MODIFICATIONS OF BERYLLIUM AND IRON IN FILMS CONDENSED ONTO COLD SUBSTRATES

B. G. LAZAREV, E. E. SEMENENKO, and A. I. SUDOVTSOV

Physico-Technical Institute, Academy of Sciences, Ukrainian S.S.R.

Submitted to JETP editor August 10, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) 40, 105-108 (January, 1961)

A study has been made of the variation with temperature of the electrical resistance of films of beryllium, iron, and copper, condensed onto substrates cooled with liquid helium, hydrogen, or nitrogen. In the beryllium films the existence of two low-temperature modifications, obtained under differing conditions of condensation, was discovered. One of these modifications becomes superconducting at ~ 8° K and exists over the temperature region up to ~ 40° K; the other becomes superconducting at ~ 6° K and is stable up to at least 130° K. In the iron films a polymorphic transition is found at a temperature of ~ 40° K. No polymorphic transitions are observed in copper films.

It is well known at the present time that certain metals, at least bismuth and beryllium, are not superconductors in the bulk state (down to 10^{-2}° K), while in films produced by low-temperature condensation they do show superconductivity, at relatively high temperatures (bismuth films, at ~ 6° K[1,2]; beryllium films, at ~ 8° K[3,4]).

In the present communication the results are presented of a further study of the superconducting properties and the temperature dependence for beryllium films, in connection with the question of the occurrence in them of new modifications.

In view of the data appearing in the literature concerning the possibility of low-temperature polymorphism in iron,[5] the electrical conductivity of films of this metal was also studied. Films of copper — a metal which has no low temperature modifications — were also investigated by the same method.

Production of the films and measurements of their electrical conductivity were carried out in the apparatus represented schematically in Fig. 1. The glass capsule 9 was evacuated to a pressure of 10^{-7} mm Hg, and pumping was continued with heating at this pressure for several hours; following this, the capsule was sealed off and placed in the helium cryostat. During evaporation of the metal to be studied the capsule was immersed in liquid helium. Below 4.2° K the temperature was controlled by helium vapor pumping, while for production of temperatures above 4.2° a jacket 1 in the form of a Dewar vessel was lowered over the capsule, whereupon the desired temperature was established within it with the aid of the heater 4.

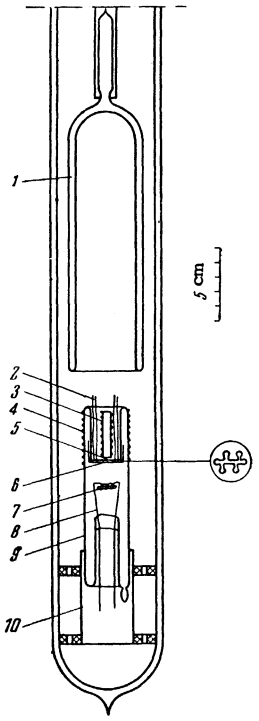

FIG. 1. Apparatus for production of films and measurement of their electrical conductivity: 1 – jacket in the form of a Dewar vessel; 2 – platinum leads from film; 3 – resistance thermometer; 4 – heater; 5 – polished glass surface onto which the film is condensed; 6 – mask defining the form chosen for the film; 7 – charge of metal to be evaporated; 8 – platinum leads for the evaporator; 9 – glass capsule; 10 – sleeve for centering capsule in cryostat.

Warming of the films was usually conducted at a rate of 2 deg/min. From 4.2 to 300° K the temperature was measured with the platinum or indium resistance thermometer 3, while from 4.2 to

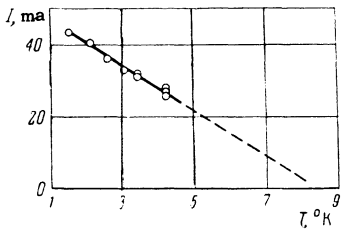

FIG. 2. Curve showing dependence of critical current upon temperature for one of the films.

1.23° K, it was determined from the vapor pressure of the helium bath. The electrical resistance of the thermometer and of the films was measured on a PPTN-1 potentiometer.

For destruction of superconductivity in beryllium films by current, the capsule could be filled with liquid helium subsequent to the deposition of the film.

In a previous paper[4] it was reported that beryllium films produced by low temperature condensation have a polymorphic transition at ~ 30° K. The films were obtained by rapid evaporation (evaporation time ~ 10 sec, temperature of the beryllium charge ~ 1500° C) onto a substrate cooled by liquid helium, and had a sharply-defined superconducting transition in the vicinity of 8 — 9° K. The same transition temperature is obtained by extrapolation of the curve showing the temperature dependence of the critical current (Fig. 2). The superconducting modification is preserved under heating to ~ 30° K. The region over which it exists is characterized by a horizontal segment in the curve showing the temperature variation of the electrical conductivity of the film, in the range from 8.5 to 30°K. Films heated to this temperature show, upon re-cooling, the same properties as freshly-condensed ones — the same complete superconducting transition is present in the same temperature region.

Heating of the films to 60° K leads to the disappearance of the superconducting modification, and this limiting heating temperature falls somewhat with increasing annealing time.

Films produced by condensation onto a substrate cooled with liquid hydrogen, following the same evaporation process, behave in a similar fashion.

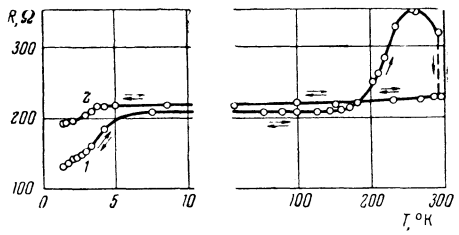

FIG. 3. Variation of electrical resistance with temperature for a beryllium film produced by slow condensation at low temperature: curve 1 – for the film after deposition; curve 2 – for a film maintained at room temperature 360 hours.

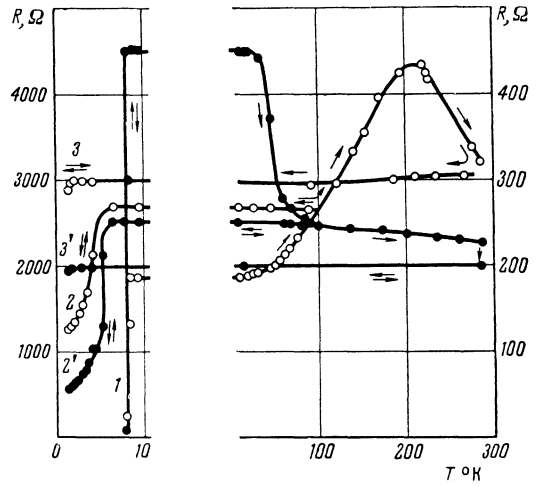

FIG. 4. Variation of electrical resistance with temperature for two beryllium films produced by slow condensation onto a surface cooled by liquid helium: 1 – initial curves; 2 and 2′ – after heating to 80° K; 3 and 3′ – following annealing at 290° K for 1 hr. Left-hand resistance scale refers to curves 1, 2, 3; right-hand, to curves 1, 2′, 3′.

It has recently become known that the mechanisms of evaporation of beryllium from the solid and liquid states are different.[7] While the beryllium evaporates primarily from the solid phase in the form of diatomic molecules, evaporation from the liquid phase proceeds chiefly in the atomic state. It was expected that condensation of vapor existing in such different states would influence the state of the films produced. A difference in the properties of films formed by slow evaporation (from the solid state) and films produced by rapid evaporation (from molten charges) is in fact observed.

Evaporation from solid beryllium (evaporation time ~ 1000 sec, charge temperature ~ 900° C) produces films that possess, in all probability, still another superconducting modification. The superconducting transition for these films (curve 1, Fig. 3) is smeared out over the region from 6° K on down. This second superconducting modi-

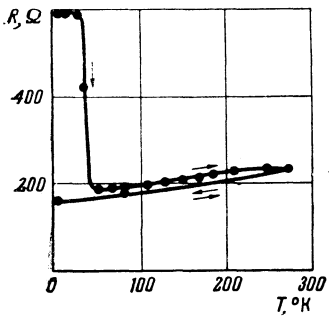

FIG. 5. Variation of electrical resistance with temperature for an iron film produced by condensation onto a surface cooled by liquid helium.

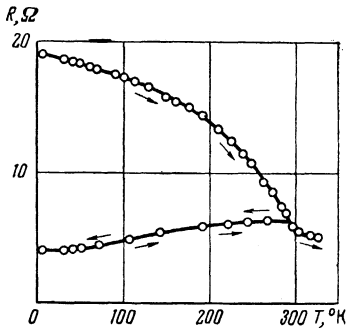

FIG. 6. Variation of electrical resistance with temperature for a copper film produced by low temperature condensation.

fication is stable to more elevated temperatures. Heating of the films to 130° K leads to no change in the second superconducting modification — the same fall in resistance below 6° K persists upon re-cooling. Moreover, the second superconducting modification can be obtained by slow evaporation onto a substrate cooled with liquid nitrogen. The temperature dependence of the electrical conductivity for films produced in this fashion is also shown in Fig. 3. After annealing at room temperature for 360 hrs. the film, on re-cooling still has a pronounced drop in electrical resistance below 5° K (curve 2).

Evaporation from the solid phase of beryllium onto a substrate cooled by liquid helium (Fig. 4) evidently leads to a mixture of the two superconducting beryllium modifications. The first superconducting modification has a sharp superconducting transition at ~ 8.4° K (curves 1 and 1′). This modification exists up to 30° K, while heating to 60° leads to its complete disappearance. Before annealing, the first modification, which becomes superconducting at the higher temperature (~ 8.4° K), apparently shunts the second modification, with the lower superconducting transition temperature (~ 6° K). The second modification is revealed following warming of the film to 60° K and subsequent cooling (curves 2 and 2′, Fig. 4). It is preserved when the film is maintained for as long as may be desired at a temperature of 130° K. Further, the second modification survives briefly (1 — 2 hrs) heating to room temperature (curves 3 and 3′). To be sure, this modification is considerably more stable when condensed slowly onto a wall cooled by liquid nitrogen (Fig. 3).

Analysis of curves showing the temperature dependence of the electrical conductivity is, evidently, a sensitive method for detection of polymorphism in metals. This circumstance can clearly be regarded at present as definitely established.

In a series of experiments, low temperature polymorphism has been found by the present method in bismuth,[1,2] beryllium,[3,4] gallium,[2] lithium, sodium, and potassium.[8] In bismuth, beryllium, and gallium, the existence of the new phases is further confirmed by their superconductivity. It is of interest that for bismuth there probably occurs in the film one of the modifications which exists at high pressures. This is evidently also the case for gallium; the same situation should be looked for in beryllium as well.

It seemed of interest also to investigate iron, for which, according to the data available,[5] the existence of a low temperature modification is possible. A curve showing the variation of electrical resistance with temperature for one of the iron films studied is presented in Fig. 5. This film was condensed onto a substrate cooled by liquid helium (evaporation time ~ 2 hr).

In the vicinity of 40° K there occurs a sharply-defined, irreversible drop in the electrical resistance. It appears that in iron there is indeed a low temperature modification produced which is stable up to 40° K. We should remark that superconductivity was not detected in any of the eleven films studied.

For comparison, we present the R(T) curve (Fig. 6) obtained for a copper film condensed at 4.2° K. No low temperature modifications have been found for this metal[9]. The curves are monotonic; they have none of the characteristic features typical of such curves for metals which possess new modifications in freshly-condensed films. Thus, low temperature modifications in freshly-condensed films have been observed for a whole series of metals: two in gallium, two in beryllium, one in bismuth, one in iron, and two each in sodium, lithium, and potassium.

[1] N. V. Zavaritskiĭ, Dokl. Akad. Nauk SSSR **86**, 687 (1952).

[2] W. Buckel and R. Hilsch, Z. Physik. **138**, 109, 136 (1954); F. Baumann, Nachr. Akad. Wiss. Göttingen, Math-physik Kl. IIa **15**, 285 (1956).

[3] Lazarev, Sudovtsov, and Smirnov, JETP **33**, 1059 (1957), Soviet Phys. JETP **6**, 816 (1958).

[4] Lazarev, Sudovtsov, and Semenenko, JETP **37**, 1461 (1959), Soviet Phys. JETP **37**, 1035 (1960).

[5] Mikhaĭlov, Nikulin, Reĭnov, and Smirnov, J. Tech. Phys. (U.S.S.R.) **29**, 931 (1959), Soviet Phys.-Tech. Phys. **4**, 844 (1960).

[6] A. I. Shal'nikov, Nature **142**, 74 (1938); JETP **10**, 630 (1940). N. E. Alekseevskiĭ, Dokl. Akad. Nauk SSSR **24**, 27 (1939); JETP **10**, 1392 (1940).

[7] Amonenko, Ryabchikov, Tikhinskiĭ, and Finkel', Dokl. Akad. Nauk SSSR **128**, 977 (1959).

[8] Lazarev, Semenenko, and Sudovtsov, JETP **39**, 1165 (1960), Soviet Phys. JETP **12**, 811 (1961).

[9] E. Feldtkeller, Z. Physik **157**, 65 (1959).

Translated by S. D. Elliott
19