, but departs appreciably from the Andrew estimate, leading to 95$\mu$. As to the charge transport at room temperature, the bulk mean free path of Table 1 is somewhat shorter than those obtained by Niebuhr[15] from considerations on the electrical behaviour of polycrystalline films vacuum deposited onto quartz substrates at various temperatures. This may be explained by takinginto account that the results of Niebuhr are very doubtful, since they refer to a carrier density of only 0.12 electron per atom, which is much smaller than the concentrations found by all the other authors.

II) Lead – The number of conduction electrons is consistent with that determined by Aleksandrov[7] (0.64 electron/atom), and confirms the findings of a recent investigation performed by Reale[16] about the electrical properties of epitaxial films grown on {100} faces of NaCl single-crystals (0.72 electron/atom), but is only a half of that expected on the basis of measurements of Chambers[S] (1.24 electrons/atom). However, the sharp decrease in the free electron concentration which, according to our data for tin and lead, should occur on passing from a multivalent non-transition metal of the fifth period to the corresponding one of the sixth is supported by a comparison between the carrier densities of the elements preceding tin and lead in the periodic table, showing that in the groups II and III the number of electrons per atom reduces from 0.32-0.40 for cadmium[7] to 0.15 for mercury[2,17], and from 0.57-0.59 for indium[18,19] to 0.12-0.15 for thallium[19,20], respectively. Furthermore, the resistivity ratio is of the usually found order of magnitude, while the bulk mean free path at 4.2" K is in reasonable agreement with the zero-field value of 130$\mu$ derived by Aleksandrov through square-law extrapolation from the results of experiments made in a field of 640 oe so as to suppress the superconductivity, while the bulk mean free path at 293° K is nearly equal to the free flight path of 75Å required to interpret the thickness dependence of the conductivity observed by Reale in the above-mentioned work.

III) Titanium, zirconium and hafnium – The values of r, (and then also those of L, at liquid-helium temperature) are'about a thousand times as small as in tin and lead. Such a discrepancy could indicate that the holes contained in the unfilled *d* band of the transition metals behave like mobile impurity atoms not only able to contribute to the residual resistance, but also capable of affecting the temperature-dependent component of Matthiessen's law, which explains why titanium, zirconium and hafnium

specimens do not obey the low-temperature form of the Gruneisen equation, in contrast with tin and lead samples. The resistivity ratio of titanium agrees with those obtained by Gould *et al.*[21] for 4000- to13900-Å-thick epitaxial films vacuum deposited on single-crystal mica substrates, which varied from 33.3 to 68.3, but is higher than was estimated by various other investigators[22-25], who, however, perhaps have used somewhat less pure materials: an analogous conclusion may be drawn from a comparison of our resistivity ratios for zirconium and hafnium and the measurements of Friebertshauser and McCamont[2']. The results obtained for $N_b$ are compatible with the generally accepted electronic structure of the transition elements, according to which only the valence electrons of the s band participate in the charge-transport processes (since the contribution of those of the *d* band can be neglected because of their large effective mass), and the s band holds about 0.6 electron per atom with an effective mass of the order of the normal mass[26]. Besides, both the concentrations of the carriers and their bulk mean free paths at 293° K are in fairly good accord with those deduced by the writer for the metals of the vanadium and chromium families[27] and the eighth group[28] from considerations based on a combined analysis of the electrical and optical characteristics of thin films. As to the findings of other investigators, it must be remarked that calculations made by Hacman[29] and Singh and Surplice[30] for titanium gave room-temperature mean free paths of 330 and 285 Å, respectively, which are much longer than ours, but leave us at a loss, since the carrier density of 0.01-0.02 electron/atom to which they lead is too small to be acceptable, while data comparable with ours were obtained by Ptushinskii and Stasyuk[31], whose measurements of the resistivity of titanium films condensed on polished glass substrates at 78 or 300" K, and tested at both these temperatures, show that the bulk mean free path of the electrons may range from 19 to 150 Å.

## b) Surface-Scattering Parameter

As for *p*, that can be thought of as the geometrical mean of the fractions of carriers incident on the film-substrate and vacuum-film interfaces which are specularly reflected[32], let us point out that its values are nearly proportional to those of the cohesive energy of the metals, as was already noticed both in the case of the transition elements of the groups V, VI and VIII[27,28] and in that of the trivalent metals of the aluminum family[19]. Since the probability of elastic scattering from the film surfaces should increase as their roughness is reduced, it follows that they are smoother the stronger the interatomic binding forces. Moreover, *p* is always higher at 4.2' K than

at 293° K, in full agreement with the results of investigations carried out by Abelès and Thèye[33] on annealed polycrystalline gold films vacuum deposited onto fused silica substrates, from which one derives that p becomes larger the longer L,. This may be easily explained if one considers that the analogy with the scattering of light from partially diffusing surfaces shows that p must increase with the angle of incidence with respect to the suface normal, as was suggested by various authors[34–36], if one takes into account that a lengthening of the mean free path of the carriers favours their deflection toward the direction of the electric field applied to make the measurements, so that they are led to travel nearly parallel to the plane of the film, which obviously implies that the surfaces are struck at grazing incidence.

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