The Transition into the Intermediate State of Hollow Superconducting Cylinders*

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The transition from the superconducting to the intermediate state has been investigated for hollow tin cylinders with various ratios of inner to outer radii. Thermodynamic arguments show that for values of this ratio greater than $(2^{\frac{1}{2}}/2)$ the free energy in the normal state becomes less than that in the superconducting state at applied fields less than one half the critical field. The experimental results indeed show that for ratios of inner to outer radii greater than $(2^{\frac{1}{2}}/2)$ the intermediate state begins to appear at less than one-half the critical field, whereas for smaller ratios the intermediate field appears at one-half the critical field.

1. INTRODUCTION

IT has been pointed out in the previous paper by Gittleman[1] that according to Peierls[2] the transition from the superconducting to the intermediate state for a cylinder should occur at an applied field H_0 equal to one-half the critical field H_c. In the work described in the previous paper, however, it was found that for the particular hollow cylinder used, this transition occurred at $H_0=0.34H_c$ rather than $H_0=0.50H_c$. In the present paper we shall show that this behavior follows from requirements of thermodynamic equilibrium, and shall report on further measurements in support of this theory.

2. THERMODYNAMIC CONSIDERATIONS

In order to work out a complete thermodynamic theory, at a given temperature, one should compare at each field value the free energies of the superconducting state, the intermediate state, and the normal state. The most stable state will be that one which has the smallest free energy. However, the calculation of the free energy of the intermediate state is very difficult, and depends somewhat on the details of the model one uses. We shall show that it is possible to gain considerable insight into the behavior of the hollow cylinder by considering only the free energies of the superconducting state and the normal state, and that one can in fact account qualitatively for Gittleman's result and our more extensive experiments. We now proceed with this more restricted program.

One can write the first law of thermodynamics for the body as follows:

$$TdS=dU+IdH_0,$$

where T is the absolute temperature, S the entropy, U the internal energy, H_0 the applied field, and I the *total* magnetic moment of the sample.[3] Then the Helmholtz free energy becomes

$$F=f_0(T)V-\int_0^{H_0} IdH_0,$$

where $f_0(T)$ is the free energy per unit volume in the absence of a magnetic field, and V is the volume of the superconductor.

Denoting by the subscripts n and s, respectively, the normal and the superconducting states, and putting

$$f_{0n}-f_{0s}=H_c^2/8\pi,$$

where H_c is the critical field value at temperature T, the difference between the total free energy in the normal state and that in the superconducting state for a *solid* cylinder of volume V becomes

$$F_n-F_s=[H_c^2/8\pi-H_0^2/4\pi]V,$$

when H_0 is transverse to the axis of the cylinder. Accordingly, $F_n=F_s$ when

$$H_0=H_c/\sqrt{2}>H_c/2.$$

For H_0 less than $H_c/\sqrt{2}$, F_n is greater than F_s, and for H_0 greater than $H_c/\sqrt{2}$, F_n is less than F_s. As at any value of the applied field H_0 the equilibrium state of the sample is that for which the free energy has its smallest value, the transition from the superconducting to the normal state *in the absence of an intermediate state* would occur at $H_0=H_c/\sqrt{2}$. The intermediate state does exist, however, indicating that the free energy of this intermediate state must become less than that of the superconducting state at an applied field less than $H_c/\sqrt{2}$. For the solid cylinder this occurs at $H_c/2$.[2]

For a *hollow* cylinder of volume V_H the difference in free energies between the normal and superconducting states is

$$F_n-F_s=[H_c^2V_H/8\pi-H_0^2V_s/4\pi], \qquad (1)$$

where V_s is the volume of a solid cylinder having the same outer radius as the hollow one. Thus, it can be seen that the magnetic part of the free energy difference $(H_0^2V_s/4\pi)$ is independent of the size of the hole,

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[1] J. Gittleman, preceding paper [Phys. Rev. 92, 561 (1953)].
[2] R. Peierls, Proc. Roy. Soc. (London) A155, 613 (1936).
[3] Considerable confusion exists in the literature concerning the proper expression for the magnetic part of the free energy. The thermodynamic variables used above are the proper ones for our problem, and we use the expression for the free energy given by E. C. Stoner, Phil. Mag. 23, 833 (1937), which we have convinced ourselves is correct.

whereas the temperature dependent part $(H_c^2V_H/8\pi)$ becomes smaller with increasing inner radius. Hence, at a given temperature, the larger the inside radius, the smaller will be that H_0 for which $F_n=F_s$, and for all value of this inside radius $F_n=F_s$ for $H_0<H_c/\sqrt{2}$.

For sufficiently small values of the inner radius, however, $F_n=F_s$ for values of the applied field still greater than $H_c/2$, the value at which the intermediate state begins to occur. For such thick-walled hollow cylinders, therefore, the transition to the intermediate state still occurs at $H_0=H_c/2$. But beyond a certain value of the inner radius, the value of the applied field at which $F_n=F_s$ becomes less than $H_c/2$, and so one can expect that for such thin-walled cylinders the intermediate state should begin to appear at $H_0<H_c/2$, the critical value of H_0 being dependent on the size of the inner radius.

To show this dependence more clearly one can rewrite Eq. (1) in the form

$$F_n-F_s=\left[\frac{H_c^2}{8\pi}-\frac{H_0^2}{4\pi}\left(\frac{a^2}{a^2-b^2}\right)\right]V_H,$$

where a and b are respectively the outer and inner radii of the hollow cylinder.

When $F_n=F_s$, one sees that

$$2(H_{0e}/H_c)^2=1-(b/a)^2,$$

where H_{0e} is the applied field for which $F_n=F_s$. Figure 1 is a plot of $\sqrt{2}H_0/H_c$ *vs* b/a. ABC is the locus of points for which $F_n=F_s$. When the cylinder is solid, i.e., $b=0$, $\sqrt{2}H_{0e}/H_c=1$, when $b\rightarrow a$, $\sqrt{2}H_{0e}/H_c\rightarrow 0$. For $b/a<\sqrt{2}/2$, $\sqrt{2}H_{0e}/H_c>\sqrt{2}/2$; in other words, $H_{0e}>H_c/2$. For cylinders with $b/a<0.707$, hence, one would expect the inception of the intermediate state to occur for $H_0=H_c/2$, and the point for such cylinders should be along DB. For $b/a>\sqrt{2}/2$, $H_{0e}<H_c/2$, and for these ratios one would expect the points to fall a little below the curve BC. That is to say, we reason that if at a given applied field less than $H_c/2$, the normal state has a lower free energy than the superconducting state, then we expect that an intermediate state can almost certainly exist at a somewhat smaller field value.

3. EXPERIMENTAL DETAILS AND RESULTS

As in the experiments described by Gittleman,[1] bismuth probes were used to measure the magnetic field. As we were primarily interested only in the value of the field at which it begins to penetrate into the superconducting cylinder, only one probe was used and this was placed at the outer equator of the cylinder. This probe consisted of a bismuth wire about 3 cm long, held closely to the surface of the cylinder by being placed in a groove scratched in a lucite holder which fitted snugly around the cylinder. Thin copper wires were brought to the ends of the probe by means of additional grooves and these wires, as well as the probe, were kept in place by small drops of Duco cement. Electrical contact between the wires and the probe was obtained by painting their points of contact with conducting silver paint.

The detecting apparatus was that described by Gittleman,[1] and the same method was used to calibrate the bismuth probes. Similar also was the preparation of the hollow cylinders. They were cast from spectroscopically pure tin obtained from Johnson-Matthey and Company. The thickest cylinder (Sample I) was made simply by machining off the casing of the mold, leaving in place its brass core. For the next three wall thicknesses (Samples II, III, and IV) the brass core was pushed out, and the inside diameter of the tin cylinder was successively reamed out to the required value. A new casting was made for the thinnest cylinder (Sample V), and in this case again the core of the mold (here made of copper) was kept inside the cylinder, and the outside diameter machined to the required value.

For each cylinder, the general variation of the magnetic field at the outer equator is the same. As the applied field is increased (all measurements were performed with increasing field), the measured field initially increases linearly with the applied field. The slope of this increase should be two; since the probes were some small distance from the cylinder surface, the observed slopes are about 1.9. At a certain value of the applied field this linear increase of the equator field changes abruptly. At this point the magnetic field begins to penetrate into the hollow cylinder through the 'window' at the poles,[1] so that the field at the outside equator no longer increases twice as fast as the applied field. The manner of the further variation of the equator field will be discussed presently.

The points on Fig. 1 show the observed values of $\sqrt{2}H_0/H_c$ as a function of b/a, the ratio of inner to outer radii of the cylinder. H_0 is the applied field at which the increase of the equator field changes abruptly, and hence also the field at which penetration of the cylinder first occurs and the intermediate state begins. H_c is the

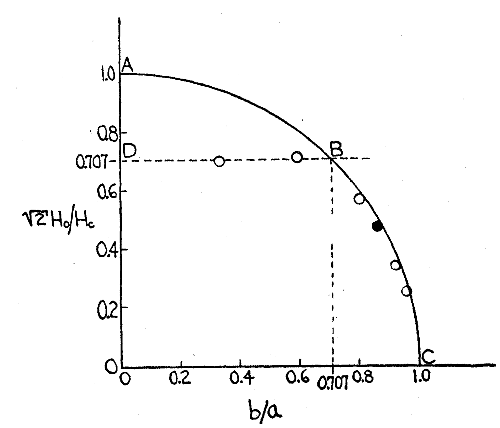

FIG. 1. The ratio of the applied magnetic field at which penetration begins to the critical field is plotted as a function of the ratio of inner to outer radii. The solid point was measured by Gittleman.

critical field at the temperature of the measurement; in all cases this temperature was about 2.61°K with a critical field corresponding to 5.3 amperes of coil current.

The points in Fig. 1 show that, as predicted above, the intermediate state begins at $H_0 = H_c/2$, i.e., $\sqrt{2}H_0/H_c = \sqrt{2}/2$, for $b/a < \sqrt{2}/2$. For $b/a > \sqrt{2}/2$, the free energies of the normal and superconducting states become equal at smaller applied fields, and here, as expected, the experimental points fall just below curve BC.

Figure 2 is a composite of the variation of equator field with applied field for the different samples. In all cases there is an initial increase in the observed field with slope nearly equal to two, followed by a sharp break. The subsequent behavior, however, varies in different samples.

In Sample I (largest wall thickness), while the sample was in the intermediate state, the observed field at the equator remained constant even though the applied field was changed, until the latter reached the critical value after which the observed field was equal to the applied field for all large field values. In this sample all time effects were negligible, in the sense that when the applied field was changed, the observed field followed (or did not follow) in a time comparable to the time constant of our detecting apparatus, which was a few seconds. Thus, as far as we can tell, this sample behaved in all respects like a solid cylinder, at least in increasing field. Beginning with Sample II, upon reaching the intermediate state, the time effects became of the order of minutes, and the observed field showed a characteristic "overshoot" behavior. That is to say, when the applied field was increased, the observed field initially increased also, and then slowly decayed to an equilibrium value. Generally speaking in the subsequent samples, this irreversible behavior became more pronounced and occurred over a larger range of values of the applied field, with the resulting more complicated form of the curves in Fig. 2. In Fig. 2 we have plotted the equilibrium values of the observed field.

4. DISCUSSION

It should be noted that in Sec. 2, we have compared the *total* free energies of the body in the normal and superconducting phases. However, Gorter and Casimir[4] have proved that if one considers an infinitesimal volume in the superconducting phase, then this volume will become normal only if the field at its surface equals the critical value. In the case of an infinitely long cylinder, this will occur when the applied field is equal to or greater than half of the critical value, independently of whether the cylinder is solid or hollow. However, despite the proof just quoted, the cylinders in these experiments do attain the state of lowest total free energy, in which normal regions are present in applied fields appreciably less than $H_c/2$. The question raised by this contradiction can be broken into two separate parts. We may first ask how nuclei of normal metal[5] form in fields less than the critical value; secondly, given some nuclei, we may inquire how they grow into the final equilibrium state. The first question is easily answered; in our experiments we had finite cylinders which therefore had sharp corners at their ends, so that the field at the ends most probably exceeded the critical value and thus provided a source of nuclei. The second question we cannot at present answer.

We must remark, however, that we would expect that in a hollow sphere at the surface of which there are no places where the field can be locally quite large, there would be great likelihood of superheating because of the difficulty of nucleation. That is to say, one can show using the methods of Sec. 2, that in a hollow sphere, when $b/a > 0.69$, the normal state has a lower free energy than the superconducting state for applied fields less than $\frac{2}{3}H_c$, corresponding to a field at the equator less than H_c. However, due to the difficulty of nucleation, we think it most probable that the spherical sample would not attain the state of lowest total free energy, but would superheat until the applied field was equal to $\frac{2}{3}H_c$. This conclusion is supported by the work of Babiskin[6] on a hollow lead sphere, for which $b/a = 0.814$. Babiskin did not observe penetration until the applied field slightly exceeded $\frac{2}{3}H_c$.

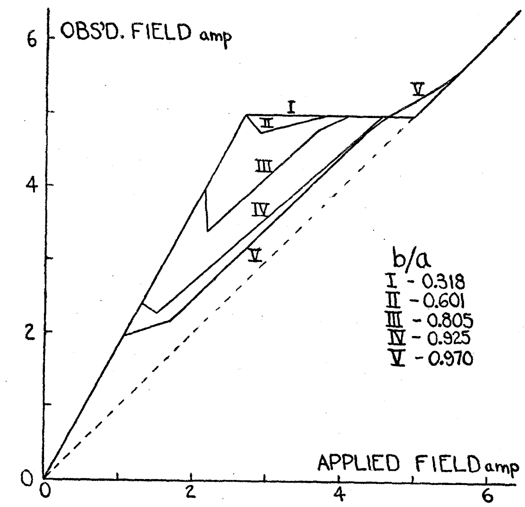

FIG. 2. The magnetic field observed at the equator is plotted as a function of the applied field for the various samples. The dashed line has a slope of one.

In conclusion, it gives us great pleasure to thank Mr. A. Siemons for his technical assistance and Dr. P. R. Weiss for many helpful discussions.

[4] C. J. Gorter and H. G. B. Casimir, Physica 1, 305 (1933).

[5] The problem involved in nucleation above should not be confused with recent examples in which nucleation was governed by surface energy, e.g., M. Garfunkel and B. Serin, Phys. Rev. **85**, 834 (1952). Here, nuclei are unstable because their volume free energy is too large.

[6] J. Babiskin, Phys. Rev. **85**, 104 (1952).