Investigation of the thermal properties of thin aluminum films

Yu. A. Volkov, L. S. Palatnik, and A. T. Pugachev

Khar'kov Polytechnic Institute

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A method and results of an investigation of the thermal conductivity and diffusivity of thin films are presented. The samples are films without substrates; they are heated by Joule heat inside an electron-diffraction chamber. The temperature fields are calculated on the basis of the electron diffraction patterns obtained with the heated films. The thermal conductivity coefficient (λ) and the diffusivity coefficient (k) are found on the basis of the one-dimensional heat-conduction equation for a current-carrying film. The thermal properties of annealed aluminum films 500–1100 Å thick are investigated in the 300 to 500°K temperature range. The experimental dependence of λ on the thickness can be satisfactorily described by the Fuchs theory in the case of diffuse scattering of the electrons by the film surface. The specific heat is calculated on the basis of the measured values of λ and k. The specific heat of the film is close to that of bulk aluminum.

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INTRODUCTION

It is known that the thermal properties of thin metal films can differ significantly from the properties of the bulk material.[1–5] However, attempts to investigate experimentally the thermal properties of thin metal films were undertaken only recently.[6–9] The experiments were devoted mainly to the thermal conductivity and pertained to temperature regions near or above the Debye temperature, and the results were treated from general points of view of the geometrical and structural singularities of thin films.

The purpose of the present study was to investigate experimentally the influence of the dimensions on the thermal properties of thin films. Most interesting but most difficult to study experimentally is the thickness interval 10^2–10^3 Å. The investigation was preceded by the development of a comprehensive method that makes it possible to determine the thermal conductivity and the temperature diffusivity with the same samples and to calculate the heat capacity from these data.

EXPERIMENTAL PROCEDURE

To determine the thermal properties it is necessary to have experimental data on the space-time distribution of the temperature in the sample and information on the amount of released or absorbed energy. The properties are calculated from the equation of thermal conductivity for a given experiment. The method consisted in the following. A rectangular film removed from a substrate was secured with both ends to a special adapter and placed in the object chamber of an electron diffraction chamber (Fig. 1). The film was heated in the vacuum by direct current flowing through it. We measured the current and the resistance of the film. At a given value of the current we plotted a series of electron diffraction patterns from different sections. From these patterns we then constructed the distribution of the temperature along the heated film:

$$T(x)=T\left(\pm\frac{L}{2}\right)+\frac{1}{\varkappa}\frac{\Delta\Phi_{hkl}(x)}{\Phi_{hkl}}, \tag{1}$$

where $T(\pm L/2)$ is the temperature at the ends of the film, $\varkappa$ is the coefficient of thermal expansion of the film, equal to the value of $\varkappa$ of bulky metals,[10] $\Delta\Phi_{hkl}$ is the change, due to heating, of the diameter of the diffraction ring (hkl) on the electron diffraction pattern from the second with coordinate x.

After taking the electron diffraction patterns, the electron beam was aimed on the center of the film. The electron diffraction patterns were obtained by kinematic photography, whereby the diffraction pattern is photographed through a narrow slit on a moving photographic plate.[11] In kinematic electron diffraction photography, the electron beam is modulated by an alternating electromagnetic field of frequency 50 Hz. The electron diffraction pattern obtained in this manner is a family of sinusoids. The electric circuit of the film was open during the course of photography. The kinematic electron diffraction pattern registered the changes in the diameters of the diffraction rings as functions of the time. The time was reckoned from the instant when the current is turned off, as revealed on the diffraction pattern by the start of the change of Φ_{hkl}. Modulation of the beam produced a reliable time scale on the diffraction pattern.

The one-dimensional equation on the thermal conductivity of a thin current-carrying film in vacuum is

$$\frac{\partial T}{\partial\tau}=k\frac{\partial^2 T}{\partial x^2}-2k\frac{\sigma\varepsilon}{\lambda t}[T^4-T_0^4]+k\frac{J^2\rho}{m^2t^2\lambda}, \tag{2}$$

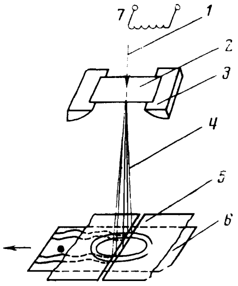

FIG. 1. Experimental setup for the investigation of the thermal properties of thin films: 1—electron beam, 2—film, 3—adapter holders, 4—diffraction cone, 5—screen width slit, 6—photographic plate, 7—solenoid for the modulation of the electron beam.

where ρ is the resistivity, ε is the integrated emissivity into a hemisphere, σ is the Stefan–Boltzmann constant, T_0 is the ambient temperature, J is the current flowing through the film, and t and m are respectively the thickness and width of the film.

For stationary temperature fields, Eq. (2) reduces to a form that is convenient for the reduction of the experimental data

$$J^2R=-2\lambda mt\frac{dT}{dx}\Big|_{x=L/2}+2m\sigma\int\limits_{-L/2}^{L/2}\varepsilon(T^4-T_0^4)\,dx, \tag{3}$$

where R is the total resistance of the film. If R_i and $T_i(x)$ are measured at several values of J_i, then λ and ε can be determined from a system of equations in the form (3).[7]

A study of the nonstationary temperature fields makes it possible to determine the thermal diffusivity of thin films.[9] After turning off the current, the film is cooled and its nonstationary temperature field is described by the equation

$$\frac{\partial T}{\partial \tau}=k\frac{\partial^2 T}{\partial x^2}-2k\frac{\sigma\varepsilon}{\lambda t}[T^4-T_0^4] \tag{4}$$

with initial and stationary boundary conditions

$$T(x,0)=T(x),\ T(\pm L/2,\tau)=T_0.$$

To determine k it is necessary to solve (4) for some point $\tilde{x}$ at different values of k and to measure $T(\tilde{x},\tau)$. The thermal-diffusivity coefficient is determined from the comparison of the experimental $T(\tilde{x},\tau)$ curves with those calculated for the different k. The nonlinear equation (4) was integrated with a computer by a finite-difference method.[12] We used the values of λ and ε obtained in the solution of the stationary problem. Since $\lambda = kcd$, simultaneous solution of the stationary and nonstationary problems makes it possible to determine the specific heat of thin films, if data on their density (d) are available.

No account was taken in the heat balance equation (2) for the elementary section of the film of a number of terms, such as the heating by the electron beam, the Thomson heat, the thermal conductivity of the residual gas, or the emission from the lateral surface of the film. A special investigation was made of the heating of films by the electron beam in order to choose the optimal conditions for obtaining the static and kinematic electron diffraction patterns. According to a precision measurement of the film resistance as a function of the current density of the electron beam (j), the heating at $j \lesssim 10^{-5}$ A/cm^2 does not exceed one degree. The heating of the film by the beam was therefore disregarded. Estimates based on the experimental data on the temperature fields of the film have shown that it is possible to neglect also the Thomson heat and the thermal conductivity of the residual gas.[13,14] Calculation of the contribution of the thermal conductivity to the heat balance were made difficult by the lack of information on the composition, partial pressure, and accommodation coefficients of the residual gases in the electron diffraction chamber. The estimates were therefore performed on the basis of oxygen and nitrogen with unity accommodation coefficients. The contribution of the radiation from the lateral surfaces were negligibly small, since the total surface area of the film exceeded the lateral surface by four or five orders of magnitude.

An advantage of the proposed procedure is the comprehensive investigation of the thermal properties of thin films without substrates, with the structure monitored by diffraction during the source of the experiment.

The objects of the investigation were aluminum films 500–1100 Å thick, prepared by a crucibleless method. Aluminum 99.999% pure and with $R_{300}/R_{4.2} > 2\times10^3$ was evaporated in a vacuum of 10^{-5} Torr from a drop melted by induction and freely suspended in an electromagnetic field of an inductor.[15,16] The rate of condensation was 10^2 Å/sec. The substrates were cover glasses on which a sublayer of NaCl was deposited in vacuum beforehand. After condensation, the films were annealed at 500 °K for five minutes. The sample were separated from the substrate by dissolving the NaCl sublayer in water and were fished out with the adapter holders. The ends of the films were clamped to the holders. The adapter with the film was placed in the electron diffraction chamber. The reliability of thermal contact was monitored against the electric resistance of the film, and also by electron diffraction measurements of the temperature at the point $x=\pm L/2$ as functions of the current through the film. The temperature $T(\pm L/2)$ was independent of the current. This demonstrates the good thermal contact between the film and the adapter.

When the static electron diffraction patterns were obtained, the diameter (D) of the bombarded section was 0.015 cm. The electron-beam current density did not exceed 10^{-6} A/cm^2. To obtain the kinematic patterns we used $D=0.13$ cm, $j\lesssim10^{-5}$ A/cm^2, a slit width 0.02 cm, and a film velocity 2 cm/sec. The diameters of the (220), (311), (331), and (420) diffraction rings on the static and kinematic electron diffraction patterns were measured with a UIM-21 microscope with accuracy ±0.0005 cm. This corresponded to a temperature measurement error ±5°.

RESULTS AND DISCUSSION

The film was regarded in the calculation as a thin plane-parallel plate. As shown by microphotometric measurements of semi-transparent samples, the thickness drop in the investigated section of the film (6–8 mm) did not exceed 2%. According to electron-microscopy data, the objects were solid polycrystalline films of single-block thickness. The average block dimension in the plane of the film ($\mathscr{L}$), measured from the dark-field photographs was two or three times larger than the film thickness. Electron microscope photographs of the rolled-up films yielded information on the microrelief of their surfaces.[17] The microrelief was smaller by one order of magnitude than the thickness, so that the real film surface was smooth enough.

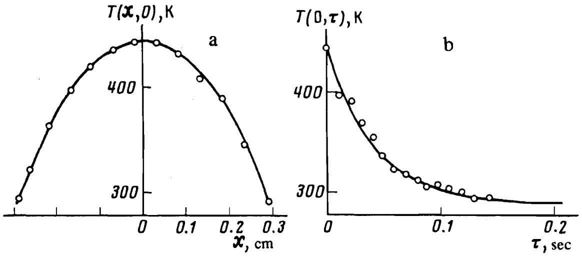

FIG. 2. Temperature distribution along an aluminum film 500 Å thick (Fig. a). Fig. b shows the time variation of the temperature at the center of the film after turning off the current; points—experiment, curve—solution of Eq. (4) with a computer at $k = 0.7$ cm^2 sec^{-1}.

Figure 2 shows the temperature fields of an aluminum film 500 Å thick. The temperature drop between the center and the ends of the film was 150°. At the indicated accuracy of the temperature measurement, this made it possible to construct reliably the temperature fields. The temperature gradient changed from zero at $x = 0$ to a value $\sim 10^3$ deg/cm at the point $x = \pm L/2$. At such large gradients it is necessary to estimate the contribution of the Thomson heat to the heat balance of the heated section of the film. Estimates performed under the assumption that the Thomson coefficients of the films and the bulk material are equal show that the Thomson heat is smaller by almost two orders of magnitude than the Joule energy. We have therefore disregarded it in Eq. (2). These estimates are confirmed also by the symmetrical form of the stationary temperature fields.

Thermal conductivity. The results of the experimental determination of the thermal properties of thin aluminum films are summarized in Table I. As seen from these data, the thermal conductivity coefficient increases with increasing thickness, and at $t \gtrsim 10^3$ Å its value practically coincides with the data for bulk metal. This behavior of the thermal conductivity as a function of the thickness at high temperatures, where the coefficient of thermal conductivity and electric conductivity are connected by the Wiedemann–Franz law, is predicted by the theories of size effects developed for electrically conducting films.[1,3,4] In the case when the electron mean free path (l_0) is commensurate with the film thickness, the classical theory of the external size effect predicts the relation[1,4]

$$\frac{\lambda}{\lambda_0} \approx \frac{\sigma}{\sigma_0} = 1 - \frac{3}{2\gamma}(1-p) \int_1^\infty \left(\frac{1}{a^3} - \frac{1}{a^5} \right) \frac{1-e^{-\gamma a}}{1-pe^{-\gamma a}} da, \tag{5}$$

where $\gamma = t/l_0$; p is the reflection coefficient and ranges from zero for diffusion reflection of the electrons by the film surfaces to unity in the case of specular reflection.

The theory has been developed for single-crystal objects, but can be used also for polycrystalline films, but those whose thickness subtends over only one block, and for which $\mathscr{L} \gg l_0$. In the case $l_0 \gtrsim \mathscr{L}$ but $l_0 \ll t$ (columnar shape of the blocks), it is necessary to take into account the contributions of the block boundaries to the conductivity (the internal size effect)[3]:

$$\sigma_b/\sigma_0 = 3[{}^1/_3 - {}^1/_2\alpha + \alpha^2 - \alpha^3 \ln(1 + 1/\alpha)], \tag{6}$$

where $\alpha = l_0 r/\mathscr{L}(1 - r)$ and r is the coefficient of electron deflection from the block boundaries.

At $l_0 \gtrsim \mathscr{L}$, the external and internal effects can be commensurate and the dependence of the conductivity on the thickness can be due to scattering of the electrons both from the surfaces and from the boundaries of the blocks, the dimensions of which, as a rule, increase with increasing film thickness.[5] To compare experiment with theory it is necessary to have information not only on the dimensions and shape of the blocks, but also on the concentration and distribution of the defects of the crystal lattice. An analysis of the electron-microscopy photograph shows that the predominant type of defects in the investigated film are the block boundaries. This still leaves open the question of other defects that cannot be resolved by microscopy. There are, however, indirect data evidencing perfection of the blocks. Thus, annealing of aluminum condensates obtained by induction, with thickness on the order of 10^6 Å, brings the physical properties closer to those of the bulk metal.[16]

Structural investigations and data on the reflection coefficient make it possible to estimate the contribution of the boundaries to the conductivity. At a value $r = 0.15$ for thin films of aluminum[3] and $l_0 = 320$ Å, it follows from (5) that $1 - \sigma_b/\sigma_0 = 0.05$. Thus, the model of the structure of the investigated films (single-block in thickness and appreciable excess of block dimension over the mean free path) allows us to neglect the internal size effect and to compare the experimental data on the thermal conductivity with the Fuchs theory.

Figure 3 shows the results of the experiment and a plot of the coefficient of thermal conductivity against thickness for the case of diffuse scattering of the electrons by the surface of the film. The data needed for plotting the curve were taken from the literature.[4] The results of the comparison offer evidence of good agreement between experiment and theory.

Thermal diffusivity and heat capacity. The experimental results on the thermal diffusivity of the films show that with increasing thickness the diffusivity coefficient increases, and at thicknesses $\sim 10^3$ Å it reaches the value of k for bulk aluminum, namely 0.94 cm^2 sec^{-1}. From the experimentally obtained values of the thermal conductivity and diffusivity, we calculated the specific heat. The information needed for this purpose on the film density was taken from the literature. The published data based on a comparison of the mass

TABLE I. Experimental data on aluminum films.

t, Å	$\mathscr{L}$, Å	λ, W/cm-deg	k, cm^2/sec	c, J/g-deg
500	10^3	1.6	0.7	0.86
740	$1.5 \cdot 10^3$	2	0.85	0.87
1100	$2.5 \cdot 10^3$	2.2	0.95	0.85
Bulk aluminum	–	2.2–2.3	0.94	0.89

Note. t—film thickness, $\mathscr{L}$—average block dimension in the film plane, λ—coefficient of thermal conductivity, k—coefficient of thermal diffusivity, c—specific heat.

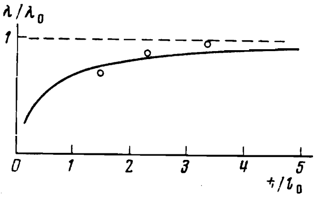

FIG. 3. Change of the ratio of the thermal-conductivity coefficient of aluminum films to the bulk value as a function of the normalized thickness.

thickness (the quartz-vibrator method, the calorimetric method) and the geometric thickness (multiple-wave interferometry) offer evidence that the film density at the investigated thicknesses, within a measurement accuracy 3–5%, coincides with the density of the bulk metal.[18–20] In this case the specific heat of the films does not depend on the thickness and coincides, within the ~ 10% accuracy limit of the measurement procedure, with the data for the bulk metal. It follows also that the thermal conductivity is the main cause of the change in the diffusivity of thin films.

Thus, the experimental data on the thermal conductivity and diffusivity of thin films of aluminum, with structure close to equilibrium, is well described by the classical theory of the size effect. A deviation of the specific heat of the films from the value for the bulk metal can be expected only at low temperatures, where the size factor can greatly influence the value of c.[2]

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Thermodynamics of disordered Heisenberg ferromagnets near the threshold concentration (percolation threshold)

E. F. Shender

Nuclear Physics Institute, USSR Academy of Sciences, Leningrad

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The temperature and concentration dependences of the specific heat and magnetization for a disordered Heisenberg ferromagnet in which the concentration x of magnetic atoms is close to the percolation threshold x_c are calculated with the aid of a scaling hypothesis formulated earlier for the percolation problem. The dependence of the Curie temperature on $x-x_c$ is also obtained.

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In solid solutions of magnetic and nonmagnetic materials, in the framework of a model in which nearest magnetic neighbors interact, macroscopic magnetic order arises only if the concentration x of magnetic atoms exceeds the threshold value x_c determined by percolation theory. For $x<x_c$ the probability of existence of an infinite connected cluster of magnetic atoms is equal to zero, while for $x>x_c$ this probability is nonzero and so macroscopic magnetic order appears at sufficiently low temperatures. The thermodynamics of such systems, both with Ising and with Heisenberg interactions of the localized spins, has been investigated repeatedly with the aid of high-temperature and concentration expansions.[1] However, near the percolation threshold, for $|x-x_c|/x_c \ll 1$, because of the poor convergence of the corresponding series, these methods have been found ineffective: it has not been possible to obtain by means of them the temperature and concentration dependences of the thermodynamic quantities.

In the present paper the thermodynamics of disor-