Free-energy surfaces for superconducting $Y_1Ba_2Cu_3O_7$

K. S. Athreya, O. B. Hyun, J. E. Ostenson, J. R. Clem, and D. K. Finnemore
Ames Laboratory, U. S. Department of Energy and Department of Physics, Iowa State University, Ames, Iowa 50011
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Magnetization studies were undertaken to determine the change in free energy of the superconducting state of $Y_1Ba_2Cu_3O_7$ with changes in magnetic field and temperature. Close to the transition temperature T_c magnetic flux moves easily and reversibly in these materials so that magnetization is a thermodynamically reversible variable. Hence, the free-energy surfaces can be measured and quantities such as entropy and specific heat can be derived. Magnetization is found to be linear in $(T_c-T)^2$ near T_c. The free-energy surface shows substantial changes with magnetic field all the way up to 92 K, well outside the usual H_{c2} vs T plots derived from resistivity or ac susceptibility data.

INTRODUCTION

The nature of the phase transition at the superconducting transition temperature, T_c, has been the subject of intense study by specific-heat, C_H, measurements. Rather strong fluctuation effects have been seen in some measurements[1] as expected from fairly standard arguments.[2] There is, however, considerable disagreement among various samples[1,3,4] and some doubt about the overall magnitude of the electronic contributions because the lattice term is so large. Our goal in this work is to study the Gibbs free-energy surface for these materials via magnetization measurements in order to determine directly the electronic contribution to the free energy and the specific-heat changes that occur as a magnetic field is applied.

From the free-energy surfaces one can then derive the entropy and specific heats by standard thermodynamic arguments. If magnetic flux moves easily in a sample and there is essentially no flux pinning, then the sample is in thermodynamic equilibrium and Gibbs free energy at field H is related to the value at $H=0$ by the relation

$$G_0-G_H=\int_0^H MdH' \tag{1}$$

where M is the magnetization and H' is a dummy variable of integration. The entropy S is then given by

$$S_0-S_H=\frac{d}{dT}(G_0-G_H) \tag{2}$$

and the specific heat is given by

$$C_0-C_H=-T\frac{d^2}{dT^2}(G_0-G_H)\,. \tag{3}$$

The only criterion for applying these equations is thermodynamic equilibrium. For the $Y_1Ba_2Cu_3O_2$ superconductors, there is a small temperature window between 86 and 92 K where the magnetization is reversible to an accuracy of better than 1%. In this range, then, the free-energy surface can be obtained.

To illustrate the effects being considered here, we have shown the free energy of a typical type-II superconductor in Fig. 1. As shown by the sketch in Fig. 1(a), the normal-state electronic free energy is illustrated as that of a free-electron gas $G_n=-1/2\gamma T^2$ where γ is the electronic specific-heat coefficient. The superconducting free energy G_0 will lie below this line for $T<T_c$ as shown on the sketch. As a magnetic field is applied at any given temperature T the free energy G_H rises and it eventually reaches G_n at H_{c2}. The temperature dependence $G_H(T)$ might be similar to the dashed line of Fig. 1(a).

In an ordinary type-II superconductor like Nb, the jump in specific heat at T_c changes with magnetic field in the manner shown by Fig. 1(b). The dominant feature of these data is that the temperature at which the jump occurs is suppressed considerably along the H_{c2} vs T line but the magnitude of the jump, ΔC, changes relatively little. In the new high-T_c superconductors, the dominant effect of applying H is to suppress the magnitude of the jump with relatively little suppression of T_c as sketched in Fig. 1(c).[1,3] Our goal here is to measure the free-energy surface near T_c and directly probe these changes in free-energy surfaces and, thus, indirectly probe the changes in

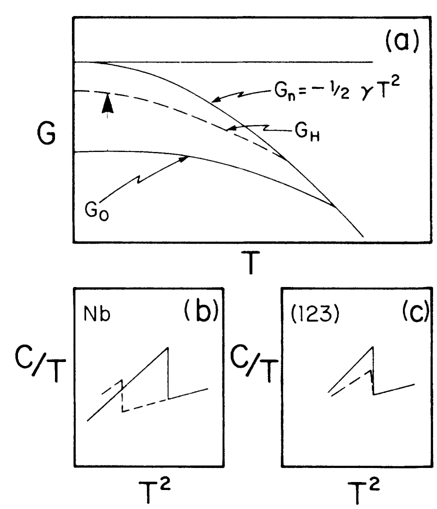

FIG. 1. Sketches to illustrate the expected behavior: (a) Gibbs free-energy curves for the normal state G_n, the superconducting state G_0, and the intermediate state G_H. (b) Specific-heat jump of Nb in $H=0$ and $H=1020$ Oe. (c) Specific-heat jump of (1:2:3).

electronic specific heat with magnetic field. The purpose is to look for fluctuation effects near T_c and to study the phase transition at T_c with increasing magnetic field.

EXPERIMENT

Grain-aligned $Y_1Ba_2Cu_3O_7$ (1:2:3) samples were chosen for these studies instead of single crystals because large single crystals may not have been fully oxygenated and there seemed to be traces of paramagnetic inclusions, probably CuO_2, in our large single crystals. This gave a small normal-state susceptibility which differed from sample to sample. With the grain aligned samples there was little difficulty getting full oxygenation and very little paramagnetic signal above 93 K. There was, however, a reproducible background magnetization from the epoxy and there also was some misalignment of a few degrees for the various crystallites.[5]

A series of grain aligned samples were prepared having a large grain size, on the order of 20 to 40 μm, and a rather sparse array of twin planes. Electron microscopy shows the twin plane spacing to be in the 0.1 to 0.3 μm range for the samples reported here. Starting materials were repeatedly ground, pressed into a pellet, and reacted at 890 °C to give a homogeneous mixture of the components. The sample was then ground, pelletized, reacted at 970 °C and slow cooled in oxygen to give a large grain (~0.1 mm) material. This was then ground and sieved to give a uniform grain size. This was then sent through the oxygen cycle one last time. It was mixed with liquid epoxy, placed in an 8-T magnetic field at room temperature, and the epoxy was allowed to harden. The room-temperature anisotropy of the susceptibility causes the alignment.[5] About 50% of the volume of the sample was (1:2:3) superconductor. The rest was epoxy.

Static magnetization measurements were made by pulling the sample through a Quantum Designs SQUID magnetometer. Data for $M(H,T)$ usually were taken in sequences by changing T at fixed H. Constant field sweeps were used because the normal-state magnetization of the sample plus epoxy is almost independent of temperature over the region of the measurement 86 to 110 K, but there is a significant change with magnetic field in the range from 0 to 5 T. The use of constant H sweeps makes it easier to subtract the background susceptibility of the epoxy.

RESULTS

Raw magnetization data, M_R, for a grain aligned sample in epoxy is shown in Fig. 2 for $H=0.1$ T. Between 103 and 93 K the magnetization is nearly constant. The background normal-state magnetization plus the contribution from the epoxy is determined by least-squares fitting these data between 93 and 110 K to a straight line to get a normal state value, M_n, shown by the dashed line. This is then extrapolated to 86 K. The superconducting state magnetization $M=M_R-M_N$ is indicated by the arrows on Fig. 2. The zero-field-cooled data (open circles) are essentially the same as the field-cooled data from T_c to the irreversible temperature, T_{irr}. The value of M is independent of the temperature and magnetic field history of the sample over the entire range from 92 to 86 K so the magnetization is thermodynamically reversible. It is important to remember here that the percentage hysteresis for applied fields comparable to H_{c1} is much larger than hysteresis for $H \gg H_{c1}$. The area under the magnetization curve for $0 < H < 300$ Oe, however, is less than 1% of the total area and so an error even as large as a factor of 2 due to hysteresis in this range would not change $G_0 - G_H$ by more than 1%.

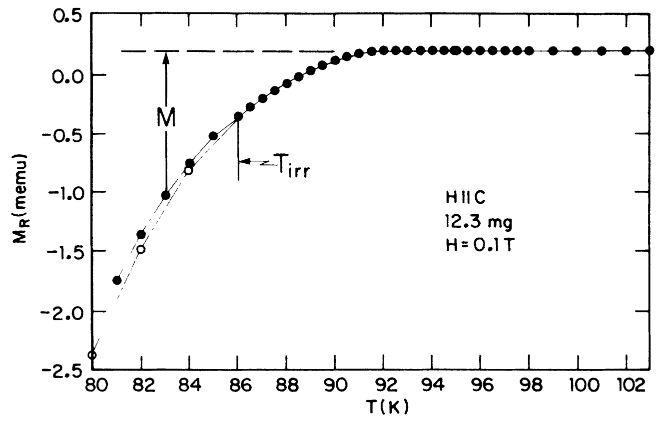

FIG. 2. Raw magnetization data. Dashed line denotes an extrapolation of normal-state data. T_{irr} is the temperature of first irreversible behavior.

As shown in Fig. 3 it is consistently found that $M^{1/2}$ is linear in T just as was found for La-Sr-Su-O.[6] A surprising feature of the data is that an extrapolation of $M^{1/2}$ to $M=0$ gives an apparent transition temperature T_H that is not suppressed with magnetic field nearly as rapidly as the H_{C2} vs T plots normally derived from experiments which depend on vortex motion such as resistivity and ac susceptibility.[7] These data, in fact, more closely resemble the specific-heat results where the temperature at which the specific-heat jump ΔC occurs is suppressed very little with magnetic field.[1,3]

The Gibbs free-energy surfaces derived from Eq. (1) are shown in Fig. 4 for H||c. Corresponding surfaces for

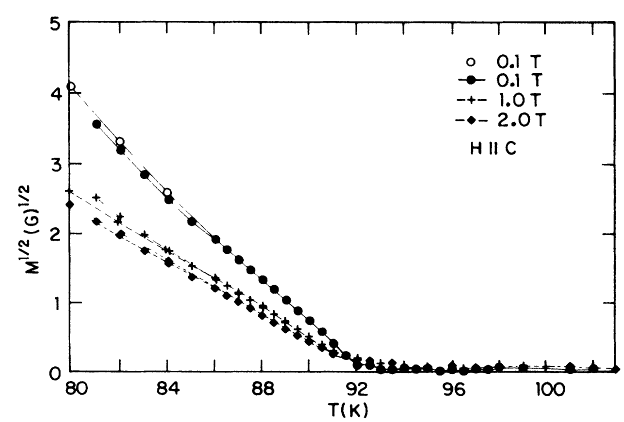

FIG. 3. $M^{1/2}$ vs T plot to show that T_H changes very little with magnetic field.

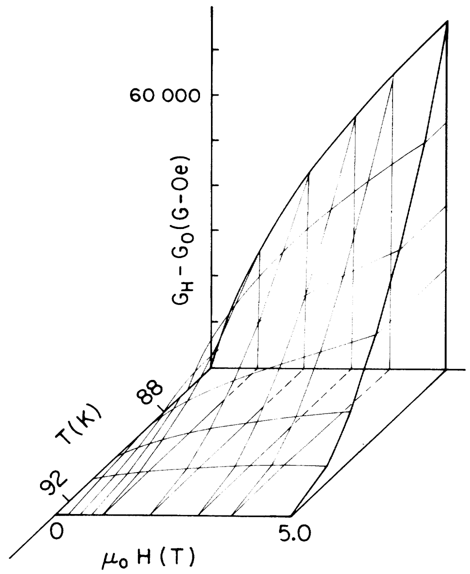

FIG. 4. Gibbs free-energy surface for $Y_1Ba_2Cu_3O_7$ close to T_c.

H⊥c are of similar shape but the values are substantially smaller at the same H and T. These surfaces, in turn, can be used to derive the change in specific heat with magnetic field. It is important here to point out that these data are derived from the change in free energy, $G_H - G_0$, shown by the arrow in Fig. 1(a). A plot of these data for both **H**∥**c** and **H⊥c** is shown in Fig. 5.

The magnetization data and the corresponding Gibbs free energy show several remarkable features. First, extrapolation of magnetization data such as those shown in Fig. 3 to $M=0$ implies an onset of superconductivity above 92 K for all fields up to 5 T. Hence, the transition

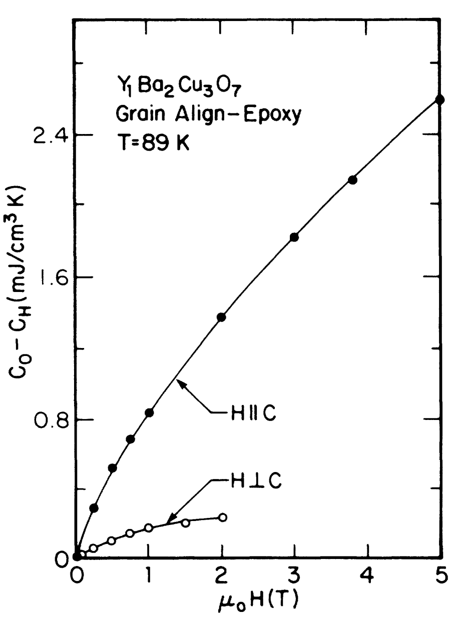

FIG. 5. Magnetic field dependence of $C_0 - C_H$ for both parallel and perpendicular fields.

drops at most 0.5 K for a 5-T field increase. If this onset is identified as the upper critical field, then the slope of the H_{c2} vs T line must be at least 10 T/K, a value much larger than many reports.[7,8] Within the accuracy of these measurements, in fact H_{c2} vs T could be a vertical straight line. As has been pointed out by Yeshurun and Malezemoff[7] and Tinkham,[8] resistive and ac inductance measurements which give 1.5 T/K slopes are probably an underestimate. These static magnetization data give a much larger value. If the twin planes act as weak links, then the sample would behave like a stack of thin films very close to T_c.

A second feature is that the free energy and the specific-heat difference, $C_0 - C_H$, derived from it is highly anisotropic, giving a jump at T_c which is 5 times larger for H parallel to the c axis than it is for H parallel to the a-b plane, as shown in Fig. 5. This presumably reflects the anisotropy in the effective mass and the penetration depth.

A third feature is that the specific-heat difference, $C_0 - C_H$, remains large over the entire range of reversibility from 88 K to T_c. Unfortunately, irreversibility occurs so the subsequent reduction at lower temperatures observed by direct specific-heat measurements could not be observed.

CONCLUSIONS

There is a narrow temperature interval about 6-K wide close to T_c where the magnetization curves are thermodynamically reversible to an accuracy of 1%. This permits the measurement of free-energy surfaces and the derivation of the entropy and specific-heat functions. The data show that there is a substantial free-energy change with magnetic field all the way up to 92 K in qualitative agreement with earlier specific-heat results.[1,3] This behavior is quite different from the behavior of Nb. It may be that flux motion along twin planes causes some phase decoupling and, hence, a smaller specific-heat jump at T_c. The origin of these effects could possibly lie in the fluctuation effects[1] but other fundamental factors could also contribute. A full theory of changes in fluctuations with magnetic field will be required to understand these data.

As pointed out by Malozemoff and co-workers,[7] it is difficult to define an H_{c2} in these materials because they do not behave like conventional type-II superconductors. Attempts to measure the thermodynamic critical field curve (H_c vs T) from these data[9,10] have been frustrated by the fact that the 8 T used by Bezinge, Jorda, Junod, and Muller and the 5 T used by Finnemore *et al.*[10] do not reach H_{c2} at temperatures below 91 K. Above 91 K, there may be a problem with sample inhomogeneity. It should be remembered that dissipative measurements, either resistivity or ac susceptibility, depend on vortex motions whereas static magnetization depends on Meissner screening currents. There clearly is a substantial change in the free energy of the sample with magnetic field well above the usual H_{c2} vs T line having a slope of 1.5 T/K. More detailed measurements and a better theory of the phase transition at T_c may be needed. The kinks in M vs H curves and resistive transitions reported previously may not be true type-II H_{c2}'s.[7]

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