

nucleons in the low energy region ( $\sim 100$  Mev) for which these effects are not negligible.

The mean number of gray plus sparse black prongs is 0.77 (Table II). Taking into account relative numbers of gelatin and Ag-Br stars, we can roughly estimate<sup>26</sup>

<sup>26</sup> J. Hadley and H. York (see reference 4) have investigated deuterons and tritons ejected from carbon, copper, and lead nuclei by 90-Mev neutrons. The ratios of deuteron production cross sections to total inelastic cross sections were found to be 0.12 for carbon, 0.067 for copper, and 0.042 for lead. The cross section for tritons was found to be one-tenth that for deuterons and effectively zero for heavier particles. The assumption that these ratios are the same for the 400-Mev case is a reasonable upper limit. Therefore, one would expect that the mean number of pick-up deuterons and tritons per gelatin stars (using carbon value) would be at the most 0.12 and 0.01, respectively. In Ag-Br we would expect something intermediate between copper and lead or approximately 0.05 and 0.005 as the mean number of deuterons and tritons, respectively.

that at the most 6–8 percent of the gray or sparse black prongs could be pick-up deuterons and 1 percent could be pick-up tritons. These effects are small and do not affect any of the general conclusions reached treating all gray and sparse black prongs as protons.

#### ACKNOWLEDGMENTS

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## The Formation of a Boundary between Normal-Conducting and Superconducting Metal\*†

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An experiment is described in which a superconducting sample is arranged so that part of it is in the normal state and part of it is superconducting. The boundary surface is thus a single, large area rather than the complicated boundaries that exist between normal and superconducting regions when a sample is in the intermediate state. We find that there is a large difference between the magnetic field at which the superconducting-normal state transition occurs and the magnetic field at which the normal-state-superconducting transition occurs. These results are in agreement with the thermodynamic theory of the phase transition. The thermodynamic theory, coupled with an assumption about the nature of the surface energy between superconducting and normal metal is used to show how the hysteresis determines the ratio of this surface energy to a characteristic dimension of the superconductor. A measure of this ratio is given in the temperature region between 3.37°K and 3.68°K for superconducting tin.

### I. INTRODUCTION

**B**ELOW the critical temperature, the normal state can be restored in a superconductor by the application of a sufficiently large magnetic field.<sup>1</sup> The nature of the transition to the normal state depends on the details of the geometry of the sample relative to the magnetic field. For the special case of a large diameter, infinite cylinder in a uniform, longitudinal magnetic field, the transition occurs abruptly at a definite value of the magnetic field. This value of the field is called the critical field  $H_c$  and for a given metal depends only on the temperature. (At the critical temperature  $T_c$ , the critical field  $H_c$  is zero.) For other geometries, such as an ellipsoid, or a cylinder in a transverse field, the conditions are somewhat different. The magnetic

field is distorted around the edges of the superconductor and thus has greater values at some points on the surface than at others. The complications which arise when the sample does not have a zero demagnetization require the introduction of a new state—the intermediate state.<sup>2</sup> The intermediate state is not a pure state, but is a complicated structure of superconducting and normal domains.<sup>3–5</sup> The domains were observed by Meshkovsky and Shalnikov<sup>5</sup> to have diameters of about 0.1 cm.

Since all experiments to determine the critical field are carried out on finite cylinders, which have nonzero demagnetization, the transition from the superconducting to the normal state in a longitudinal field for such cylinders occurs with the formation of an intermediate state, usually at the ends of the cylinder. Since the intermediate state consists of small domains of superconducting and normal regions, the transition

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<sup>1</sup> H. Kammerlingh Onnes, *Leiden Comm.* **122b** (1911); *Leiden Comm.* **124c** (1911); *Leiden Comm. Suppl.* **35** (1913).

<sup>2</sup> C. J. Gorter and H. Casimir, *Physica* **1**, 305 (1934).

<sup>3</sup> L. Landau, *Nature* **141**, 688 (1938).

<sup>4</sup> A. Shalnikov, *J. Phys. U.S.S.R.* **9**, 202 (1945).

<sup>5</sup> A. Meshkovsky and A. Shalnikov, *J. Phys. U.S.S.R.* **11**, 1 (1947).

can take place by the growth of the final phase from an already established nucleus of that phase, and the corresponding displacement of a superconducting-normal boundary. Thus, the transition of a finite cylinder in a longitudinal magnetic field does not take place abruptly over the complete cylinder but grows from an established nucleus of the final phase.

The experiments of deHaas, Voogd, and Jonker,<sup>6</sup> Misener,<sup>7</sup> and more recently Desirant and Shoenberg<sup>8</sup> show that the creation of the intermediate state in a long cylinder in a transverse magnetic field requires more energy than is expected from the simple thermodynamic argument. It is assumed that the additional energy is required to create the surfaces between the normal and superconducting phases. Landau<sup>9</sup> has shown that the existence of the domain structure of the intermediate state depends on the surface energy between the normal and the superconducting phases. Andrew<sup>10</sup> has analyzed the transition of a long cylindrical conductor in a transverse field and explained the results of Desirant and Shoenberg,<sup>8</sup> who observed that the transition from the superconducting state to the intermediate state occurs at a slightly higher external magnetic field than is required to create the critical field at the surface of the cylinder. The aforementioned authors also observed a hysteresis in the transition; that is the field at which the transition from the superconducting state to the intermediate state takes place is greater than the field at which the reverse transition takes place.

In view of the complicated structure of the intermediate state, it is of interest to investigate the normal-superconducting transition with the creation of a single surface between the normal and superconducting metal, and with the growth of the final phase taking place without the benefit of a small domain of that phase to act as a nucleus. The experiment to be described has accomplished this by the application of a small, constant magnetic field  $h$  over a small central section of a long cylindrical sample, while the sample as a whole has been carried through the transition from the superconducting to the normal state by the application of an additional uniform longitudinal magnetic field  $H$  over the whole sample.

Neglecting the surface energy between phases, one would expect that when the sum of the two fields,  $H$  and  $h$ , reaches the critical field the central section would make a transition from the superconducting state to the normal state while the remainder of the sample would remain superconducting until the field  $H$  reached the critical value  $H_c$ , at which point the whole sample would pass into the normal state. On decreasing  $H$ , the

TABLE I. Hysteresis in transition field.

Temperature <sup>a</sup> (°K)	$H_0$ (oersteds)	$h$ (oersteds)	$V_c/V$	Sample coil nos. <sup>b</sup>	$\Delta h$ (oersteds)
3.681	6.9	2.77	0.25	2 and 3	1.3
3.681	6.9	2.77	0.25	2 and 3	0.9
3.681	6.9	5.54	0.25	2 and 3	0.6
3.679	7.5	2.16	0.125	3	1.3
3.679	7.5	2.70	0.25	2 and 3	1.2
3.675	7.9	1.35	0.125	2	1.2
3.675	8.0	1.35	0.125	1	1.2
3.675	8.0	1.35	0.125	3	1.2
3.675	8.1	1.35	0.125	4	1.3
3.675	8.2	2.70	0.125	1	1.9
3.659	10.5	1.62	0.25	2 and 3	1.5
3.659	10.1	2.70	0.25	1 and 2	1.8
3.649	12.0	2.70	0.125	2	2.4
3.649	12.0	2.70	0.125	3	2.4
3.647	12.0	5.40	0.125	2	1.8
3.647	11.9	5.54	0.25	2 and 3	1.6
3.608	14.6	2.77	0.25	2 and 3	1.2
3.608	16.4	2.77	0.25	2 and 3	1.0
3.608	16.6	2.82	0.625	1, 2, 3, 4, 5	1.0
3.605	18.0	5.54	0.25	2 and 3	1.6
3.566	23.8	5.54	0.25	2 and 3	1.7
3.541	27.5	2.07	0.25	2 and 3	1.8
3.541	27.5	8.31	0.25	2 and 3	1.3
3.372	51.3	2.77	0.25	2 and 3	1.9
3.372	51.3	13.75	0.25	2 and 3	1.2
3.372	51.3	27.7	0.25	2 and 3	1.3
3.372	51.3	27.7	0.25	2 and 3	1.5

<sup>a</sup> Temperatures were obtained from helium vapor pressure-temperature scale published by Royal Society Mond Laboratory, Cambridge, June, 1949, and are described by H. van Dijk and D. Shoenberg, *Nature* **164**, 151 (1949).

<sup>b</sup> The column labeled Sample coil nos. indicates which sections of the sample coils carried the current, and thus which section of the sample was in the field  $h$ .

transitions would be expected to occur at the same field values.<sup>11</sup>

The experiment to be described consisted of an investigation of the superconducting-normal transition in both increasing and decreasing magnetic field  $H$ , with several different values of the field  $h$ , and at several different temperatures as shown in Table I.

## II. EXPERIMENTAL DETAILS

(a) *Samples*.—The samples were prepared from Johnson-Matthey spectroscopically pure tin (99.998 percent Sn). They were cast in glass capillaries of diameter 0.15 cm and were 8.0 cm long. After the samples were grown into single crystals, five coils (each having a 1.0 cm length) were wound over the central five centimeters of each sample. These coils were used to supply the field  $h$ . They will be referred to as the sample coils.

(b) *Measurements*.—The transitions were observed by changes in the average susceptibility of the sample, which was deduced from measurements of the magnetic moment of the sample in a longitudinal field. The magnetic moment was measured by determining the change

<sup>6</sup> deHaas, Voogd, and Jonker, *Physica* **1**, 281 (1934).

<sup>7</sup> A. D. Misener, *Proc. Roy. Soc. (London)* **A166**, 43 (1938).

<sup>8</sup> M. Desirant and D. Shoenberg, *Proc. Roy. Soc. (London)* **A194**, 63 (1948).

<sup>9</sup> L. Landau, *J. Phys. U.S.S.R.* **7**, 99 (1943).

<sup>10</sup> E. R. Andrew, *Proc. Roy. Soc. (London)* **A194**, 98 (1948).

<sup>11</sup> In this case, since we are neglecting surface energy, there would be no Meissner effect, as is pointed out by F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1950), Vol. I, Sec. 21.

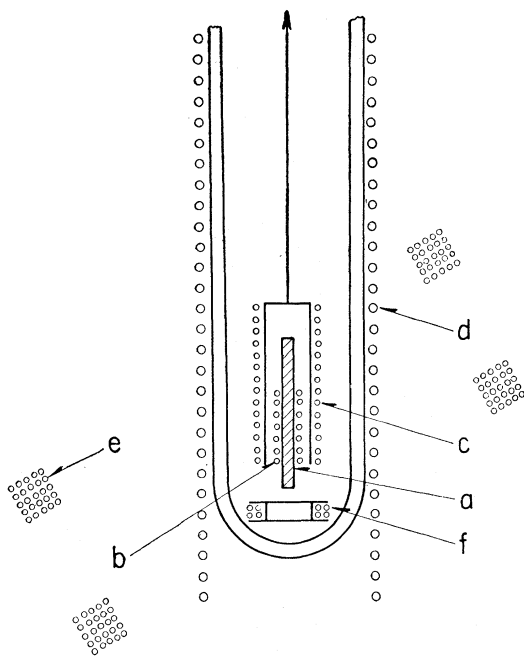


FIG. 1. Experimental arrangement.

in flux through a pick-up coil, as the pick-up coil was moved from a position enclosing the sample to a position not enclosing the sample.<sup>12</sup> The change in flux was measured with a ballistic galvanometer.

The general arrangement is shown in Fig. 1. A sample *a* was mounted inside a helium Dewar with the sample coils *b*. The pick-up coil *c* was arranged so that it could slide over the sample. Around the helium Dewar was a long solenoid *d* to supply the field *H*. Surrounding the whole apparatus was a large pair of Helmholtz coils *e* which was used to cancel the earth's magnetic field over the region of the sample. A heater *f* was placed in the bottom of the helium Dewar insuring thermal equilibrium throughout the liquid helium bath.

The data were taken by determining the magnetic moment of the sample at constant temperature (as given in Table I), and at various values of the magnetic field *H*. Care was taken to determine any hysteresis by changing the field *H* in one direction only. This was done at several values of the temperature, and for several values of the field *h*, applied over different central sections of the sample from 1 to 5 cm in length. The temperature was maintained constant by monitoring the vapor pressure over the helium bath, to within 0.2 mm of Hg. The pressure was measured with a mercury manometer.

### III. EXPERIMENTAL RESULTS

The data observed in the manner described in Sec. II are shown plotted in Figs. 2 and 3. All the curves have sample-susceptibility as ordinate and the magnetic field

<sup>12</sup> The essential features of this method are described by D. Shoenberg, Proc. Roy. Soc. (London) A175, 49 (1940).

*H* as abscissa. From these figures, with the exception of 3(*b*) and 3(*c*), it is clear that the sample is not always in the same state at a given value of the field *H*, but that it can exist in two different states, corresponding to greatly different susceptibilities, over a large range of values of the field *H*.

Figure 2(*a*) shows the transition for the field *h* equal to zero and is the usual type of transition curve in a longitudinal magnetic field. The transition is very sharp, going from the superconducting state to the normal state in about 0.2 oersted. There is no hysteresis in this transition, the points for decreasing field following the curve for increasing field. § The critical field, *H*<sub>0</sub>, as can be seen from this figure, is 11.8 oersteds.

Figure 2(*b*) is plotted from data taken at the same temperature but with the sample field *h* equal to 5.40 oersteds, over a one centimeter length of the sample. It is to be noted that between 6.6 oersteds and 9.0 oersteds the whole sample remains superconducting, in increasing field, even though the field on a one centimeter section exceeds the critical field at that temperature by as much as 2.4 oersteds. At 9.0 oersteds a transition is made to a mixed state, where the section inside the sample coil goes into the normal state and the remainder of the sample stays superconducting. Since the coil producing the field *h* covers about 25 percent of the part of the sample covered by the pick-up coil, we note that the susceptibility value of about 0.75 ( $-1/4\pi$ ) corresponds to the value expected for the mixed state. As the field *H* approaches the critical field the susceptibility increases to zero corresponding to the whole sample being in the normal state. On decreasing the field *H*, the transition to the mixed state occurs when *H* equals the critical field just as in the increasing field case. The transition from the mixed state to the superconducting state, however, does not occur until the field on the section in the sample coil drops to the critical field, corresponding to  $H = H_0 - h$ .

Figures 2(*c*) and 2(*d*) show the same form as 2(*b*), but in the cases represented, the field *h* is 2.70 oersteds causing the transitions to the mixed state to occur at higher values of the field *H*, but at the same values of the total field on the section in the sample coil. The data plotted in Figs. 2(*c*) and 2(*d*) were taken on different sections of the sample, to check on the possibility of the effect being caused by a characteristic of a particular section. No effect was found. Other sections of the sample were also used with the same negative result.

Figure 3(*a*) is a curve plotted with data obtained with the field *h* over a 2.0 centimeter length of the sample. It is to be noted that the mixed state has a susceptibility corresponding to a normal region of twice the size of the mixed state shown in Figs. 2(*b*), 2(*c*), and 2(*d*) with

§ Note added in proof.—Mr. W. H. Wright has recently conducted experiments using the same sample. He has found that if the magnetic field is brought to several times the critical value and allowed to remain there for a sufficient time, the subsequent decreasing field magnetization curve shows supercooling. This is in agreement with the thermodynamic arguments,

the 1.0 centimeter coil, in agreement with our model of the mixed state. The other characteristics of the curve are the same as those in Figs. 2(b), 2(c), and 2(d) except that the temperature is slightly lower, and thus the critical field slightly greater.

The data shown in the curves of Figs. 3(b) and 3(c) were obtained under somewhat different conditions. The full 5.0 centimeter length of the sample solenoid was used and the field  $h$  was in the opposite direction to the field  $H$ . This arrangement is equivalent to having the sample coils on the ends of the sample. Thus, for these two cases the normal region could grow out from the ends where there was an intermediate state, and therefore, a nucleus of the normal state at fields well below the critical field. The transitions in Figs. 3(b) and 3(c) from the superconducting state to the mixed state occur just at the point where the field on the end sections reaches the critical field in both increasing and decreasing field  $h$ , thus differing markedly from the results obtained with the sample coil at the center. Although there is no hysteresis in the value of the field  $H$  at which the transitions occur, there is a large hysteresis in the value of the susceptibility for increasing and decreasing field. In the case of decreasing field, when the transition from the normal state to the mixed state occurs, there must be formed in some region of the sample an intermediate state, thereby giving the observed smaller value of the susceptibility in decreasing field than in increasing field. This intermediate state region remains even after the section on the ends goes into the superconducting state. Data were not taken for lower field values to determine where the intermediate state disappeared and whether it disappeared discontinuously. At very small values of the field, however, the sample was completely superconducting and no frozen-in magnetic moment was observed.

Figure 3(d) shows part of a curve plotted from data taken when the sample was mechanically shocked at

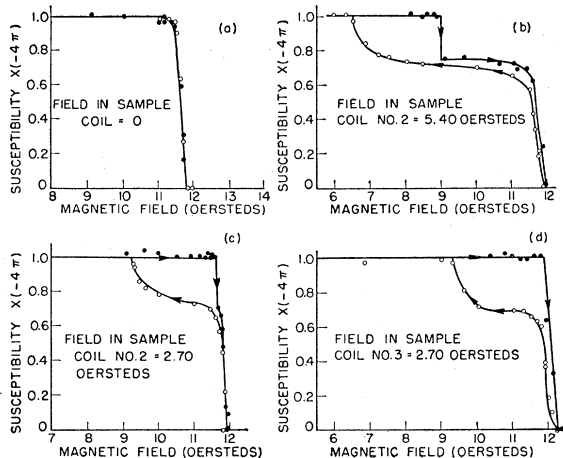


FIG. 2. Experimental curves of susceptibility versus magnetic field  $H$ .

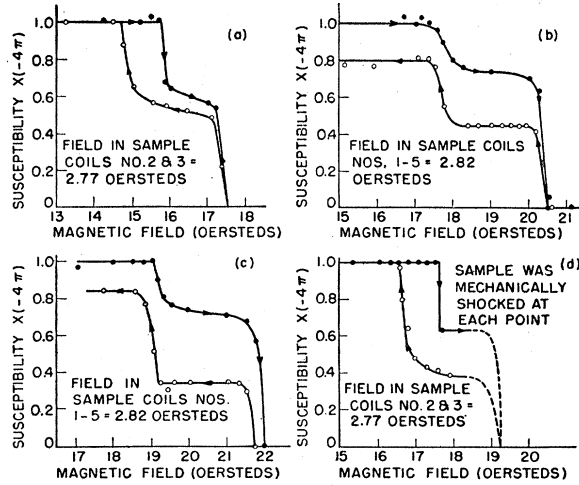


FIG. 3. Experimental curves of susceptibility versus magnetic field  $H$ .

each value of the field  $H$ . The jarring made no essential difference in the characteristics of the curves.

We call the difference in the values of the field  $H$ , at which the superconducting-mixed-state transition occurs in increasing and decreasing magnetic field, the width of the hysteresis  $\Delta h$ . Table I shows the values of  $\Delta h$  obtained under various experimental conditions. We note that  $\Delta h$  is essentially constant and is apparently independent of the temperature, the dimensions of the sample coil, and the value of the field  $h$ . There may be a small change in  $\Delta h$  with temperature, but the scatter in the values is so large that any small changes are not detectable. It should be noted that in all of the figures, except Figs. 3(b) and 3(c), the transition from the superconducting state to the mixed state in increasing field  $H$  is discontinuous; while the transition in the opposite direction, while sharp, is not discontinuous.

#### IV. DISCUSSION

##### A. Thermodynamic Theory of the Superconducting-Normal State Transition

We shall follow the thermodynamic theory of the superconducting-normal state transition developed by Gorter and Casimir.<sup>2</sup> The most stable phase of any system at constant temperature and magnetic field,<sup>13</sup> is that phase which has the minimum value of the Gibbs free energy. London<sup>11</sup> gives for the Gibbs free energy per unit volume of the normal phase  $g_n$  and the superconducting phase  $g_s$  of an infinite cylinder of large radius in a longitudinal field  $H$ ,

$$8\pi g_s = 0, \quad 8\pi g_n = H_c^2 - H^2. \quad (1)$$

We omit the same term in each expression which depends on temperature only. These latter terms are not sig-

<sup>13</sup> The thermodynamic variables considered here are magnetic field, temperature, and magnetization per unit volume.

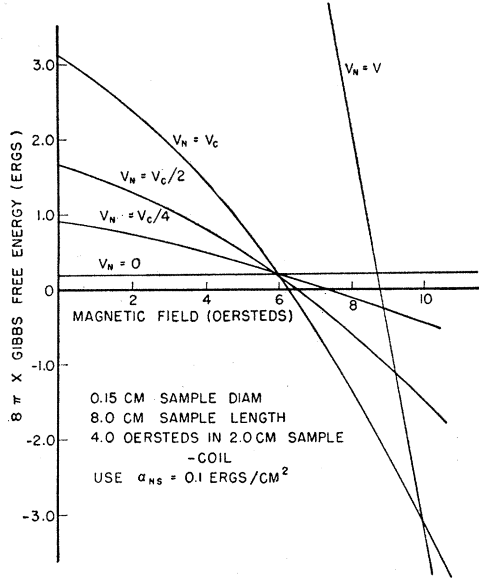


FIG. 4. Gibbs free energy of the mixed state *versus* magnetic field for various volumes in the normal state.

nificant because we are interested only in differences between  $g_n$  and  $g_s$ .  $H_c$  is the critical field at any given temperature, and  $H$  is the applied field.

We apply these equations to the case of interest and consider a finite cylinder of volume  $V$  and surface  $S$  in a uniform longitudinal field  $H$  with an additional uniform field  $h$  on a central section having a volume  $V_c$  and a surface  $S_c$ . We obtain for the total Gibbs free energies

$$8\pi G_s = 8\pi\alpha_s S,$$

$$8\pi G_n = [H_c^2 - (H+h)^2]V_c + (H_c^2 - H^2)(V - V_c) + 8\pi\alpha_n S,$$

where  $\alpha_s$  and  $\alpha_n$  are the surface energy densities at a superconducting-insulator boundary and a normal conductor-insulator boundary, respectively. We must now consider a third possible phase—the mixed phase. This phase is not to be confused with the intermediate state which is sometimes called the mixture state, but rather refers to that configuration where the volume  $V_c$  is normal, and the remainder of the cylinder is superconducting. The Gibbs free energy for this mixed phase is given by

$$8\pi G_m = [H_c^2 - (H+h)^2]V_c + 8\pi\alpha_n S_c + 8\pi\alpha_s(S - S_c) + 8\pi\alpha_{ns}A_{ns},$$

where  $\alpha_{ns}$  is the surface energy density on a superconducting-normal surface, and  $A_{ns}$  is the total area between normal and superconducting material.

It is convenient to select the zero of Gibbs free energy as the free energy of the superconducting phase. This is done by subtracting  $\alpha_s S$  from each of the three free

energies. The expressions become

$$8\pi G_s = 0,$$

$$8\pi G_n = [H_c^2 - (H+h)^2]V_c + (H_c^2 - H^2)(V - V_c) - 8\pi(\alpha_s - \alpha_n)S,$$

$$8\pi G_m = [H_c^2 - (H+h)^2]V_c + 8\pi\alpha_{ns}A_{ns} - 8\pi(\alpha_s - \alpha_n)S_c.$$

If  $H_0$  is the value of  $H$  at which the transition from superconducting to normal phase occurs for  $h=0$ , then

$$H_0^2 V = H_c^2 V - 8\pi(\alpha_s - \alpha_n)S,$$

$$H_0^2 V_c = H_c^2 V_c - 8\pi(\alpha_s - \alpha_n)S_c,$$

where we assume that the area of the ends of the sample are small compared to the total area.

Thus, we have

$$8\pi G_s = 0,$$

$$8\pi G_n = [H_0^2 - (H+h)^2]V_c + (H_0^2 - H^2)(V - V_c), \quad (2)$$

$$8\pi G_m = [H_0^2 - (H+h)^2]V_c + 8\pi\alpha_{ns}A_{ns}.$$

The most stable phase at any value of the magnetic field can now be determined by observing which of Eqs. (2) has the smallest value. Clearly any other mixed phase that can be formulated will have a larger free energy, at any value of the magnetic field  $H$ , than at least one of the three phases assumed.

The theory outlined above is the usual thermodynamic theory. We see that this theory predicts that the superconducting-mixed-state transition will occur at a value of the field  $H$  slightly greater than  $H_0 - h$ , and that the transition will occur at the same value of the field  $H$  in both increasing and decreasing magnetic field. The experimental results given in Sec. III are in contradiction to these conclusions.

## B. Mechanism of the Superconducting-Normal-State Transition

The experimental results force us to appreciate that it is not sufficient to know only the most stable phase at any given magnetic field. It is also necessary to consider the mechanism by which a transition is made from one phase to a second phase. We can expect the transition to occur only if the system can go from one phase to the other phase without increasing its free energy anywhere on the path.

If we consider the transition that takes place in going from the superconducting phase to the mixed phase, we see that this must occur by the growth of a small normal region out to the volume  $V_c$ . Thus we must consider the Gibbs free energy everywhere along this path.

For a volume  $V_n$  in the normal state, we see from the third of Eqs. (2) that the free energy of the mixed

state  $G_m$  is given by

$$8\pi G_m = \begin{cases} [H_0^2 - (H+h)^2]V_n + 8\pi\alpha_{ns}A_{ns}, & V_n \leq V_c \\ [H_0^2 - (H+h)^2]V_c + (H_0^2 - H^2)(V_n - V_c) \\ \quad + 8\pi\alpha_{ns}A_{ns}, & V_n \geq V_c. \end{cases} \quad (3)$$

As long as the normal volume extends over a region of the sample that is long compared to the diameter of the sample, the area  $A_{ns}$  remains constant. However, when  $V_n$  gets very small the shape of the normal region will take a shape which will reduce the surface energy to as small a value as possible while still keeping the energy stored in the magnetic field small. This shape will be assumed to be approximately a hemisphere with a flat surface on the surface of the cylinder.

Figure 4 is a plot of the Gibbs free energy as a function of the magnetic field  $H$ , for various values of the normal volume  $V_n$ . For simplicity,  $A_{ns}$  is taken as constant and equal to the area of a sphere with the same diameter as the sample. The surface energy density used is the value 0.1 erg per square centimeter as determined by the thin measurements of Pontius.<sup>14</sup> This value is not reliable for this purpose, but it serves to illustrate the argument. The curves show that even above that field at which  $G_m$  is less than  $G_s$  for  $V_n = V_c$  there are curves of  $G_m > G_s$  for smaller values of  $V_n$ . Thus, the path that must be taken in going from the superconducting state to the mixed state requires an increase in the free energy.

The argument aforementioned is somewhat oversimplified. We have considered that the surface energy appears on a mathematical surface. This is not actually the case, as can be realized from the consideration of the usual penetration depth, which indicates a transition region between normal and superconducting regions. If we now ascribe a characteristic length  $R_0$  to this transition region, then for all regions  $V_n$  having a radius smaller than  $R_0$ , the "surface" energy is distributed over the whole volume of the region and is no longer to be considered a surface energy but must be considered a volume energy.

We can now rewrite the first of Eqs. (3) for regions  $V_n$  small compared to  $R_0^3$ . The shape of the regions is assumed to be hemispherical. We have

$$8\pi G_m = [H_0^2 - (H+h)^2]V_n + 24\pi V_n \alpha_{ns} / R_0, \quad V_n < R_0^3. \quad (4)$$

Figure 5 is a plot of the free energy *versus* the volume in the normal state, using Eqs. (3) for large  $V_n$  and Eq. (4) for small  $V_n$ . The shape of the boundary is taken to be constant for large  $V_n$ , changing to a hemisphere when the volume  $V_n$  becomes the order of magnitude of the cube of the radius of the sample.

### C. Analysis of Experimental Results

We now discuss our experimental observations in terms of the theory preceding.

<sup>14</sup> Pontius, Phil. Mag. 24, 787 (1937).

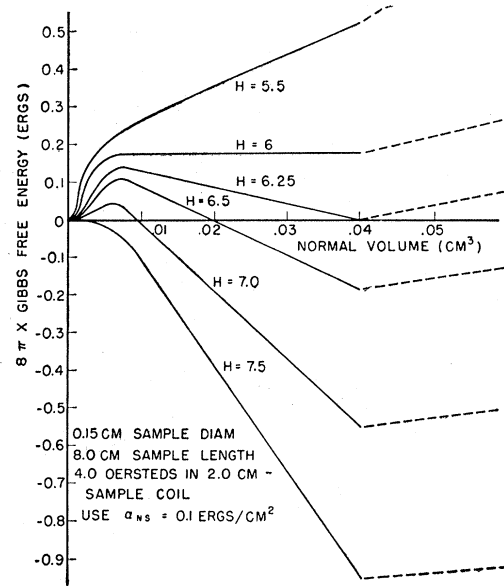


FIG. 5. Gibbs free energy of the mixed state *versus* volume in the normal state for various values of the magnetic field.

The transition from the superconducting state to the mixed state cannot occur when the mixed state has the same free energy as the superconducting state if there is a surface energy, since the path from the superconducting state to the mixed state requires an increase in the free energy. The transition cannot occur until the field  $H$  is so large that the free energy decreases everywhere along the path. Thus, the observed hysteresis is expected. This value of field,  $H_1$ , can be found by setting  $dG_m/dV_n = 0$  at  $V_n = 0$ . This yields  $(H_1 + h)^2 - H_0^2 = 24\pi\alpha_{ns}/R_0$ , or, since  $H_1 + h = H_0 + \Delta h$ ,

$$2H_0(\Delta h) + (\Delta h)^2 = 24\pi\alpha_{ns}/R_0.$$

In the approximation  $\Delta h \ll H_0$ ,

$$H_0(\Delta h) = 12\pi\alpha_{ns}/R_0. \quad (5)$$

The values of  $H_0$  and  $H_1$  can be found accurately experimentally since  $H_0$  is the transition field when  $h$  is equal to zero [Fig. 2(a)], and  $H_1$  is the field at which the transition from the superconducting to the mixed state takes place. The former is quite sharp, occurring in a region of less than 0.2 oersted, and the latter is discontinuous. However, the spread in the values from experiment to experiment indicates that there are other factors which may critically effect  $\Delta h$ . The most important factor may be the magnitude of the transverse component of field in the region of the sample. This is determined by the percentage cancellation of the earth's field and by the alignment of sample in the field  $H$ . These two factors may easily have given a variation of from 0.1 to 0.2 oersted in the transverse component of field from one experiment to the next. In addition small temperature drifts between the time  $H_0$  was

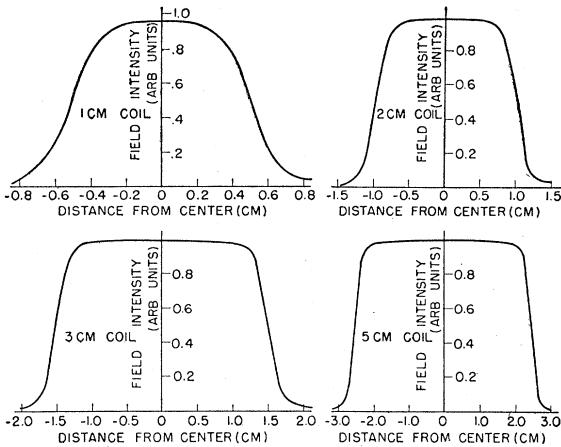


FIG. 6. Field intensity as a function of distance from the center of the sample coil.

determined and the time  $H_1$  was determined would cause the observed scatter.

From Fig. 5 we see the reason for the fact that the transition from the superconducting state of the mixed state is discontinuous. Consider the transition occurring for  $H$  equal to 7.5 oersteds. At this value of field the free energy of the mixed state is considerably smaller than the free energy of the superconducting state, and the slope of the free energy *versus* normal volume curve is very steep as soon as  $V_n$  is slightly greater than zero. We therefore expect a discontinuous transition from the superconducting state to the mixed state, since as soon as a small volume becomes normal the transition proceeds rapidly, decreasing free energy all along the path. If we now consider the transition from the mixed state to the superconducting state in decreasing field  $H$ , we see that the transition cannot occur when the free energy of the two states are equal since the path requires an increase in the free energy. In this case, the transition cannot occur until the field  $H=H_2$  is so small that the free energy decreases everywhere on the path or for  $dG_m/dV_n=0$ , for  $V_n=V_c$ . This yields

$$H_2+h=H_0, \quad (6)$$

since for large  $V_n$ ,  $A_{ns}$  is a constant. We have always observed the reverse transition to occur at precisely this field value.

The reason that the transition is not discontinuous in this last case is not apparent from this analysis. We note, however, that we have been assuming that the field  $h$  is constant over the region  $V_c$ . This is not quite correct as may be seen from Fig. 6, in which appear the magnetic field distributions for various sample-coil lengths. The field  $h$  has a maximum value at the center and decreases very slowly until it reaches the width of

the sample coil, at which point there is a sharp decrease in field. The small nonuniformity over the center section slightly modifies the family of curves plotted in Fig. 5, causing the straight portion of each of them to become concave upwards. As a result, the relative minima which occur in Fig. 5 at  $V_n$  equal to  $V_c$  do not occur at exactly that value, but move to smaller values of  $V_n$  as the field  $H$  is decreased. In the neighborhood of  $H=H_2$  the relative minimum moves rapidly to smaller values of  $V_n$  until the minimum disappears completely at  $H=H_2$ . This discussion does not appreciably affect the transition in increasing field since the free energy curve is very steep at the field  $H_1$ .

Equation (5), taken with the result that  $\Delta h$  is essentially constant over the range of temperatures considered, indicates that  $\alpha_{ns}/R_0$  varies approximately as  $H_0$ , or approximately as the critical field. At  $H_0=30$  oersteds,  $\alpha_{ns}/R_0 \sim 1$  erg/cm<sup>3</sup>. If we now relate the dimension  $R_0$  to the region of long-range order suggested by Pippard<sup>15,16</sup> and Bardeen,<sup>17</sup> we find that  $\alpha_{ns} \sim 10^{-4}$  ergs/cm<sup>2</sup> at  $H_0=30$  gauss and for  $R_0 \sim 10^{-4}$  cm. And if  $R_0$  is assumed to remain approximately constant, then the surface energy varies approximately as the critical field.

In conclusion, we review some implications of this experiment. There seems to be ambiguity in the usual definition of the critical field. This experiment gives reason to believe that in the ideal case of an infinite cylinder, there will be two different transitions, one in increasing field and one in decreasing field, neither occurring at the value of field where the two phases are in equilibrium. This ambiguity can readily be removed by the usual expedient of using long but finite cylinders. In addition the experiment implies that there is a maximum amount of supercooling or superheating that can be attained in a superconductor and that this can be determined from the ratio  $\alpha_{ns}/R_0$ . We might expect that the velocity at which superconductivity (or normal conductivity) is propagated from the point of nucleation is related to the gradient of the Gibbs function, and thus to the degree of supercooling (or superheating), as has been shown by Faber.<sup>18</sup>

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<sup>17</sup> J. Bardeen, Phys. Rev. **81**, 1070 (1951).

<sup>18</sup> T. E. Faber, Nature **164**, 277 (1949).