Size Effects in Thin Superconducting Indium Films

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Measurements of residual resistivity, superconductive critical temperature, and critical magnetic field have been carried out on indium films ranging in thickness from 650 to 126 000 A. The thickest films had the bulk critical field and critical temperature. The variation of residual resistivity with thickness is consistent with Fuchs' model if one assumes an intrinsic resistivity ρ_0 of 1.31×10^{-8} ohm cm and an intrinsic mean free path l_0 of 152 000 A. The value of $\rho_0 l_0$ so obtained was 2.0×10^{-11} ohm cm^2. The critical temperature was found to be a systematic function of film thickness, increasing with decreasing thickness. The magnitude of this change in critical temperature is in good agreement with a simple model relating critical temperature to elastic stresses in the films. The penetration depth, as calculated from the critical field by means of the London theory or the Ginzburg-Landau theory, was found to increase with decreasing film thickness. This result is consistent with a nonlocal model and implies a coherence length of approximately 2600 A.

INTRODUCTION

In order to study size effects in superconductors, indium films of high chemical purity were deposited in a vacuum of about 10^{-6} mm Hg at a rate of about 1000 A/sec onto fused quartz substrates held at approximately 80°K. The thicknesses studied ranged from 650 to 35 000 A. Several films about 100 000 A in thickness which had been deposited on substrates at room temperature were also studied.

The film properties measured were the normal state electrical resistance, the critical temperature for superconductivity, and the critical magnetic field, i.e., the magnetic field necessary to switch the films from the superconductive state to the normal resistive state. From these quantities, the residual resistivity, effective film thickness, and penetration depth were obtained.

MEASUREMENTS

The residual resistivity of each film was calculated from the ratio of the resistance at room temperature to the residual resistance, assuming Matthiessen's law and assuming that the temperature-dependent portion of the room temperature resistivity is the same as that of bulk indium, which has been measured by White and Woods.[1] The film thickness d was calculated from the room temperature and residual resistances in the following way:

$$d=\rho_i(295)L/W(R_{295}-R_0), \qquad (1)$$

where $\rho_i(295)$ is the intrinsic resistivity at 295°K, obtained from White and Woods' data; L is the film length; W is the film width; R_{295} is the resistance at 295°K; and R_0 is the residual resistance.

Using a Garrett[2] type solenoid to apply a uniform tangential magnetic field, the critical field of the film, h_c, was measured by observing the abrupt increase in resistance as the film changed from the superconductive to the normal state. The observed transitions were quite sharp, generally taking place over a field interval of one percent of the critical field or less. The transitions were independent of measuring current over a current range of several orders of magnitude except very near the critical temperature, T_c, where the field produced by the measuring current is comparable to the specimen critical field. However, hysteresis effects were observed in the thicker films, i.e., the field at which the superconductive to normal state transition took place was larger than that field at which the normal to superconductive transition occurred. The temperature and thickness dependence of this hysteresis is similar to that observed by Zavaritski[3] on indium films and in general is in agreement with the predictions of the Ginzburg-Landau[4] theory. This data will be discussed in a subsequent paper. In all of the results to follow, the critical field quoted is that field at which the destruction of the superconductive state took place. To avoid edge effects,[5–7] all of the specimens were cut into a four-terminal pattern from a block of film.

The films and the solenoid were parallel within about one degree or less. Hence the component of field normal to the film was about 1–2% of the tangential field. Because of the large demagnetizing factor for a thin superconductive film, the films were rotated to that position which minimized demagnetization effects. In addition, Helmholtz coils were used to compensate the horizontal component of the earth's magnetic field. The films were suspended in a liquid helium bath which could be pumped upon by a 13 CFM forepump to achieve the necessary temperatures. With this arrangement, the temperature range 1.2–4.2°K was covered. During each critical-field determination, the helium was maintained at a constant temperature using a bellows-operated manostat and a thermal regulating device similar to that described by Sommers.[8] The relative accuracy of

[1] G. K. White and S. B. Woods, Rev. Sci. Instr. **28**, 638 (1957).
[2] M. W. Garrett, J. Appl. Phys. **22**, 1091 (1951).
[3] N. V. Zavaritski, Doklady Akad. Nauk S.S.S.R. **85**, 749 (1952).
[4] V. L. Ginzburg and L. D. Landau, Zhur. Eksp. i Teoret. Fiz. **20**, 1064 (1950).
[5] E. T. S. Appleyard, J. R. Bristow, H. London, and A. D. Misener, Proc. Roy. Soc. (London) **A172**, 540 (1939).
[6] G. J. Kahan, R. B. DeLano, Jr., A. E. Brennemann, and R. T. C. Tsui, IBM J. Research Develop. **4**, 173 (1960).
[7] Hollis L. Caswell, J. Appl. Phys. **32**, 105 (1961).
[8] H. S. Sommers, Jr., Rev. Sci. Instr. **25**, 793 (1954).

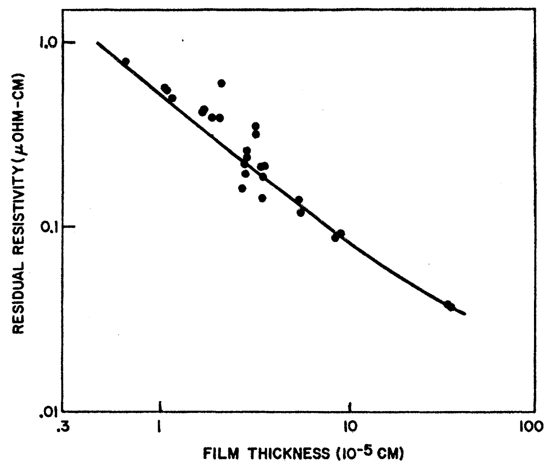

FIG. 1. Residual resistivity of thin indium films and Fuchs' relation for $\rho_0=0.0131$ μohm cm, $l_0=152\,000$ A.

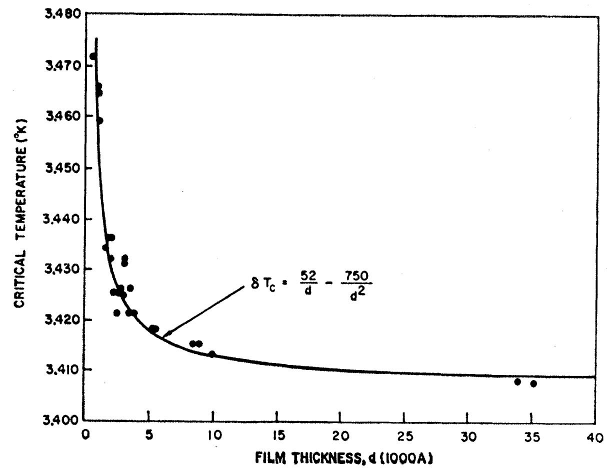

FIG. 2. Thickness dependence of superconducting critical temperature of indium films.

the critical-field values is about ±0.1 gauss; the absolute accuracy, ±1%. All of the temperatures were determined from measurements of the vapor pressure of the helium bath and were deduced from the 1958 He scale of temperature.[9] The accuracy of the temperature measurements was estimated to be ±0.003°K.

For some of the films the critical temperature was measured directly by observing the temperature at which the resistance became zero. For the remaining films, T_c was deduced by an extrapolation of the critical field vs temperature data to zero critical field.

RESULTS

In Fig. 1 is shown the variation of residual resistivity with film thickness. Also shown is a theoretical curve calculated from Fuchs'[10] relation.

This is a calculation of the increase in resistivity in a thin plate of film over that of the "bulk" metal arising from the limitation of the normal mean free path by the boundaries of the specimen. In order to fit the experimental data over the range 600–35 000 A, it was necessary to postulate a "bulk" resistivity of 0.0131 μohm cm and a "bulk" mean free path of 152 000 A. These values correspond to an equivalent point impurity concentration of roughly 0.03 at. %. As calculated from the above values, $\rho l=2.0\times10^{-11}$ ohm-cm^2. This is in poor agreement with unpublished data by D. C. Roberts,[11] who found $\rho l=0.89\times10^{-11}$ ohm-cm^2, and with the data obtained by Dheer,[12] who found $\rho l=0.6\times10^{-11}$ ohm-cm^2. To fit the data of Fig. 1 with Fuchs' relation using the ρl values measured by Dheer or Roberts, one must postulate that the intrinsic or "bulk" resistivity of the films is itself a function of thickness. For the Dheer measurement, the variation of intrinsic resistivity is from 0.0302 μohm-cm for the 35 000 A film to 0.378 μohm-cm for the 640 A film. It is difficult to envision a tenfold variation in the chemical purity of the films, since they were all evaporated under quite similar conditions. Hence, if there is a true variation in "bulk" resistivity, it must be the result of grown-in defects such as dislocations, stacking faults, large angle grain boundaries, etc.

In Fig. 2 is shown the dependence of critical temperature upon thickness for some of the indium films studied. The critical temperatures of several indium films, 80 000–125 000 A in thickness, which had been evaporated onto substrates held at room temperature, were 3.408±0.003°K. This value is in good agreement with measurements on bulk indium; e.g., 3.407±0.001°K reported by M. D. Reeber[13]; also 3.4075±0.0005°K and 3.4085±0.005°K reported for two specimens by Shaw, Mapother, and Hopkins.[14]

For films thinner than 10 000 A, there is a sharp increase in T_c with decreasing thickness. One explanation of this is that the increase in T_c is associated with stresses in the films. Lock[15] observed that for tin films evaporated onto various substrates, the critical temperatures were higher or lower than that of bulk tin, depending upon whether the coefficient of expansion of the substrate material was lower or higher, respectively, than that of the tin. From this, Lock concluded that the shifts in T_c of the films were due to strains caused by differential contraction of film and substrate upon cooling from toom temperature to T_c. In further support of this contention, Lock found that tin films which had been removed from their substrates had critical temperatures close to that of bulk material. Zavaritski[16]

[9] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Research Natl. Bur. Standards **64A**, 1, (1960).
[10] K. Fuchs, Proc. Cambridge Phil. Soc. **34**, 100 (1938).
[11] See T. E. Faber, Proc. Roy. Soc. (London) **A241**, 531 (1957).
[12] See E. A. Davies, Proc. Roy. Soc. (London) **A155**, 407 (1960).
[13] M. D. Reeber, Phys. Rev. **117**, 1476 (1960).
[14] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).
[15] J. M. Lock, Proc. Roy. Soc. (London) **A208**, 391 (1951).
[16] N. V. Zavaritski, Doklady Akad. Nauk S.S.S.R. **78**, 665 (1951).

also attributed variation in the critical temperatures of evaporated films to differential contraction of film and substrate.

That stress effects can produce changes in T_c of the order of magnitude of those observed can be seen from simple considerations. On being cooled from room temperature to 3.4°K, polycrystalline indium undergoes a contraction of magnitude[17] $\Delta l/l_{273}=-7.3\times10^{-3}$. On the other hand, the vitreous silica substrate increases slightly in length,[18] $\Delta l/l_{273}=+0.1\times10^{-3}$. Clearly, at 3.4°K, the indium films are under biaxial tensile stress, caused by the differential contraction of film and substrate. If the yield stress of the films were not exceeded, the volume strain would be approximately $\Delta V/V_{273}\approx7.4\times10^{-3}$, including Poisson contraction. Using the results of Jennings and Swenson,[19] who found $\delta T_c=17.6(\Delta V/V)$, a hydrostatic strain of this magnitude would produce a shift in T_c of $+0.13$°K. This is considerably larger than the observed shifts. In fact, as has already been pointed out, the thicker films exhibit the bulk critical temperature. Hence one must conclude that plastic flow takes place in the films, relieving the large thermal stresses which would otherwise be present. On this basis one might interpret the variation of T_c with film thickness to be a result of the variation of critical yield stress with thickness. A simple model[20] predicting such a variation is one which assumes that plastic flow will occur by the motion of dislocations whose ends are pinned at grain boundaries or at the upper and lower surfaces of the film. For such a model, the minimum shear stress for slip is given by the relation

$$\sigma=Gb/L, \qquad (2)$$

where G is the shear modulus, b is the Burgers vector for the slip, and L is the distance between the pinning points. The shear stress is in turn related to the tensile stress P by the relation[21]

$$P=\sigma/\cos\phi\ \cos\lambda, \qquad (3)$$

where λ is the angle between the slip direction and the axis of tension, and ϕ is the angle between the normal to the slip plane and the axis of tension. In these films, L, the distance between pinning points will be of the order of magnitude of the film thickness, d. Hence, combining Eqs. (2) and (3) the minimum uniaxial stress will be given by the expression,

$$P_{\min}=[Gb(\cos\phi\ \cos\lambda)^{-1}/d]. \qquad (4)$$

Let us now calculate $P_{\min}$. Indium has a face-centered

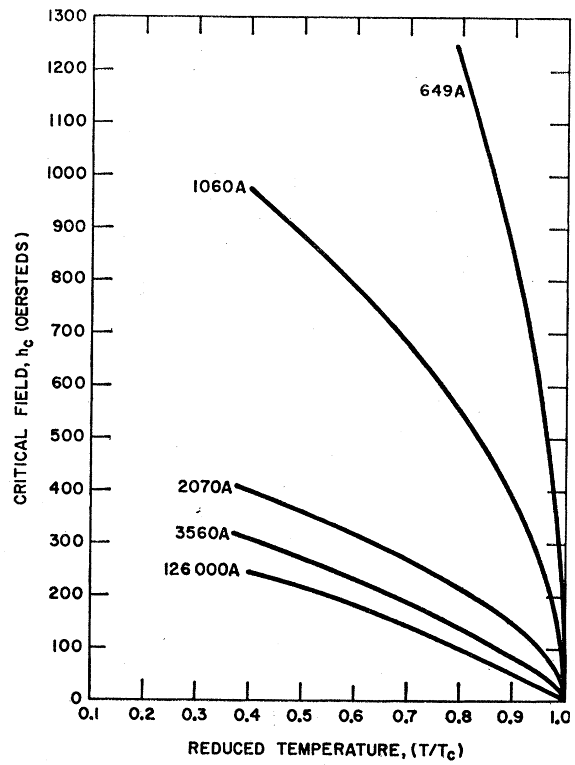

FIG. 3. Critical magnetic field of indium films.

tetragonal structure in which the c/a ratio is approximately 1.08 at low temperatures[22]; i.e., the lattice structure is nearly face-centered cubic. It therefore seems reasonable to assume that slip will be most likely to occur in {111} planes along [110] directions.[21] It has been found from x-ray measurements[23] that the films have a preferred orientation with the {101} planes parallel to the substrate. One can now calculate $P_{\min}$ from Eq. (4); for b is equal to 3.2 A; $(\cos\phi\ \cos\lambda)^{-1}$ is equal to 2.4, and G is given by the expression $(C_{11}-C_{12}+C_{44})/3$. Using the elastic constants measured by Chandrasekar and Rayne,[24] G equals 0.77×10^5 atm. Substituting these values into Eq. (4), one obtains

$$P_{\min}=6.0\times10^5/d, \qquad (5)$$

where $P_{\min}$ is in atmospheres and d is in angstrom units. The relationship found by Jennings and Swenson between hydrostatic pressure and shift in T_c is

$$\delta T_c=-4.36\times10^{-5}P_{\text{hyd}}+5.2\times10^{-10}P_{\text{hyd}}^2. \qquad (6a)$$

Since one may think of a hydrostatic stress as being equivalent to three mutually perpendicular uniaxial stresses, the effect of biaxial stress will be roughly two-thirds of a hydrostatic stress of the same magnitude.

[17] C. A. Swenson, Phys. Rev. **100**, 1607 (1955).
[18] R. B. Scott, *Cryogenic Engineering* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1959), see p. 332.
[19] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).
[20] See for example, J. W. Mentor and D. W. Pashley, *Structure and Properties of Thin Films*, edited by Neugebauer, Newkirk, and Vermilyea (John Wiley & Sons, Inc., New York, 1959).
[21] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Oxford University Press, London, 1958).
[22] J. Graham, A. Moore, and G. V. Raynor, J. Inst. Metals, **84**, 86 (1955).
[23] R. Crosby (private communication).
[24] B. S. Chandrasekhar and J. A. Rayne, Phys. Rev. Letters **6**, 3 (1961).

Therefore, on the basis of the above postulates, one might expect the variation of T_c with film thickness to be given by the relation

$$\delta T_c = (52/d) - (750/d^2), \tag{6b}$$

obtained by substituting Eq. (5) into (6a). In Fig. 2 is shown the plot of Eq. (6b). The agreement with the data is good.

In Fig. 3 are shown some representative critical field data for indium films ranging in thickness from 649 A to 126 000 A. The critical field values for the 126 000 A film and for several other very thick films agreed with one another within 0.1% and were in good agreement with the values reported for bulk indium. The critical field as extrapolated to 0°K for these films was $h_0 = 283.5 \pm 2\%$ oersteds which compares well with the value of 285.7 ± 0.5 oe reported by Shaw, Mapother, and Hopkins.

In a recent paper,[25] Ittner showed that the penetration depths of thin tin films, calculated from critical magnetic field data using the London model, varied with film thickness in a way consistent with a nonlocal model. This result is also true for thin indium films. The relation between critical field and penetration depth given by the London theory[26] is

$$H_c^2/h_c^2 = 1 - (2\lambda/d)\tanh(d/2\lambda), \tag{7}$$

where h_c is the film critical field, H_c is the bulk critical field, d is the film thickness, and λ is the penetration depth. From Eq. (7), one can calculate the penetration depth from the film thickness and critical field. In Fig. 4 are shown values of $\lambda(0)$, the value of $\lambda(T)$ extrapolated to $T = 0$°K, for the thinner films. For comparison, the curves calculated by Ittner are also shown. One is calculated for a coherence length ξ_0 equal to 2560 A and an intrinsic or "bulk" electronic mean free path of 1000 A; the other is calculated for a coherence length of 2560 A but for infinite bulk mean free path. Clearly, the penetration depths calculated from Eq. (7) are in qualitative agreement with Ittner's calculations.

On the other hand, one really should not calculate penetration depth from critical field data using the London model. In the first place, the London theory does not properly take account of the surface energy between normal and superconductive regions. In addition, the London theory is a "weak field" theory and hence may not properly describe phenomena taking place at the critical field. A theory which does not have these shortcomings, but which is still a local theory, is that proposed by Ginzburg and Landau. In this theory are contained the quantities H_c, the critical field of a bulk specimen; δ_0, the penetration depth in weak field; x, a theoretical parameter, which is approximately 0.1 for

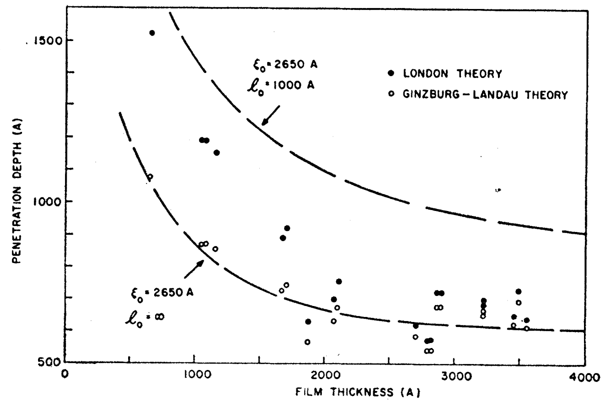

FIG. 4. Dependence of penetration depth upon thickness for indium films. The dashed curves are based on a theoretical calculation by Ittner.

indium; and ψ, an "effective" wave function of the "superconducting electrons." The critical field of a film is related to the above quantities and to the film thickness. For thin films, Ginzburg and Landau assert that one can with sufficient accuracy assume $\psi = \psi_0 =$ constant within the superconductor. This is equivalent to setting $x = 0$ and results in a considerable simplification of the relations. Under the latter assumption, the following relations are obtained for h_c, the film critical field [reference 4, Eqs. (61) and (62)]:

$$(h_c/H_c)^2 = [\psi_0^2(2-\psi_0^2)/1-(1/\eta)\tanh\eta], \tag{8}$$

where $\eta = \psi_0 d/2\delta_0$.

$$(h_c/H_c)^2 = [4\psi_0^2(\psi_0^2-1)\cosh^2\eta/1-(1/2\eta)\sinh 2\eta]. \tag{9}$$

It has recently been shown by Gorkov[27] that the Ginzburg-Landau equations follow from the microscopic theory of superconductivity, if one identifies the quantity ψ as being proportional to the energy gap Δ, and if one is restricted to small Δ (and hence small ψ). In practice this situation is always realized at temperatures close to T_c, but may not be at temperatures below T_c. Therefore, the validity of Eqs. (8) and (9) is somewhat in doubt at $T = 0$. It was pointed out by Abrikosov,[28] however, that the Ginzburg-Landau relations, which are based on an expansion of the free energy F_s in powers of $(\psi)^2$ should be valid at temperatures well below T_c in the case of thin films, since $\psi_0 \ll 1$. It can be shown from Eqs. (8) and (9) that for the indium films, ψ_0 is less than 0.1 for films thinner than about 1700 A. Further, since ψ_0 is small for the thin films, it follows that Δ is also small, which implies that Gorkov's derivation may also be valid in this case. At any rate, δ_0 has been calculated for the thin indium films in the limit $T = 0$ and the values are shown in Fig. 4. It is evident that the values of δ_0 are in reasonable agree-

[25] W. B. Ittner, III, Phys. Rev. **119**, 1591 (1960).
[26] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1.
[27] L. P. Gorkov, Soviet Phys.—JETP, **9**, 1364 (1959).
[28] A. A. Abrikosov, Doklady Adad. Nauk S.S.S.R. **86**, 489 (1952).

ment with Ittner's calculation for $\xi_0=2560$ A and infinite "bulk" electronic mean free path.

The values of penetration depth shown in Fig. 4 may be compared to measurements of the penetration depth of bulk single-crystal indium specimens by Dheer,[29] who reports $\lambda(0)=423$ A–485 A depending upon orientation. Measurements of $\lambda(0)$ for indium films were also reported by Lock,[21] who obtained $\lambda(0)$ equal to 540 A–708 A for films ranging in thickness from 1970 A to 9580 A, respectively.

To see whether 2560 A is a reasonable coherence length, let us calculate ξ_0. From the Bardeen, Cooper, and Schrieffer theory,[30] the coherence length ξ_0 is related to the Fermi velocity v_0 and the energy gap at 0°K, $\epsilon(0)$, by the relation

$$\xi_0=\hbar v_0/\pi\epsilon(0). \tag{10}$$

The Fermi velocity can be calculated from the electronic resistivity ρ, mean free path l, and effective mass m^* from the relations[31]

$$m^*v_0=ne^2\rho l, \tag{11}$$

and

$$m^*v_0=\tfrac{1}{2}h(3n/\pi)^{\frac{1}{3}}, \tag{12}$$

where n is the density of the conduction electrons, and e is the electronic charge. The effective mass can in turn be calculated from the coefficient of the electronic specific heat γ from the expression[32]

$$m^*=7.3(nV_m{}^3/na)^{-\frac{1}{3}}m\gamma, \tag{13}$$

where n_a is the number of atoms per unit volume, V_m is the molar volume, m is the electronic mass, and γ is in units of millijoules/mole-deg².

When Eqs. (10)–(13) are combined, one obtains

$$\xi_0=1.68\times10^{-2}V_mh^3/me^2N_0{}^{\frac{1}{3}}\epsilon(0)\gamma\rho l, \tag{14}$$

where N_0 is Avogadro's number and h is Planck's constant. Substituting into Eq. (14) the values $\epsilon(0)=1.82kT_c$ obtained from recent tunneling experiments[33]; $V_m=15.37$ cm³ from Swenson's data[17]; $\gamma=1.7$ millijoules/mole deg² which is the average of calorimetric values obtained by Clement and Quinnell[34] and Bryant and Keesom[35]; and $\rho l=0.6\times10^{-11}$ ohm-cm² from Dheer's measurement, ξ_0 comes out to be 4300 A which agrees well with the value 4400 A calculated by Davies.[12] If one takes $\rho l=2.0\times10^{-11}$ ohm-cm² calculated previously from the resistivity data, then $\xi_0=1300$ A. However, if one uses the value of ρl obtained by Roberts, $\rho l=0.89\times10^{-11}$ ohm-cm², then ξ_0 equals 2900 A which is in reasonable agreement with the data of Fig. 4. In view of the spread of values which can be obtained for ξ_0, it seems reasonable that ξ_0 might be about 2600 A.

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[29] P. N. Dheer, Proceedings of Cambridge Conference on Superconductivity, July, 1959 (unpublished).
[30] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[31] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, England 1953) p. 248.
[32] P. H. Keesom and N. Perlman, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. XIV.
[33] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[34] J. R. Clement and E. H. Quinnell, Phys. Rev. **92**, 258 (1953).
[35] C. A. Bryant and P. H. Keesom, Phys. Rev. Letters **4**, 460 (1960).