

## TEMPERATURE DEPENDENCE OF THE CHARGE TRANSPORT IN ALKALI METAL FILMS

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### ABSTRACT:

The behaviour of the resistivity of vacuum-deposited thin solid films of alkali metals was observed to depart from the predictions of the Fuchs-Sondheimer size-effect theory with decreasing condensation temperature: the deviation takes place when the mean free path of the conduction electrons becomes comparable with the average linear dimension of the grains of the film. A second change in the electrical properties occurs at a critical crystalline-to-amorphous transformation temperature below which the deposit exhibits a highly disordered liquid-like structure. The results derived on modifying the Fuchs-Sondheimer treatment so as to include both phenomena are in reasonable agreement with the observations.

### I. INTRODUCTION

If one of the dimensions of a metal sample becomes very small, as in the case of films whose thickness is so reduced as to be comparable with the mean free path of the conduction electrons in the bulk metal, then the

surfaces of the specimen behave as a sort of structural imperfection imposing a geometrical limitation on the movement of the charges. Hence the electrical conductivity of a thin film shall depend on a size effect which may be studied by introducing the boundary conditions at the film surfaces into the Boltzmann distribution equation according to the well known charge transport theory worked out by Fuchs<sup>1</sup> and Sondheimer<sup>2</sup> for a free electron gas and a spherical Fermi surface<sup>3,4</sup>. This theory leads to a relation between resistivity and thickness which involves both the bulk metal value of the mean free path of the carriers at the Fermi level and a parameter describing the average probability of their specular reflection from the film surfaces, that was deduced from the roughness of the surfaces by taking into account the angular distribution of the electrons incident on them and using a formula proposed by Soffer<sup>5</sup>.

The Fuchs-Sondheimer treatment is based on the assumption that the film can be thought of as a homogeneous, isotropic slab of bulk material, so that it should be applied only in the case of single-crystal and amorphous layers: however, it may be extended to polycrystalline films, even if they consist of grains whose average diameter in the direction of the electric field,  $d_g$ , is less than the background mean free path of the electrons within the crystal lattice,  $\lambda_b$  (some values of which are listed in Table 1), on condition that also another size effect is considered, the one associated with the scattering of the carriers by the grain boundaries, which can be represented as an arrangement of partially reflecting, randomly spaced planes, oriented perpendicular to the direction of the current and acting as an assembly of parallel  $\delta$ -function potentials<sup>6</sup>.

Table 1. Background mean free path of the electrons within a grain for the alkali metals at various temperatures: the values are expressed in ångströms

Metal	77°K	123°K	173°K	273°K	Melting point
Li	900	569	210	115	64
Na	1892	1283	623	343	223
K	1265	952	612	374	270
Rb	1154	784	383	226	185
Cs	656	467	262	160	138

The influence of the sample size on the transport processes was already discussed in previous works<sup>7</sup>, where it was examined how the electrical conductivity, the temperature coefficient of resistivity, the thermoelectric power, the thermal conductivity, the field-induced changes of resistivity and the piezoresistive properties of a film are affected by its thickness. The aim of the present investigation is a reasonable explanation of the electrical behaviour exhibited by alkali metal films vacuum condensed at various temperatures, that has been interpreted by adapting the Fuchs-Sondheimer model to the structural characteristics of the specimens and generalizing the calculations to include the internal size effects arising in fine-grained polycrystalline films.

## II. EXPERIMENTAL DETAILS

Alkali metal films 500 Å thick were vacuum deposited on very flat, optically polished hard glass substrates held at temperatures between 77°K and the melting point of the metal: before film condensation, the substrates had been degassed by baking in vacuum at 350°C for 24h and cleaned afterwards by both ultrasonic agitation at 50kc and ionic bombardment using a glow discharge of 5 kV.

Lithium was evaporated with a 270° beam deflection electron gun from a copper water-cooled crucible, while the other metals were sublimated from a multiple source consisting of a quartz tube with several holes and heated by a tungsten coil: the pressure during condensation was of the order of  $10^{-8}$  torr for lithium,  $10^{-7}$  torr for sodium,  $10^{-6}$  torr for potassium,  $5 \times 10^{-6}$  torr for rubidium and  $10^{-5}$  torr for caesium. Both the film thickness and the deposition rate were carefully controlled with a piezoelectric quartz crystal oscillator.

The sheet resistivity of the film and its change with temperature were determined by means of a dc Wheatstone bridge connected with the film by two terminals sealed in the substrate ends, which had been coated with electrodes of gold vacuum deposited prior to the film condensation. The results thus found are shown as solid lines in Figs. 1 and 2, where the ratios of the film resistivity and its temperature coefficient to the corresponding macrocrystalline bulk quantities have been plotted as a function of temperature: each of the data points represented in the figure was derived by averaging the values obtained for several square-shaped samples.

To minimize the chemical contamination due to oxidation or adsorption



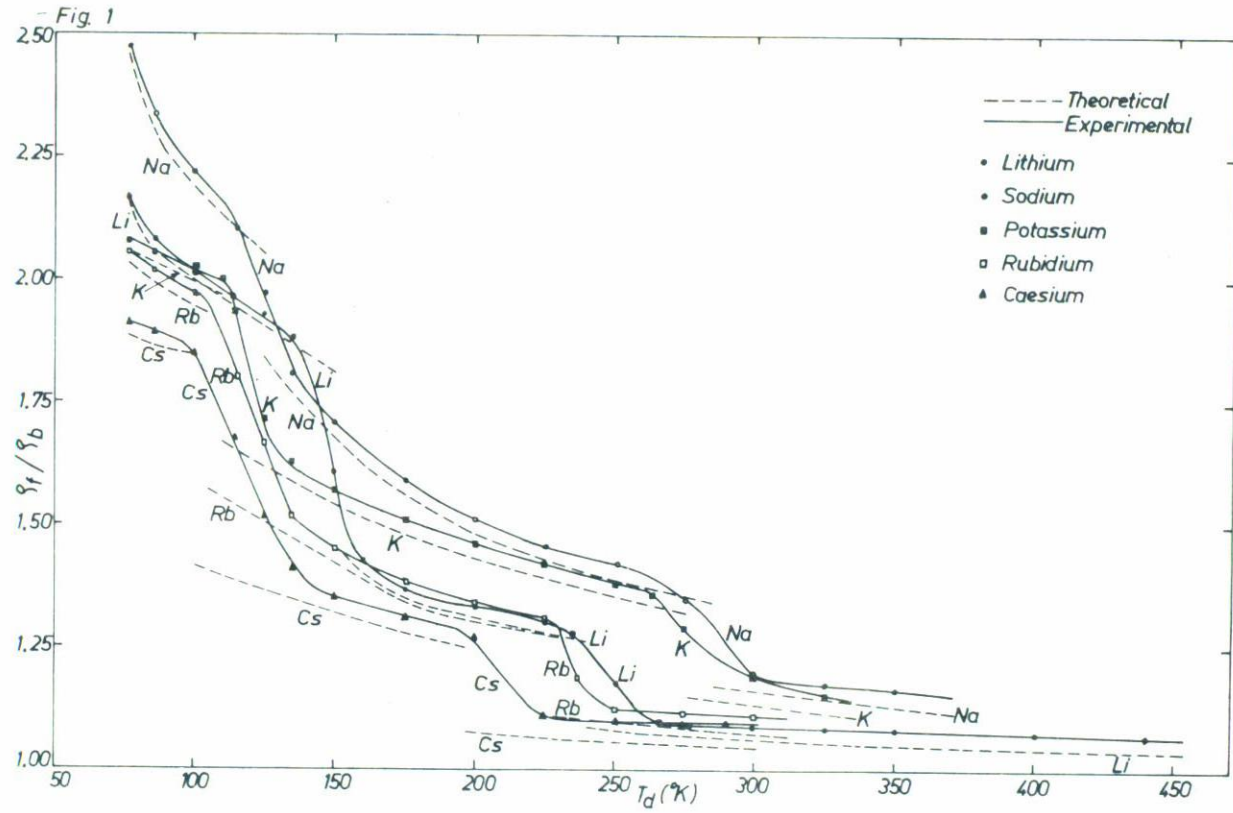


Fig. 1. The ratio of the resistivity of the film to that for the macrocrystalline bulk metal, as a function of the condensation temperature, for alkali metal films 500 Å thick vacuum deposited on glass substrates.

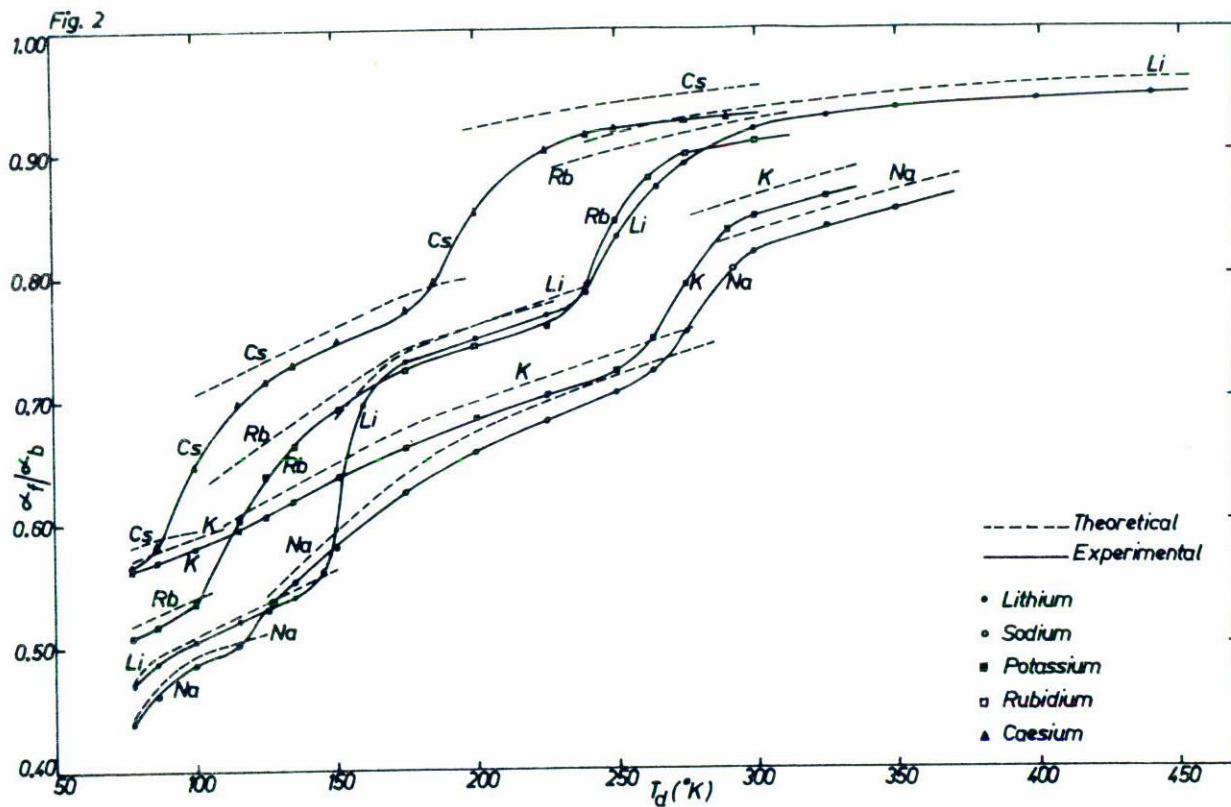


Fig. 2. The ratio of the temperature coefficient of resistivity of the film to that of the macrocrystalline bulk metal, as a function of the condensation temperature for alkali metal films 500 Å thick vacuum deposited on glass substrates.

of some other residual gases and to avoid the structural deformation arising from differential thermal expansion between metal and glass, all the tests were performed on freshly evaporated films kept at the same pressure and temperature at which their condensation took place.

Since a reliable interpretation of the experimental results is possible only if the film structure is perfectly known, every sample was examined very accurately in an electron microscope, and then analysed by electron diffraction. The main features exhibited by the films are the following: 1) when the deposition temperature  $T_d$  is lower than a critical value  $T_c$  of the order of  $T_m/3$ , where  $T_m$  is the melting point of the bulk metal, broad, halo-type diffraction patterns are observed, that may be explained as due to a highly disordered, amorphous-like structure: this result agrees with Komnik's<sup>5</sup> considerations on the condensation process; 2) for  $T_d > T_c$  the deposits are crystalline and consist of grains whose average linear dimension in the plane of the film is comparable with the film thickness and increases with the condensation temperature: as a rise of  $T_d$  will produce a reduction of the mean free path of the electrons, a temperature  $T_g$  shall then exist at which  $d_g = \lambda_b$ .

From the examination of the structural properties and their comparison with the electrical ones we obtained:  $T_c = 150^\circ \text{K}$  and  $T_g = 240^\circ \text{K}$  for lithium;  $T_c = 125^\circ \text{K}$  and  $T_g = 285^\circ \text{K}$  for sodium;  $T_c = 110^\circ \text{K}$  and  $T_g = 277^\circ \text{K}$  for potassium;  $T_c = 105^\circ \text{K}$  and  $T_g = 228^\circ \text{K}$  for rubidium;  $T_c = 100^\circ \text{K}$  and  $T_g = 197^\circ \text{K}$  for caesium.

### III. THEORETICAL PROCEDURE

#### a) Polycrystalline Films: Case where $T_d > T_g$

To interpret the behaviour of deposits condensed at temperatures higher than  $T_g$ , so that  $d_g > \lambda_b$ , the film resistivity,  $\rho_f$ , and its temperature coefficient,  $\alpha_f$ , were expressed by the formulae<sup>4</sup>

$$\rho_f = \rho_0 \Phi_p(b)/b \quad (1)$$

$$\alpha_f = \frac{1}{\rho_0} \frac{d\rho_0}{dT} \left\{ 1 - \Phi_p(b) \frac{d[b/\Phi_p(b)]}{db} \right\} \quad (2)$$

where  $\rho_0$  and  $d\rho_0/dT$  are the resistivity of a massive specimen of the film material held at the same temperature and having the same structure as the film (which for  $d_g > \lambda_b$  can be practically equated to the intrinsic resistivity of a single-crystal,  $\rho_b$ ) and its derivative with respect to the absolute temperature, while  $\Phi_p(b)$  is a function given by<sup>1, 2</sup>

$$\Phi_p(b) = b \left[ 1 - \frac{3(1-p)}{2b} \int_1^\infty \left( \frac{1}{x^3} - \frac{1}{x^5} \right) \frac{1 - \exp(-bx)}{1 - p \exp(-bx)} dx \right]^{-1}, \quad (3)$$

derived by inserting the boundary conditions at the film surfaces into the Boltzmann equation for the distribution function of the conduction electrons, but ignoring the contribution to the film resistivity due to charge scattering at grain boundaries, that when  $d_g > \lambda_b$  may be neglected without appreciable errors.

The non-dimensional quantity  $b$  can be represented in terms of the film thickness,  $t$ , and the carrier concentration,  $N$ , using the expression

$$b = (2te^2\rho_0/b)(\pi N^2/3)^{1/3}, \quad (4)$$

where  $b$  indicates Planck's constant and  $e$  the electronic charge;  $p$  is the fraction of electrons incident on the film surfaces which are specularly reflected, called the scattering parameter: in the absence of tangential correlation of the surface asperities it may be written as<sup>5, 10</sup>

$$p = \exp [-(2\eta \cos \theta)^2 (3\pi^2 N)^{2/3}], \quad (5)$$

where  $\eta$  is a parameter representative of the roughness of the surfaces, giving the root mean square height deviation from a flat configuration, which may be determined by assuming that the heights of the asperities are distributed statistically in Gaussian fashion about a suitable mean value, and  $\theta$  is an appropriate average angle of reflection of the electron wave vectors as measured from the surface normal, which can be calculated by taking into account the angular distribution of the carriers striking the surfaces. As in the alkali metals  $N$  corresponds to the number of atoms per unit volume, eq. (5) shows that the probability of elastic scattering at the film surfaces will increase with the nearest neighbour distance.



On substituting (4) and (5) in (3), and then (3) in (1) and (2), the temperature dependences of  $\rho_f/\rho_b$  and  $\alpha_f/\alpha_b$  plotted as dashed curves on the right side of Figs. 1 and 2 were found. Here  $\alpha_b$  denotes the temperature coefficient of resistivity corresponding to  $\rho_b$ .

b) Polycrystalline Films: Case where  $T_d < T_g$

If the films are deposited at a temperature lower than  $T_g$ , but higher than  $T_c$ , so as to produce microcrystalline layers where  $d_g < \lambda_b$ , another resistivity component shall be taken into account, the one associated with the interactions of the conduction electrons with the grain boundaries. To determine the value of this new contribution the Mayadas-Shatzkes<sup>6</sup> model was applied, where the crystal boundaries are treated as a series of partially reflecting, randomly spaced parallel planes, oriented perpendicular to the direction of the current flow, with an average separation  $d_g$ , and behaving as an array of smooth, short-ranged  $\delta$ -function potentials.

On these assumptions a computation of  $\rho_f$  and  $\alpha_f$  using eqs. (1) and (2) entails replacing  $\rho_0$  and  $\Phi_p(b)$  by the relations

$$\rho_0 = \rho_b / F(c) \quad (6)$$

$$\Phi_p(b) = b \left[ 1 - \frac{6(1-p)}{\pi b F(c)} \int_0^{\pi/2} \int_1^{\infty} \left( \frac{1}{x^3} - \frac{1}{x^5} \right) \frac{\cos^2 \omega}{H^2(x, \omega)} \frac{1 - \exp(-bxH(x, \omega))}{1 - p \exp(-bxH(x, \omega))} d\omega dx \right]^{-1} \quad (7)$$

with

$$F(c) = 3 \left[ 1/3 - c/2 + c^2 - c^3 \log_e(1 + 1/c) \right] \quad (8)$$

$$H(x, \omega) = 1 + c/\cos \omega (1 - 1/x^2)^{1/2}, \quad (9)$$

where  $c$  is a numerical parameter depending on both the crystal size and the grain-boundary effects. To make a direct comparison between this procedure and the Fuchs-Sondheimer theory,  $c$  must be expressed in the form

$$c = [b(1-q)/2e^2 \rho_0 d_g q] (3/\pi N^2)^{1/3}, \quad (10)$$



where  $q$  denotes a transmission coefficient giving the average probability of charge transfer across the grain boundaries, that can be derived from considerations on the mechanism of electron tunneling through the potential barriers existing between the crystallites.

Solving eqs. (1) and (2), the results represented as broken curves in the centre of Figs. 1 and 2 were obtained.

### c) Amorphous Films ( $T_d < T_c$ )

When the condensation occurs below a critical temperature  $T_c$ , always lower than  $T_g$ , and of the order of  $T_m/3$ , the films exhibit a very disordered, liquid-like structure, as evidenced by electron diffraction patterns.

To study the electrical properties of such deposits the same procedure as in the case (a) may be applied, since the medium is isotropic and the only size effect is that concerning the surfaces of the film. However, it shall be noted that in this case the background resistivity  $\rho_0$  due to the scattering of the carriers by the thermal vibrations of the atoms (electron-phonon collisions) and to their interaction with structural defects is rather different from  $\rho_b$ .

If one assumes that a crystalline-to-amorphous transformation can be treated as a melting process, then  $\rho_0$  may be derived from the equation

$$\rho_0 = \rho_b \exp [2(S_a - S_c)/3kN] \quad , \quad (11)$$

where  $k$  is Boltzmann's constant, while  $S_a$  and  $S_c$  are the entropies per unit volume of the amorphous and crystalline phases, respectively: obviously,  $S_a$  includes also the configurational contribution arising from the disorder of the structure.

Introducing now (11) into (1), (2) and (4), and following the lines of the Fuchs-Sondheimer treatment, the dashed curves shown on the left side of Figs. 1 and 2 resulted.

The discontinuities between the branches of the theoretical curves obtained using the three models described in this section, may be easily understood if one considers that the changes in the charge transport mechanism due to the structural transformations produced by varying the deposition temperature, cannot occur so suddenly as it was supposed in the mathematical procedure.

#### 4. DISCUSSION OF RESULTS AND CONCLUSIONS

Figs. 1 and 2 show that the theoretically predicted temperature dependence of  $\rho_f/\rho_b$  and  $\alpha_f/\alpha_b$  is in good agreement with the observations, though the fit is not complete. Apart from the neighbourhood of  $T_C$  and  $T_g$ , where obviously a comparison is meaningless, the film resistivity and its temperature coefficient are respectively higher and lower than would be expected on the basis of eqs. (1) and (2): the difference between calculations and measurements increases with both the pressure in the vacuum chamber and the deposition temperature.

All these discrepancies may be explained by assuming that even at pressures between  $10^{-5}$  and  $10^{-8}$  torr the free surface of the films can be contaminated by small traces of oxide and physisorbed impurities able to produce a reduction in the conductivity and temperature coefficient of resistivity, that obviously will become more evident the thinner the film. This hypothesis is supported by the rise of both the conductivity and the temperature coefficient of resistivity with improving vacuum conditions or increasing film thickness observed by comparing the behaviour of samples of different thicknesses deposited and tested at various pressures, and explains why the deviation from theory is less the lower the pressure at which the films were produced and measured (that was raised with the atomic number in proportion to the volatility of the metal, from  $10^{-8}$  torr for lithium to  $10^{-5}$  torr for caesium, to avoid the reevaporation of the atoms of the film) or the colder the substrate (as the thermal agitation activates the diffusion of foreign atoms over the free surface of the film, facilitating thus their capture by adsorption sites).

Experiments performed using lithium films prepared and held in a vacuum better than  $10^{-8}$  torr show, however, that from about  $10^{-9}$  torr on down the film resistivity and its temperature coefficient give up decreasing and increasing, respectively: one can then assume that at such a pressure the adsorption phenomena have become quite negligible.

However, even at  $10^{-9}$  torr the values of  $\rho_f$  and  $\alpha_f$  are larger and smaller, respectively, than in the theoretical predictions, but in this case the difference reduces with raising  $T_d$ . Therefore, the discrepancies between calculations and measurements illustrated in Figs. 1 and 2 cannot be completely attributed to the film contamination. The residual departure noticed in specimens evaporated and investigated at  $10^{-9}$  torr may be interpreted by supposing that the fraction of carriers elastically scattered from the film surfaces is less than would result from (5), and does not remain constant as in the idealized model considered in the mathematical treatment, but increases with the condensation temperature.



This explanation is reasonable, as we have assumed that the values of  $p$  deduced from considerations on the structural characteristics of the film-vacuum interface can be used also for the substrate-film interface, while the proportions of electrons specularly reflected at the top and bottom surfaces of the film could be different<sup>11</sup>, and the second could be smaller, since obviously the bottom surface must have the same roughness as the substrate, whereas the asperities of the top surface may be partially smoothed by a diffusion mechanism which is enhanced by increasing the deposition temperature.

However, a study of the influence of the thermal agitation on the surface mobility of vapour atoms of the alkali metal captured by the free surface of the film during the condensation process, shows that in the low temperature region the residual deviation from theory in the absence of contamination should be greater than is observed in ultra-high-vacuum deposited lithium films. This may be explained by considering that the lower is the temperature, the more small-angle electron-phonon interactions become effective in deflecting the electrons toward the film surfaces for further scattering, which entails a shortening of the electron mean free path used in the Fuchs-Sondheimer theory<sup>12</sup>, and can then balance partially the decrease of  $p$  arising from the reduction in the atom surface mobility.

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#### RESUMEN

Se observó que el comportamiento de la resistividad de películas sólidas delgadas de metales alcalinos, depositadas en el vacío, se desvía de las predicciones de la teoría de Fuchs-Sondheimer sobre el efecto del tamaño: la desviación tiene lugar cuando la trayectoria media libre de los electrones de conducción es comparable con la dimensión lineal promedio de los granos de la película. Ocurre un segundo cambio en las propiedades eléctricas, a la temperatura crítica de transformación de cristalino a amorfo, abajo de la cual, el depósito muestra una estructura altamente desordenada, semejante a un líquido. Los resultados obtenidos al modificar el tratamiento Fuchs-Sondheimer de modo que incluya ambos fenómenos, están razonablemente de acuerdo con las observaciones.