levels do not provide many levels for electrons to fall into in transition from the filled band to the empty band, thereby improving the chances of completion of the transition. This state of affairs will permit a continuous supply of electrons to the conduction band for emission, and at the same time provide a minimum number of levels to trap possible secondary electrons. The desirability of having the bottom of the allowed empty band as high as or higher than the potential energy of an electron in vacuum outside the emitter has been pointed out by Bruining and De Boer.[7]

Many investigators have found that the so-called oxides of barium and magnesium (prepared by raising the temperature of the metal in the presence of oxygen) have maximum secondary yields in the neighborhood of three or four. Strictly speaking, these are not simple oxides; they are, in the writer's opinion, oxides with too little or too much impurity to allow them to be really good secondary emitters. They are, however, better emitters than conductors are.

The author expresses here his appreciation for the encouragement and advice of Professor Lloyd P. Smith who suggested this problem. The writer is also indebted to Professor Hans Bethe for valuable discussions, and to Professor D. H. Tomboulian for assistance with evaporation problems.

---

[7] H. Bruining and J. H. De Boer, Physica 6, 836 (1939).

OCTOBER 1 AND 15, 1942 PHYSICAL REVIEW VOLUME 62

Studies in Superconductivity*

II. Evaporated Lead Films

W. F. Brucksch, Jr.† and Waldemar T. Ziegler
Cryogenic Laboratory, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

(Received June 29, 1942)

The electrical and magnetic properties of evaporated lead films of several thicknesses (1000–3000A) have been studied in the superconducting state. The films exhibited transition temperatures (in zero magnetic field) of 7.23±0.03°K irrespective of thickness. The disappearance of resistance (99 to 1 percent) usually occurred within a range of 0.10°. The depression of the transition temperature with increase in measuring current I_c was found to be greater the thinner the film, all films showing larger depressions than a 254-micron lead wire ($T_c = 7.20$°K). The depression of the transition temperature in several magnetic fields (0–80 oersteds) perpendicular to the plane of the film was found to depend upon thickness, the thinner films requiring larger external fields to produce a unit depression. The I_c *versus* T_c curves obtained exhibit inflection points not heretofore observed, while the H_c *versus* T_c curves obtained suggest the existence of a similar phenomenon. The effect of measuring current on the depression of the transition temperature in constant magnetic fields also has been studied.

In the course of the development of a superconducting bolometer suitable for the measurement of small amounts of infra-red radiation[1] the properties of evaporated lead films of several thicknesses and tin, lead, columbium, and tantalum wires of various sizes were investigated in the superconducting state. It is the purpose of this and a subsequent paper to present some of the results obtained in these studies, since we believe them to have an interest quite apart from their original intent.[2] In general our studies were

---

* From a dissertation submitted to the Board of University Studies of The Johns Hopkins University by W. F. Brucksch, Jr. in conformity with the requirements for the degree of Doctor of Philosophy.

† Present address: U. S. Rubber Company, Detroit, Michigan.

[1] Andrews, Brucksch, Jr., Ziegler, and Blanchard, Rev. Sci. Inst. 13, 281 (1942), hereafter referred to as Paper I.

[2] Some of the material to be discussed has already been presented before meetings of the American Physical Society. See Brucksch, Jr., Ziegler, Blanchard, and Andrews, Phys. Rev. 59, 688 (1941); Brucksch, Jr., Ziegler, Horn, and Andrews, *ibid.*, 60, 170 (1941) (Abstracts).

confined to the measurement of the change of the electrical resistance of the test specimen with temperature in several magnetic fields (0–80 oersteds) and with various measuring currents. From these measurements we were able to deduce the change of the superconducting "transition temperature" T_c with the measuring current I_c (the critical current) and the applied external magnetic field H_c (the critical field). Throughout this paper the transition temperature T_c is taken to be that temperature in the transition range at which the resistance of the sample is equal to one-half that which it is in the normal state just above the transition range.

EXPERIMENTAL PART

The lead films were prepared by evaporation of the metal from a heated tungsten filament in a high vacuum onto soft glass bases at room temperature. These glass bases were provided with two tiny sealed-in platinum leads to which current and potential leads could be attached. The resistance of the film was followed during deposition and various thicknesses obtained by varying the time of deposition.

The soft glass bases were of two sorts: (a) flat ribbons and (b) glass "bows." They were made by drawing an ordinary microscope slide into a thin ribbon approximately 1 mm wide and 0.5 mm thick. The "bow" type of film support was designed for the aforementioned radiation studies,[3] and arranged so that the glass ribbon (on which the film was to be deposited) was sealed to the glass base only at the ends.

After the films were deposited at room temperature they were inserted in the cryostat and usually cooled to about 80°K the day after they had been prepared.

The low temperature cryostat used in these studies has been described in Paper I and will not be discussed in detail here. The sample to be studied was mounted on the top of the copper helium vessel in a horizontal position. The current and potential leads were soldered to wires passing around the massive helium vessel and thence to the outside.

Three methods of mounting were used. *Method I:* The glass base on which the film was deposited was suspended between binding posts by means of the electrical leads. These binding posts were attached to (but insulated electrically from) a copper plate which was then soldered to the helium vessel. *Method II:* The glass base on which the film was deposited was cemented directly to the copper plate which was then inserted as in Method I. *Method III:* The film was mounted as described in Method I. However, the copper plate was supported on glass rods in such a manner as to afford poor thermal contact with the helium vessel. (This arrangement was later used for radiation studies.)

We believe that the thermal contact afforded by Method II may be described as very good, by Method I as moderately good, and by Method III as poor.

All electrical measurements were made with White and Type K potentiometers and sensitive galvanometers manufactured by the Leeds and Northrup Company. Potential measurements were made to ±0.2 microvolt.

The measurement of the temperature of the test sample was carried out by means of a constantan resistance thermometer ($R=624\Omega$ at 4.2°K) *wound on the outer surface of the helium vessel.* Measurements of potential permitted *a relative* temperature[4] measurement to be made with an accuracy of ±0.008°. The resistance thermometer was calibrated with a helium gas thermometer of the type described by Woodcock.[5] This acted as a helium vapor pressure thermometer below 2.5°K. Using the normal boiling point of helium (4.22°K) as a fixed point we obtained the following results[6] for the transition temperatures of tin, lead, and columbium metals: $T_c(\text{Sn})=3.60°$; $T_c(\text{Pb})=7.20°$; $T_c(\text{Cb})=9.58°$. These may be compared with the generally accepted values for these transitions: $T_c(\text{Sn})=3.73°$;[7] $T_c(\text{Pb})=7.2°$;[8] and $T_c(\text{Cb})=9.3°$.[9] Inasmuch as we did not correct for gas

---

[3] Andrews, Brucksch, Jr., Ziegler, and Blanchard, Phys. Rev. **59**, 1045 (1941).

[4] All temperatures reported in this paper refer to these relative temperatures, since their accuracy relative to one another is much greater than their absolute accuracy. If absolute temperatures are desired cognizance must be taken of the errors discussed below.

[5] A. H. Woodcock, Can. J. Research **A16**, 133 (1938).

[6] These are discussed more fully in Paper III of this series.

[7] Silsbee, Scott, and Brickwedde, J. Research Nat. Bur. Stand. **18**, 295 (1937). W. Tuyn and H. K. Onnes, Leiden Comm. **181** (1926).

[8] H. K. Onnes and W. Tuyn, Leiden Comm. **b160** (1922).

[9] Meissner, Franz, and Westerhoff, Ann. d. Physik **17**, 593 (1933).

imperfection (which would tend to make our temperature scale too high above 4.2° and too low below 4.2°) we have taken the above results as indicating the error in our absolute temperature scale.

The magnetic field was produced by a solenoid (22 cm long; 12 cm mean diameter) immersed in liquid nitrogen. The solenoid was wound in such a manner that the field produced was perpendicular to the plane of the film, the film being located approximately at the center of the solenoid. By varying the exciting current from 0 to 200 milliamp. fields of 0 to 80 oersteds could be produced.[10]

RESISTANCE *VS.* TEMPERATURE MEASUREMENTS

After the film had been mounted but prior to cooling the cryostat a measurement of the resistance of the sample was made at room temperature (~25°C). This has been called R_0. Additional values of the resistance were obtained at the boiling point of liquid N_2 (77°K), liquid H_2 (20.4°K), and the lowest solid hydrogen temperature (~14°K) reached prior to expansion of the helium gas.[11]

In the temperature range 12.5–4.2°K the helium vessel was cooled in steps by partial expansion of the enclosed gas. When the sample being studied was found to have lost its resistance (i.e., become superconducting) cooling by expansion was stopped. The helium vessel was then allowed to warm up gradually (warming rate~0.05° per minute) which it did due to the heat leaks into the apparatus from the environment (12–13°K). Measurements of temperature (resistance thermometer) *vs.* time and resistance of film *vs.* time permitted a determination of the resistance of the film as a function of temperature.

Critical field studies were made by adjusting the external field to the desired value, cooling the sample until it became superconducting, and then following the above procedure for obtaining the R *vs.* T curve.

Critical current studies were carried out by first cooling the sample well below its normal transition temperature and then adjusting the current through the film to some value below that required to destroy superconductivity. The helium vessel was then allowed to warm slowly (~0.03–0.05° per min.). As the temperature of the sample approached the transition temperature corresponding to this current the galvanometer beam began to show the restoration of a small fraction of the total resistance (perhaps 0.1–1 percent), and then within an interval of ~0.01° the remainder of the resistance appeared. In order to prevent damage to the film as well as to the galvanometer the restoration of the normal resistance was used to operate a relay which cut off the current within the space of 0.1–1 second.

After superconductivity had been destroyed by a given current, the current was decreased, the circuit reestablished, and the cycle repeated on the same "warm-up." In this way the variation of transition temperature with critical current was obtained.

EXPERIMENTAL RESULTS

Table I summarizes the properties of and the results obtained for lead films of various thicknesses, with small measuring currents (~10^{-4} amp.) in zero applied magnetic field.

Film thicknesses were obtained in two ways. An *electrical* thickness was calculated from the length and width (average dimensions: 16 mm and 1.5 mm, respectively) and electrical resistance of the film at *room temperature*. In this we assumed the metal to have normal resistivity and density. A *chemical* thickness was determined after the electrical experiments were completed by chemical analysis[12] for the mass of the film studied. By assuming a normal density this method gave thicknesses with an estimated maximum error of 20–25 percent.

On the basis of the chemical thickness studies the films fall into three groups: 3000A, 1400A, 900A. An examination of the electrical thicknesses shows three *corresponding* groups: 2300A, 400A, and 70A. With one exception the R/R_0 ratio just above the superconducting region (column 7, Table I) shows corresponding groups.[13]

---

[10] These fields were calculated from the expression for the field at the center of a solenoid whose length is several times its mean diameter.

[11] Liquid helium was produced by the Simon expansion method.

[12] The method employed was a variation of that described by J. H. Yoe, *Photometric Chemical Analysis*, Vol. 1 (Wiley, 1928), p. 250.

[13] It seems reasonable to assume that the thinner the film the larger would be the R/R_0 ratio just above the transition,

Table I. Summary of data on lead films.

Film	Method of support	R_0 (ohm)	R/R_0				Thickness (A)		T_c	ΔT°[2]	
			80°K	20.4°K	14°K	7.3°[1]	Electrical	Chemical		1–99%	10–90%
7A[a]	I	12.98	0.2506	0.0486	0.0304	0.0198	2100	3300	7.24	0.08	0.02
7B[a]	I	10.81	0.2556	0.0534	0.0347	0.0237	2600	2700	7.25	0.10	0.03
9A[a]	I	84.51	0.2747	0.0754	0.0553	0.0459	380	1600	7.24	0.08	0.06
9B[a]	I	59.47	0.2692	0.0711	0.0501	0.0406	550	1200	7.20	0.03	0.01
10A[a]	II	405.0	0.4492	0.2933	0.2789	0.268	70	1000	7.21	0.11	0.05
10B[a]	II	451.3	0.4601	0.3052	0.2909	0.279	70	900	7.22	0.18	0.05
13A[b]	III	42.41	0.2664	0.0684	0.0509	0.0419	460	1400	6.93	0.11	0.08
13B[b]	III	51.24	0.2621	0.0635	0.0407	0.0358	380	1200	7.02	0.10	0.06
14A[b]	III	109.6	0.2566	0.0656	0.0473	0.0367	140	1500	7.11	0.10	0.07
14B[b]	III	499.7	0.2593	0.0681	0.0513	0.0411	50	1100	6.94	0.13	0.06
Bulk Pb[3]			0.221	0.0269	0.0101				7.2[4]		

[a] Ribbon base.
[b] "Bow" base.
[1] Temperature at top of transition range.
[2] The temperature range corresponding to restoration of the indicated resistance.
[3] Leiden Comm., Supplement 58 to Nos. 169–180.
[4] Onnes and Tuyn, Leiden Comm. **b160** (1922).

We conclude, therefore, that regardless of which criterion of thickness is used the *relative* thickness of the three groups is approximately correctly given.

In zero magnetic fields the transition temperatures T_c of films 7A–10B were 7.23±0.03°K (Table I). The R *vs.* T curves for these films were smooth curves with a transition range of the order of 0.05–0.15°. These observations are in accord with those of Onnes and Tuyn[14] as well as measurements made by us for lead wires[15] and indicate that our films behaved like bulk metal in these respects.

On the other hand, films 13A–14B, which were placed in the cryostat immediately after preparation and were cooled to 80°K, within 4–5 hours thereafter exhibited transition temperatures definitely below 7.2° as well as transition curves of a somewhat more irregular form. The poorer thermal contact between the films and the helium vessel afforded by the method of mounting III) may be partly responsible, but since the transitions were always determined during *warming*, the values for T_c reported in Table I are to be regarded as upper limits. However, we believe that the anomalies observed with these films are due primarily to the fact that at room temperature annealing of the film is a rather slow process,[16] and hence the films 13A–14B had not been allowed sufficient time to come to equilibrium.[17]

Figure 1 presents a summary of H_c *vs.* T_c for various film thicknesses (chemical), including two of the "unannealed" films. Figures 2 and 3 present data for I_c *vs.* T_c in the absence and presence of a magnetic field, respectively. The magnetic fields were usually limited to the values 0, 40, and 80 oersteds, the critical currents to 100 milliamperes or less. In each of these figures experimental data for a 25-micron lead wire is included for comparison.

DISCUSSION OF RESULTS

An inspection of the curves in Fig. 1 shows, if the unannealed films be excluded, that the thinner the film the greater is dH_c/dT_c. As the film thickness becomes larger (3300A) the slope much more nearly approaches that for 25-micron wire ($dH_c/dT_c \cong 170$ oersteds per deg.) which approximates that for bulk lead ($dH_c/dT_c \cong 120$ oersteds per deg.).[7] Similar results have been observed for annealed evaporated mercury film by Appleyard, Bristow, London, and Misener.[17]

The experimental results with critical currents in zero magnetic field (Fig. 2) show that the thinner the film the smaller the critical current required to produce a given lowering of the

---

because of the effect of strains within the metal lattice arising (a) from the surface forces of the substrate and (b) from imperfect annealing. These effects are difficult to disentangle. See Appleyard and Bristow, Proc. Roy. Soc. **172A**, 530 (1939).

[14] H. K. Onnes and W. Tuyn, Leiden Comm. **b160** (1922).

[15] See Paper III of this series.

[16] See, for example, R. Suhrman and H. Schnackenberg, Zeits. f. Elektrochemie **47**, 277 (1941).

[17] Similar results have been obtained for unannealed mercury films by Appleyard, Bristow, London, and Misener, Proc. Roy. Soc. **A172**, 540 (1939). On the contrary Shalnikov (Nature **142**, 74 (1938)) has found an ***increase*** in transition temperature for ***unannealed*** lead films deposited at 4.2 K.

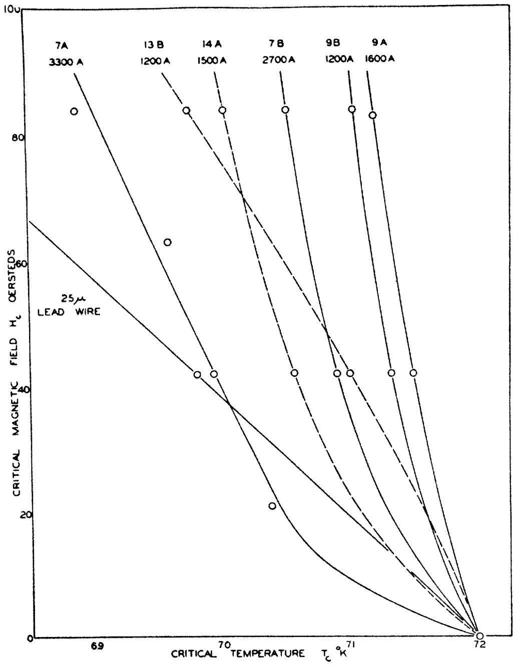

FIG. 1. Variation of transition temperature T_c with applied magnetic field for lead films of several thicknesses. The 25-Pb wire curve has a third point (not shown) at 6.8°K for 84 oersteds.

transition temperature. By comparison with the lead wires it is seen that the films are much more sensitive to current in the superconducting state than is a wire of the same metal. The resistance was always restored in a very abrupt fashion, the transition range being of the order of 0.01°. This effect was independent of the method of mounting the film in the cryostat. Shalnikov[17] has observed similar effects for evaporated lead and tin films.

Figure 3 shows the results obtained when critical current studies were made in constant magnetic fields. An inspection of the curves shows that the combined effect of current and field results in a greater lowering than one would expect from a combination of the data given in Figs. 1 and 2. Moreover, the *excess* lowering of T_c is larger the greater the magnetic field being ~0.06° and ~0.14° for fields of 42 and 84 oersteds, respectively. Hence it is seen that a much smaller current is required to destroy superconductivity in a film which is in a magnetic field than would be predicted on the basis of a combination of H_c *vs.* T_c and I_c *vs.* T_c curves of the sort given in Figs. 1 and 2.

A consideration of the curves in Fig. 1 shows them to be concave upward, although the thickest film seems to have an inflection point in its H_c *vs.* T_c curve. Likewise, with low critical currents the $I_c - T_c$ curves (Fig. 2) are all concave upward, but show inflection points.

We have been unable to find any published data for films which indicate the existence of an inflection point in the H_c *vs.* T_c and I_c *vs.* T_c curves. Extensive studies of mercury films in varying fields down to 100 oersteds by Appleyard, Bristow, London, and Misener gave curves which were concave downward.[18] This is true generally for bulk metal samples,[19] although a slight upward concavity of H_c *vs.* T_c has been found for some samples of tantalum wire in low fields.[20]

Shalnikov[17] has made critical current studies for very thin lead and tin films. The I_c *vs.* T_c curves reported by him are concave downward, but the measurements are confined to temperatures below 4.2° where large currents (0.15 amp.) are required to destroy superconductivity. Below $T_c = 7$°K our curves are also concave downward.

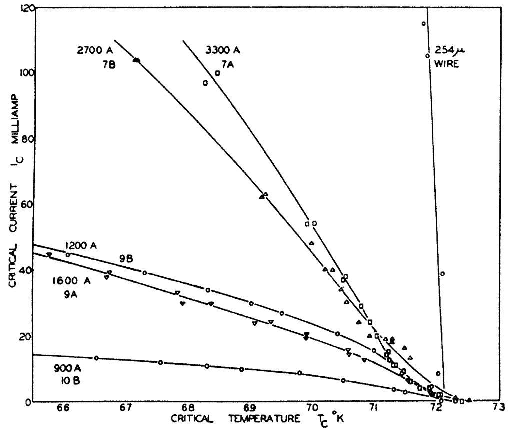

FIG. 2. Variation of transition temperature T_c with measuring current (in zero applied magnetic field) for lead films of several thicknesses.

---

[18] Reference 17. These investigators give data for a single Hg film 2410A thick which permits one to deduce the shape of the H_c *vs.* T_c curve for fields from 60–130 oersteds. Within this range the curvature is still concave downward.

[19] See D. Schoenberg, *Superconductivity* (Cambridge University Press, 1938), p. 107.

[20] K. Mendelssohn and J. R. Moore, Phil. Mag. **21**, 532 (1936); Silsbee, Scott, and Brickwedde, reference 7.

The *simultaneous* occurrence of the upward concave nature of the H_c *vs.* T_c and I_c *vs.* T_c for low magnetic fields and critical currents is consistent with the generally accepted view that the action of the critical current in destroying superconductivity is to be associated with the magnetic field produced by the current. Hence the occurrence of the effect in the two sets of measurements arrived at in entirely different ways leads us to believe the effect to be real.

Several possible objections to this conclusion may be raised. Conceivably the constantan resistance thermometer used for temperature measurements might have exhibited an anomalous resistance in the range 7.0–7.25°K.[21] However, a plot of potential across the thermometer *vs.* time during a slow "warm-up" was always perfectly smooth in this range. Hence we conclude that no such anomaly exists here.

Also heating effects on the one hand might be assumed to invalidate the measurement of I_c *vs.* T_c while the assumption that the applied field varied linearly with applied solenoid current might also be incorrect. The fact that the observed slope of the H_c *vs.* T_c curve for Pb and Sn wires (unpublished results) is constant (i.e., linear curve) shows that the effect is associated with the films and *not* with an erroneous temperature or magnetic field scale. In addition since the method of mounting the films (Methods I, II) did not affect the presence of the anomalous curvature the argument that heating effects are responsible loses much of its force. We conclude, therefore, that the effects observed are to be associated with the films themselves and not with the method of making the measurements.

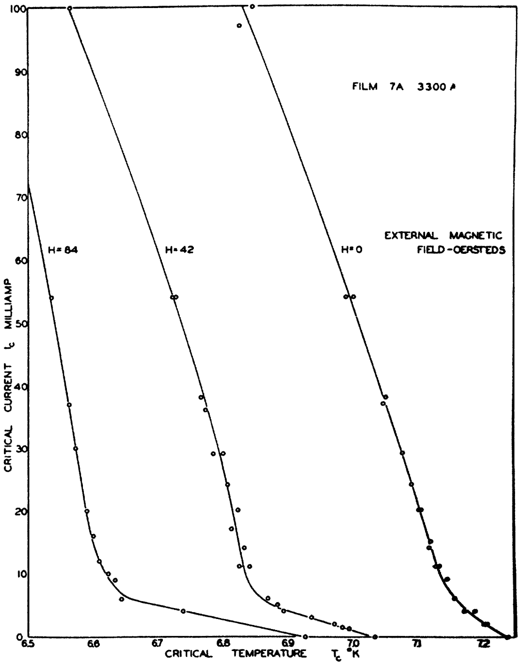

FIG. 3. Variation of transition temperature T_c with measuring current for Pb film 7A in several constant magnetic fields.

ACKNOWLEDGMENTS

We wish gratefully to acknowledge grants-in-aid from the Research Corporation which covered the expense of equipment, operation, and technical assistance. We wish to thank the Rockefeller Foundation for a grant providing for research assistance. We also wish to express our thanks to Mr. F. Hubbard Horn for helping with the electrical measurements, to Messrs. Warren DeSorbo and Robert Goodwin for the chemical analysis of the lead films, and to Dr. E. R. Blanchard for help in the production of the liquid hydrogen used.

---

[21] See Onnes, Leiden Comm. **b219**, 13 (1932).