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On the Influence of Aggregation on the Magnetic Phase Transition of Evaporated Superconducting Thin Films*

Abstract: An investigation was made of the magnetic phase transition of thin, superconducting Sn films. In evaporated films, because of the sloping edges, broad magnetic field transitions are generally found. This paper shows that such "penumbra" effects can be eliminated by raising the temperature of the substrate during evaporation. The lack of penumbra effect was due to the aggregation of the film. The transition curves of such films displayed hysteresis.

Introduction

Recently superconductivity has found an important application in computer devices;[1-3] however, the operational speed of devices constructed of bulk material, such as wire or coils, is greatly limited. Thin films, because of a relatively high resistance in the normal state, promise to provide a means for increasing speeds to the degree required for computer applications. These devices utilize the superconducting-to-normal transition caused by the application of an external magnetic field of magnitude H_c. This paper reports a study of this magnetic phase transition. In view of the general complexity of this problem, this work is restricted to the problem of evaporating films which display sharp transition curves when measured by resistance methods.

The critical field of a film increases with decreasing thickness because the incomplete exclusion of the magnetic field lowers the energy imparted to the film. For this thickness dependence, London[4] derived the expression

$$h_c/H_c=[1-2\beta d\cdot \tanh(\beta d/2)]^{-1/2},$$

where d = thickness of film;

$1/\beta = \lambda=\lambda_0[1-(T-T_c)^4]^{-1/2}$;
= penetration depth of the magnetic field;

λ_0 = penetration depth at $T=0°K$,
$\approx$ 500 A for tin;

h_c = critical field of the film;

H_c = critical field of the bulk.

Field transitions of thin evaporated films have been investigated by several authors. The earlier work[5-9] has been discussed thoroughly by Shoenberg.[10] Lock[7] studied the penetration depth of a magnetic field into a superconductor by means of a magnetic method. Appleyard et al[8] determined the critical magnetic fields of thin films of mercury by resistance measurements in a way similar to our method. They pointed out that in strip-shaped films the transition curves were strongly influenced by the edges of the films, i.e., the width of the transitions was increased by the edge or penumbra. Since an evaporation mask must be of finite thickness, the penumbra can never be completely prevented. The penumbra is a narrow strip surrounding the main part of an evaporated film in which the film thickness changes gradually to zero. Because of the increase of critical field with decreasing film thickness, it is possible for the penumbra to remain in the superconducting or intermediate state even though the main part of the film has returned to the normal state. Thus the transition curve becomes broad and varies appreciably with the measuring current.

To overcome these difficulties, Appleyard et al[8] designed a disk-shaped sample in which the measuring current flows from one electrode to the other only by passing through a considerable area of uniform film. From these samples the authors obtained transition curves displaying less edge effects than those of strip-shaped samples. However, the disk geometry could not be used for our special purpose.

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Since the penumbra of a film which causes the broad field transitions is an area of decreasing thickness, it can be best considered by investigating the growth and structure of evaporated films. This was the subject of several electronmicroscopic investigations, e.g., Scott, McLaughlan, and Sennet,[11] Sennet and Scott,[12] and Levinstein;[13] it was also discussed thoroughly by Mayer.[14]

During the first stages of film deposition, small droplets are formed. As the deposition continues, the droplets grow and start to combine with each other, forming aggregates. Finally the spaces between these aggregations are filled, and the film becomes continuous. Because of this growth process, continuity occurs only at a certain thickness, which depends upon such parameters as substrate temperature, evaporation conditions, evaporant and substrate material, and nucleation centers.

Experimental apparatus

For the investigation reported here, thin films of tin were vacuum deposited onto substrates at varying temperatures. The evaporations were performed in a commercial bell jar vacuum system. For additional pumping an internal cold trap, as described by Meissner,[15] was installed. With this system, pressures of about 1×10^{-7} mm Hg were obtained before the evaporation was started. These pressure measurements were taken by an ionization gauge located inside the bell jar in a position such that the opening of the gauge was directed toward the substrate.

During the actual film deposition, pressures not better than 5×10^{-7} mm Hg were maintained despite thorough outgassing of the evaporation source. The deposition rates were approximately 50 A/sec, and the source-to-substrate spacing was 8″. With faster deposition rates, the pressure during the evaporation increased to the low 10^{-6} mm Hg region. It is evident, therefore, that in our system the outgassing of the melt determined the residual pressure during the film deposition. This means that no severe contamination of the evaporated films should have occurred.

The evaporation mask (a 0.005″ stainless steel plate with the sample pattern milled out) was clamped against the glass microscope slide which served as the substrate. During each deposition, four films were deposited simultaneously, two of them on one substrate.

Figure 1 **Geometry of a test sample.**
l=2 cm, w=0.025 cm. The width of the voltage lines is approximately 0.0625 cm.

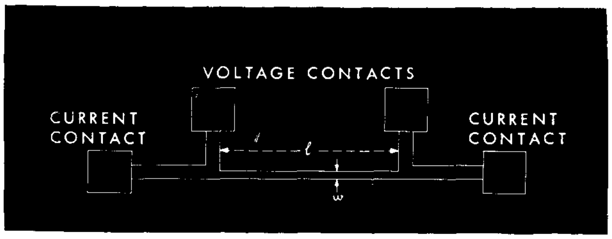


Figure 2 **Aggregation of a film deposited on a substrate maintained at a temperature of about 110°C. Magnification 10,000 ×.**

The geometry and dimensions of a test sample are shown in Fig. 1. Over the area of such a film, the thickness uniformity was calculated to be ±1%, which was sufficient for the investigation reported in this paper. After completion of the electrical tests, the thickness measurements were performed by multiple-beam interferometry.

Testing these samples consisted of measuring the resistance as a function of magnetic field. The measuring current was varied from 10 μa to 10 ma. The output across the voltage contacts was read by a precision potentiometer. A solenoid coil similar to that calculated by Garret[16] provided the necessary magnetic field parallel to the sense-current flow and parallel to the major axis of the film. The fields were measured with an accuracy of ±3%. During the test, the samples were immersed in liquid helium, the temperature of which was varied by changing the pressure above the bath. The pressure measurement was determined to an accuracy of ±0.3 mm. This corresponds to a maximum error over the temperature region measured of ±0.005°K.

Experimental results and discussion

- *Penumbra effects*

Films deposited onto substrates at different temperatures differ appreciably in their reflectivity. Cooling the substrate to nitrogen temperatures resulted in films having high reflectivity, indicating a smooth surface and therefore small grains or aggregates. Films deposited onto substrates at elevated temperatures were found to be strongly aggregated (Fig. 2) and to have low reflectivity.

In a film with sloping edges one might expect that the thinner parts of the penumbra are still disintegrated while the main part of the film is continuous (schematically pictured in Fig. 3b). Under such conditions the penumbra should not contribute to the electrical properties of the film.

Figures 4a and 4b show pictures of such film edges obtained by the transmission light microscopy. The area along the edge of the film which was deposited at 80°C (Fig. 4b) has a broken-up structure. This is not true for the film deposited onto a nitrogen-cooled substrate (4a).

The film deposited onto the cool substrate displayed a pronounced penumbra effect, i.e., a very broad transition curve dependent on the measuring current (Fig. 5). Films deposited onto substrates at elevated temperatures (Figs. 6 and 7), however, exhibited a quite different behavior. These transition curves were very sharp, sometimes almost discontinuous and similar to those observed in pure bulk material. Traces of superconductivity far above H_c, found by Appleyard et al[8] with the disk-shaped sample, did not appear in these transition curves. Also these transition curves were reproducible and did not vary with the measuring current I_s, as long as I_s was small compared to the critical current I_c. In our tests, I_s was varied from 10 μa to 10 ma. This measuring current independence eliminated the possibility that penumbra effects were involved in the measurements, although the films were deposited through the same mask and at the same source-to-substrate distance as the films deposited onto cold substrates which showed such strong effects. These experiments confirmed the assumptions about the influence of aggregation upon the film edges as outlined above.

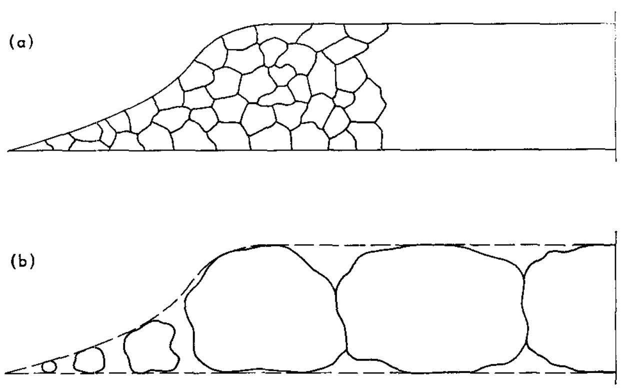
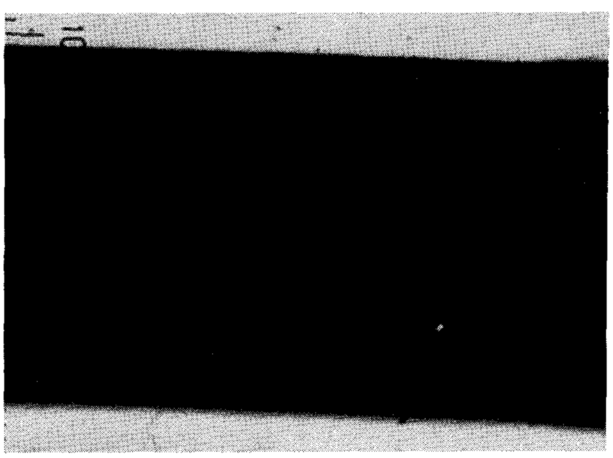


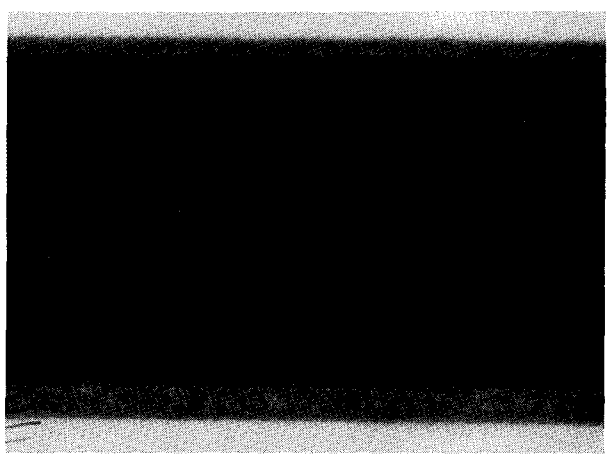
Figure 3 **Schematic drawing of film edge.**
(a) Film consists of small crystallites
(b) Film is agglomerated.

- *Hysteresis effects*

From Figs. 6 and 7 it can also be seen that films whose transition curves are not influenced by the film edges displayed a strong hysteresis effect, i.e., for increasing magnetic fields the film remained completely superconducting until a certain value of the field H_c was reached. For decreasing magnetic fields, the film remained in the normal state until the field was lowered to $H_l<H_c$. The field strength H_l could be considerably less than H_c. The functional relationship between hysteresis and temperature was not alike for all films. Most of them displayed an almost constant amount of hysteresis over the entire temperature range, e.g., it was $(H_c-H_l)/H_c=0.2$ for the film whose transition curve is shown in Fig. 6. This was not always true, especially not for those films which were deposited at the highest substrate temperature and exhibited the largest amount of hysteresis. Close to T_c, the ratio $(H_c-H_l)/H_c$ was as high as 0.45, but for lower temperatures the quantity (H_c-H_l), rather than the ratio, was constant.

Figure 4 **Light microscope pictures of films, magnification 140 ×.**
(a) Substrates cooled with liquid nitrogen during film deposition.
(b) Substrate temperature 80°C.





The phase transitions of films deposited onto liquid-nitrogen-cooled substrates, as shown in Fig. 8, displayed only little hysteresis. In this film the penumbra area was removed mechanically. The hysteresis was $(H_c - H_l)/H_c = 7\%$ = constant over the entire temperature range.

A very interesting fact is that films deposited simultaneously displayed the same amount of hysteresis. It was also found that the hysteresis of films when remeasured after several weeks remained unchanged, even after the films had been covered by a layer of SiO.

The phase transition from the normal to the superconducting state occurred sharply (Figs. 6 and 7) but not discontinuously. If the field was decreased slowly, a resistance between 0 and R_N (resistance of the film in the normal state) could be stabilized. If the field was increased again, this resistance value was maintained until the field reached H_c. Similar behavior was observed for the transition from the superconducting to the normal state. In other words, one might say that "stopping" on either the upward or downward leg of the hysteresis loop was possible (Fig. 9).

Such hysteresis effects sometimes can be caused by impurities, as found by Decker, Mapother, and Shaw[17] for lead. In this case the hysteresis was due to frozen-in magnetic moments at impurity centers. But, since films deposited on cold substrates displaying less hysteresis should not have less impurities, we may conjecture that impurities are not the cause for the effects we observed.

Hysteresis effects in pure superconductors were studied by Faber,[18] although by flux methods, not by resistance methods. In sophisticated experiments with a tin rod he found that a nucleation process is necessary to initiate the phase transition. He found that very pure material does not include enough nucleation centers to start the superconducting phase transition when the magnetic field is lowered to the value of H_c, i.e., the normal phase of the superconductor can be maintained below H_c. This effect is called "supercooling." The converse effect "superheating" was found to be negligible.[19] When the transition finally occurred at a value of the field $H_l < H_c$, it started in very localized areas (flaws) and from these it spread immediately over the entire rod.

The amount of supercooling Faber found was smaller than the hysteresis effects we observed. Moreover, in Faber's experiments the sample preparation was very im-

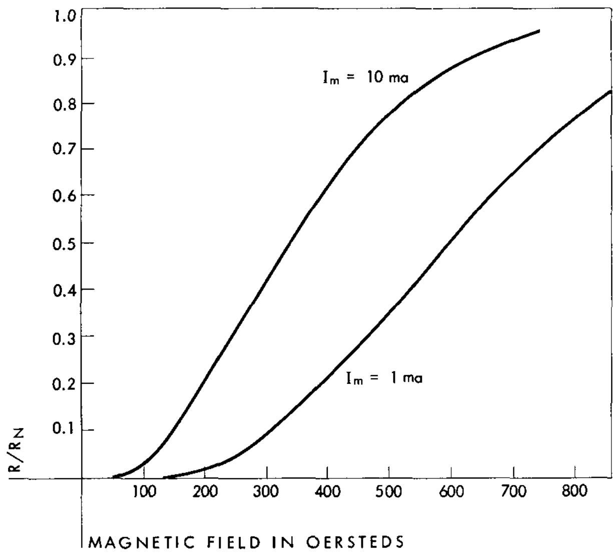


Figure 5 **Magnetic transition curve of a film deposited onto a substrate cooled by liquid nitrogen.**
I_m = measuring current; R_N = resistance of film in the normal state; temperature during measurement $T = 3.70°K$; film thickness $t = 3500$ A.

Figure 6 **Phase transition of a tin film deposited onto a warm substrate (about 60°C).**
Film thickness $t = 5450$ A; measuring temperature $T = 1.888°K$; resistance ratio $R_{291}/R_{4.2} = 83$; R_N = resistance of film in the normal conducting state.

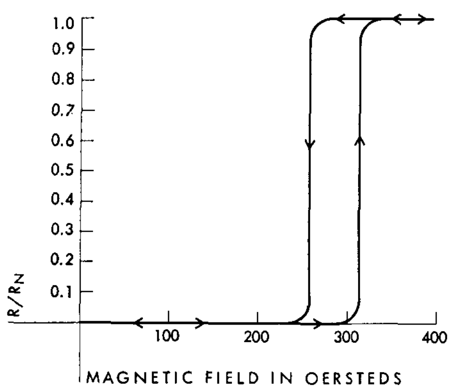
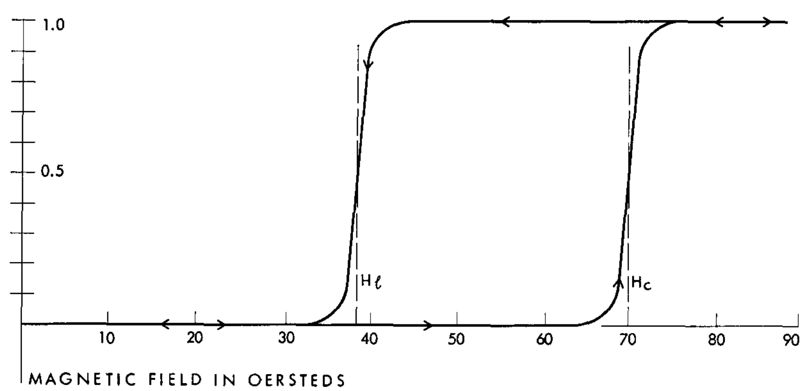


Figure 7 **Phase transition of film deposited onto a substrate at $T = 80°C$.**
Film thickness $t = 7000$ A; measuring temperature $T = 3.363°K$; resistance ratio $R_{291}/R_{4.2} = 135$.



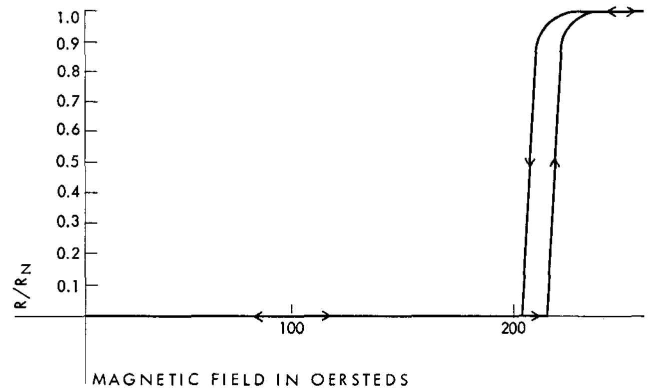


Figure 8 **Phase transition of a film deposited onto a substrate cooled by liquid nitrogen, penumbra removed mechanically.**
Film thickness t=3400 A; measuring temperature T=2.6°K.

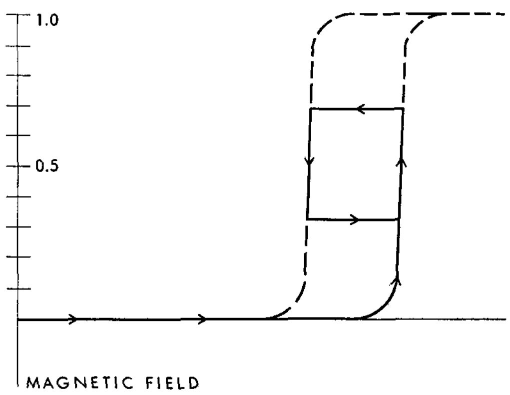


Figure 9 **Stabilization of the intermediate state of films displaying hysteresis effects.**

portant. Even handling the samples changed the amount of supercooling.

These results are very much in contrast to our findings; namely, films deposited simultaneously displayed the same amount of hysteresis. Since it is virtually impossible to produce films having identical flaws, we feel the hysteresis we found was a property of the film. Only in aggregated films was there a considerable amount of hysteresis. It is suggested, therefore, that the aggregation of the films is the determining factor. Grain boundaries possibly may prevent the superconducting phase from spreading over the specimen after the transition is started in one spot, thus causing a supercooling phenomenon.

With respect to these conclusions it is interesting to note that Shoenberg[20] and Whitehead[21] observed a considerable amount of supercooling in mercury colloids, which depended on the size of the particles. A theoretical explanation of these effects was tried by Pippard[22] in terms of the two-fluid model and the long-range parameter. Though the results on colloidal particles cannot be directly applied to thin films, we see a parallelism to our work insofar as the size of the droplets influenced the hysteresis, i.e., the size of the colloidal particles in one case, the size of the aggregates in the other.

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