Superconducting Transition Width in Pure Gallium Single Crystals*

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The superconducting transition in 99.9999% pure gallium single crystals was investigated. The change in mutual inductance at 23 Hz of a pair of coils containing the sample was used to monitor the transition. In long, thin single crystals, the transition was 90% complete in a temperature interval of 2×10^{-5} °K, a smaller superconducting transition width than is usually reported in the literature. This transition width corresponds to a superconducting penetration depth at 0°K of $\lambda_0 \leq 3.8\times10^{-5}$ cm, in agreement with the nuclear-resonance data of Hammond and Knight. Several factors were investigated for possible effects on the transition width. For pure single crystals, the dominant contribution to the transition width was correlated to the relative lengths of the sample and the primary coil. Samples shorter than the primary coil showed substantially broadened transitions, probably caused by a complex nucleation of the superconducting state at the blunt ends of the specimens in the weak (10^{-2}–10^{-3}-G) primary-coil magnetic field. All effects of damage on the transition width were removed by 40 h of room-temperature annealing, and the transition temperature from specimen to specimen of cut and annealed specimens was the same to within a temperature interval at least as small as the transition width. These results support the suggestion by Gregory, Sheahen, and Cochran that the critical-field curve of gallium may be used as a reliable secondary temperature standard below $T_c=1.083$°K.

I. INTRODUCTION

A VERY well-defined transition to the superconducting state in pure gallium single crystals was observed using a mutual-inductance technique to monitor the transition. In the best samples, the superconducting transition was better than 90% complete in a temperature interval of about 2×10^{-5} °K. Such a transition width is comparable with the theoretical limit on the width for the mutual-inductance method of observing the superconducting transition, as calculated from the two-fluid model and the London's equations. An ideal transition such as this is necessary for the proper study of the superconducting transition as a phase transition. It may also be possible to use such a well-defined critical temperature as a fixed point in low-temperature thermometry.[1] Consequently, the experimental conditions under which these narrow transitions were observed are reported here. The factors that were found to increase the transition width to the values usually reported in the literature (10^{-4}–10^{-3}°K) are also discussed.

II. WIDTH OF THE SUPERCONDUCTING TRANSITION

A. Theoretical Estimates of the Transition Width

The transition to the superconducting state should be "smeared" over a finite temperature interval because of statistical fluctuation in the ordering parameter that defines the states of the metal. This is a well-known result of statistical mechanics and has been applied to other phase transitions. In the case of superconductors, the fluctuations are of the "effective wave function" ψ of the Ginzburg-Landau theory or, equivalently, of the energy gap $2\Delta(T)$ of the BCS theory. Shmidt[2] and Ginzburg[3] have recently calculated the width of the superconducting transition by applying the theory of fluctuations to the Ginzburg-Landau description of superconductors. These authors show that the transition to the superconducting state should spread over a temperature interval of 10^{-14}–10^{-5} °K in pure homogeneous superconductors. A similar estimate of the width of the region of logarithmic singularity in the specific heat of a superconductor was obtained by Batyev *et al.*[4]

If real superconductors have so narrow a transition width as 10^{-14}–10^{-15} °K, there is no hope of observing such a width directly, since temperature intervals of this order of magnitude are not measurable. However, one would expect a substantially greater transition width in even the purest single-crystal superconductor if the sample is not a pure isotope. In a metal of mixed isotopic constitution, the fluctuation in the concentration of isotopes throughout the sample volume should lead to transition widths on the order of 10^{-5}–10^{-6} °K if the classical isotope effect is observed for the material, i.e., $T_c \propto M^{-1/2}$, where M is the isotopic mass of the lattice atoms. This result is based on a calculation of the fluctuation of the concentrations of a two-isotope mixture within many equal-sized cells throughout the sample. The cells are taken to be cubes

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[1] W. D. Gregory, T. P. Sheahen, and J. F. Cochran, Phys. Rev. **150**, 315 (1966).

[2] V. V. Shmidt, Zh. Eksperim. i Teor. Fiz., Pis'ma V Redaktsiyu **3**, 141 (1966) [English transl.: Soviet Physics—JETP Letters **3**, 89 (1966)].

[3] V. L. Ginzburg, Fiz. Tverd. Tela, (1960) [English transl.: Soviet Phys.—Solid State **2**, 1924 (1961)].

[4] E. G. Batyev, A. Z. Patashinskii, and V. L. Pokrovskii, Zh. Eksperim. i Teor. Fiz. **46**, 2093 (1964) [English transl.: Soviet Phys.—JETP **19**, 1412 (1964)].

of the order of the superconducting coherence length on a side, assuming this is the smallest volume for which a transition temperature has a meaning. It is further assumed that there are about equal total concentrations of each isotope and that the average isotopic mass is about 50 amu. These assumptions are well satisfied by gallium.[5]

B. Experimental Limitations on the Transition Width

It would appear from the analysis given above that transition widths of the order of 10^{-5}–10^{-6} °K should be observed in practice. In two recent studies somewhat greater transition widths were observed. Cochran[6] found transition widths of about 5×10^{-4} °K in the width of the specific-heat transition of Ta and Sn samples. Neighbor *et al.*[7] found transition widths of 3×10^{-4} °K in very pure lead specimens using both specific-heat and susceptibility methods to detect the transition. Transition widths of this order of magnitude are typically reported in the literature. Assuming that the theoretical estimates of the width are reliable, the excess transition width must be attributed to experimental causes. These may be causes related to the condition of the sample (which we investigate in this paper) or they may be inherent in the methods for observing the superconducting transition.

Defining the superconducting transition by any of the three parameters that change at T_c (the specific heat, resistivity, and penetration depth for ac fields) has inherent difficulties for studies of the superconducting transition width. The discrete temperature steps used in taking specific-heat data are fixed by statistics[8] and limit temperature resolution to about 10^{-4} °K.[6,7] Resistivity measurements of T_c and ΔT_c can be erroneous because of filimentation of the superconducting state.[9] A good compromise method for observing the transition is to measure the change in the penetration of ac fields at T_c (i.e., the Meissner effect). Such data can be taken in a continuous fashion as a function of temperature. While it is true that the properties of only the material contained in a normal-state skin depth are probed by such a technique, the skin depth can be made as large as 1000 superconducting penetration depths by the use of low-frequency ac fields. Thus, over dimensions characteristic of the superconducting state, a large amount of material is investigated. If samples are properly prepared, the sample surface down to one skin depth can be made free of strains and defects. This assumption can be checked with x-ray studies of the surface as well as by use of the transition-width data itself. A poor sample surface condition could result in anomalously large transition widths.

Use of the Meissner effect to define T_c introduces an inherent limitation on the transition width which can be measured. The penetration depth is related to the change of mutual inductance ΔM of a pair of coils containing a superconductor and may be given approximately by

$$\Delta M(T)=K(\delta-\lambda(T)) \qquad (T<T_c), \qquad K=\text{constant}, \tag{1}$$

provided the sample diameter D is greater than the normal-state skin depth δ or the superconducting-state penetration depth λ. In the superconducting state, the penetration depth has a temperature dependence given by

$$\lambda(t)=\lambda_0/(1-t^4)^{1/2}, \qquad t=T/T_c \tag{2}$$

for the two-fluid model of a superconductor.[10] Although the penetration depth has a strong temperature dependence, the 0°K value λ_0 is not achieved abruptly at T_c, so that some uncertainty may arise as to the exact temperature at which the penetration began to change. It is clear from Eq. (1) that if $\lambda_0\simeq\delta$, then *no* appreciable change of the mutual inductance will occur until $T\simeq0$°K. The criterion for observing a sharp jump of mutual inductance at T_c is that $\lambda_0\ll\delta$, a result which can be achieved by choosing a low frequency ω for the ac field in the mutual inductor primary, since $\delta\propto\omega^{-r}$, where $r=\frac{1}{2}$ or $\frac{1}{3}$ according to the classical theories of the skin depth.[11] To illustrate this more clearly, the change in mutual inductance of a pair of coils containing a superconductor has been calculated[12] exactly for a cylindrical sample without the approximation of Eq. (1) using the Londons' equations and Maxwell's equations. The results are plotted in Fig. 1. The plots for the two different values of λ_0 clearly show the dramatic effect λ_0 has on the temperature dependence of the mutual inductance. The points where $M_{(\text{super})}/M_{(\text{normal})}=\frac{1}{2}$ fit very well to the assumption

$$[\lambda(T)]_{M(\text{super})/M(\text{normal})=1/2}=\delta/2.$$

This yields, expanding $T=T_c-\Delta T$ and using the binomial approximation,

$$(\Delta T/T_c)_{M(\text{super})/M(\text{normal})=1/2}=(\lambda_0/\delta)^2. \tag{3}$$

Thus, a measurement of the half-width of the transition can be used to estimate λ_0.

III. EXPERIMENTAL DETAILS

Superconducting transitions were detected by the change in mutual inductance ΔM at 23 cycles of a pair

[5] The author wishes to thank J. E. Neighbor and R. S. Newbower for an interesting discussion concerning the transition width in mixed isotopes.

[6] J. F. Cochran, Ann. Phys. (N.Y.) **19**, 186 (1962).

[7] J. E. Neighbor, J. F. Cochran, and C. A. Shiffman, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio*, edited by J. A. Daunt *et al.* (Plenum Press Inc., New York, 1965). p. 479.

[8] J. F. Cochran, C. A. Shiffman, and J. E. Neighbor, Rev. Sci. Instr. **37**, 499 (1966).

[9] E. Maxwell and M. Strongin, Phys. Rev. Letters **10**, 212 (1963).

[10] The two-fluid predictions for λ (T) agree well with the BCS theory. See J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[11] E. H. Sondheimer, Advan. Phys. **1**, 1 (1952).

[12] This calculation appears in Appendix 1 of W. D. Gregory, Ph.D. thesis, M.I.T., 1966 (unpublished).

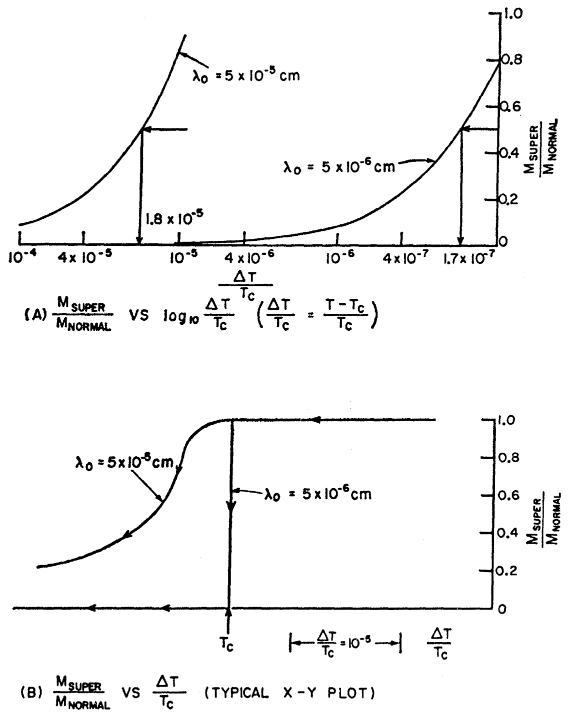

FIG. 1. The mutual inductance as a function of temperature for a pair of coils containing an infinite-cylinder superconductor. The two values used of the superconducting penetration depth λ_0 bracket the present estimate for gallium (Ref. 13). The normal-state skin depth δ was taken as 0.01 cm, appropriate for gallium at 23 Hz.

of coils containing the sample. A carbon resistor attached to the specimen served as a high-resolution thermometer. Data were taken by plotting ΔM as a function of carbon thermometer resistance with an X-Y recorder while the specimen temperature was changed slowly through T_c. The carbon resistor was then calibrated in temperature sensitivity dR/dT, using the slope of the critical-field curve at T_c, dHc/dT, or in temperature $R(T)$ against the vapor pressure of ^{3}He. The change in mutual inductance was calibrated by comparison with a standard mutual inductor.

The gallium samples used in this work were made from very pure (99.9999%) Alcoa gallium using a technique similar to that described by Yaqub and Cochran.[13] The samples were grown in Lucite molds by injecting liquid gallium into channels of appropriate size and initiating the growth of the solid phase with a piece of solid single-crystal gallium used as a seed. The seed crystal was mounted in a goniometer and usually oriented so that the sample crystal grew with the A axis of Ga parallel to the longest sample dimension.

The cryostat,[8] the experimental technique,[1] and the methods of sample preparation[1,13] have all been reported previously. The reader is referred to these publications for further details.

[13] M. Yaqub and J. F. Cochran, Phys. Rev. **137**, A1182 (1965); J. F. Cochran and M. Yaqub, *ibid.* **140**, A2174 (1965).

IV. RESULTS

A. Transition Width in Long, Thin Single Crystals

The mutual-inductance traces for long, thin single crystals of Ga are very much like the ideal trace calculated from the two-fluid model shown in Fig. 1. An example of this is the transition in a 6-in.-long by $\frac{1}{16}$-in.-square single-crystal rod shown in Figs. 2(A)–2(C). The three traces were taken with the temperature resolution progressively increased from Figs. 2(A) to 2(C). This figure illustrates the criterion used to define T_c, i.e., the point where the change of mutual inductance falls to half the maximum change between the superconducting and the normal states.

Even at the highest temperature resolution used [Fig. 2(C)], the transition still looked extremely sharp and was 90% complete within a temperature interval of 2×10^{-5} °K. In Fig. 2(C) the mutual-inductance trace was taken many times, both cooling and warming through the transition. It was observed that the transition width associated with *each pass* through the transition was far less than the combined width shown in the figure. Thus, the finite width of the tran-

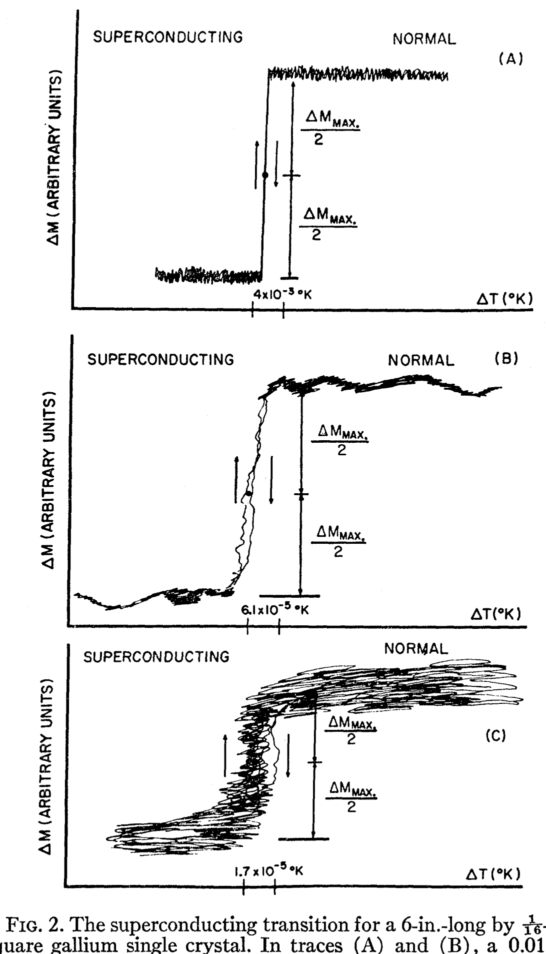

FIG. 2. The superconducting transition for a 6-in.-long by $\frac{1}{16}$-in.-square gallium single crystal. In traces (A) and (B), a 0.012-G field was used in the primary coil. In trace (C), a 0.003-G primary field was used.

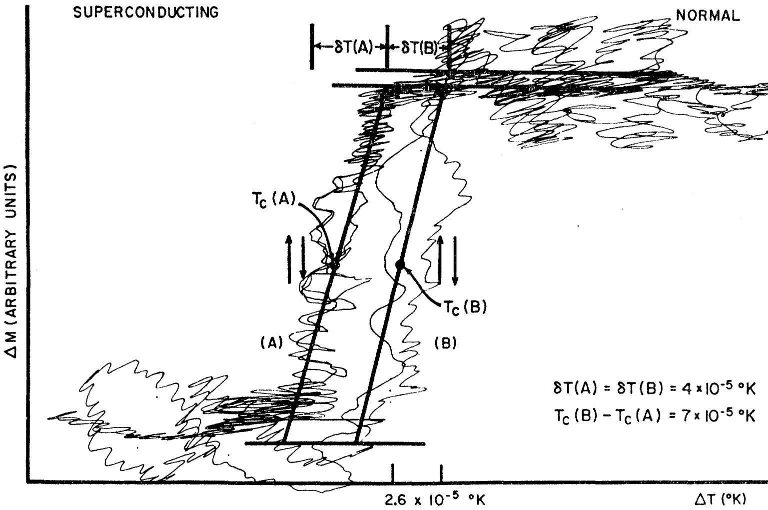

FIG. 3. The effect on the superconducting transition of a 6-in.-long by $\frac{1}{16}$-in.-square gallium single crystal of reducing the primary-coil magnetic field. (A) The transition in a 0.012-G primary field, showing $T_c = T_c(A)$ and the transition width, $\delta T(A)$. (B) The transition in a 0.003-G primary field, showing $T_c = T_c(B)$ and the transition width $\delta T(B)$.

sition in Fig. 2(C) was primarily the result of thermal and electronic noise in the apparatus. Note that the noise on *both* the X and Y axes increases as greater temperature resolution is used. The reason for this is that smaller primary-coil currents were used when greater temperature resolution was required to avoid visibly perturbing the transition with the primary-coil magnetic field.

The data of Fig. 2 show that it is indeed possible, under suitable conditions, to obtain transition traces comparable to those shown in Fig. 1. Using Eq. (3), one notes that a transition width of 2×10^{-5} °K corresponds to a value of $\lambda_0 \leq 3.8\times10^{-5}$ cm. This is compatible with the estimate of $\lambda_0 = 1.2\times10^{-5}$ cm obtained by Hammond and Knight[14] from nuclear-resonance data. The normal skin depth can also be estimated from the data of Fig. 2 by using Eq. (1). One finds that $\delta = 0.9\times10^{-2}$ cm, in reasonable agreement with calculated values of the skin depth using the resistivity data for gallium given by Cochran and Yaqub.[13]

B. Investigation of Factors Affecting the Transition Width

When the very narrow transition shown in Fig. 2 was observed, steps were taken to discover the factors limiting the transition width and to determine if the critical temperature was defined to the accuracy of the transition width ΔT. The following properties were investigated for their effect on ΔT.

1. Primary-Coil Magnetic Field

The effect of the primary-coil magnetic field on the mutual-inductance trace was investigated using another 6-in.-long by $\frac{1}{16}$-in.-square specimen. These data are shown in Fig. 3. The observation of another very narrow transition width for this specimen shows that the data in Fig. 2 were not due to a freak specimen. One can see that decreasing the field from 0.012 G [Fig. 3(A)] to 0.003 G [Fig. 3(B)] shifts T_c but does not reduce the transition width ΔT. The transition temperature did not change further as the field was reduced further from 0.003–0.001 G.

The shift in T_c from Fig. 3(A) to 3(B) can be calculated from ΔH the difference in the mutual-inductor primary fields used in (A) and (B) and the value of $(dH_c/dT)_{T_c}$ for Ga of -92.5G/°K taken from Ref. 1. This estimate is

$$\frac{\Delta H}{(dH_c/dT)_{T_c}} = \Delta T_c = 10^{-4}\,°\text{K}.$$

The shift in T_c measured directly from Fig. 3 is 7×10^{-5} °K, in substantial agreement with this figure.

It is clear that the transition widths in Fig. 3 were not produced by the primary-coil magnetic field, since changing this field by a factor of 4 produced no change in the width. As with the other 6-in.-long sample (Fig. 2), this width seems to be limited by the noise seen in the mutual-inductance trace.

2. Metallurgical Condition of the Sample

An attempt was made to determine whether residual effects of impurities, strain and damage, or polycrystalline structure could cause the transition widths of 10^{-4}–10^{-3} °K reported in the literature. Polycrystalline specimens with transitions broadened to 10^{-3} °K by differential thermal contraction between crystallites were found, but the back reflection x rays for such specimens were like Debye-Scherrer patterns and would be clearly distinguishable from the perfect Laue photographs for our specimens. The addition of 4 at. wt. % of silver to gallium broadens the transition to 5×10^{-3} °K but decreases the resistance ratio of the specimens from 10^5–10^2 and should also be detectable. The effects of strain and damage on the transition are also completely avoided if the specimens are annealed sufficiently at room temperature (melting point of gallium = 29.8°C). Table I shows that damaged

[14] R. H. Hammond and W. D. Knight, Phys. Rev. **120**, 762 (1960).

TABLE I. The effects of various kinds of damage on the T_c of single-crystal Ga plates.

Sample thickness (mil)	ΔT_c [a] (m°K) run No. 1[b]	ΔT_c [a] (m°K) run No. 2[c]	Treatment
1	−0.009	+0.009	Bent (45° at center)
1	+0.091	+0.009	Epoxied to Cu plate
2	+0.017	+0.089	Untouched, control sample
1	+0.205	−0.071	Smeared with epoxy

[a] $\Delta T_c = T_c$ (thin plate) $- T_c$ (bulk sample).
[b] Run No. 1—plates undamaged.
[c] Run No. 2—plates damaged, then annealed 40 h at room temperature.

specimens, annealed 40 h at room temperature, show no residual effect on T_c. Table II shows that annealing beyond 40 h is unnecessary. Ten hours of annealing was not found to be sufficient, however. These results are consistent with the effects of annealing on the resistance ratio of gallium specimens reported by Weissberg and Josephs.[15]

3. *Sample Holder*

The possible effect on the transition width of temperature gradients in the specimen and specimen holder was investigated using a mutual inductor with three secondaries equally spaced along one primary. The difference in transition temperature at all three positions, both cooling and warming through T_c for six samples each long enough to fit through all three secondaries was $\Delta T_c = (+0.012 \pm 0.013)$ m°K. For the same samples, each cut into three pieces, then annealed 40 h at room temperature, epoxied together with copper wire and replaced in the secondary coils, we found $\Delta T_c = (-0.007 \pm 0.05)$ m°K. This shows that temperature gradients were negligible and once again that 40 h annealing is quite sufficient to remove any effects on T_c of the damage due to cutting the specimens.

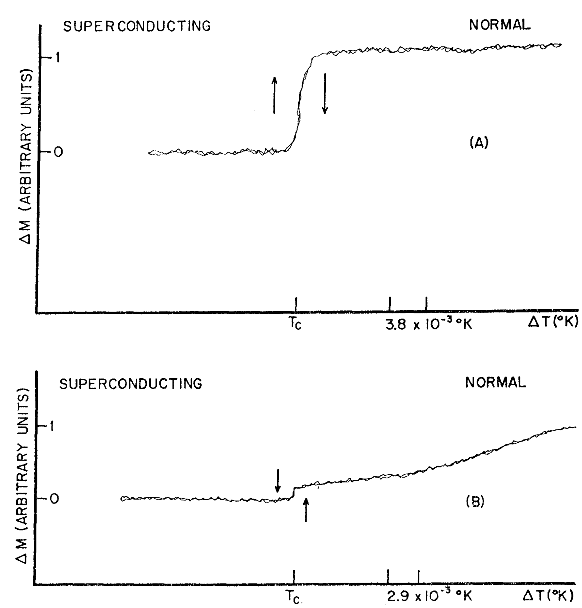

FIG. 4. The superconducting transitions in a 1-mil-thick by 1-in.-long by ¼-in.-wide single-crystal gallium plate before and after coating with epoxy resin. The change of mutual inductance from 0–1 corresponds to a 100% complete transition. (A) *Before* coating with epoxy. (B) *After* coating with epoxy.

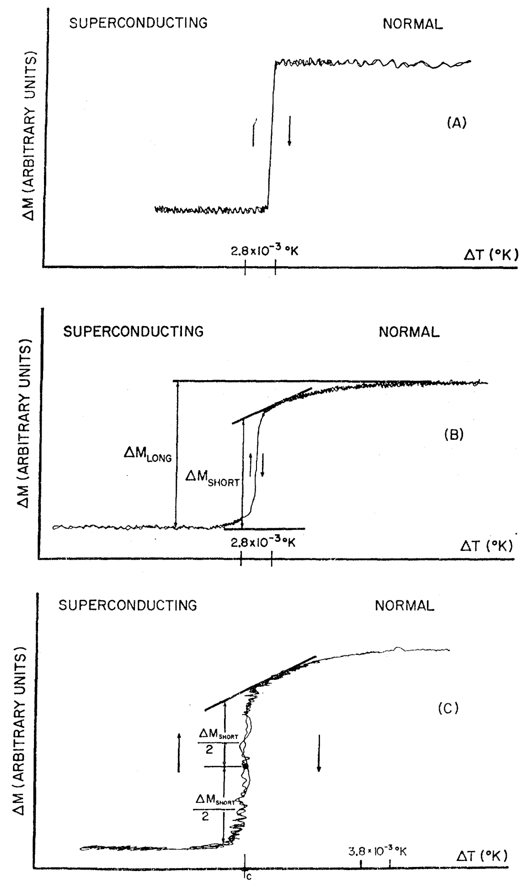

FIG. 5. The superconducting transition for three Ga single crystals with different sample shapes. (A) The transition in a sample 6-in. long by $\frac{1}{16}$-in. square. (B) The transition in a 2-in.-long piece cut from the 6-in.-long sample. (C) The transition in a 7-mil-thick by 1-in.-long and ¼-in.-wide plate.

One effect on the transition due to the sample holder was discovered. The normal side of the transition was smeared, because of differential contraction of the sample with the epoxy[16] binding of the sample to the sample holder, for any sample with the epoxied part in the primary coil. Figure 4 shows the increase of this effect when the amount of epoxy is substantially increased. However, as noted in Table I, this effect does not shift T_c if the smeared part of the transition

[15] L. R. Weissberg and R. M. Josephs, Phys. Rev. 124, 36 (1961).

[16] Stycast No. 2850 FT epoxy resin, manufactured by Emerson and Cummings, Inc., Canton, Mass.

TABLE II. The effect of annealing on the T_c of single-crystal gallium plates.

Sample thickness (mil)	ΔT_c [a] (m°K) run No. 1[c]	ΔT_c [a] (m°K) run No. 2[d]	$\Delta^2 T_c$ [b] (m°K) (run No. 2) − (run No. 1)	Annealing time beyond 40 h (h)	Total annealing time (h)
7	+0.100	0.00	−0.100	31	71
1	+0.076	−0.084	−0.160		
5	+0.114	+0.066	−0.048		
1	+0.078	+0.070	−0.008	116	156
2	+0.016	+0.018	+0.002		
2	+0.088	−0.027	−0.115		

[a] $\Delta T_c = T_c$ (thin plate) $- T_c$ (bulk sample).
[b] $\Delta^2 T_c = \Delta T_c$ (run No. 2) $- \Delta T_c$ (run No. 1).
[c] Run No. 1—ΔT_c measured after 40 h anneal at room temperature.
[d] Run No. 2—ΔT_c measured after extra annealing time beyond 40 h as indicated.

is eliminated in defining T_c by using $\frac{1}{2}(\Delta T_{c(\text{short})})$ as demonstrated in Figs. 5(B) and 5(C). The epoxy effect was found to be even more pronounced in indium samples (data not shown here).

4. *Sample Geometry*

The most substantial effect broadening the transition was correlated with the relative lengths of the sample and the primary coil. No other dimension of the sample appeared to matter. Figure 5 shows the transitions of one sample that was longer than the primary coil (one of those with $\Delta T \approx 2\times10^{-5}$ °K, discussed earlier) and two other specimens shorter than the primary but radically different in the rest of their geometry. Besides the epoxy smearing discussed above, one can see that the superconducting side of the transition is also smeared for the short specimens. This effect might be due to complicated nucleation of the superconducting state at the blunt ends of the specimens when these ends are in the primary-coil magnetic field. However, the magnitude of this effect is quite startling since the primary-coil fields used were only 10^{-2}–10^{-3} G. One can see from Fig. 5 that this effect tends to broaden the transition 100 times from 10^{-5} to 10^{-3} °K, requiring a demagnetizing coefficient of about 100 to explain this width using simple theories of the intermediate state.[17]

V. CONCLUSIONS

The superconducting transition width in long, thin gallium single crystals was found to be 2×10^{-5} °K or less. This width agrees with that expected from the two-fluid model and the Londons' equations and corresponds to a value of $\lambda_0 \lesssim 3.8\times10^{-5}$ cm, in agreement with the data of Hammond and Knight.[14]

The effects of several parameters on the transition width were investigated. The transition width showed a correlation to the length of the specimens in a fashion that cannot be explained by simple intermediate-state theories. Specimens which were longer than 5-in. primary coil exhibited the narrowest transitions $\Delta T \approx 10^{-5}$ °K while any shorter specimens had transition widths on the order of 10^{-3} °K. It is possible that the presence of the blunt ends of the shorter specimens in the primary coil resulted in a complicated nucleation of the superconducting state which smeared the transition over a 10^{-3} °K temperature interval.

Polycrystalline structure and impurities produced the expected smearing of the transition. Bent and annealed single crystals showed no residual effects on the transition provided annealing took place for 40 h or more at room temperature. The pressure of an epoxy bond at one end of the specimen to ensure thermal contact with the cryostat was shown to broaden the transition somewhat but did not substantially shift T_c. This resistance of the gallium superconducting transition to perturbing effects is further evidence that the gallium critical-field curve is a reliable secondary standard[1] for temperature below $T_c = 1.083$ °K.

Finally, we note that when the Ga superconducting transition is observed with the mutual-inductance technique used in this investigation, the critical temperature can be determined to 10^{-5} °K for specimens longer than the primary coil and to 10^{-4} °K for shorter specimens. This makes possible the study of minute effects on the transition temperature of Ga or other similar pure single-crystal materials. One such study has been completed, concerning the effect of boundary scattering on the critical temperature of pure gallium single crystals. This work will be reported at a later date.

ACKNOWLEDGMENT

The author wishes to thank Professor J. F. Cochran for encouraging this work. The cryostat used for this investigation was designed by Professor Cochran.

[17] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), 2nd ed., p. 25.