PECULIARITIES OF THE PROPERTIES OF BISMUTH LAYERS CONDENSED AT LIQUID-HELIUM TEMPERATURE

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Abstract

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Academician of the Academy of Sciences of the Ukrainian SSR B. G. LAZAREV,
V. M. KUZ' MENKO,
A. I. SUDOVTSOV, V. M. MEL' NIKOV

PECULIARITIES OF THE PROPERTIES OF BISMUTH LAYERS CONDENSED AT LIQUID-HELIUM TEMPERATURE

It was shown earlier that ytterbium (ˆ1) and iron (ˆ2), in layers obtained by condensation onto substrates cooled with liquid helium, remain in a modification different from that of the bulk metal (evidently amorphous) only up to a certain (critical) thickness. If during condensation the layer thickness exceeds the critical value, the metal abruptly transforms into its usual modification at liquid-helium temperature. It was assumed that, by analogy with ytterbium and iron, a critical thickness is apparently characteristic of all metallic films obtained by low-temperature condensation and possessing metastable phases different from the phases in the bulk state (ˆ2).

Of special interest from this point of view are nonsuperconducting metals that, upon low-temperature condensation, form superconducting phases. These include, in particular, bismuth and beryllium. If a critical thickness also exists for layers of these metals, then, evidently, upon its attainment in the course of condensation, superconductivity should disappear because of the transition of the metal to the usual nonsuperconducting modification.

The present communication is devoted to the discovery of a critical thickness in bismuth layers. As is known, bulk bismuth is not a superconductor down to the lowest temperatures. Hilsh (ˆ3) showed that bismuth layers obtained by condensation onto a substrate cooled with liquid helium are superconducting at a temperature of 6° K. As was subsequently shown by electron diffraction, freshly condensed bismuth layers have an amorphous structure. Upon annealing them above 14–20° K, superconductivity disappears, which is associated with a phase transition to normal crystalline bismuth (4,5). By the present time, bismuth layers condensed at liquid-helium temperature have been investigated in detail over a wide range of thicknesses ($3 \cdot 10^{-7} \div 2 \cdot 10^{-5}$ cm) (3-8), and in all cases they were superconducting.

Fig. 1. Diagram of the upper part of the working ampoule for obtaining metallic layers.

Figure 1 schematic

Figure 1: Figure 1 schematic

1 –ampoule body, 2 –substrate, 3 –platinum current leads, 4 –platinum potential leads

In the present work, bismuth layers were obtained by condensation in high vacuum onto a glass substrate cooled with liquid helium, according to the method described earlier (9,10). In order to improve heat removal, the temperature of the helium bath was maintained below 2° K (He II region). The disk geometry of the films proposed by N. E. Alekseevskii was used, allowing–

···allowing work with specimens in which the influence of the edges is minimal. The diagram of the upper part of the working ampoule with the substrate for obtaining such layers is shown in Fig. 1. The specimen obtained in such an ampoule had the form of a disk, at the center and at the edge of which there were electrodes for measuring the electrical resistance. In order to obtain purer specimens, part of the charge was evaporated with the substrate shutter closed. In this case, part of the bismuth with the gas adsorbed on it was evaporated and the tungsten heater was degassed. The initial bismuth had a purity of 99.9999%. The evaporation rate averaged 100–300 Å/min. The layer thickness was determined by an interferometric method.

The experimental results confirmed our assumption regarding the existence of a critical thickness in bismuth layers. Figure 2 presents a plot of the change in the resistance of a bismuth layer during condensation. In the initial period of evaporation, a superconducting modification of bismuth is formed, having the usual temperature dependence of resistance upon annealing (Fig. 3), from which it is evident that the phase transition from the amorphous to the crystalline state occurs in the temperature interval 12–35° K. The resistance of the layer by the end of the transition increases almost 20-fold. Bismuth layers with similar characteristics are formed only up to a certain thickness. From Fig. 2 it is seen that if, in the process of continuous condensation, this critical thickness is reached, a sharp step-like appearance of resistance occurs, characterizing an irreversible transformation into the ordinary nonsuperconducting modification. The value of the critical thickness for bismuth is approximately 600 Å. It should be noted, however, that this value depends strongly on the purity of the specimens. Thus, a bismuth specimen obtained from an unpurified charge by the indicated method undergoes a phase transition upon reaching a thickness of about 1300 Å. Figure 4 presents a plot of the dependence of resistance on the temperature of a bismuth layer of critical thickness (condensation was stopped at the moment resistance appeared (Fig. 2)).

Fig. 2. Change in the resistance of a bismuth layer during condensation; condensation rate ~350 Å/min.

The presence of superconductivity of the bismuth layer in the process of contin-

Fig. 2. Change in the resistance of a bismuth layer during condensation; condensation rate ~350 Å/min

Figure 2: Fig. 2. Change in the resistance of a bismuth layer during condensation; condensation rate ~350 Å/min

Fig. 3

Figure 3: Fig. 3

uous condensation in the steady regime indicates that overheating of the layer does not exceed the critical temperature, equal to 6° K. Moreover, an additional experiment using a previously condensed indium film, serving as a temperature indicator during the condensation of bismuth onto it, showed that the overheating is no more than 2° above the temperature of the helium bath (i.e., the temperature of the bismuth layer during condensation did not exceed 4° K).

As is seen from Fig. 4, at temperatures below 6° K there is a small reversible jump of resistance on the curve $R(T)$. It corresponds to the superconducting transition of the remnants of the amorphous phase (apparently located along the edges of the disk), which completely pass into the crystalline state after annealing to 25° K. The transition of the remnants of the amorphous bismuth phase into the crystalline phase corresponds to a small rise of resistance on the curve $R(T)$ in the region 10-20° K. Remnants of the amorphous phase were observed in all the layers investigated, with thicknesses from 600 to 1300 Å. It was not possible to obtain thicker layers because of their cracking during condensation.

It is curious that as early as 1952 N. V. Zavaritskii (^{6}) observed in separate experiments, during the condensation of bismuth, a sudden change in the color of the film condensed on the side surface of the instrument. A gray specimen acquired a greenish color in transmitted light. In this region of green coloration the specific resistance

turned out to be several times greater than in the region of gray coloration. They also found that the green coloration of the film appears as the temperature of the specimen is raised and is accompanied by an increase in its resistivity. He suggested that the abrupt change in the coloration of the specimens, occurring during condensation, is associated with their partial transition into the nonsuperconducting state owing to possible local overheating. In light of the present work, it seems obvious that the phenomenon observed by Zavaritskii was connected with the film reaching the critical thickness.

Fig. 3. Curve of the temperature behavior of the electrical resistance of a bismuth layer of thickness ~ 500 Å/min. 1 –irreversible course of the resistance during annealing; 2 –reversible course of the resistance of the deposited layer. A –segment of the curve characterizing the superconducting transition of the freshly condensed layer.

Fig. 4

Figure 4: Fig. 4

Fig. 4. Curve of the temperature behavior of the electrical resistance of a bismuth layer of critical thickness (~ 600 Å). 1 –irreversible course of the resistance during annealing; 2 –reversible course of the resistance of the deposited layer. A –initial segment of the curve.

Let us also note that in bismuth layers obtained by condensation on a substrate covered with a mask, in order to obtain films of a ribbon shape convenient for measurement ([6,9,10]), it is very difficult to observe the critical thickness. In this case, because of the thinner wedge-shaped edges, bismuth layers often remain superconducting even at thicknesses greater than the critical one, which masks the change in resistance during the phase transition. Sometimes, upon reaching the critical thickness, resistance appears abruptly; however, it often disappears (superconductivity reappears) when the layer is held for some time after the end of condensation at the temperature of the helium bath. This is apparently analogous to the observed fact that superconductivity appears in freshly condensed bismuth layers only after a certain holding time at the temperature of the helium bath or after warming the layer to $8 \div 10$°K ([11]). What processes occur in this case is still unclear, but the observed phenomenon is apparently connected with the presence of edges in layers of supercritical thickness, since all 14 disk films investigated in the present work became superconducting immediately after the onset of condensation (Fig. 2) and until the critical thickness was reached.

Thus, not all bismuth layers obtained by low-temperature condensation are superconducting. If the thickness of the layer in the proces-

condensation exceeds the critical value, bismuth crystallizes in its ordinary modification.

The existence of a critical thickness in bismuth layers can be explained by a change in the thermodynamic conditions in thin films ([12]).

Physico-Technical Institute
Academy of Sciences of the Ukrainian SSR
Moscow

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