

Investigation of disordered bismuth and cadmium films

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An investigation has been made of electrical properties of bismuth and cadmium films deposited through a superfluid helium layer at a temperature of about 0.5 K. Films prepared under these conditions are insulating up to thicknesses of $\sim 100 \text{ \AA}$; the appearance of conduction is due to modification of the film structure on increase of their thickness. Films of thickness slightly exceeding that corresponding to the onset of conduction exhibit semiconducting properties; a further increase of the thickness results in a transition to the metallic state. In this state the films of both metals are superconducting and their critical temperatures ($T_c \approx 1.1 \text{ K}$ for cadmium and $T_c \approx 5 \text{ K}$ for bismuth) are practically independent of the resistance. The superconducting transitions have been observed in films of resistance $R_{\square} \leq 2 \times 10^5 \Omega$. The resistivity ρ of films with $R_{\square} \approx 10^5 \Omega$ is $\sim 0.1 \Omega \cdot \text{cm}$ and in the case of greater thicknesses, when ρ is practically independent of thickness, it is found that $\rho \approx 10^{-3} \Omega \cdot \text{cm}$.

Experimental studies of metal films formed by evaporation on a substrate covered by a superfluid helium layer^{1,2} have revealed unusual electrical properties. The main idea behind these experiments was to study the films formed as a result of condensation of atoms of kinetic energy much lower than in the case of the usual evaporation in air. The effective retardation of the metal atoms was ensured by the characteristics of the interaction between moving particles and the superfluid liquid. As long as the velocity of an atom v exceeds the critical velocity of superfluid motion $v_c \approx 60 \text{ m/s}$, the mean free path should be on the order of the interatomic distance, whereas at lower velocities the mean free path should be governed by temperature and at low temperatures it could be long, thus ensuring that the mean free path exceeds the distance from the surface of the liquid helium to the substrate on which a film is being deposited. This specific impurity atom motion in superfluid helium leads, on the one hand, to a considerable reduction in the kinetic energy and momentum of the condensing metal atoms and, on the other, makes it possible to avoid mutual collisions and coalescence of metal atoms to form clusters on the way from the surface of the liquid to the substrate.

We shall report the results of an experimental investigation of bismuth and cadmium films prepared by such condensation of metal atoms through a superfluid helium layer. We shall also give the results of a study of ordinary cold-deposited films of the same metals.

I. EXPERIMENTAL METHOD

1. Construction of the deposition system

A schematic diagram of the deposition system is shown in Fig. 1. A beam of atoms from an evaporator 7 condensed on a substrate 10 located in the low-temperature part of the system under a layer of liquid helium. The evaporator–substrate distance was 7.5 cm. The bulk of the power dissipated in the evaporator was removed by copper screens 8 cooled with liquid nitrogen circulated along a coiled pipe soldered to a copper disk 1. A series of diaphragms in a beam entry tube limited the power of the radiation propagating from the radiator to the low-temperature part of the system.

The system was located in the upper part of a conventional glass Dewar slightly above the level of liquid helium.

It was cooled by supplying helium to the cover of the vacuum jacket by the thermomechanical effect (the helium temperature was about 1.5 K). This made it possible to heat and subsequently cool the system without losing helium from the Dewar by evaporation. It was found that 3 liters of helium poured into the Dewar was sufficient to operate the system for 4.5 h.

The low-temperature part of the system was located inside a vacuum jacket 2 and cooled by a cryostat operating on the basis of pumping of helium-3 vapor. Helium-3 was pumped by a DRN-50 mercury diffusion pump and the minimum temperature achieved without admission of helium-4 into the system was 0.33 K; supplying helium increased the temperature because of the additional heat associated with the flow of helium inside a superfluid film and the temperature of the bath during the deposition of metal films through helium was 0.46 K.

The equilibrium helium vapor pressure at $T = 0.46 \text{ K}$ was $3 \times 10^{-6} \text{ Torr}$, which corresponded to good vacuum; however, in the presence of a superfluid film its flow in the direction of the temperature gradient (in the present case upward along the tube used to admit the beam) and evaporation in the warmer parts of the system could increase considerably the actual pressure. This effect was avoided by employing a special helium film suppressor (similar construction was used for the same purpose in solution cryostats described in Refs. 3 and 4).

This film suppressor consisted of two large-surface copper structures forming a film evaporator 9 and a helium vapor condenser 4 (Fig. 1). The condenser 4 was at the helium-3 bath temperature and the evaporator was attached to the thin-walled beam entry tube; the temperature of the evaporator could be raised by a special heater. The helium film followed a path identified by dashed lines in Fig. 1; in the course of its travel toward the beam entry tube the film reached the evaporator and, if the evaporator was supplied with sufficient power, the film evaporated completely and then condensed on the cold parts of the system.

The optimal power supplied to the film suppressor was found by trial and error and amounted to 2 mW; this value was in agreement with the known velocity flow of a helium film and the minimum value of the perimeter of the path of the film, which in our system was 3 cm. When the heater in

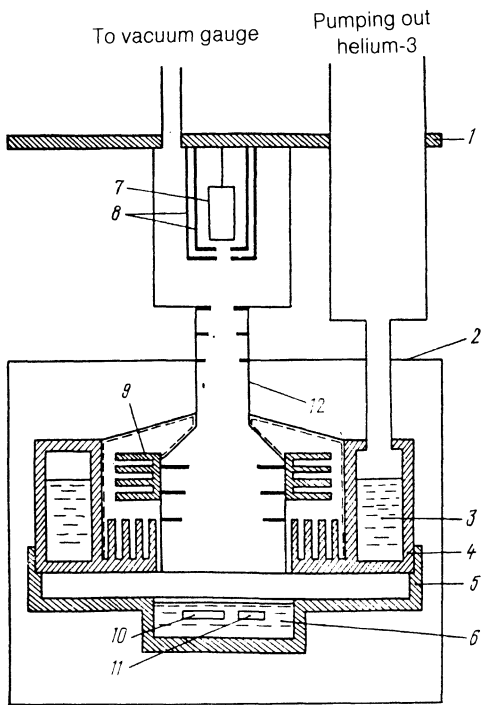


FIG. 1. General layout of the evaporation system: 1) copper disk; 2) vacuum jacket; 3) helium-3; 4) casing; 5) lower part of the system; 6) helium-4; 7) metal evaporator; 8) heat screens; 9) helium film evaporator; 10) substrate; 11) quartz resonator for thickness measurements; 12) tube for admission of a beam of metal atoms.

the film evaporator was switched on, the helium pressure in the upper part of the beam entry tube fell by a factor of approximately 100 and became equal to the saturated vapor pressure at the temperature of the experiment. The temperature of the helium-4 bath fell by 2–3 mK; this effect was due to the fact that when the suppressor was working, the process of helium film evaporation occurred at a lower temperature, so there was a corresponding reduction in the heat content of the condensing gas.

It would undoubtedly be of interest to compare the properties of metal films deposited through helium with the properties of conventional cold-deposited films of the same metals cold-deposited in the same system. Vacuum evaporation was carried out by replacing the lower part of the system (5 in Fig. 1) by a different part (Fig. 2). A soldered stainless steel tube with a flange 5 was attached to the copper bottom of the system. An indium seal was used to support a substrate 3 (with a diameter of 1 cm) on the flange. A mask 1 was placed above it, with apertures for the formation of the required geometry of the investigated film. The region under the substrate could be filled with liquid helium, which also served as a heat-exchange medium for cooling the substrate. A heater 6 made it possible to heat the substrate before the deposition (the same procedure could be used to heat the substrate to room temperature even after helium had been poured into the Dewar).

Figure 3 shows the construction of a metal evaporator. The body of the evaporator was made of molybdenum and it had two cavities which were closed by molybdenum covers. A heater of tantalum wire, wound on a ceramic aluminum oxide cylinder was placed in the upper cavity. The evaporat-

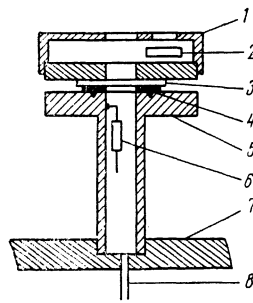


FIG. 2. Substrate support used during evaporation in vacuum: 1) mask; 2) thickness measuring instrument; 3) substrate; 4) indium seal; 5) flange; 6) heater; 7) lower part of the system; 8) capillary for admission of helium.

ed metal was located in the lower cavity; an aperture in the upper cover, 1 mm in diameter, was used to release a beam of the metal atoms being evaporated. A tantalum foil tube placed inside the aperture prevented the escape of any liquid metal from the evaporator. The evaporator was wrapped in silver foil in order to reduce the effects of thermal radiation. Heating to 700 °C, when bismuth evaporated, was achieved with a power consumption of 4 W in the evaporator. The temperature of the evaporator was monitored with a copper-constantan thermocouple.

2. Measurement techniques

The evaporation process was monitored employing a shift of the resonance frequency of a quartz resonator located in the direct vicinity of the substrate (Figs. 1 and 2). Use was made of a quartz crystal with a resonant frequency of about 10 MHz. The sensitivity of the quartz resonator was determined in special experiments in which a known amount of tin was deposited by evaporation and was equal to $2 \times 10^{-9} \text{ g cm}^{-2} \text{ Hz}^{-1}$; converted to the thickness this amounted to $\sim 30 \text{ Hz}/\text{\AA}$.¹⁾ Relative measurements of the film thickness yielded results with an error of at most 0.1 Å, while the error in the absolute values was governed by the precision of calibration and amounted to about 10%.

Our substrates were polished single-crystal sapphire plates 0.5 mm thick (the deviation of the sixfold axis from the normal to the substrate was a few angular minutes). Cathode sputtering was used to deposit platinum electrodes

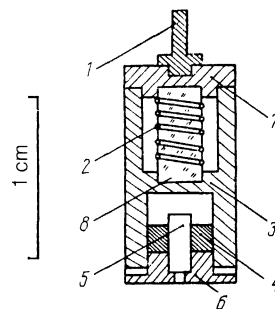


FIG. 3. Metal evaporator: 1) holder; 2) heater; 3) casing; 4) metal being evaporated; 5) foil tube; 6) lower cover; 7) upper cover; 8) ceramic cylinder.

on the substrates (Fig. 4). The scattering effect of liquid helium was as follows: The narrow parts of the film were somewhat thinner and these experiments were carried out using a simpler electrode geometry (Fig. 4b). Platinum poles, soldered to the measuring leads, were used as the film contacts.

The film resistance was measured under dc conditions. The voltages in the current were determined either with the aid of F-30 digital voltmeters or with VK2-16 electrometers, which was done in the case of high-resistivity films.

In addition to measuring electrodes, we evaporated a platinum heater on the side of a substrate opposite to that used for the evaporation via helium; this heater could raise the substrate temperature to 400 °C directly in the system. In the case of cadmium films such vacuum heating made it possible to remove cadmium from the substrate and thus prepare the system for the next evaporation. In the case of bismuth the heating process was used to remove possible volatile contamination from the substrate.

3. Sequence of operations

Before film deposition the system was pumped out by a sorption pump for 24 h and then heated to 80 °C for several hours. After such conditioning the pressure in the system was $(2-5) \times 10^{-5}$ Torr. The system was then cooled to liquid nitrogen temperature and disconnected from the pump.

After helium was poured into the outer Dewar, a thermomechanical pump was switched on. It delivered helium to the cover of the vacuum jacket; this resulted in an effective sorption of the residual gases on the surfaces of the system kept at helium temperature. After 5–10 min the sapphire substrate was heated to 400 °C for a period of 2–3 min (in the case of vacuum evaporation the substrate was heated to room temperature); during this time the temperature of the system as a whole hardly increased. Heating in high vacuum was used in final cleaning of the substrate.

Gaseous helium-4 was admitted into the low-temperature part of the system after heating of the substrate. This was followed by further cooling of the system and helium condensation. The helium admitted to the system was subjected to preliminary purification by removal of helium-3 impurities with the aid of the thermomechanical effect (the cleaning method was described in Ref. 5). Condensation of gaseous helium involved passage through a carbon trap cooled with liquid nitrogen, a porous nickel filter, and a long capillary (internal diameter 0.1 mm); a large part of the capillary was kept at liquid helium temperature. The thick-

ness of the liquid helium layer above the substrate (0.5–1 mm) was deduced from the volume of the condensed gas, which gave values accurate to within ~ 0.1 mm.

In the case of cadmium films the completion of the measurements was followed by heating the system to a temperature in the range 80–100 K and removal of helium by pumping. Then, switching on the supply of liquid helium to the vacuum jacket (to ensure high vacuum), we followed the same substrate heating program as at the beginning of the experiment, and cadmium was evaporated from the substrate. This evaporation of cadmium made it possible to carry out repeated experiments in which films were deposited without opening the system to the atmosphere. Experiments with deposition of bismuth through a liquid helium layer or by vacuum evaporation required replacement of the substrates after each experiment.

II. MOTION OF METAL ATOMS IN LIQUID HELIUM

At the deposition temperature the saturated vapor pressure above liquid helium was negligible and the metal atoms traveled from the evaporator to the surface of the liquid without encountering helium atoms. The velocity of the metal atoms reaching the surface of helium (500–600 m/s) exceeded the velocity of sound in liquid helium, $v_s = 240$ m/s. For such supersonic atoms the layer of superfluid helium behaves as an ordinary liquid and the mean free path should be of the order of the interatomic distance (the case of retardation of heavy supersonic atoms in normal helium was considered theoretically in Ref. 6 and it was found that the range of these atoms to the stopping point was 50 Å).

Deceleration of metal atoms in superfluid helium can be regarded as a consequence of the emission of Cherenkov radiation of normal excitations in a superfluid liquid. For atom velocities $v > v_s$ we would expect mainly the emission of phonons, whereas for $v < v_s$ the emission of phonons would be impossible and further retardation should occur as a result of emission of rotons. Such retardation accompanied by the formation of quasiparticles is possible as long as the metal atom velocity exceeds the critical velocity of superfluid motion v_c and the atoms with lower velocities can interact only with the quasiparticles present in helium.⁷

It should also be pointed out that a neutral impurity atom in liquid helium should clearly be surrounded by a sphere of solid helium, by analogy with the case of positive ions.²⁾ The radius of such an aggregate can be estimated by comparing the energy of the polarization interaction of a helium atom with a point charge $U_1 = A/r^4$ and the energy of the van der Waals interaction with a heavy impurity atom $U_2 = B/r^6$. If r_1 is used to denote the radius of a positive ion in helium, the corresponding radius of a neutral atom is $r_2 = (A/B)^{1/6} r_1^{2/3}$. The values of the constants A and B are known to within the nearest order of magnitude (see Refs. 9–11) and the ratio of these constants is given by $(A/B)^{1/6} \approx 1 \text{ \AA}^{1/3}$; since $r_1 \approx 7 \text{ \AA}$ (Refs. 9 and 10), it follows that $r_2 \approx 4 \text{ \AA}$.

Formation of a solid helium sphere around a metal atom,³⁾ which naturally occurs after deceleration to the velocity $v \approx v_c$, increases the effective mass of an atom and further reduces its velocity (this process occurs with conservation of momentum). The magnitude of the effect should be of order 50% for cadmium and somewhat less for the heavier bismuth.

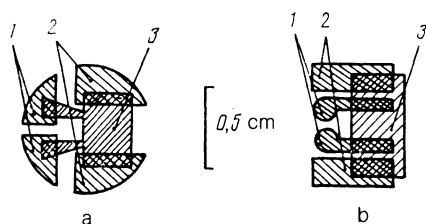


FIG. 4. Geometry of the film and measuring electrodes in the case of evaporation in vacuum (a) and evaporation through a helium layer (b): 1) potential electrodes; 2) current electrodes; 3) investigated film.

We thus find that a neutral metal atom in liquid helium may be surrounded by a layer of localized helium atoms and that the resultant aggregate may move at a velocity much lower than v_c . As pointed out already, such a slow atom may interact only with excitations present in superfluid helium, but at temperatures $T \ll 0.5$ K there are practically no rotons in helium, whereas phonons at such lower temperatures have little effect on the motion of a heavy particle because of the smallness of the scattering cross section and of the transferred momentum. In other words, the motion of a metal atom in a superfluid liquid after deceleration to $v \ll v_c$ should occur without a change in the absolute value and direction of velocity, by analogy with the motion of a free particle in vacuum.

We shall now consider the influence of the existence of a shell of localized helium atoms on the formation of a metal film. First of all, the energy of the interaction of metal atoms with one another is several times greater than the energy of their interaction with helium atoms, and the presence of a helium shell cannot disturb the approach of metal atoms (helium atoms should then be simply pushed out into the liquid).⁴⁾ One should point out nevertheless that the presence of a shell consisting of helium atoms should slow down the process of approach between metal atoms and this in turn should increase the time during which the evolution of the condensation energy takes place (we are speaking here of the binding energy which is released as a result of condensation of atoms of zero kinetic energy). This may reduce greatly the local overheating of the resultant metal film during condensation of atoms, especially as some of the condensation energy may be transferred directly to helium atoms which have left the localized states in the investigated liquid.

III. PROPERTIES OF FILMS PREPARED BY EVAPORATION IN VACUUM

Investigations of the usual cold-deposited bismuth and cadmium films had a number of purposes. The properties of bismuth films, particularly their superconductivity, had been investigated thoroughly and the agreement between our results and the published data should make it possible to check that the film evaporation conditions in our system yielded were sufficiently clean. Cold-deposited cadmium films were investigated much less^{12,13} and the results reported below are of intrinsic interest.

When films were evaporated in vacuum the substrate temperature was kept at about 0.5 K, exactly as in the case of evaporation through helium. The appearance of conduction was monitored by applying a potential difference of 1 V to the current contacts of a film during evaporation; this was done using a series resistance of $10^9 \Omega$. The sensitivity of the current was somewhat better than 10^{-10} A, and we could detect the appearance of conduction when the conductance reached $10^{-10} \Omega^{-1}$. The experiments were then continued as follows: The film thickness was increased somewhat and electrical properties of the film were investigated in the temperature range 0.35–2.1 K (in the case of bismuth films the upper limit of this interval was increased to a temperature exceeding the critical temperature of the superconducting transition of the film in question). We thus investigated a batch of films of different thicknesses in the course of the same experiment.

A significant conductance appeared in films of both metals with the same thickness $d = 10 \text{ \AA}$. Thin and high-resistance films exhibited semiconductor-type temperature dependence of the resistance. An increase in the thickness reduced the resistance rapidly and its temperature dependence disappeared practically completely (low-resistance films of these metals were superconductors and we are speaking here of temperatures above the critical temperature of the superconducting transition).

According to current theoretical ideas, an important role in the process of conduction in two-dimensional disordered systems is played by localization and electron interaction. In films of relatively low resistance these effects give rise to quantum corrections to the classical metallic conductance. This is known as the weak localization regime and the temperature dependence of the conductance $\sigma_{\square}(T)$ (see, for example, the review in Ref. 14) is as follows:

$$\frac{\sigma_{\square}(T)}{\sigma_{\square}(T_1)} = 1 + \frac{\ln(T/T_1)}{R_1 \sigma_{\square}(T_1)}. \quad (1)$$

Here, T_1 is some arbitrary temperature and $R_1 \sim 2\pi^2 \hbar / e^2 \approx 80 \text{ k}\Omega$ (e is the electron charge); the actual value of this constant depends on the details of the interaction of electrons and on the inelastic scattering mechanisms.

At high resistances a transition takes place to the strong localization regime, i.e., to the case when all the electrons are localized and the process of conduction involves activated jumps of electrons from one localized state to another. The temperature dependence of the conductance under conditions of low-temperature hopping conduction is described by the Mott law,¹⁵ which in the two-dimensional case is

$$\sigma_{\square}(T) = \sigma_{\square}^{(0)} \exp\{- (T_0/T)^{1/2}\}. \quad (2)$$

At present there are also other theoretical models of hopping conduction (see Refs. 16 and 17), but the results of our measurements fit in fact the Mott dependences.

Figure 5a shows the dependences $\sigma_{\square}(T)$ plotted using the Mott coordinates, whereas Fig. 5b gives the results using the coordinates corresponding to Eq. (1). It is clear from these parts of the figure that when the film thickness is increased, a transition takes place from the exponential Mott dependence of Eq. (2) to the logarithmic dependence of Eq. (1). Interesting results were obtained for a 12- \AA thick film: All the points which deviated from the straight line in Fig. 1a at temperatures above 1 K fitted very well the straight line in Fig. 5b; this nature of the dependence shows that the transition from the strong to the weak localization on increase in temperature occurs in a very narrow temperature interval, so that there is no transition region between the different types of dependence.

Figure 6 shows the superconducting transitions in cadmium films of different thickness (similar results for bismuth films were given in Ref. 2). The corresponding dependences of the critical temperature on R_{\square} are plotted in Fig. 7. In qualitative agreement with the theoretical predictions,^{21,22} we found that the films of both metals exhibited a reduction in T_c as the film resistance increased, so that the superconducting transition was no longer exhibited by films with resistances in the range $R_{\square} > 15 \text{ k}\Omega$ in the case of bismuth and $R_{\square} > 10 \text{ k}\Omega$ in the case of cadmium.

An increase in the thickness revealed considerable dif-

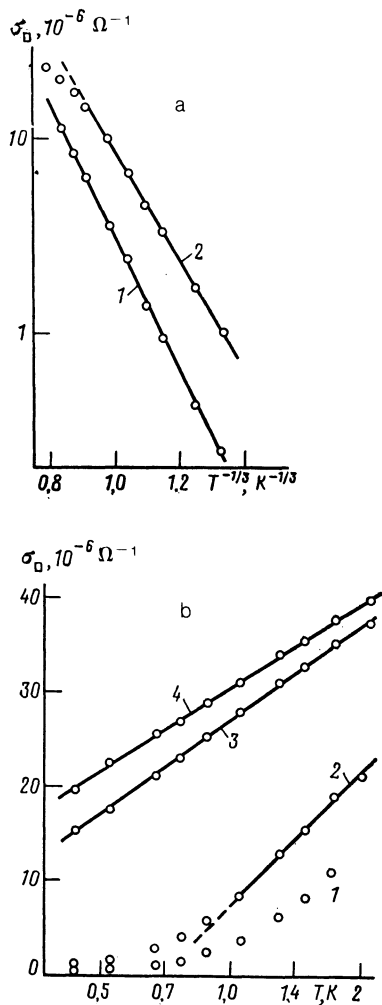


FIG. 5. Temperature dependence of the conductance of bismuth films plotted using different coordinates: 1) $d = 11 \text{ \AA}$; 2) $d = 12 \text{ \AA}$; 3) $d = 16.3 \text{ \AA}$; 4) $d = 16.3 \text{ \AA}$ (after heating to 7 K).

ferences in the behavior of bismuth and cadmium films: In the case of bismuth the temperature T_c increased monotonically as R_{\square} was reduced, whereas in the case of cadmium the initial rise of T_c with increasing thickness and reduction in the film resistance changed to a decrease of this temperature (Fig. 7a). This behavior of cadmium films was most probably due to the onset of crystallization of the initially amorphous structure.

In the case of thin films it would be natural to expect an amorphous structure for cold-deposited films of any metals. The stability of a metastable amorphous state is governed by the height of the potential barriers hindering the motion of atoms to positions expected in an equilibrium crystal structure. In the case of some metals, such as bismuth and gallium, the amorphous state is fairly stable and the transition to the crystalline state in thin films occurs only close to room temperatures. The transition of films to the crystalline state at low temperatures occurs at higher thicknesses and is of avalanche nature: A fluctuation-induced transition in a small part of the film releases a considerable energy which overheats the film and thus stimulates the transition to the crystalline state in a large part or the whole of the film.

However, we can also imagine a situation when the

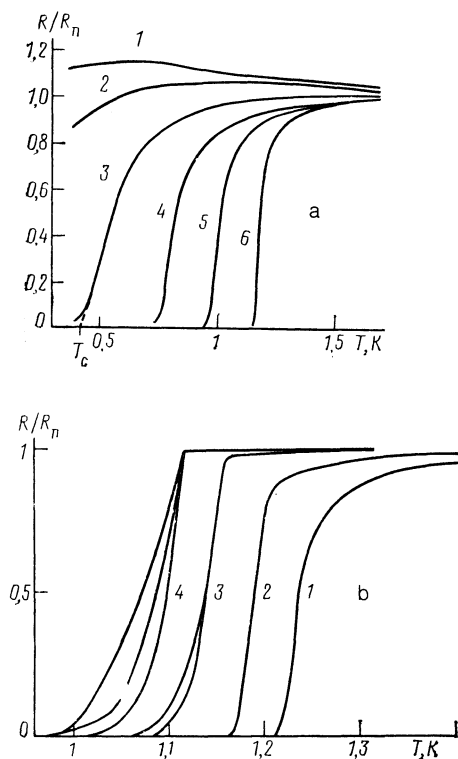


FIG. 6. Superconducting transitions in Cd films. a) High-resistance films (the dashed part of the curve shows the method of determination of T_c): 1) $d = 11.3 \text{ \AA}$, $R_{\square} = 12.2 \text{ k}\Omega/\square$; 2) $d = 11.6 \text{ \AA}$, $R_{\square} = 9.2 \text{ k}\Omega/\square$; 3) $d = 12.2 \text{ \AA}$, $R_{\square} = 5.4 \text{ k}\Omega/\square$; 4) $d = 13.1 \text{ \AA}$, $R_{\square} = 2.9 \text{ k}\Omega/\square$; 5) $d = 14.4 \text{ \AA}$, $R_{\square} = 1.64 \text{ k}\Omega/\square$; 6) $d = 17.2 \text{ \AA}$, $R_{\square} = 0.7 \text{ k}\Omega/\square$. b) Low-resistance films, investigated using different values of the measuring current i : 1) $d = 22.2 \text{ \AA}$, $R_{\square} = 300 \Omega/\square$; 2) $d = 28.4 \text{ \AA}$, $R_{\square} = 160 \Omega/\square$; 3) $d = 44 \text{ \AA}$, $R_{\square} = 73 \Omega/\square$, $i = 10 \mu\text{A}$; 4) $d = 70 \text{ \AA}$, $R_{\square} = 35 \Omega/\square$, $i = 4 \mu\text{A}$, $i = 10 \mu\text{A}$, $i = 20 \mu\text{A}$.

height of the potential barriers is low. In this case the perturbations in the film, which appear as a result of condensation of single atoms, may be sufficient to result in a local modification of the structure without any significant overheating of the film relative to the substrate. It seems to us that this is the nature of the process of crystallization of cold-deposited cadmium films.

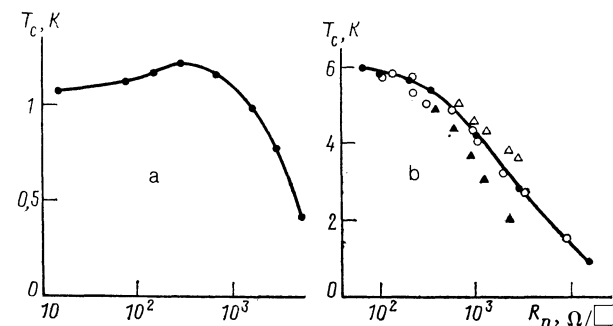


FIG. 7. Dependence of the critical temperature on the resistance of cadmium (a) and bismuth (b) films. Different symbols represent the results obtained in different investigations: \bullet) our results; \circ) results from Ref. 18; \blacktriangle) results from Ref. 19; \triangle) results from Ref. 20.

Since the temperature of the superconducting transition of crystalline cadmium (0.52 K) is less than T_c of the amorphous modification, ordering of the structure should lower T_c , as was indeed found in our experiments. Such crystallization could disturb the homogeneity of the film and inclusions of a phase with a lower critical temperature could cause redistribution of the current in the film and this might destroy the superconductivity in regions with the maximum current density. Therefore, the experimentally observed dependence of the shape of the superconducting transition curve on the measuring current (Fig. 6b) is in agreement with the hypothesis of gradual crystallization.

Lowering of the critical temperature with increasing thickness of cold-deposited films has been reported also for other metals (aluminum and tin,¹⁹ mercury,²³ and beryllium²⁴⁻²⁶); all these metals exhibit crystalline modifications with a lower critical temperature than that of amorphous films. In the case of beryllium this effect can also be explained by gradual crystallization of the films²⁵; films of beryllium with $d > 100 \text{ \AA}$ also exhibit a dependence of the shape of the superconducting transition curve on the measuring current.

IV. PROPERTIES OF FILMS EVAPORATED THROUGH A LIQUID HELIUM LAYER

The experiments carried out on cadmium and bismuth were slightly different. As pointed out already, it was possible to evaporate cadmium films repeatedly without taking the system apart: This allowed us to carry out a wide variety of experiments on cadmium. Four experiments were carried out on bismuth films. In each of them we studied the effects of additional evaporation on the films. It was found that the properties of the films were independent of the thickness of the helium layer in the range 0.1–1 mm and of the temperature of the helium bath right up to 0.52 K (helium vapor prevented evaporation of bismuth at higher temperatures).

1. Onset of conduction

We observed conduction in the films prepared by evaporation through helium at thicknesses much higher than those needed for the onset of conduction in the case of the vacuum-evaporated films. For example, in the case of cadmium the process of conduction appeared for films $d \approx 60 \text{ \AA}$ thick, whereas in the case of bismuth films this happened at $d \approx 120 \text{ \AA}$. These values of the thickness were purely nominal, because the real density of the films could differ from the density of bulk crystalline samples used in conversion of the results of our measurements. A more satisfactory characteristic was clearly the surface density of atoms in a film, and the value of this density when conduction appeared was practically the same for both metals: $\approx 3.5 \text{ at/\AA}^2$.

Films of thicknesses slightly exceeding the thickness for the onset of conduction had a high resistivity and the resistance depended strongly on the applied potential and on temperature; this was why we could not determine the film resistance in the ohmic region. Figure 8 shows the dependence of the current through cadmium films on their thickness when a constant potential $V = 1$ volt was applied to a film. Clearly, the conductivity rose by two orders of magnitude as the film thickness increased by just by 1 \AA ; such a rapid rise of the conductivity suggested that the thickness d_c

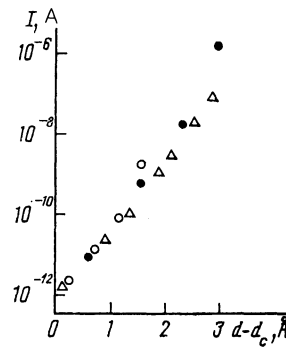


FIG. 8. Dependence of the current on the thickness of cadmium films near d_c ; the potential difference across the film was $V = 1$ volt. The different symbols represent different helium experiments.

at the onset of conduction was determined quite accurately, irrespective of the measurement method. This high increase of the conductivity as a function of the film thickness near d_c was observed also for bismuth films.

The structure of the films of thickness approaching d_c was very unstable and even slight heating resulted in irreversible changes of the resistance. This effect was exhibited by our cadmium films when they were heated to 1–1.5 K, whereas in the case of bismuth films this happened even at temperatures below 1 K. Figure 9 shows irreversible changes in the resistance with increasing temperature, which were due to modification of the film structure. It is clear from this figure that an increase in the film thickness made the films more stable and that significant changes in the resistance of the films for $d \approx 200 \text{ \AA}$ was observed only as a result of heating to 20–30 K.

The experiments on cadmium demonstrated also that in films of thickness $d < d_c$ we could induce conduction by heating a film (the annealing curves obtained for two such films are presented in Fig. 9). The temperature needed for this transition rose rapidly on reduction in the film thickness (Fig. 10).

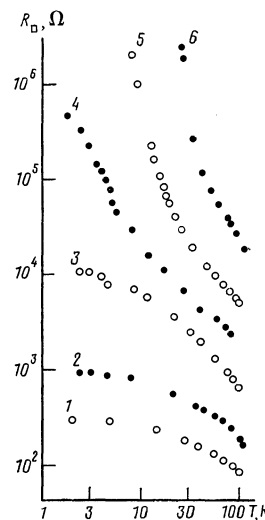


FIG. 9. Annealing curves of cadmium films of different thicknesses: 1) $d = 226 \text{ \AA}$; 2) $d = 124 \text{ \AA}$; 3) $d = 100 \text{ \AA}$; 4) $d = 76 \text{ \AA}$; 5) $d = 74 \text{ \AA}$; 6) $d = 63 \text{ \AA}$.

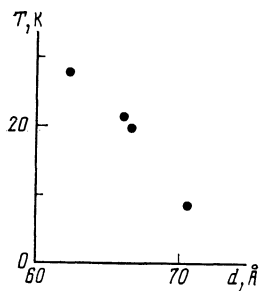


FIG. 10. Temperature of the onset of conduction as a function of the film thickness (at a fixed temperature when the film resistance was $10^7 \Omega/\square$).

The appearance of conduction only for very thick films and the extreme sensitivity of the film structure to an increase in temperature demonstrated that the appearance of conduction during evaporation was not a simple effect of an increase in the thickness but was due to modification of the film structure under the influence of the condensing atoms themselves, which became stronger on increase in the thickness.

A clear confirmation of this conclusion was provided by our experiments on bismuth. A film 128 Å thick had a resistance of 20 M Ω/\square at the evaporation temperature; when this film was heated to 1.28 K and then cooled again, its resistance fell to 420 k Ω/\square . Evaporation of a further 1.6 Å of bismuth had in fact no influence on the film resistance, but the subsequent heating to just 1.1 K reduced considerably the resistance; after cooling to the temperature at which evaporation took place (0.46 K) it became 110 k Ω/\square . Such an underestimate of the resistance was due to the fact that the condensation of additional atoms resulted in disturbance of the equilibrium of the film structure, which was the cause of the modification occurring as a result of a small increase in temperature. In other words, in the case of a conducting film one could condense a practically insulating layer of bismuth and the process of condensation of atoms did not result in modification of the already annealed film. This result also demonstrated that the deceleration of metal atoms in liquid helium was very effective and the influence of condensing atoms on the film structure was in any case weaker than heating of a film to 1.25 K.

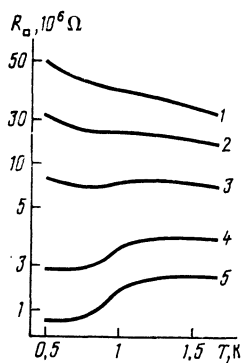


FIG. 11. Temperature dependence of the resistance of a Cd film ($d = 71.5 \text{ \AA}$) obtained on application of different potential differences V (mV): 1) 15; 2) 30; 3) 70; 4) 300; 5) 700.

2. Superconducting properties

Bismuth and cadmium films with a resistance $R_{\square} \geq 10^8 \Omega$ exhibited typical semiconductor-type temperature and electric-field dependences of the conductivity and showed no signs of a superconducting transition. A reduction in the resistance by additional evaporation or annealing of a film revealed a characteristic nonmonotonic behavior of the temperature dependence of the conductivity, which became clearer as the applied potential increased (Fig. 11). An increase in the potential difference across a film practically destroyed the temperature dependence of the resistance at high and low temperatures, so that this dependence approached a form typical of a superconducting transition in respect of the shape of the curve, but with a nonzero resistance below T_c .

Figure 12 illustrates superconducting transitions in cadmium films with different values of the resistance in the normal state (similar results for bismuth were published earlier²). It was found that films of both metals with a resistance in the normal state $R_n \leq 2 \times 10^5 \Omega/\square$ had the zero resistance below T_c , i.e., there were true superconductors.

The temperature of the superconducting transition in the films formed by evaporation through helium was practically independent of the resistance in the normal state throughout the range of resistances in which there were at least some manifestations of the superconductivity. The critical temperature of the cadmium films was 1.1 K and that of bismuth films was 5 K. Note that T_c of the films evaporated across helium was considerably less than for the conventional cold-deposited films of the same metal (since the criti-

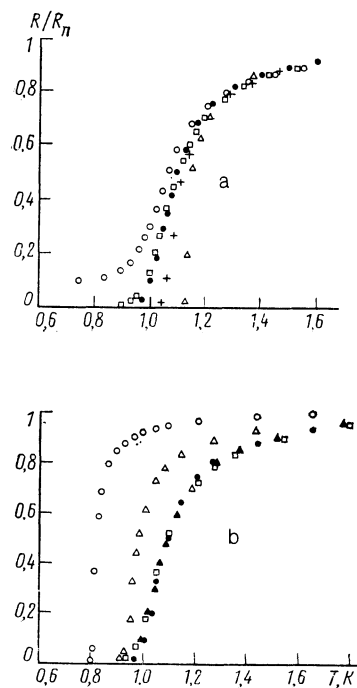


FIG. 12. Superconducting transitions in cadmium films: a) After heating to temperatures less than 2.5 K: \circ) $d = 75 \text{ \AA}$, $R_n = 1840 \text{ k}\Omega/\square$; \square) $d = 81 \text{ \AA}$, $R_n = 132 \text{ k}\Omega/\square$; \bullet) $d = 87 \text{ \AA}$, $R_n = 17.6 \text{ k}\Omega/\square$; $+$) $d = 112 \text{ \AA}$, $R_n = 4.4 \text{ k}\Omega/\square$; \triangle) $d = 189 \text{ \AA}$, $R_n = 0.82 \text{ k}\Omega/\square$. b) After heating to various temperatures T_1 : \square) $d = 79 \text{ \AA}$, $T_1 = 4.3 \text{ K}$, $R_n = 288 \text{ k}\Omega/\square$; \blacktriangle) $d = 87 \text{ \AA}$, $T_1 = 1.9 \text{ K}$, $R_n = 28.6 \text{ k}\Omega/\square$; \bullet) $d = 87 \text{ \AA}$, $T_1 = 4.4 \text{ K}$, $R_n = 17.6 \text{ k}\Omega/\square$; \triangle) $d = 79 \text{ \AA}$, $T_1 = 61.5 \text{ K}$, $R_n = 13.2 \text{ k}\Omega/\square$; \circ) $d = 87 \text{ \AA}$, $T_1 = 117 \text{ K}$, $R_n = 1 \text{ k}\Omega/\square$.

cal temperature of the vacuum-deposited films depended on the thickness, it was meaningful to speak only of the limiting value T_{c0} obtained for $R_{\square} \rightarrow 0$). In the case of bismuth films the difference between the critical temperatures was $\Delta T_c \approx 1$ K. The value of ΔT_c was more difficult to determine for cadmium films because crystallization of the films formed by vacuum evaporation made it impossible to determine accurately the critical temperature of thick amorphous cadmium films. Extrapolation of the dependence of T_c on R_{\square} for relatively thin films with $R_{\square} = 0$ (Fig. 7a), yielded an approximate estimate $T_{c0} \approx 1.3$ K. Therefore, the ratio $\Delta T_c / T_{c0} \approx 0.2$ was approximately the same for films of both metals.

The superconducting transitions in cadmium films after heating to various temperatures are demonstrated in Fig. 12b. As long as the temperature did not exceed 5–7 K, the superconducting transition curve did not change its profile and annealing at higher temperatures resulted in a considerable shift of the superconducting transition toward lower temperatures. The fall of T_c was obviously due to crystallization of the films, exactly as in the case of the conventional cold-deposited cadmium films discussed above.

In the case of cold-deposited bismuth films it is known that heating results in an abrupt transition to a nonsuperconducting crystalline state; this transition is accompanied by a considerable increase in the resistance. Bismuth films prepared by evaporation through helium exhibited a similar transition, but in this case it was spread over a temperature interval 10–15 K. The dependence of the temperature of this transition on the film thickness was weaker than for vacuum-deposited films: The temperature of the onset of the rise of the resistance as a result of increase in temperature changed from 40 K (for a film with $d = 230$ Å) to 50 K (for a film with $d = 140$ Å).

3. Discussion of results

It follows from the above experimental results that practically all the electrical properties of films formed by evaporation across a superfluid helium layer differed considerably from the properties of ordinary cold-deposited films.⁵⁾ These differences include also the appearance of conduction at much higher film thicknesses and a change in the film structure at very low temperatures (significant irreversible changes in the resistance during heating began at temperatures of ≈ 1 K); moreover, the superconducting properties of these films were found to be anomalous.

We first consider the superconducting properties. At present it can be regarded as firmly established that because of the two-dimensional localization effects, an increase in the surface resistance of the films R_{\square} should reduce the critical temperature of the superconducting transition, approaching zero for $R_{\square} \approx 10$ k Ω . At somewhat higher values of $R_{\square} \approx 30$ k Ω a metal–insulator transition should occur in the two-dimensional case. This conclusion follows from practically all the theoretical calculations and numerous experiments on cold-deposited films of different metals (these cold-deposited films were characterized by a high homogeneity and a comparatively high resistance making the samples a convenient object for such investigations). On the other hand, films evaporated through a liquid helium layer indicate that T_c of the resistance is completely independent;

a superconducting transition with zero residual resistance was observed right up to $R_{\square} \approx (2-3) \times 10^5 \Omega$.

The most probable cause of such unusual behavior is an anomalously large thickness of the films when sets in conduction. In view of their thicknesses, our films should therefore be regarded as three- and not two-dimensional. A film with $R_{\square} \sim 10^5 \Omega$, where electrons should be strongly localized because of their two-dimensional nature, can be regarded as a weakly localized three-dimensional object. In the three-dimensional case (see Ref. 27) the value of T_c may not vanish even at the localization threshold and approach to the threshold then results in broadening of the superconducting transition. It therefore follows that superconducting properties of our films at least do not contradict the hypothesis of their three-dimensional nature.

Figure 13 shows how $\rho^* = R_{\square} d^*$ depends on the film thickness d^* (we shall use this notation in order to stress the arbitrary nature of our value of the thickness). The value of ρ^* has the meaning of the resistivity (the film density may be only less than the density in the bulk samples and, consequently, the true values of the resistivity may even exceed somewhat the values of ρ^* given in this figure). It is clear from Fig. 13 that the resistivity of the films deposited through helium, even in the case of large thicknesses (where ρ^* is practically independent of d^*), exceeds tens of times the resistivity of both cold-deposited metal films. Such a high resistivity indicates that the mean free path of electrons in these films is of the order of the interatomic distance. In objects of this kind we should observe a particularly strong reduction in the electron diffusion coefficient D and the correction should be of the order of

$$\Delta D/D \sim -(a/l)^2 \quad (3)$$

where a is the interatomic distance and l is the mean free path. In the case when $l \sim a$, this correction is not small and an estimate given by Eq. (3) may be inaccurate, but nevertheless it is natural to assume that the diffusion coefficient is then small and the diffusion time of an electron from one surface of a film to the other is $t = d^2/D$ (d is the true film thickness) and it will exceed the inelastic scattering time. Under these conditions the films in the metallic-conduction region represent three-dimensional objects which are close to the metal–insulator transition (an analysis of high-resis-

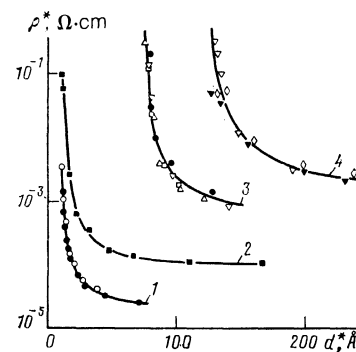


FIG. 13. Dependence of the electrical resistivity on the film thickness. Different symbols represent different helium experiments. Evaporation in vacuum: 1) cadmium film; 2) bismuth film. Evaporation across helium: 3) cadmium film; 4) bismuth film.

tance films acting as insulators is outside the scope of the present paper).

Figure 13 gives results which are somewhat arbitrary because of some indeterminacy in the value of d^* used in constructing Fig. 13, whereas Fig. 14 gives the dependence of R_{\square} on the directly measurable surface density of atoms n_s in the film. The coincidence of the dependences $R_{\square}(n_s)$ for such very different metals as bismuth and cadmium is surprising; on the other hand, it is difficult to imagine that such a coincidence in a wide range of changes in R_{\square} could be accidental.

In discussing the structure of our films, we should mention that they are less dense than the films obtained by vacuum evaporation. This is because in the latter case the kinetic energy of the condensing atoms cannot result in local overheating of the structure; we must bear in mind also the considerable momentum of the atoms in the direction of the substrate, which should increase the density of the film. In the opposite case, when the evaporation takes place through a superfluid helium layer, the substrate receives atoms with extremely low values of the kinetic energy and momentum. In this situation one could expect many more disordered structures.

Numerical modeling of the structure of these films in the limiting case of zero energy of the condensing atoms was reported in Ref. 28 (in these calculations the atoms were represented by hard spheres and the attraction between them was assumed to fall rapidly with the distance). These calculations yielded the structure of the most strongly disordered phase possible in a system of hard spheres. In spite of the fact that this model is somewhat primitive, it seems to us that it provides a correct approach to the experimental situation, and possibly to those structures which are obtained as a result of evaporation through a helium layer.

The density of such a model structure is almost 2.5 times less than that in the close-packed case. We can easily assume that in the case of such a low average density a film represents an insulator even if it consists of metal atoms. The appearance of conduction in our experiments was associated with the change in the film structure with increasing thickness. The change in the structure should be particularly noticeable in the case of thick films because an increase in the thickness enhances the degree of nonequilibrium and weakens the stabilizing influence of the substrate atoms at fixed positions. It should be stressed that any modification should

increase the density and the short-range order and thus give rise to conduction.

It is at present difficult to say whether the change in the structure under the influence of condensing atoms occurs during the growth of a film or whether such changes require a certain degree of instability of the structure, which is achieved only in the case of large thicknesses. The coincidence of the dependences $R_{\square}(n_s)$ for bismuth and cadmium (Fig. 14) makes the second possibility more probable. In fact, it is difficult to see how the process of continuous modification can give rise to conduction for the same value of n_s in the case of different metals; it is much more natural to consider a situation where up to a certain thickness the structure is formed initially, as proposed in the model of Ref. 28, without any changes during film growth. In this case both bismuth and cadmium films are simply identical because in the model of hard spheres all properties are determined by the value of n_s (it should be noted that the diameters of bismuth and cadmium atoms are practically identical). An increase in n_s in the film produces a considerable number of regions which are close to the stability limit, and condensation of the already slowed-down atoms should result in their modification; this modification may be significant and may give rise to conduction.

If we adopt this viewpoint, we must assume that right up to values of n_s close to the onset of conduction, i.e., up to $n_s \approx 3$ atoms/Å, the film structure is close to that found by calculation in Ref. 28. This gives the thickness $d \approx 130$ Å; a further increase in n_s does not increase the film thickness, but reduces it because of modification of the structure that increases the film density. Hence, we can estimate the critical value of the resistivity ρ_c at which the superconducting transition characterized by zero residual resistance is observed. Clearly, ρ_c is fairly high and amounts to $0.2 \Omega \cdot \text{cm}$.

It should be interesting to compare this value of ρ_c with the results reported for other objects and characterized by a high resistivity as well as superconductivity. Samples used in the published investigations on this topic were formed by simultaneous evaporation of a metal and an insulator. Among the numerous combinations of this kind the simplest and easiest to understand is the structure of granulated aluminum films formed by evaporation in oxygen. This method made it possible to prepare very homogeneous films with extremely small granules (~ 30 Å) whose resistivity could vary within wide limits because of variation in the oxide layer thickness on the granules. Superconducting transitions were reported to be exhibited by superconducting films of aluminum,²⁹⁻³¹ with a critical temperature practically independent of ρ ; the maximum values of ρ at which the true superconductivity was observed amounted, as in our experiments, to about $0.2 \Omega \cdot \text{cm}$. Approximately the same values of ρ_c were reported in Refs. 23 and 32 for cold-deposited mercury films.

It follows from the above analysis that in the case of three-dimensional objects there is a critical value of the resistivity, $\rho_c \approx 0.2 \Omega \cdot \text{cm}$, which is independent of the actual structure, at which superconductivity vanishes. It would be of interest to determine whether samples with such high values of ρ are metals or insulators in the normal state at $T > T_c$. Using the Mott concept of the existence of the minimum metallic conductance, we could say that they should be insulators, because $\rho_c \gg 1/\sigma_{\min} \approx 5 \cdot 10^{-3} \Omega \cdot \text{cm}$. However, it has

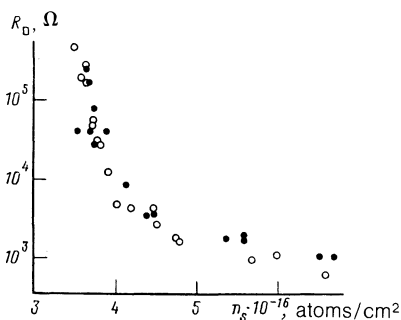


FIG. 14. Dependence of R_{\square} on the surface density of atoms: ● bismuth films; ○ cadmium films.

been recently confirmed experimentally and theoretically with some degree of error (see, for example, the reviews in Refs. 33–35), that even in the limit $T \rightarrow 0$ the metal–insulator transition may occur as a result of a gradual reduction in σ right down to $\sigma = 0$. Therefore, at present there are no serious objections against the possible existence of a metal with such values of the resistivity. Interpretation of the temperature and magnetic-field dependences of the conductivity (see, for example, Refs. 29 and 31) at finite temperatures is not very reliable, because there is no self-consistent theory describing the behavior of metallic objects near the metal–insulator transition. It is possible that a more reliable criterion of this transition would be when superconductivity disappears.

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- ¹⁾In the conversion we used the density of bulk crystalline samples of cadmium and bismuth.
- ²⁾In the case of some impurity atoms there are fairly accurate numerical calculations of this effect⁸; for example, the number of helium atoms associated with a xenon atom is 14.
- ³⁾This shell is only nominally solid helium; in fact, it represents a single layer of helium atoms localized near a metal atom, and, consequently, these helium atoms do not participate in the motion of the liquid.
- ⁴⁾A solid helium layer coats not only the condensing atoms but also all the solid surfaces immersed in liquid helium, including the freshly evaporated film.
- ⁵⁾The only exception is represented by cold-deposited mercury films,²³ which in many respects are similar to films evaporated across superfluid helium. The most probable reason for the similarity is an extremely low evaporation temperature of mercury (below 250 K). Experiments on mercury have stimulated our idea that the kinetic energy of the condensing atoms exerts of a considerable influence on the properties of cold-deposited films.
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