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Autor: Brändli, G. / Montanarini, M. / Olsen, J.L.

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Size Effect and Diffusion in Sandwich Structures Made from Pure and Impure Indium

by **G. Brändli, M. Montanarini**[1]) and **J. L. Olsen**

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, Zürich, Switzerland

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Abstract. Foils of indium and of an indium-lead alloy were rolled together to form sandwich structures with a total thickness of 0.2 mm having from 2 to 8000 alternating layers of pure and alloyed material. In these samples, in which the layer thickness varied over several orders of magnitude, the size effect in d.c. electrical conduction was compared with Fuchs' calculation and with calculations based on his model. The diffusion rate of lead in these specimens was investigated experimentally and theoretically.

The earliest experimental demonstration of a size effect in the electrical conduction in thin metal specimens was made on chemically deposited films. Since then a great deal of work on size effects has been carried out on thin evaporated films, and also on relatively thick rolled plates or foils of very pure metal (see e.g. [1]). Between the evaporated films and rolled or beaten foils there is a gap where sample preparation is difficult, and it is rare for one set of size effect measurements on comparable specimens to extend over both ranges of thickness.

The experiments described here were carried out to close this gap and also to seek evidence for the existence of widely different mean free paths at different parts of the Fermi surface in indium. In addition the diffusion rate of lead in indium was determined.

Experiments

A new technique was introduced to prepare indium films with thicknesses ranging from 0.1 mm to $2.5 \cdot 10^{-5}$ mm. Two foils, one of very pure indium (99.9995% purity), and the other of an In-4 at.% Pb alloy were superimposed and rolled to a total thickness of 0.2 mm. This caused the two materials to become cold welded together. A part of the resulting sandwich was kept as a first sample. The remainder was cut into two parts. One was put on top of the other, and the double sandwich again reduced to 0.2 mm thickness by rolling. This procedure was repeated until a final sample having 2^{13} layers each 250 Å thick was obtained. Thus 13 samples were prepared, each of thickness 0.2 mm, and with the layer thicknesses, d, forming a geometric series. To avoid diffusion of lead from the alloy into the pure indium layers the rolling was carried out in a cold room at a temperature of $-20\,°C$. The samples were immersed in liquid nitrogen immediately after preparation.

[1]) Now at the Institut für Kristallographie und Petrographie, Eidgenössische Technische Hochschule, Zürich.

The d.c. conductivity was measured, using a four terminal voltage current method, at the temperatures of liquid nitrogen and liquid helium. The resulting conductivity ratios were plotted on a logarithmic scale against the reciprocal layer thickness as shown by the points in Figure 1. The first two points are the conductivity ratios of pure indium plates of 2 and 0.2 mm thickness. These are corrected for a hypothetical attached In-Pb layer, since in the sandwiches at nitrogen temperature about 30% of the current flows in the In-Pb layers.

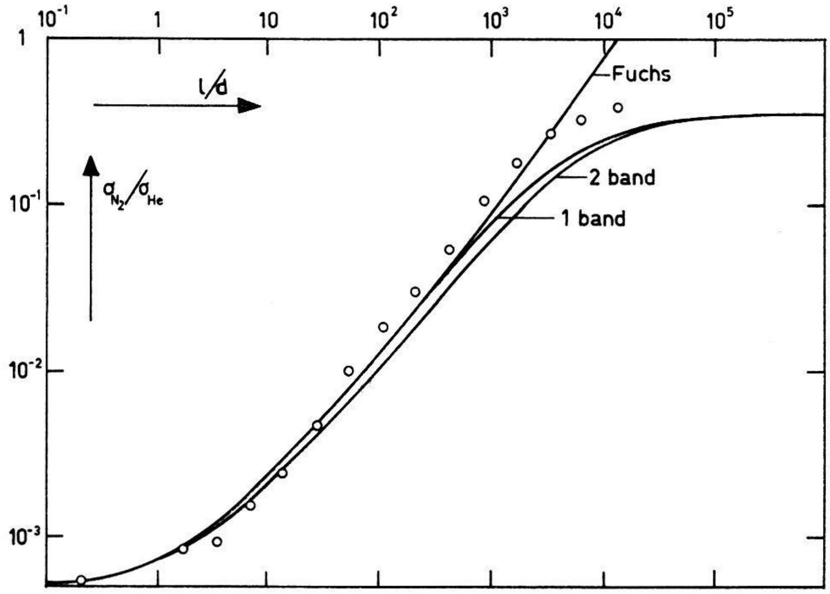

Figure 1

Measured ratios of the conductivity at nitrogen and helium temperatures of sandwich structures are plotted against l/d, where l is the mean free path in pure bulk indium at helium temperature and d is the layer thickness. l is chosen to be 0.35 mm to fit the curves which are calculated from Fuchs' [2] model or from a sandwich structure model assuming one conductivity band or two bands with equal parts of the Fermi surface area, but mean free paths differing by a factor of 10.

In Figure 1 the experimental points are compared with three different theoretical curves: (i) Fuchs' [2] calculation for a simple film, (ii) an analogous calculation for an infinitely extended sandwich structure, and (iii) the same, but assuming a two band model with two different mean free paths. These calculations are explained in detail below.

(i) Fuchs [2] found that the decrease in conductivity due to surface scattering of conduction electrons is given by:

$$\frac{\sigma}{\sigma_b} = 1 - \frac{3}{2\,k} \int_1^\infty dt\,(1/t^3 - 1/t^5)\,(1 - e^{-kt})\,\frac{1-p}{1-p\,e^{-kt}}\,, \tag{1}$$

where σ and σ_b are the conductivity of the film and a bulk specimen of the same material. $k = d/l$, where d is the film thickness, and l the mean free path in the bulk specimen. p is the probability that an electron hitting the surface is reflected specularly. Since In-4 at.% Pb is a solid solution, there is some diffusion of lead atoms across the interface to form a very thin layer of gradually changing lead concentration.

Electrons reaching this layer are therefore reflected diffusely by large angle scattering at the lead impurities, so that $p = 0$. The Fuchs curve in Figure 1 is fitted to the experimental curves by chosing the best fit for the thicker specimens. This corresponds to $l = 0.35$ mm at helium temperature. The conductivity ratio of a bulk sandwich is calculated from the thickest measured specimens. These values for the parameters are used unchanged for the models (ii) and (iii).

(ii) When the size effect reduces the mean free path, l_p, in the pure layers to the length, l_i, of the mean free path in the impure layers, Fuchs' calculation is no more applicable to the sandwich samples, since the conductivity of the impure sample can no longer be neglected. In specimens with very thin layers one then expects that the electrons will pass through several pure and impure layers before they are scattered at a lead impurity. The conductivity ratio should therefore tend asymptotically to the conductivity ratio of a bulk specimen made from In-2 at.% Pb.

We have calculated the behaviour of a sandwich structure using CHAMBERS' [3] formula and taking an infinite number of layers with alternating values for the mean free paths. Electrons meeting the interface are allowed to pass undisturbed into the adjacent layers. The effective conductivity, σ_p, in the *pure* layers, having a bulk conductivity, σ_{pb}, as a function of layer thickness, d, then becomes:

$$\frac{\sigma_p}{\sigma_{pb}} = f(k_p, k_i) = 1 - \frac{3}{2\,k_p} \int_1^\infty dt\,(1/t^3 - 1/t^5)\,(1 - e^{-k_p t}) \times \left\{1 - \frac{(k_p/k_i)\,(1 - e^{-k_i t}) + e^{-k_i t}\,(1 - e^{-k_p t})}{1 - e^{-(k_p + k_i)\,t}}\right\}, \quad (2)$$

where $k_p = d/l_p$, and $k_i = d/l_i$. The conductivity, σ_i, in the *impure* layers with bulk conductivity, σ_{ib}, is then,

$$\frac{\sigma_i}{\sigma_{ib}} = f(k_i, k_p)\,. \quad (3)$$

The conductivity of the sandwich is a parallel connection of (2) and (3) weighted properly. We assume that the area of the Fermi surface is the same for In-Pb and In, i.e. that $\sigma_{pb}/l_p = \sigma_{ib}/l_i$. The conductivity, σ_s, of the sandwich is then given by

$$\frac{\sigma_s}{\sigma_{sb}} = \left(\frac{\sigma_p}{\sigma_{pb}}\,l_p + \frac{\sigma_i}{\sigma_{ib}}\,l_i\right)/(l_p + l_i)\,, \quad (4)$$

where σ_{sb} is the conductivity of a sandwich with layers too thick to show size effect. The parameters for the numerical computation of σ_s have been deduced from the resistivity ratio of bulk pure and impure samples, assuming the validity of Matthiessen's rule, and using the same values of l_p at helium temperature and $\sigma_{sb} = \sigma_b$ as in (i).

(iii) We have mentioned above that this experiment was carried out to test Fuchs' calculation over several orders of magnitude in conductivity and film thickness, and also to search for any evidence of the existence of two mean free paths in indium. If there are two mean free paths, l_1 and l_2 ($l_1 > l_2$), then for $l_1 > d > l_2$ only those electrons with the longer free path will suffer surface scattering and show a size effect. When $l_1, l_2 > d$, however, then all electrons will have a size effect. This has been used by COTTI, FRYER and OLSEN [4], and by COTTI [5] to explain why abnormally small Fermi surface areas are calculated from size effect results while the anomalous skin effect [6] gives values closer to those expected theoretically. Simple considerations lead to the expectation that if the Fuchs curve is made to fit the results for thick specimens then the experimental points will fall below this curve once the shorter free path becomes size dependent.

We assume that the phonon scattering at nitrogen temperature ($T \simeq \Theta_D$) is nearly isotropic, i.e. that at this temperature only one mean free path exists. Likewise in the impure layers at helium temperature, where large angle impurity scattering is dominant, we consider only one mean free path. But in the pure layers at helium temperature small angle scattering by phonons and dislocations is important. At the parts of the Fermi surface with large curvature this small angle scattering is effective, and the mean free path small, while at the parts with small curvature the electrons have to make long random walks on the Fermi surface and have long mean free paths.

The 'two band curve' in Figure 1 is calculated assuming for one half of the Fermi surface a mean free path 10 times shorter than that of the other half at helium temperature. All other assumptions are the same as in (ii). The two band model is calculated using the following formula:

$$\frac{\sigma_p}{\sigma_{p\,b}} = \left(\frac{\sigma_{p\,1}}{\sigma_{p\,1\,b}}\, S_1\, l_1 + \frac{\sigma_{p\,2}}{\sigma_{p\,2\,b}}\, S_2\, l_2\right) / (S_1\, l_1 + S_2\, l_2)\,, \tag{5}$$

where S_1 and S_2 are the areas of the Fermi surface having mean free paths l_1 and l_2, respectively.

The result of the two band calculation is not very spectacular, a second mean free path does not result in a localized jump of the curve but rather in a parallel displacement of the entire curve, which might now be fitted to the experimental points by a different choice of the values of the mean free paths.

Diffusion is a complicating factor in this experiment. To study this problem we have made experiments and calculations. The experiments consisted in tempering the specimens for a certain time at an elevated constant temperature. After this the conductivity ratio was remeasured. The calculations are given below.

The spatial distribution of the lead concentration in a sandwich structure before diffusion is shown schematically in Figure 2a. The state after a certain diffusion is given in Figure 2b. After a time, t, the distribution of the lead initially located in the impure layer between 0 and $+ d$ can be calculated as a function of the coordinate, z, measured perpendicular to the layers:

$$c(z, t) = \frac{1}{2}\, c_0 \{\operatorname{erf}[(z + d)/2\sqrt{D\, t}] - \operatorname{erf}[z/2\sqrt{D\, t}]\}\,, \tag{6}$$

where *erf* is the tabulated integral over gaussian curves, c_0 is the initial lead concentration in the impure layer and D is the diffusion constant. After long diffusion times more than one impure layer contribute to the lead concentration at a certain point z. We therefore have to sum over several functions of the type (6), each arising from one impure layer. For specimens with very few layers reflection of the diffusing lead atoms at the open surfaces has been taken in account, too.

It is known that in solid solutions of lead in indium the residual resistivity is approximately proportional to the lead concentration (see e.g. GYGAX [7]). The lead distribution would therefore give us directly the resistivity at helium temperature for all z, if no size effects were present. These we have taken in account by making the very crude assumption that Matthiessen's rule is valid for the size effect, and that a size induced resistivity may simply be added to the residual resistivity. This is shown by the dashed line in Figure 2. At nitrogen temperature we have added the temperature dependent resistivity instead, this is nearly equal to the residual resistivity of the impure layers.

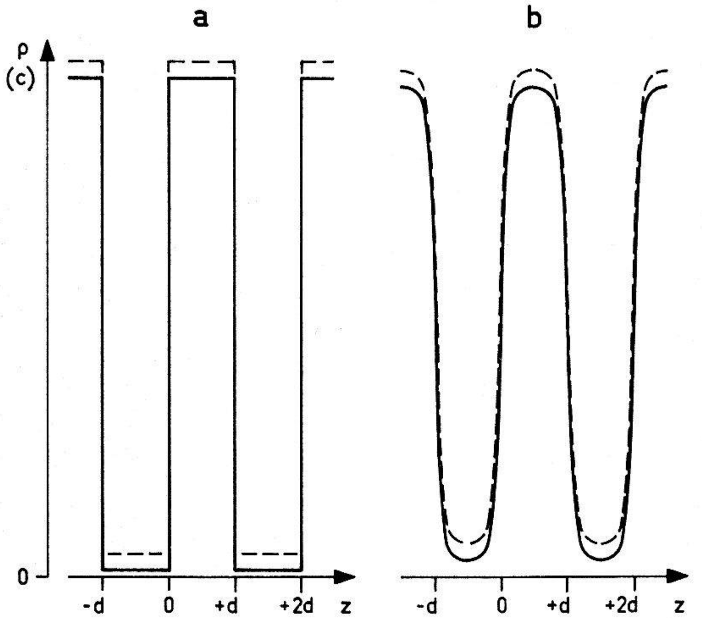

Figure 2

At the left, curve a, is shown the variation of lead concentration, c, and resistivity, ϱ, before diffusion as a function of coordinate, z, perpendicular to the layers. Curve b shows the same at time, t, after diffusion. The dashed lines indicate how we have added the size dependent part of the resistivity assuming Matthiessen's rule.

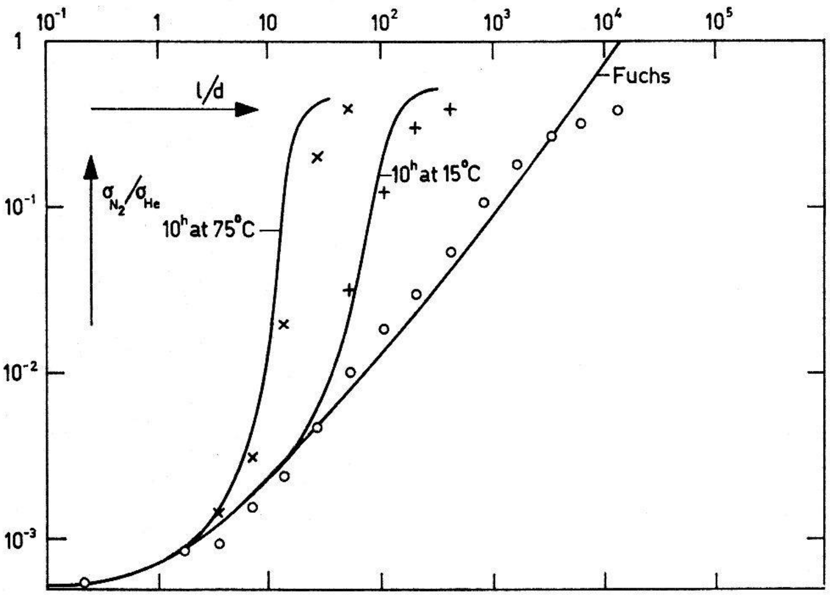

Figure 3

Comparison of measured conductivity ratios before and after diffusion with calculated curves assuming the model of Figure 2 and based on diffusion data of thallium in indium measured by Eckert and Drickamer [7].

The model presented here for calculating the effective conductivity in a sandwich structure as a function of diffusion rate is only valid for specimens with thick layers, small size effect, and a relatively high resistivity in the impure layers. For thin layers a calculation analogous to formula (2) but with a continously varying lead concentration would be necessary. This would, however, lead to a threefold nonanalytical integral for the effective conductivity.

In Figure 3 theoretical curves and measured points are compared. For the diffusion constant, D, in equation (6) we have used the data of ECKERT and DRICKAMER [8] on diffusion of thallium in indium. The measured points lie somewhat lower than the calculated curves. We conclude from this and from other experiments, not shown in Figure 2, that the activation energy of lead in indium is about 3% higher than that of thallium in indium, and further that diffusion between sample preparation and our first measurements is negligible except for the last three or four specimens. We do not know, however, how quickly diffusion processes go on during the rolling of the specimens. Such a diffusion is probably responsible for the relatively low conductivity at helium temperature of all samples having very thin layers.

In discussing these experiments we conclude that sandwich structures of the kind described can give information on the size effect over several orders of the ratio of size to free path, and that they offer a method for measuring the diffusion rate of substances that cannot be traced radioactively. The preparation of the sandwiches could undoubtedly be greatly improved.

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References

[1] G. BRÄNDLI and J. L. OLSEN, Mat. Sci. Engng. *4*, 61 (1969).
[2] K. FUCHS, Proc. Cambridge Phil. Soc. *34*, 100 (1938).
[3] R. G. CHAMBERS, Proc. Roy. Soc. *A 202*, 378 (1950).
[4] P. COTTI, E. M. FRYER and J. L. OLSEN, Helv. phys. Acta *37*, 585 (1964).
[5] P. COTTI, Phys. kondens. Mat. *3*, 40 (1964).
[6] N. DHEER, Proc. Roy. Soc. *A 260*, 333 (1961).
[7] S. GYGAX, Phys. kondens. Mat. *4*, 207 (1965).
[8] R. E. ECKERT and H. G. DRICKAMER, J. Chem. Phys. *20*, 13 (1952).