Boundary Scattering Effects on the Superconducting Transition Temperature of Indium*

ERNEST A. LYNTON AND DAVID MCLACHLAN
Rutgers University, New Brunswick, New Jersey
(Received November 16, 1961)

We have compared the superconducting transition temperature, T_c, of indium foils about 6 μ thick with that of an indium wire of diameter 250 μ. The foils were cold-rolled and then carefully annealed. At low temperatures the electron mean free path in the foils was primarily determined by scattering from the boundaries, as indicated by measurements of their residual resistivity. The transition temperature of the foils is lower than that of the wire by small but measurable amounts which agree with decreases in T_c found in experiments with impure indium specimens of comparable resistivity. We conclude that the present measurements give additional support to the idea that limiting the electronic mean free path in indium results in a decrease in transition temperature independent of the mechanism determining the free path.

INTRODUCTION AND DESCRIPTION OF THE EXPERIMENT

PREVIOUS measurements at this laboratory have shown that the critical temperature of tin, indium, and aluminum is decreased when the normal electronic mean free path l is limited by impurity scattering[1,2] and by mechanical defects.[3] The effect has also been observed in quenched tin containing dislocations,[4] in tin irradiated by electrons[5] and by neutrons,[6] in dilute solutions of tin and of indium in a number of experiments,[7–9] and in impure tantalum.[10] We have now made measurements on thin foils of very pure indium, in which the electron mean free path is limited by scattering from the foil boundaries.

When one looks for possible size effects on T_c, it is important to use specimens which in every respect other than size have the properties of well-annealed and homogeneous bulk material. This is generally not the case for evaporated films, colloidal particles, or whiskers. Lock[11] as well as Ginsberg and Tinkham[12] have reported values of T_c for very thin evaporated indium films as high as 3.88°K, compared to a value of 3.41°K for bulk material. Increases in the critical temperature of cold-worked foils and evaporated films have also been found by Von Minnigerode[13] in a number of elements. More recently Toxen[14] has investigated this rise in T_c systematically with a series of evaporated indium films between 650 and 35 000 A, and has found that, as had been suggested by Lock, the increase in T_c of these films can be simply related to the existence of elastic stresses in them. For colloidal mercury particles with a diameter of the order of a few hundred A, Whitehead[15] found a rise of T_c of about 0.040°K, which is also attributed to strains. The work of Lutes[16] on tin whiskers of diameter down to about 10^{-4} cm did not include accurate determinations of T_c, but he does report considerable broadening of the magnetic transition at lower temperatures, and also ascribes this to strain. Appreciable broadening of the transition was also found by Androes and Knight[17] in the 100-A tin films in which they measured the Knight shift. The critical temperature of these films was lower than that of annealed bulk material.

In any of these film, colloidal, or whisker samples, the change in T_c due to the nonideal elastic conditions can completely mask the small effect which, on the basis of our previous measurements,[1,2] one can expect to be due to a decrease in the electronic mean free path. We therefore decided to use only cold-rolled foils which were then annealed, although even in the thinnest samples we could prepare the change in T_c was just measurable. The specimens were hand-rolled between Teflon strips, and this yielded material of approximately 6 μ average thickness as determined by weighing. Strips about 2 to 3 mm wide and 2 cm long were then cut from this, mounted in the low-temperature apparatus, and annealed at room temperature for at least a week before the measurements.

The low-temperature apparatus consisted primarily of a massive copper block which provided sufficient

* This work was supported by the National Science Foundation and the Rutgers Research Council.
[1] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957).
[2] G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).
[3] W. Joiner and B. Serin (private communication). See also B. Serin, *Proceedings of the Seventh International Conference on Low-Temperature Physics* (University of Toronto Press, Toronto, 1960), p. 391.
[4] W. DeSorbo, J. Phys. Chem. Solids **15**, 7 (1960).
[5] W. Dale Compton (private communication to B. Serin).
[6] J. Blanc, B. B. Goodman, G. Kuhn, E. A. Lynton, and L. Weil, *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1960), p. 393.
[7] S. Wipf and B. Coles, Proceedings of the Conference on Superconductivity, Cambridge, 1959 (unpublished); see also B. Coles, IBM J. Research Develop. **6**, 68 (1962).
[8] M. D. Reeber, Phys. Rev. **117**, 1476 (1960).
[9] D. P. Seraphim, C. Chiou, and D. T. Quinn, Acta Met. (to be published).
[10] J. I. Budnick, Phys. Rev. **119**, 1578 (1960); see also D. P. Seraphim, D. T. Novick, and J. I. Budnick, Acta Met. **9**, 446 (1961).
[11] J. M. Lock, Proc. Roy. Soc. (London) **A208**, 391 (1951).
[12] D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).
[13] G. von Minnigerode, Z. Physik **154**, 442 (1959).
[14] A. M. Toxen, Phys. Rev. **123**, 442 (1961).
[15] C. S. Whitehead, Proc. Roy. Soc. **A238**, 175 (1956).
[16] O. S. Lutes, Phys. Rev. **105**, 1451 (1957).
[17] G. M. Androes and W. D. Knight, Phys. Rev. **121**, 779 (1961).

thermal inertia to smooth out rapid temperature fluctuations of the helium bath in which it was immersed. The indium foils were placed loosely into wide grooves cut into the upper, horizontal face of this block, which had previously been coated with a thin layer of GE No. 7013 varnish for electrical insulation. The parts of the current and potential leads in contact with the samples were themselves made of indium, and were cold-welded to the samples by pressing gently. Care was taken to maintain enough slack in the samples so as to prevent subsequent strain upon cooling due to differential expansion. One of the grooves of the copper block contained a length of 0.010-in.-diam indium wire extruded from the same pure material. This wire served as the "bulk" reference sample. The block further contained a carbon resistance thermometer cemented into a hole into which it fitted tightly. This thermometer was calibrated against the vapor pressure of the helium bath.

The critical temperature of the specimens was determined as that point at which their resistance fell to one-half of its normal value. All readings were taken while the temperature was decreasing and with the earth's field compensated to within a few percent. The potential across one of the thin foils was connected through a microvolt amplifier to one of the pens of a double-pen recorder. The low-temperature foil resistances were of the order of 250 μohm, and required a measuring current of only 1–2 ma for adequate deflections. The second pen of the recorder followed the off-balance of a microvolt potentiometer which measured the potential drop across the carbon thermometer. A galvanometer with an optical multiplier was connected directly across the "bulk" sample, which has a low-temperature resistance of 26 μohm. With a measuring current of 10 ma, this resulted in a galvanometer deflection of about 2 cm in the normal state. When this deflection fell to one-half of its normal value, the observer would tap a switch producing an electrical marking signal which was superimposed on the thermometer trace of the recorder.

The procedure was to start at a temperature a few millidegrees above the highest critical temperature, and to allow the temperature to drift down at the rate of about 2–3 mdeg per minute. This was slow enough to make the transitions occur in a time long compared to the period of the galvanometer and the response time of the human and electronic recorders, yet not so slow as to obscure the value of T_c due to temperature fluctuations and variations in the thermal emf's. The midpoint of the transition of the "bulk" would appear as a marker on the thermometer trace, and a little earlier or later depending on the measuring current in the bulk sample, the transition of the foil would be indicated by the movement of its pen. In this fashion the difference between the two critical temperatures could be determined with reasonable accuracy in terms of the concurrent change in the thermometer resistance.

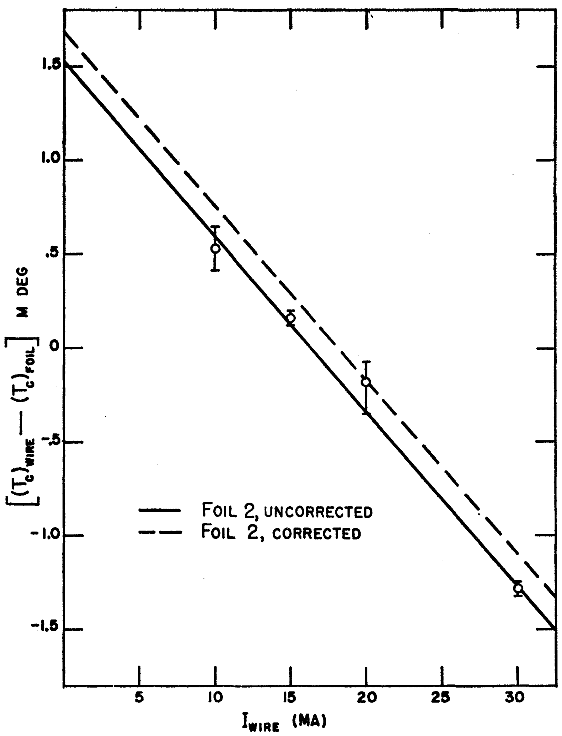

FIG. 1. Values of $\Delta T_c = (T_c)_{\rm wire} - (T_c)_{\rm foil}$, taken with a current of 1 ma through foil No. 2, plotted as a function of the measured current through the wire. The dashed curve is corrected for the effect of 1 ma through the foil.

RESULTS AND CONCLUSIONS

Our success in preparing and annealing samples reasonably free of strain and closely resembling bulk material in every respect except size was indicated by the narrowness of the superconducting transitions, which occurred within 1–2 mdeg for the wire and for foil No. 2, and within 2–3 mdeg for foil No. 1.

Allowance had to be made, of course, for the field created by the measuring currents. Rather than rely on a calculated correction, particularly questionable for the foils, we made measurements of $(T_c)_{\rm wire} - (T_c)_{\rm foil}$ as a function of measuring currents in both the "bulk" and the foils. Figure 1 shows a series of measurements of the difference in T_c, all taken with a current of 1 ma through foil No. 2, plotted as a function of the measuring current through the "bulk" sample. Each point is the average of several transitions, the flags indicating the spread in results. It is evident that even with the lowest current, 10 ma, the lowering of T_c due to the field is half as big as the temperature difference which we wish to measure, which is the value extrapolated to zero current. The correction is seen to be in the opposite direction to the actual mean-free-path effect. For small measuring currents the "bulk" transition occurred at a temperature higher than that of the foil, for larger currents the "bulk" transition moved to lower temperatures. This change in the sequence was observed quite

TABLE I. Comparison of calculated and observed changes in T_c.

Specimen	$\rho\times10^3$	$(\Delta T_c)_{calc}$ (mdeg)	$[(T_c)_{bulk} - (T_c)_{foil}]_{calc}$ (mdeg)	$[(T_c)_{bulk} - (T_c)_{foil}]_{meas}$ (mdeg)
Foil No. 1	1.05	2.4±0.6	1.9±0.7	1.4±0.6
Foil No. 2	0.76	1.8±0.4	1.3±0.5	1.7±0.6
Wire	0.21	0.5±0.1		

unequivocally, and allows us in spite of the smallness of the effect to extrapolate with confidence to a ΔT_c value in zero measuring current. The current correction for the foils was much smaller, and was obtained by measuring T_c differences with varying foil currents and constant bulk current. This yielded corrections of the order of one-tenth of the observed mean-free-path effect: approximately 0.18 mdeg/ma for foil No. 1, and 0.16 mdeg/ma for foil No. 2. The dashed line in Fig. 1 is corrected by this latter amount.

Applying these corrections for the foil currents to the T_c values extrapolated to zero wire current yielded values for the difference in T_c between each of the foils and the "bulk" wire which we list in the last column Table I. The critical temperature of the foils is lower than that of the bulk. This and the magnitude of the change are in excellent agreement with the results of Chanin *et al.*[2] on impure indium, according to which

$$\Delta T_c = -(2.3\pm0.6)\rho, \tag{1}$$

where

$$\rho = R_{4.2}/\{(R_T - R_{4.2})[1-\alpha(T-273)]\}. \tag{2}$$

α is the known temperature coefficient of resistivity for indium, and $R_{4.2}$ and R_T are the resistances measured at 4.2° and at room temperature T, respectively. The second column in the table lists the values of ρ for our foils and wire, as calculated from their measured resistances, and the next column gives the corresponding values of ΔT_c as calculated from (1). Subtracting the change in T_c of the wire from that of each of the foils yields the differences in T_c between foils and wire to be expected if the boundary scattering has the same effect as impurity scattering. The values are shown in column four, and are seen to agree very well with the measured values in column five.

As a check on our basic assumption that in the foils the electrons are predominantly boundary scattered, one can use Dingle's calculations[18] of the conductivity of thin films. Dingle computes the ratio of foil resistivity to that of bulk material for different ratios of foil thickness to bulk mean free path. Taking for this last about 0.045 cm, and a bulk value of $\rho\approx10^{-4}$,[19] one finds that films of thickness $a\approx6\ \mu$ should have $\rho\approx10^{-3}$, which is just what we measure for our films. Another check is to calculate the effective mean free path in the foils, l_{eff}, using the known value of the ideal bulk conductivity at 273°K,[20] and the temperature-independent value of σ/l, as calculated from anomalous skin effect measurements.[21] One obtains for foil No. 1 $l_{eff}\approx7\ \mu$, for foil No. 2 $l_{eff}\approx10\ \mu$. This too is in agreement with Dingle's calculations, according to which for very thin films the effective mean free path varies as

$$l_{eff}\approx a\ln(l_0/a). \tag{3}$$

For our films $l_0/a\approx75$, and l_{eff} should therefore be somewhat larger than the film thickness a. Again this is consistent with our results, so that our assumption of boundary scattering seems to be well substantiated.

We believe, therefore, that this work clearly establishes, in spite of the small magnitude of the effect, that in indium the critical temperature is lowered when the normal electronic mean free path decreases as a result of boundary scattering. In view of the similarity between our previous results on indium[2] and those on aluminum and tin,[1,2] it appears probable that the same conclusion can be drawn for these other elements. Together with previously cited evidence that the same effect occurs when the mean free path is limited by other means, this convinces us that the initial lowering of T_c in aluminum, indium, and tin is indeed a true mean-free-path effect independent of the mechanism determining the free path. Serin[22] has pointed out that both the magnitude and the extent of this effect support Anderson's suggestion[23] that when the mean free path decreases to a value comparable to the bulk range of coherence, the critical temperature decreases by a fractional amount of the order of the square of the fractional anisotropy of the superconducting energy gap.

ACKNOWLEDGMENT

We are very pleased to acknowledge our gratitude to Professor B. Serin for a suggestion initiating this work, and for many subsequent discussions.

[18] R. B. Dingle, Proc. Roy. Soc. (London) **A201**, 545 (1950); see also E. H. Sondheimer, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1952), Vol. 1.

[19] J. L. Olsen, Helv. Phys. Acta **31**, 713 (1958).

[20] G. K. White and S. B. Woods, Rev. Sci. Instr. **28**, 638 (1957).

[21] P. N. Dheer, Proc. Roy. Soc. (London) **A260**, 333 (1961).

[22] B. Serin, reference 6, p. 391.

[23] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959); reference 6, p. 298.