Superconducting Transition in Aluminum*

J. F. Cochran, D. E. Mapother, and R. E. Mould†
Physics Department, University of Illinois, Urbana, Illinois
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Techniques have been developed which make it possible to examine the detailed properties of the superconducting transition under rigorously isothermal conditions down to temperatures of about 0.8°K. The superconducting behavior of an accurately ellipsoidal single crystal of pure aluminum has been studied by using a high-precision ballistic induction method which is particularly well suited for studying the reversibility of the transition. The problem of accurately determining the thermodynamic critical field, H_c, from magnetic induction measurements is discussed.

The experimental results show that aluminum always supercools by a substantial amount if the applied magnetic field is reduced from a value greater than a characteristic value, H_n, which is the field necessary to destroy the last detectable trace of superconductivity in a super to normal transition. The value of H_n appears to be slightly greater than H_c. Some aluminum specimens are found to exhibit two discreet supercooled transition fields depending upon the magnitude of the excursion in the applied field beyond H_c. This effect (termed the quench effect) appears to indicate that the superconducting phase can survive in microscopic regions within the specimen at fields far above the critical field, and it is possible to determine quite accurately the field, H_q, which is necessary to quench such local regions. The available evidence is consistent with the model proposed by Faber according to which the persistent superconducting traces are associated with localized strain configurations in the metallic lattice.

1. INTRODUCTION

The basic superconducting properties of aluminum are not known with the degree of precision that exists in the case of the easily measurable elements such as tin. The critical temperature of aluminum lies just below 1.2°K, and comparatively few precise measurements have been made in this temperature region owing to the difficulties associated with the establishment of the stable and accurately known temperatures which such measurements require.

This paper is the first of two articles which will present the results of an investigation whose object has been the accurate determination of the critical constants of the superconducting transition in aluminum. Part I describes the procedures followed in making precise ballistic induction measurements under conditions of exceptionally good temperature stability down to temperatures of about 0.8°K. The measuring techniques used in this work provide a detailed picture of the magnetic changes which occur in the specimen as it is taken through the superconducting to normal transition and vice versa (hereafter designated as *S-N* or *N-S* transitions), revealing certain qualitative features of the transitions which have not received close attention in previous work. The discussion of the results in Part I is largely confined to the qualitative aspects, and the presentation of precise numerical values for the critical constants of the transition in aluminum will be given in Part II.

2. EXPERIMENTAL

A. Cryostat

The cryostat designed for this investigation is based on the scheme originally described by Blaisse, Cooke, and Hull[1] for reducing the temperature by pumping through a small orifice over an adiabatically isolated bath of liquid helium. The orifice reduces the efflux of helium from the bath due to Rollin Film flow, thus greatly reducing the quantity of gas to the pumping system. This permits the achievement of low pressures over the helium bath with vacuum pumps of moderate capacity.

A cross-sectional view of the working portion of the cryostat is shown in Fig. 1, and a schematic diagram of the complete apparatus appears in Fig. 2. The inner bath is pumped by a C.V.C. oil-diffusion pump (VMF-100) backed by a C.V.C. booster pump (VKB-08) and a Cenco Hypervac-23 forepump.[2] Temperatures as low as 0.76°K have been achieved under some circumstances, but no great effort has been expended to reach lower temperatures. The pumping tube above the inner bath in Fig. 1 is $\frac{1}{4}$-inch diameter Cupro-nickel of 0.006-inch wall thickness, and it terminates at an orifice of 0.030-inch diameter where it connects to the inner vessel. With this pumping tube and orifice, a temperature of about 0.8°K could be reached regularly. The pumping line contains a large throttle valve (about 4-inch diameter) immediately in front of the diffusion pump which is used to reduce the pumping speed at the inner bath and thus approximately control the temperature of the inner bath. The inner bath is thermally isolated by a vacuum jacket which is continuously pumped by a diffusion pump. Unless otherwise noted, all parts of the lower assembly are made of brass.

Since the metal construction of the cryostat prevents visual observation of the inner liquid level, the following scheme is employed to fill the inner vessel and

* This work has received partial support from the Office of Ordnance Research.
† This work was done while on leave from the Preston Laboratories, Butler, Pennsylvania.

[1] Blaisse, Cooke, and Hull, Physica 6, 231 (1939).
[2] These specifications are given to permit estimates of the available pumping capacity, but better pumps for this purpose are available.

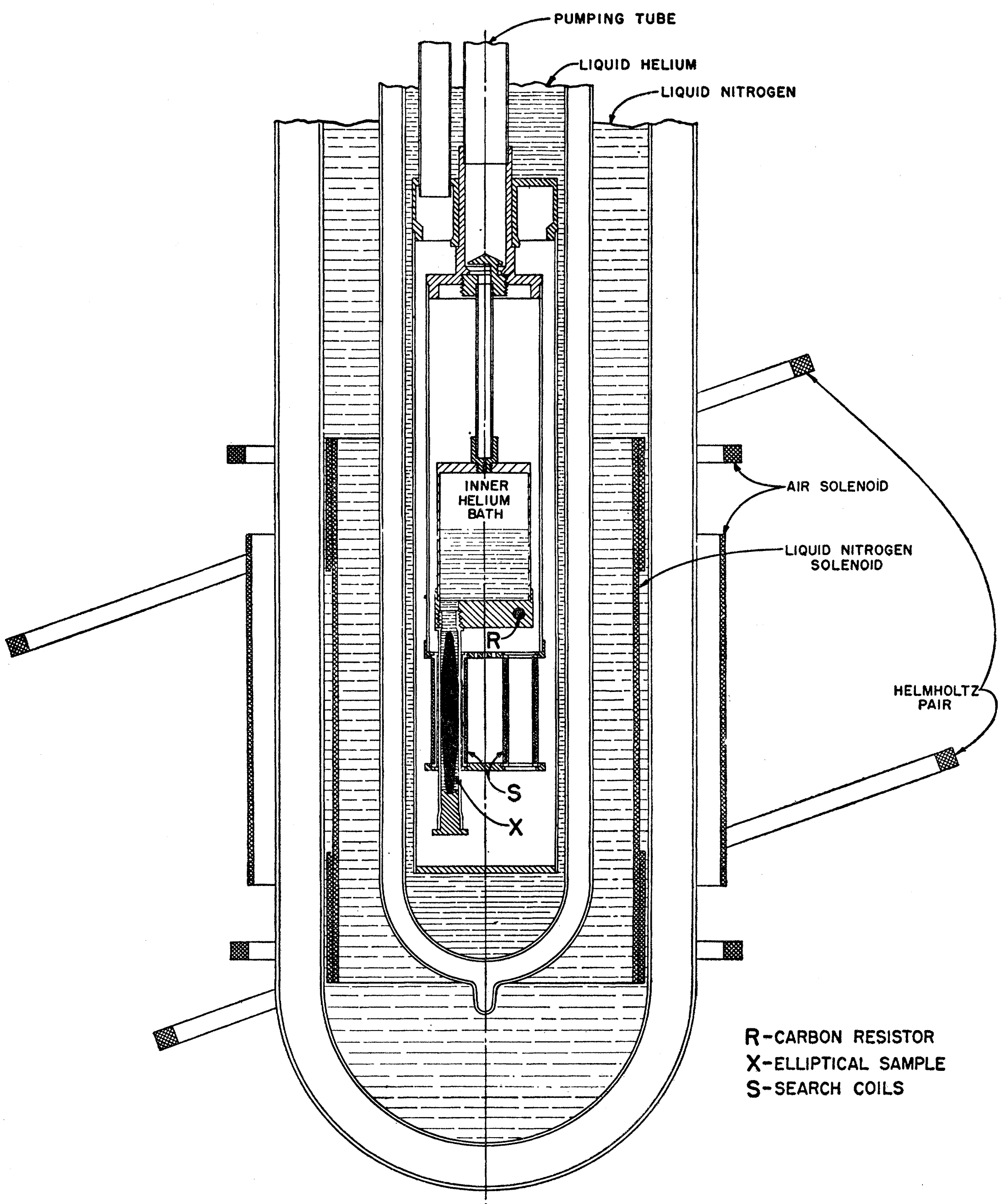

FIG. 1. Cross section of the working region of the cryostat. Mechanical details of the bobbins for the solenoids have been omitted for simplicity, but the dimensions and placement of the windings are drawn to scale.

monitor the liquid level within it. An external tank of known volume is filled with helium gas at about 200 psi. The helium is then slowly bled from this tank, condensed in a coil immersed in the outer helium bath, and discharged into the inner system just above the small pumping tube. The throttle valve closes off the inner system from the pumps during this operation. The pressure drop in the tank from which the gas is being bled provides an indication of the quantity of liquid condensed in the inner system. The subsequent level of the liquid in the inner bath is determined by measuring the volume of gas discharged from the fore-pump. Although the volume of the inner vessel is only about 40 cc, the loss of helium in pumping through the orifice is sufficiently small that one filling of liquid will last for about 30 hours operation.

The superconducting specimens under observation are held loosely in cylindrical appendages (called sample

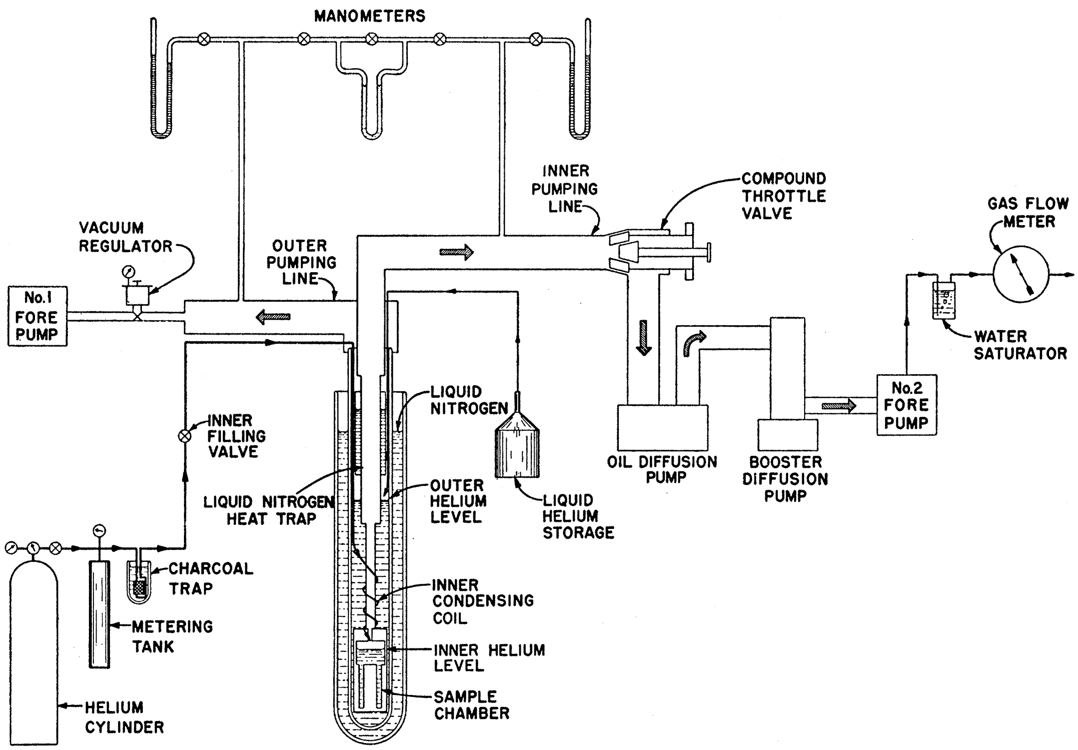

FIG. 2. Schematic diagram of the complete cryostat.

tails) which project from the bottom of the inner vessel. The specimens are immersed in liquid He II, an arrangement which assures excellent thermal contact with the inner bath. The specimens are inserted into the sample tails by means of removable soldered plugs at the bottom of each tail. It is desirable for the sake of the specimen that the solder used have a low melting point, and, for the sake of the magnetic measurements, that it be nonsuperconducting. These two requirements have been met satisfactorily by the use of a solder consisting of a eutectic mixture of bismuth and cadmium which has a melting point near 140°C and which, unlike most soft solders, does not become superconducting down to the lowest temperatures that we can reach.[3] We have found this solder to work very nicely but potential users are cautioned to avoid overheating it since the consequences of inhaling cadmium oxide fumes are severe and often fatal.[4]

The search coils used in the magnetic measurements are clamped in a rigid support which keeps them from touching the inner container. This mounting prevents the conduction of heat to the inner bath through the electrical leads to the search coils. The heavy bottom of the inner vessel is made of copper and a carbon resistance thermometer is mounted in this piece.

[3] We are indebted to Dr. R. R. Hake for conducting a series of tests on various low-melting alloys which resulted in the selection of this particular solder.

[4] See, for example, *Metals Handbook* (American Society for Metals, Cleveland, 1948), p. 755.

The vapor pressure of the outer helium bath can be regulated by means of the separate pumping system shown in Fig. 2. The temperature of the outer bath can be accurately stabilized at any value between 1.5 and 4.2°K by the use of a bellows-actuated regulating valve in the pumping line. This feature is employed in the calibration of the carbon thermometer on the inner vessel.

B. Temperature Control

The temperature was determined in these measurements by using the carbon resistor mounted on the inner vessel. In order to calibrate the resistor, helium gas was introduced into the vacuum space surrounding the inner vessel, this putting the carbon resistor into good thermal contact with the outer bath. During this operation the inner system was filled with helium and closed off from the pumps. Under these circumstances the pressure prevailing in the pumping tube is the equilibrium vapor pressure of the condensed helium in the inner vessel. The vapor pressure was measured with a large-bore mercury manometer. The resistance of the carbon thermometer was determined as a function of the vapor pressure in the inner system and the vapor pressure data were converted to temperatures using the 1948 temperature scale.[5] Resistance-temperature data were obtained over the temperature range from about 4 to 1.5°K and used to determine the

[5] H. van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

best values of the constants A, B, and K in the empirical formula[6]

$$B/T=K/\log R+\log R-A.$$

This formula was then used to calculate temperatures below 1.5°K from the observed resistance values. It should be remarked that subsequent measurements have shown that this sort of extrapolation cannot be relied upon to determine the absolute temperature to better than 1 or 2%.

The resistance of the carbon thermometer was measured with a Wheatstone Bridge circuit which included provisions for eliminating lead resistance and stray emf's. The null detector was a Leeds and Northrup 9835-B stabilized dc amplifier with a built in microvoltmeter. The carbon thermometer was made from a 10-ohm $\frac{1}{2}$-watt Allen-Bradley carbon radio resistor, and its sensitivity was such that temperature variations of 10^{-4} °K were readily detectable over the range 1.2 to 0.8°K.

Because of its high sensitivity, the carbon resistor was used to maintain a very stable temperature in the inner helium bath. To stabilize the temperature, the throttle valve in the pumping line was adjusted to produce a temperature in the inner bath slightly lower than that desired for a measurement. A Type G Leeds and Northrup Millivolt Speedomax recorder, driven by the dc amplifier on the resistance bridge, was then used to actuate an on-off switch controlling the current to a constantan heater wound on the inner vessel in such a way as to keep the bridge balanced at the desired resistance value. In this way the temperature of the superconducting specimens could be held constant to within 10^{-4} °K for hours if necessary.

C. Magnetic Field Control

The method used in measuring the superconducting transitions requires the use of two separate solenoids, called the nitrogen and air solenoids after the medium in which each operates in the apparatus (see Fig. 1). The magnetic field applied to the specimen is the sum of the fields produced by these two solenoids. The nitrogen solenoid produces a large constant field which is regulated at about the value corresponding to the critical field of the specimen at the temperature of measurement. The air solenoid supplies a small field which may be made to subtract from or add to the field produced by the nitrogen solenoid. By adjusting the current in the air solenoid, the magnetic field at the specimen can be very accurately controlled within a range of field values which brackets the critical field of the specimen. Both solenoids have been based on designs recently proposed by Garrett[7] which are characterized by exceptionally homogeneous fields and by favorable geometry for applications in cryogenic apparatus.

The nitrogen solenoid design was based on Garrett's sixth order system. As indicated in Fig. 1, it is a solenoid with double-wound ends which produces a field uniform to one part in 10^3 within a roughly spherical volume about 3 inches in diameter. The solenoid is powered by a current-regulated supply capable of a maximum current of 1 ampere (corresponding to a maximum field of 100 gauss). By means of the regulator the field can be held constant to ± 0.01 gauss.

The design of the air solenoid is based on Garrett's eighth-order system which consists of a short solenoid with compensating loops at either end. For the air solenoid, the field is uniform to one part in 10^3 within a spherical volume of about 4 inches in diameter. This solenoid is powered by storage batteries. A bank of 15 precision resistors connected in series with the solenoid is so arranged that by successively shunting the resistors, the magnetic field may be increased in 15 approximately equal steps. The step interval, and hence the maximum field produced by the air solenoid, can be varied by using more or less storage batteries as required. The step interval used in the present work was 0.08 gauss, giving a maximum field of 1.2 gauss. The total span of magnetic field which could be covered stepwise was, in this case, 2.4 gauss since the air solenoid field could first be set to oppose the nitrogen solenoid field, reduced stepwise to zero, reversed, and then increased stepwise from zero, aiding the nitrogen solenoid field.

Both the nitrogen and air solenoids were calibrated with a precision of one part in 10^3 by using the paramagnetic resonance absorption line of potassium dissolved in liquid ammonia. Experimental measurements were also made to establish the boundaries of the 0.1% limits on field homogeneity for both solenoids. The homogeneity of field over the entire volume of the specimens was 0.1% or better in all measurements.

A Helmholtz pair was used to cancel the earth's magnetic field at the superconducting specimens. Critical fields measured with the solenoid fields normal and reversed indicated that 0.08 gauss of uncompensated stray field remain at the samples.

D. Specimen Preparation

All of the specimens measured in this work were prepared from 99.99% pure aluminum bar stock supplied by the Aluminum Company of America. In order to permit an accurate estimate of the demagnetizing coefficient of the specimens, all were carefully machined in the form of an ellipsoid of revolution with a major axis of 2.50 inches and a minor axis of 0.242 inch.

After machining, the specimens were recrystallized into single crystals by using the soft-mould technique

[6] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

[7] M. W. Garrett, J. Appl. Phys. **22**, 1091 (1951).

of Noggle[8] which preserves the machined dimensions. The specimens were etched to check for the existence of grain boundaries by using a solution due to Beck *et al.*[9] One polycrystal with a machined surface was studied.

E. Measurement of the Superconducting Transition

The conventional scheme, of switching off and on a magnetic field of the order of magnitude of the critical field, was not appropriate in the present investigation for two reasons. In the first place, the use of paramagnetic salt pills as thermometers was envisaged at the beginning of this work, but large changes in the magnetic field make accurate temperature stabilization impossible in this temperature range if any magnetic material is in thermal contact with the superconducting specimen. Secondly, it was desired to study the supercooling phenomenon in the aluminum transition but switching off the entire external field completely obscures this effect.

In the method adopted for this work, two identical search coils, one of which surrounds the aluminum specimen, are connected in series opposition through a sensitive ballistic galvanometer. The change of the effective permeability of the specimen as it makes an isothermal transition is determined from the galvanometer deflections when the applied magnetic field is changed by small, monotonic, stepwise increments so as to take the specimen through its critical field.

The galvanometer used in these measurements was a Leeds and Northrup 2285-e having a coil resistance of 13.2 ohms, a period of 29 seconds (undamped), and an external critical damping resistance of 600 ohms. The search coils were wound on brass bobbins insulated with a single layer of glassine paper as a precaution against short circuits between the coil and the bobbin. Each coil consisted of 9760 turns of 40-gauge heavy Formex-insulated copper magnet wire with a resistance of 1300 ohms at room temperature or about 26 ohms at liquid helium temperatures. Three of these coils were mounted in the coil support of the cryostat, two surrounding two separate specimen tails (only one tail is shown in Fig. 1), and the third, called the dummy, was located symetrically with respect to the two specimen coils but surrounded nothing. Switching arrangements permitted the connection of either of the specimen coils in series opposition with the dummy coil through the galvanometer. The combined resistance of two search coils at helium temperature was substantially less than the critical damping resistance of the galvanometer and so the galvanometer responded more or less as a fluxmeter.

Figure 3(a) is a diagramatic representation of the

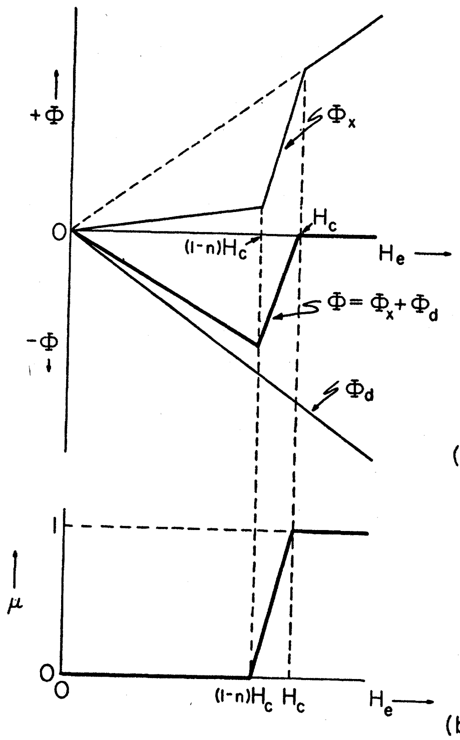

FIG. 3. (a) Variation of magnetic flux linking specimen and dummy coils for an ideal ellipsoidal superconducting specimen in a homogeneous magnetic field, H_e. (b) Variation of permeability for an ideal superconducting ellipsoid in a homogeneous magnetic field, H_e. (n = demagnetizing factor of the ellipsoid.)

flux linkage in the coil system as a function of the applied external field. In this diagram, the flux Φ_d linking the dummy is arbitrarily taken as negative, and, since the dummy coil contains no specimen, Φ_d decreases linearly with the applied field, H_e. The flux linked by the specimen coil, Φ_x, is positive since the specimen and dummy coils are connected in series opposition. Φ_x increases linearly up to the point at which the flux first begins to penetrate the specimen, but the slope has a much smaller magnitude than the slope of the Φ_d curve since flux is excluded from the volume of the specimen. For an ideal superconducting ellopsoid, the flux first begins to penetrate the specimen when the external field reaches the value $(1-n)H_c$, where n is the demagnetizing coefficient of the ellipsoid and H_c is the critical field of the specimen. Between the values $H_e=(1-n)H_c$ and $H_e=H_c$, the magnetic flux progressively penetrates the specimen, the process being represented in Fig. 3(a) as a linear rise in the Φ_x curve. For values of H_e greater than H_c, $|\Phi_x|=|\Phi_d|$ since the dummy and specimen search coils are identical. The net flux linkage in the galvanometer circuit is shown by the heavy solid line in Fig. 3(a).

Expressions for the theoretical response of the present measuring method to changes in the superconducting properties of the specimen can be derived from the well-known equations which describe the macroscopic

[8] T. S. Noggle, Rev. Sci. Instr. **24**, 184 (1953).
[9] Beck, Kremer, Demer, and Holzworth, Trans. Am. Inst. Mining Met. Engrs. **175**, 372 (1948).

magnetic properties of a superconducting ellipsoid in a uniform magnetic field.[10] The net flux, Φ, linking the galvanometer circuit can be expressed as follows:

$$\Phi=\Phi_x+\Phi_d=C(H_e+f_xI)-C(H_e+f_dI), \quad (1)$$

where $C=$ the effective area-turns constant for a single search coil, $H_e=$the applied external field (i.e., the field which would exist in the absence of the specimen), $I=$the magnetic moment per unit volume of the specimen, and f_x, $f_d=$field distortion factors for the specimen and dummy coils respectively which are determined by the dimensions of the coils and the specimen but are independent of H_e. Ideally, the magnetization, I, of a superconducting ellipsoid in a uniform field, H_e, can be written

$$I=(B-H_e)/[4\pi(1-n)], \quad (2)$$

where $B=$the magnetic induction within the ellipsoid and $n=$the demagnetizing factor of the ellipsoid. Setting $(f_x-f_d)=f$, we obtain from (1) and (2)

$$\Phi=[Cf(B-H_e)]/[4\pi(1-n)]. \quad (3)$$

The quantity $Cf/4\pi(1-n)$ is a constant of the measurement which will be denoted hereafter as Γ.

To observe a super to normal transition the solenoids are first adjusted to give a value of H_e somewhat less than $(1-n)H_c$ for the temperature of measurement. Then, using the switching arrangement on the air solenoid described previously, H_e is increased monotonically in approximately uniform stepwise increments, and the galvanometer deflection accompanying each stepwise change is recorded. The galvanometer deflections are thus proportional to the derivative of the Φ curve at the prevailing value of H_e. Letting δd represent the galvanometer deflection resulting from the incremental change δH_e in the applied external field, and introducing the galvanometer flux sensitivity $K=\delta d/\delta\Phi$, the quantity measured may be expressed as

$$\delta d/\delta H_e=K\Gamma[(\delta B/\delta H_e)-1]. \quad (4)$$

Depending upon the magnitude of H_e, the specimen may be in either the superconducting, intermediate, or normal states with the following consequent responses:

(1) *Superconducting State:* $\delta B/\delta H_e=0$; thus

$$\delta d/\delta H_e=-K\Gamma. \quad (4s)$$

This relation makes it possible to directly determine the over-all flux sensitivity of the galvanometer-search-coil circuit. In the present measurements, the observed value was $K\Gamma=11.3$ mm/gauss.

(2) *Intermediate State:* $\delta B/\delta H_e=1/n$; thus

$$\delta d/\delta H_e=K\Gamma(1-n)/n. \quad (4i)$$

With the present specimens, n is approximately equal to 0.02 and so, in addition to a change in the sign of the galvanometer deflection, there is a 50-fold increase in the magnitude of the deflection which makes this method very suitable for the examination of the detailed features of the intermediate state.

(3) *Normal State:* $\delta B/\delta H_e=1$; thus

$$\delta d/\delta H_e=0. \quad (4n)$$

The accuracy with which this relation holds provides an experimental check on the degree of mismatch in the area turns constants for the different search coils. There is again a clean-cut change in the character of the galvanometer response to signify the transition of the specimen from the intermediate state to the normal state, and it is found in practice that the value of H_e at which the last trace of superconductivity leaves the specimen can be fixed with good precision.

In presenting the experimental results, it is desirable to characterize the magnetic condition of the specimen by a parameter whose magnitude varies within fixed limits depending upon whether the specimen is superconducting or normal, but is independent of the magnitude of H_c. The permeability of the specimen has the desired property since it varies from zero in the superconducting state to unity in the normal state. For an ellipsoid in the intermediate state the permeability, μ, may be defined according to the theory given by Peierls[11] as

$$\mu=B/H_c, \quad (5)$$

where

$$B=H_c-(H_c-H_e)/n. \quad (6)$$

These relations are in satisfactory agreement with previous experimental measurements on magnetic properties, and they have also been shown to be consistent with the thermodynamic requirements on the superconducting transition.[12] From (4), (5), and (6) an expression may be derived which expresses the specimen permeability in terms of the galvanometer deflections. Since this relation serves as the basis for the discussion of the experimental results, its derivation will be given here.

From (4) we have

$$\delta B^i=\delta H_e^i+(\delta d^i/K\Gamma); \quad (7)$$

but $B=0$ for all δH_e^i which give negative galvanometer deflections [see Eq. (4s)], and so B may be expressed as

$$B(j)=\sum_{i=1}^{j}\delta B^i=\sum_{i=1}^{j}\delta H_e^i+\frac{1}{K\Gamma}\sum_{i=1}^{j}\delta d^i, \quad (8)$$

where i is the integer denoting the ordinal number of the stepwise increase in H_e, and $i=1$ corresponds to the first stepwise increment which produces a positive galvanometer deflection. The quantity $B(j)$ denotes the magnetic induction within the specimen following

[10] See, for example, D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), Chap. II.

[11] R. Pierels, Proc. Roy. Soc. (London) **A155**, 613 (1936).

[12] D. Shoenberg, reference 8, p. 25.

the jth positive galvanometer deflection. The value $H_e=H_p$ at which flux first begins to penetrate the specimen is a well-defined property of the transition, and it will be noted that

$$\sum_{i=1}^{j} \delta H_e^i = [H_e(j) - H_p]. \tag{9}$$

Using (9) and the condition that $B=H_c$ when $H_e=H_c$, we may solve (8) for $K\Gamma$, obtaining

$$K\Gamma = (\sum_{\text{tot}} \delta d^i)/H_p = (\sum_{\text{tot}} \delta d^i)/[(1-n)H_c], \tag{10}$$

where $\sum_{\text{tot}}\delta d^i$ is the sum of all the positive galvanometer deflections observed as H_e is increased from H_p to H_c. (In the ideal case, this is the only interval of H_e in which any positive deflections would be observed.)

For brevity we introduce a new symbol to represent the normalized sum of the galvanometer deflections, defining it as follows:

$$\Delta d(j) = \sum_{i=1}^{j} \delta d^i \Big/ \sum_{\text{tot}} \delta d^i, \tag{11}$$

and $\Delta d(j)$ can be shown to be equal to the specimen permeability. Rewriting (8) by using (9), (10), and (11), we find

$$\Delta d(j) = (B - H_e + H_c - nH_c)/[H_c(1-n)]; \tag{12}$$

but from (6), $(nH_c - H_c + H_e) = nB$, and so

$$\Delta d(j) = \frac{1}{H_c}\frac{(B-nB)}{(1-n)} = \frac{B}{H_c} = \mu. \tag{13}$$

The derivation above is strictly valid only in the ideal case in which μ varies with H_e according to (5) and (6) and which is represented graphically in Fig. 3(b). The experimental transitions, while showing a general conformity with the results of this analysis, also show appreciable deviations, the nature and probable causes of which will be discussed in the following sections.

There is one experimental consideration which may be mentioned at this point. The constant of proportionality between the galvanometer deflection and the change in magnetic induction within the specimen depends on the relaxation time for flux changes in the specimen to reach equilibrium following a stepwise change in H_e. This is an intrinsic property of the specimen, not to be confused with the time constant of the galvanometer-search-coil circuit. Experience in this work has shown this relaxation time to be about 15 seconds when the specimen is in the intermediate state, while the time constant of the galvanometer system is about 2 or 3 seconds (since it is heavily overdamped by the search coils). The relaxation time is long enough to affect the integrating efficiency of the galvanometer, as evidenced by the observation that $K\Gamma$ determined from response in the intermediate state [from Eq. (10)] was about 20% smaller than $K\Gamma$ determined in the superconducting state [from Eq. (4s)]. The long relaxation time does not in itself reduce the validity of (13) so long as it is constant throughout the intermediate state. Observation of the galvanometer deflections indicated that the relaxation time was substantially constant in the intermediate state, but more detailed information would clearly be desirable.

3. RESULTS

In Fig. 4 the results of plotting experimental values of $\Delta d(j)$ against the applied field, H_e, are shown. In constructing such plots the normalizing factor, $\sum_{\text{tot}}\delta d^i$, is taken as the sum of all the positive galvanometer deflections observed in the complete transition, even though the experimental transition spreads over a range of H_e values greater than the ideal width, nH_c. Because of (13) we shall refer to this and similar plots as permeability curves, and the experimental quantity $\Delta d(j)$ will hereafter be designated as the *effective permeability* μ_e. It should be clear that μ_e, defined in this way, is an average quantity characteristic of the specimen as a whole.

To obtain a curve such as Fig. 4, the temperature of the specimen is first stabilized at a value somewhere below the zero-field critical temperature, T_c, and H_e is

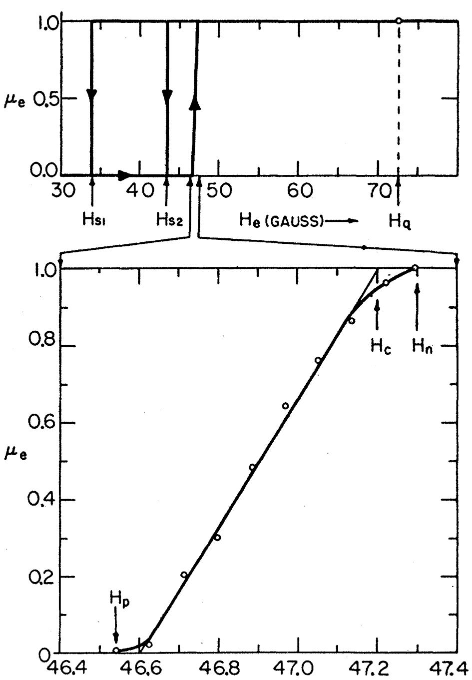

FIG. 4. Experimental permeability curve measured at a temperature of about 0.84°K. The critical parameters, H_p, H_c, H_n, H_{S1}, H_q, and H_{S2}, which are referred to in the text, are illustrated. The lower curve is a greatly expanded plot of the S-N transition shown in the upper curve.

increased from zero. The particular values H_p and H^u which mark the beginning and completion of the super to normal transition are noted on the figure. The μ_e curve is typical of the transitions observed in this work in showing a predominantly linear rise with more or less rounding near $\mu_e=0$ and 1. Because of this rounding effect, the linear portion of the permeability curve, when extrapolated to $\mu_e=0$ or 1, does not in general give either H_p or H_n. However, the value of the applied field obtained by extrapolation of the linear portion to the value $\mu_e=1$ is regarded as the best approximation to the critical field for the transition. Some arguments supporting the validity of this criterion for H_c will be given in the discussion of the following section.

If H_e is decreased from a value greater than H_n, the specimen remains in the normal state until the field is reduced considerably below H_n, and then the transition occurs abruptly at a field value which we will designate hereafter as H_{S1}. This transition is complete within one stepwidth (about 0.08 oersted) and so far as can be told experimentally it is completely discontinuous. The property of making the *N-S* transition at a field value below that for the *S-N* transition has been called supercooling and the effect has been known, since the early work of Shoenberg,[13] to be exceptionally large in the case of aluminum.

With some specimens it is found that there are two distinct supercooled transitions depending upon the

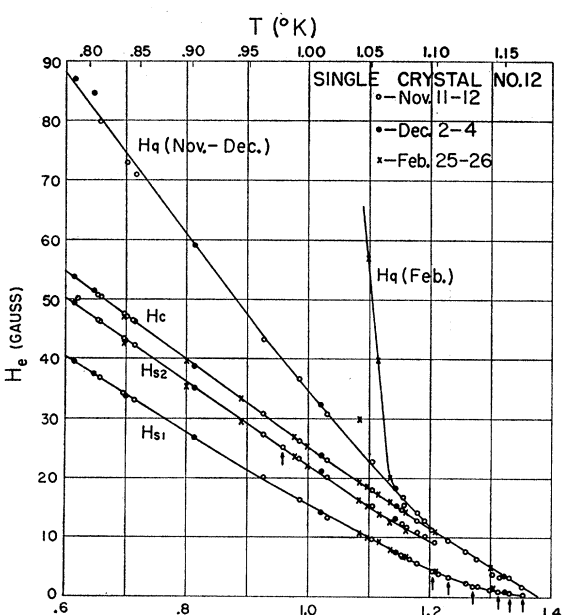

FIG. 5. Critical field curves for a pure aluminum specimen. Points determined at constant field by varying the temperature are indicated by small arrows. All other points were measured under isothermal conditions.

[13] D. Shoenberg, Proc. Cambridge Phil. Soc. **36**, 84 (1940).

magnitude of the excursion in applied field above the value H_n. We call this property the quench phenomenon, and for transitions which show this feature it is necessary to add two further particular field values to a plot such as Fig. 4. A specimen showing the quench phenomenon will not show its full degree of supercooling unless the field is first increased beyond the value H_q (the quench field). If the applied field is decreased from any value between H_n and H_q, the specimen makes a supercooled transition at a field value designated H_{S2}. The *N-S* transition at H_{S2} is, in most of its qualitative properties, the same sort of discontinuous occurrence that is observed at H_{S1}. However, in the transition at H_{S2} there is evidence of a small quantity of magnetic flux remaining in the specimen after the main precipitous drop which occurs at H_{S2}. This residual flux is rapidly expelled as H_e is reduced below H_{S2}, and its magnitude is of the order of 2 or 3% of the flux expelled in the discontinuous transition.

For completeness it should be remarked that if H_e is reduced from any value less than H_n, the permeability curve is retraced with only a small hysteresis. In other words, there is no supercooling in this case.

All of the particular field values noted in Fig. 4 are sharply defined parameters of the superconducting transition which can be accurately measured with the present technique and which show a high degree of reproducibility. Once the specimen has been cooled below the critical temperature and the temperature stabilized, no special precautions are required for the observation of these phenomena beyond manipulation of the external field in the manner described above. The results of a series of transitions observed at various temperatures are collected in Fig. 5. These measurements were made on a specimen which showed the quench phenomenon, and values of H_c, H_q, H_{S1}, and H_{S2} are plotted against the square of the temperature as determined with the carbon resistance thermometer. The quench field curve appears to cut across the critical field curve and, for temperatures greater than that corresponding to the intersection of the H_q and H_c curves, only one supercooled transition is observed. The quench field curve was reproducible for two runs between which the specimen was warmed to room temperature but not removed from the cryostat. After the second run, the specimen was removed from the apparatus and then replaced, whereupon it was discovered that the H_q curve had changed (run of February 25–26) although the H_c, H_{S1}, and H_{S2} curves remained unchanged.

The H_c curve in Fig. 5 shows a slight curvature near T_c, indicating a small deviation from a true T^2 dependence, but more recent measurements indicate the presence of a systematic error in the determination of the absolute temperature. The H_c *vs* T dependence shown in Fig. 5 is fairly close to that reported in previous work by Daunt and Heer,[14] but because of the suspected inaccuracy in the temperature a more exact analytic specification of the observed temperature dependence will be deferred until Part II.

Although the usual procedure in these measurements was to vary the applied field at constant temperature, a number of observations were made at constant applied field by varying the temperature to see whether the H_S and H_q values obtained were the same. In all cases the values measured at constant field agreed with those obtained at constant temperature to within the precision of the measurement.

Measurements were made on five different specimens which were prepared from the same lot of pure aluminum but which differed in the degree of crystalline perfection achieved. Three of the specimens were single crystals (including specimen No. 12 from which the data of Fig. 5 were obtained), one was a tricrystal, and one was a fine-grained polycrystal. In the course of the measurements on the various specimens, the measuring technique itself was refined and improved so it would serve no useful purpose to record here all the data that were obtained on all the specimens. The curves of Fig. 5 were obtained with the most refined measuring techniques on one of the best specimens and, except for the quench phenomenon, which is not observed on all specimens, they are typical results. For the present purposes it will suffice to cover the results obtained with the other specimens by a few general observations.

(1) Within the limits of error of these measurements, there was no difference between the critical field curves for any of the specimens.

(2) The degree of supercooling was about the same for two of the single crystals, but the third showed substantially less supercooling and agreed fairly closely with the supercooling properties of the polycrystal. (The H_{S1} curve of Fig. 5 represents about the largest degree of supercooling observed in this series of measurements.)

(3) The *S-N* transitions for the polycrystalline specimen were appreciably sharper than those of the single crystal specimens.

(4) There are not sufficient data from the present measurements to estimate the frequency of occurrence of the quench effect in single crystal specimens. Only one of these specimens showed the effect, but this may have been due to the circumstance that in the early measurements of this series the effect was unknown and therefore not looked for. The effect has been found again in the more recent measurements to be reported in Part II.

In the following sections, a more detailed discussion will be given of some of the features of the transition shown in Fig. 4.

[14] J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 1324 (1949).

4. SUPERCONDUCTING TO NORMAL TRANSITION

In this section, attention will be confined to the properties of the *S-N* transition between the applied field values H_p and H_n (see Fig. 4). It will facilitate the present discussion to consider the transition on a plot of μ_e *versus* h, where h is the reduced field defined as H_e/H_c. A plot of this type with a greatly expanded h scale is shown in Fig. 6. In making precise measurements on the superconducting transition, a major problem is the establishment of an accurate value of the magnetic field within the observed breadth of the transition which corresponds to the true thermodynamic critical field of the superconducting material.

A. Intrinsic Transition Width

According to the analysis presented above, the *S-N* transition in an ideal superconducting ellipsoid should, when plotted as in Fig. 6, consist of a straight line passing through the point $\mu_e=1$, $h=1$, and having a slope equal to $1/n$, where n is the demagnetizing coefficient of the ellipsoid. The absolute width of the transition is proportional to H_c and hence increases with decreasing temperature, but the relative width, as presented in Fig. 6, should be independent of the temperature. We shall call the temperature-independent relative width the *intrinsic width*, and it is of interest to see how well the predictions of the idealized theory agree with the results of an accurate measurement, and to what extent the disagreements can be explained. We shall restrict attention for the moment to data obtained below 1°K since our results show that the best approximation to ideal behavior occurs at temperatures well below T_c.

The points shown in Fig. 6 are data obtained from one specimen in observations at six different temperatures below 1°K. Since the position of the experimental points along the h axis depends upon the value assigned to the critical field, it is necessary to adopt some experimental criterion for choosing H_c. For each of the transitions in Fig. 6, H_c was determined by making a linear extrapolation of the permeability curve to the value $\mu_e=1$ on a plot such as Fig. 4. The reasons for choosing this criterion are largely intuitive in the present case since several appreciable deviations from ideal behavior are evident in the experimental transitions. However, it will be noted in Fig. 6 that this criterion results in superimposing all the transitions very nicely. The agreement between the data for different temperatures and the linearity of their common locus is noteworthy. This is what is to be expected from the idealized theory, but, unfortunately for the idealized theory and our criterion, it is not quite the right straight line.

The specimen used in these measurements was quite accurately ellipsoidal, and so it is possible to assign a fairly precise value to the demagnetization coefficient and thus to predict the slope of the transition curve. The ideal transition shape obtained in this way is

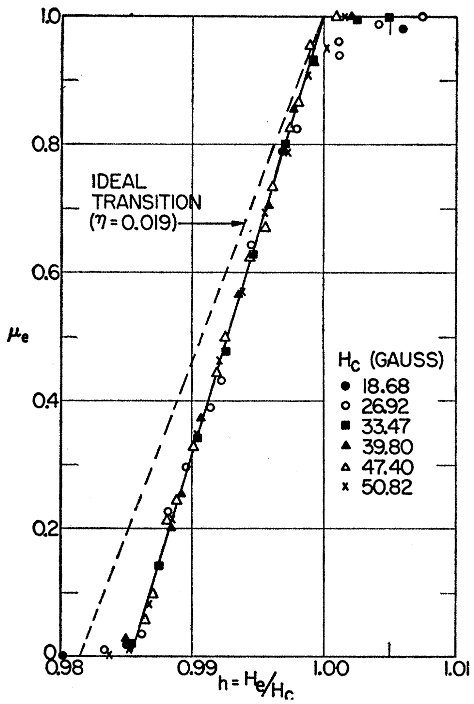

FIG. 6. Permeability curves for an ellipsoidal single crystal of aluminum measured at several temperatures below 1°K. The ideal transition shape for the ellipticity of this specimen is shown by the dashed line.

also shown in Fig. 6, and it will be noted that the experimental points indicate an intrinsic transition width which is sharper than ideal. From the dimensions of the specimen the demagnetization coefficient obtained from tabulated values[15] is 0.019, whereas the slope of the experimental transition curve indicates a demagnetizing coefficient of 0.014. To appreciate the difference in specimen dimensions implied by this difference in n values, let it be assumed that the specimen length is exactly 2.500 inches. The value $n=0.019$ corresponds to the actual specimen diameter of 0.242 inch while $n=0.014$ corresponds to a diameter of 0.202 inch. Actually the dimensions of the specimen were measured to a precision of a few thousandths of an inch, and it seems quite certain that this apparent difference in n values is something more fundamental than a matter of errors in the physical dimensions of the specimen. While the evidence of the present data is not conclusive on this point, we suggest that the extra sharpness of these transitions may be a manifestation of the free energy associated with the boundary between the superconducting and normal regions in the specimen. The role played by the boundary free energy has been ignored in the idealized theory of the intermediate state which was given above. However, the boundary free energy is positive and relatively large in the case of aluminum as evidenced by the large degree of supercooling which it shows.[16] Its effect would be to require a larger than ideal value of H_e to start the specimen into the intermediate state, which is the observed effect.

In addition to the difference between the ideal and actual slopes, further departures from ideality are evident in the rounding tendencies of the transition curves near $\mu_e=1$ and $\mu_e=0$. Observations in connection with the present work indicate that the rounding near $\mu_e=0$ is due to local flux penetration at surface irregularities or departures from perfect ellipticity, an explanation previously advanced by Maxwell.[17] The observed rounding is small with elliptical single crystals, being at most about equal to the intrinsic width of the transition. The rounding is much greater in observations on elongated cylindrical specimens which are not accurately ellipsoidal in shape. With such specimens the broadening near $\mu_e=0$ may be many times the intrinsic width.

The rounding of the transition curves near $\mu_e=1$ varies considerably from one specimen to another, and, as might be expected, it seems entirely unrelated to specimen geometry. Some correlation seems to exist between the magnitude of this rounding effect and the care taken to avoid mechanical strain in handling the specimen. With very carefully prepared single-crystal specimens, there is practically no difference between H_n and H_c. This effect is probably due to small amounts of internal strain which give rise to local regions within the specimen volume having a larger than normal critical field. (Also see the subsequent discussion on the quenching phenomenon.)

It may be remarked that rounding or smearing of experimental transition curves similar in appearance to some of the effects described above can also be caused by inhomogeneities in the applied magnetic field. We believe that the field homogeneity of the solenoids used in these measurements is sufficiently good to make any distortion of the transition curves due to this cause negligable.

To summarize the situation as observed in measurements below 1°K, it is found that the predictions of the ideal theory of the transition curve are closely fulfilled only to the extent that the actual specimens do exhibit an intrinsic broadening which is proportional to the critical field and that the permeability curves do exhibit an accurately linear rise. The theory fails to predict the slope of the permeability curves to within the precision that it can be measured, although the difference is small on the absolute scale. However, this disagreement is evidence that the theoretical basis for the procedure of determining H_c absolutely by linear extrapolation of the μ_e curve is not entirely satisfactory. For example, it is possible that the agency responsible for the disagreement between the ideal and actual slopes may also cause the entire transition to be dis-

[15] E. C. Stoner, Phil. Mag. **36**, 803 (1945).

[16] T. E. Faber, Proc. Roy. Soc. (London) **A231**, 353 (1955).

[17] E. Maxwell, Phys. Rev. **86**, 235 (1952).

placed to higher values of the magnetic field. It is not possible to know whether this is the case until the factors governing behavior in the intermediate state are better understood, although it may be expected that such a shift would be small—probably of the order of magnitude of the transition breadth. What we wish to emphasize is that the excellent experimental reproducibility of the criterion used here in determining H_c does not necessarily imply that the thermodynamic H_c for aluminum is known with the same precision with which this criterion can be reproduced owing to the theoretical uncertainty regarding conditions in the intermediate state.

B. Transitions Near the Critical Temperature

In view of the behavior shown in Fig. 6, it might be expected that the absolute magnitude of the transition width would decrease linearly with H_c as the temperature of measurement approaches the critical temperature, T_c, while the relative width (as represented in Fig. 6) would remain constant. Actually our measurements show that for temperatures approaching T_c, the absolute magnitude of the width no longer decreases linearly, while the relative width of the transition becomes larger and larger the closer T_c is approached. This characteristic is shown by the data on the reduced field plot of Fig. 7, where it will be seen that the slope of the permeability curves decreases quite markedly with decreasing values of the critical field.

The data of Fig. 7(a) were measured on the same specimen from which the data of Fig. 6 were obtained, while the data of Fig. 7(b) were obtained on two other single crystalline ellipsoids which were measured to very low values of H_c (i.e., very near to T_c). At low values of H_c, the number of experimental points per transition becomes small owing to the fixed magnitude of the incremental changes in H_e used in the present measurements. To indicate the reproducibility of the points taken at small values of H_c, the data for two separate measurements are shown on each of the transitions of Fig. 7(a). The agreement shown in Fig. 7(a) is considered satisfactory and is typical of all the measurements made in this temperature range.

The relative scarcity of points in the transitions observed near T_c leaves some latitude for individual judgment in drawing the exact shape of the permeability curve. However, we believe that these measurements clearly establish that the progressive "smearing" of the transition as T_c is approached is a reproducible property of the superconducting transition. The effect seems to be a characteristic of single-crystal aluminum specimens since similar measurements on zinc, gallium, and even polycrystalline aluminum specimens do not show this broadening effect. The fact that the broadening is absent in all but single-crystal aluminum specimens has removed our initial suspicion that the broadening effect was in some way related to the relative

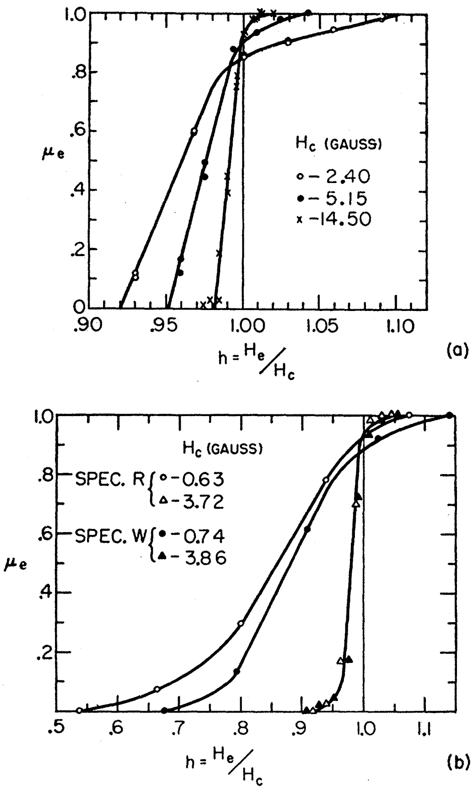

FIG. 7. Permeability curves for ellipsoidal single crystals of aluminum measured at temperatures near T_c. Curve (a) was obtained from the same specimen which yielded the curves of Fig. 6. Curve (b) shows results obtained with two different specimens which were measured very close to T_c.

resolution of the measuring method (which becomes poorer as lower values of H_c are approached).

No explanation can be offered at present for this temperature-dependent broadening, but more careful measurements are being made. Further discussion of this effect will be deferred until Part II.

5. SUPERCOOLING

The most extensive discussions of the problems of supercooling in the superconducting phase transition have been given in the recent articles of Faber,[18] and Faber and Pippard.[19] Faber introduces a parameter ϕ called the degree of supercooling which he shows to be proportional to the surface free energy per unit area associated with the boundary between the super conducting and normal phases, and which is defined as follows:

$$\phi = 1 - (H_S/H_c)^2,$$

where H_S is the value of H_e at which the supercooled transition occurs. A plot of ϕ obtained in the present measurements against the reduced temperature $t = T/T_c$

[18] T. E. Faber, Proc. Roy. Soc. (London) **A214**, 392 (1952).

[19] T. E. Faber and A. B. Pippard, *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1955), Vol. 1, Chap. IX.

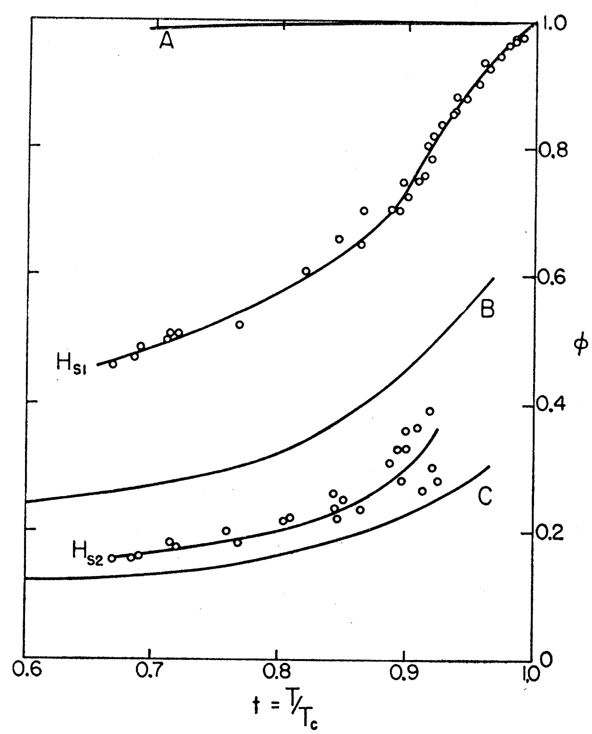

FIG. 8. Degree of supercooling *vs* reduced temperature for the two supercooled transitions observed with specimen 12 (see Fig. 5). Some data obtained in localized measurements by Faber are shown for comparison. Curve A shows results on aluminum described in reference 14. Curves B and C show results on tin described in reference 16.

is shown in Fig. 8, with some of Faber's data for tin[18] and aluminum[16] for comparison.

It should be pointed out that the measuring method employed by Faber makes it possible to determine the degree of supercooling characteristic of a small region within his specimen, whereas the method of the present work determines the degree of supercooling characteristic of the whole specimen. On the basis of Faber's observations on tin, this difference in measuring method should result in low values of ϕ in the present case since our values of H_S are, in Faber's nomenclature, characteristic of the "weakest flaw" in the entire specimen. Even so, the ϕ values observed in the present work are considerably larger than the greatest ϕ values observed in tin, and, near T_c, they are fairly close to the values observed by Faber in aluminum using the localized measuring technique.

The apparent uniqueness of the H_{S1} values observed in these aluminum measurements is in contrast with the results obtained by Faber on tin. The value of H_n which must be exceeded for supercooling to occur can be fixed as exactly as the precision of the present measuring method permits, i.e., about 0.08 gauss. If H_e is reduced from any value less than H_n the specimen will not supercool, and if H_e is reduced from any value greater than H_n the specimen always supercools to the same value, H_{S1}, within the precision of the measurement (except for the special case of the quench effect). In his measurements on tin, Faber found what amounts to a continuous range of H_n values, since within a limited range of field values a continuous increase in the magnitude of the excursion of H_e beyond H_c resulted in a continuous increase in the degree of supercooling. This behavior is attributed to the existence of an assortment of potential superconducting nuclei of various "strengths" which are successively subdued by the application of increasingly large fields. A plausible inference from the distinct character of H_n in these aluminum specimens is that the nucleating centers must be very uniform in character throughout the volume of the specimen.

The supercooled transition consists of an apparently discontinuous drop in permeability and with the 0.08-gauss limit of resolution of the measuring technique, it has not been possible to detect any width in the supercooled transition at H_{S1}. An estimate of the completeness of the Meissner effect in the supercooled transition can be obtained from the galvanometer deflections, but uncertainty regarding the integrating efficiency of the galvanometer makes it difficult to establish a precise value. The best estimate from the present data indicates that the frozen-in flux is less than 3% of the flux contained by the specimen when in the normal state immediately above H_{S1}.

6. QUENCH EFFECT

A brief description of what we call the quench effect has been given in Sec. 3. In this section, we will describe some subsidiary observations on this phenomenon and offer some conjunctures concerning their significance.

The important parameters of the quench effect are H_q, the quench field, and H_{S2}, the additional (higher) supercooled field which is observed. One of the significant features of the effect is the excellent reproducibility of H_q and H_{S2} which, as noted above, is as good as the reproducibility of the critical field or any of the other parameters of the transition. This indicates that, whatever the fundamental origin of the effect may be, it is characteristic of a stable condition in the specimen. Such evidence as exists suggests that the quench effect is very sensitive to mechanical strain in the specimen. (Note the shift in the H_q curves in Fig. 5.) The qualitative attributes of the effect can be explained in a consistent manner by assuming that H_q corresponds to the applied field necessary to irreversibly transform (or quench) a small trace of the superconducting phase within the specimen. According to this picture the superconducting trace, if unquenched, serves as an abnormally large nucleating center for the initiation of the N-S transition and therefore cause the supercooled transition to occur at the larger than normal field, H_{S2}.

If this hypothesis regarding the significance of H_q is correct, one question which arises is that of **the** magnitude of the volume of the superconducting trace which gets quenched at H_q. Attempts were made to ascertain this volume by careful observations to see whether any expulsion of flux could be detected when the external field was raised through the value H_q. By working at the lowest temperatures where H_q is relatively large, some enhancement of the sensitivity of the galvanometer to a Meissner effect in a microscopic volume is achieved. In these measurements the over-all sensitivity was such that an S-N transition in a spherical volume of about 10^{-3} cm^3 could be detected, but nothing could be seen. Unfortunately this observation is rather inconclusive since it merely puts an unexciting upper limit on the size of the hypothetical superconducting volume, but it is the best that could be done with the equipment.

Experiments were made to see whether the specimen showing the quench effect possessed more than one quench field. Within the range of field which could be produced by the solenoids (about 100 gauss) there was only one H_q value as was evidenced by the fact that only two supercooled transitions could be observed (one at H_{S2} occurring when H_e was reduced from any value between H_n and H_q, and one at H_{S1} occurring when H_e was reduced from any value greater than H_q). To see whether there was any H_q value above the maximum field that could be produced by our solenoids, the specimen was warmed to a temperature of about 1.25°K, i.e., well above T_c. As has been pointed out by Faber,[18] this procedure amounts to a thermal quenching of the superconducting phase which is equivalent to the application of a larger magnetic field than could be generated by the solenoids. The temperature was then reduced to the temperature of measurement with H_e established at a value greater than the H_q for the temperature of measurement, and, finally, the N-S transition observed as H_e was reduced. The result of this procedure was always a supercooled transition at the same value, H_{S1}, that was observed even when H_e was reduced from a value only slightly exceeding H_q. It will also be noted in Fig. 5 that the H_{S1} curve is a smooth, continuous locus over the whole temperature range. This evidence indicates that there was only one quench field at any given temperature.

Because of the limitations of the measuring techniques employed here, it is difficult to say anything about the fundamental nature of the agency responsible for the quench effect without moving into the realm of pure speculation. However, from the various observations which have been made, there emerges a plausible picture of a small superconducting domain which collapses irreversibly under the influence of the field H_q. That it is a single domain is suggested by the facts that the quench field appears to be correlated with some special strain configuration in the aluminum lattice, and that the magnitude of H_q is so sharply defined. If there were several domains they would have to be very similar to account for the sharpness of H_q, and the chance of the random occurrence of several identical strain configurations in the same specimen seems to us decidely less probable than the occurrence of a single exceptional strain configuration. A superficial inspection of Fig. 5 might prompt the suggestion that the strain configuration produces a localized region having the critical field curve given by H_q, but the substantial difference between the magnitudes of H_q and H_c, together with the irreversible nature of the collapse of the domain at H_q, makes such an explanation seem untenable. It seems most reasonable to attribute the presence of the reluctant superconducting domain to the effect of an anomalous boundary free-energy contribution in the vicinity of a microscopic strain configuration.

The suggestion has been made by Faber that the nucleation centers which determine the degree of supercooling are associated with loops of dislocations within the metal lattice.[18] The evidence for this assertion rests on the observations that all supercooling phenomena seem to be very strain-dependent and that Faber's detailed observations indicate that the dimensions of the nuclei for the supercooled transitions are of the order of 10^{-3} or 10^{-4} cm. The present work adds further evidence to support the importance of strain but, because of the averaging character of the measurements, it is not possible to draw any significant conclusions regarding the dimensions of the nuclei. However, it is perhaps of interest to remark that if it should be true that the superconducting nucleus responsible for the quench effect is indeed single and characteristic of a particular dislocation configuration, then the quench effect may provide a useful experimental technique for the study of dislocations. The quench effect can be roughly likened to the process in a Geiger-Müller tube in that a single microscopic event serves to initiate a large macroscopic process. Perhaps dislocation experts will be able to make something of this.

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