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Free energy of thallium-based superconductors

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Free-energy surfaces have been determined for both $Tl_2Ba_2Ca_1Cu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ in order to determine the thermodynamic aspects of vortex formation in the mixed state of these materials. For fields up to 5 T, the free-energy change, $G_H - G_0$, is found to be linear in temperature, over a wide temperature range, thus indicating that the specific heat is roughly independent of magnetic field. The slope of the upper critical field versus temperature plot is at least 20 T/K. These two materials obey a law of corresponding states.

INTRODUCTION

The nucleation and motion of quantized vortices in the high-temperature superconducting oxides is rather different from the corresponding behavior of familiar type-II superconductors such as the $A15$'s or Nb.[1,2] As pointed out by Gammel and co-workers,[3,4] there is very little rigidity in the flux line lattice for an interval near the upper critical field H_{c2}. Furthermore, Malozemoff and co-workers[5] have shown that there is some difficulty even defining the upper critical field because flux creep is such a major effect. Measurements of H_{c2} which depend on vortex motion and the dynamic response[6] of the vortex lattice seem to give a lower[5] value than measurements of static magnetization.[1] Explanations for these effects frequently involve the relatively large value of kT compared to the pinning potential U. An extensive review of this subject will soon appear.[5,7]

As a first step in understanding these phenomena, it is useful to map out the free energy of the superconducting mixed state as the magnetic field H, and thus the vortex density increases. This then gives a measure of the standard thermodynamic quantities such as the entropy S and the specific heat C_p. For $Y_1Ba_2Cu_3O_7$ (1:2:3) there is a window where vortices move easily enough to give thermodynamic equilibrium[1] that is only about 6 K wide, from 86 to 92 K. For the $Tl_2Ba_2Ca_1Cu_2O_8$ (2:2:1:2) and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2:2:2:3) samples reported here, however, the window of reversibility is 20–30 K wide for fields above 0.5 T. Therefore, a major portion of the H-T plane exhibits thermodynamic reversibility.

The purpose of this work is to measure the free-energy surfaces for the Tl (2:2:1:2) and Tl (2:2:2:3) phases in order to determine whether a law of corresponding states applies for these two materials and to measure H_{c2} vs T. Results also will give calculated values of the specific-heat change with H for comparison with direct C_p data,[8] which appear to show that C_p is independent of H.

EXPERIMENT

To prepare grain-aligned samples powders were ground from the respective parent material and mixed into liquid epoxy.[9] This mixture was placed in a magnetic field of 9.0 T and the epoxy was allowed to harden. X-ray rocking curves showed a mosaic spread of 1.8° full width at half maximum for the [005] peak. Magnetization data were taken by pulling the sample through a superconducting quantum interferences device coil.

RESULTS AND DISCUSSION

Irreversibility

The two extremes of low-field behavior and relatively high-field behavior are shown in Fig. 1. In the regime where H is comparable to H_{c1}, the magnetization goes negative at 120 K and falls very quickly in the region of 117 K. The $H = 20$ Oe data, shown on Fig. 1(a) are reversible to 1% between 120 and 116 K, at which point the field-cooled (FC) and zero-field-cooled (ZFC) data diverge.

At higher fields, illustrated by the 0.1- and 1.0-T data of Fig. 1(b), the reversibility range becomes much larger. It eventually extends from 120 to 25 K for $H = 5$ T. In fact, there is a very characteristic shape of M vs T for all data above $H = 1$ T in which there is a long linear region extending from 115 to well below 60 K. At lower temperature, M begins to decrease more rapidly and irreversibility becomes measurable. A plot of the irreversibility point H_{irr} versus temperature is shown as $H_{irr}^{2/3}$ vs T in Fig. 2 in order to compare these data with the ideas of Malozemoff and co-workers.[5] The $H^{2/3}$-vs-T curve is roughly linear down to 80 K, as they predicted for the Y (1:2:3) compounds and then it rises much more quickly. The surprising feature of these data is that the isolated 25-μm grains

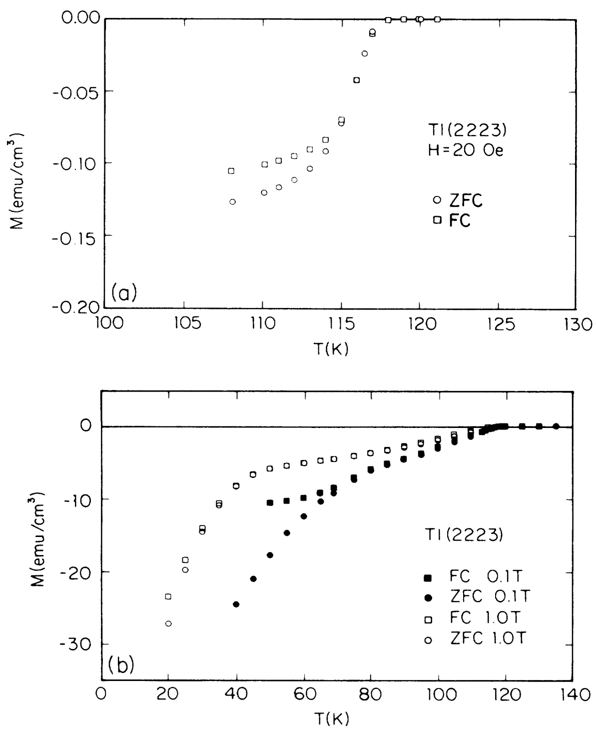

FIG. 1. (a) Temperature dependence of the magnetization for Tl (2:2:2:3) for low field of 20 Oe. (b) Temperature dependence of the magnetization for Tl (2:2:2:3) for 0.1 and 1.0 T.

in the epoxy-stabilized grain-aligned sample show such low critical currents when the thin-film data show such high critical currents.[10]

Magnetization curves

A regular grid of magnetization data was taken as a function of temperature and magnetic field. Constant

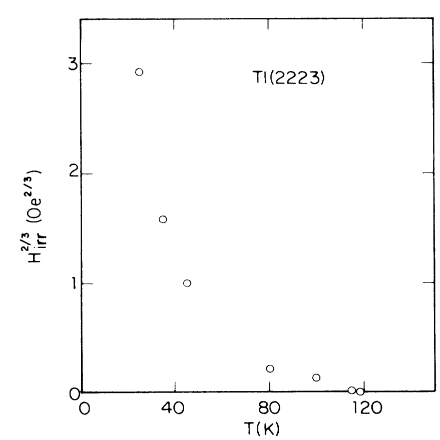

FIG. 2. Thermodynamic irreversibility for the Tl (2:2:2:3) curve defined as the temperature and field point where the magnetization changes by less than 1% in 20 min.

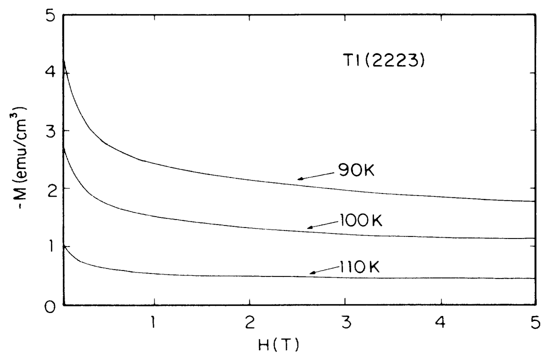

FIG. 3. Magnetization (M-vs-H) curves for Tl (2:2:2:3).

temperature cuts through this surface give the magnetization curves shown in Fig. 3. Irreversibility near H_{c1} introduces less than a 1% error in the total area and thus the Gibbs free energy for these data.

Free energy

Free-energy surfaces derived from reversible magnetization data for Tl (2:2:2:3) and Tl (2:2:1:2) are very similar to one another as illustrated in Fig. 4. Both show that $G(H)-G(0)$ is linear in T over a wide temperature range from $t=0.7$ to $t=0.95$ and then bends over to the normal-state value in approximately a 5-K interval near T_c.

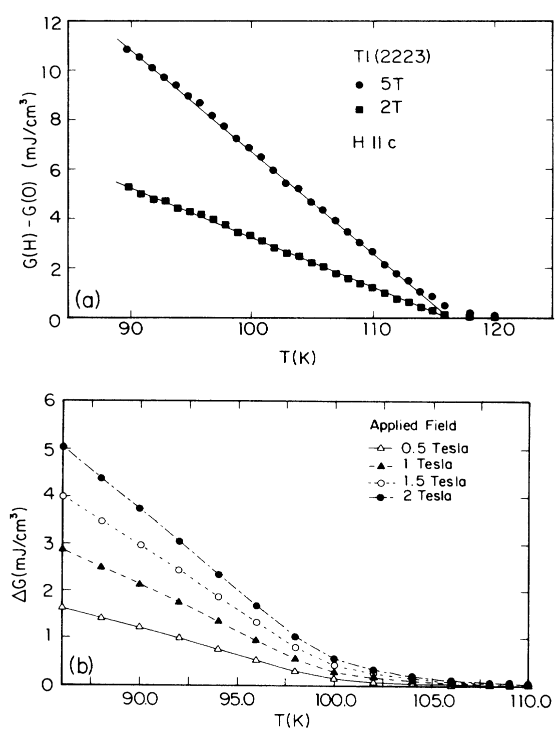

FIG. 4. (a) Free-energy curves to illustrate the linear behavior in Tl (2:2:2:3). (b) Free-energy curves to illustrate the linear behavior in Tl (2:2:1:2) for $H \| c$.

By the thermodynamic relation

$$C(H)-C(0)=-T\frac{d^2[G(H)-G(0)]}{dT^2} . \qquad (1)$$

This means that the specific heat is independent of magnetic field as was found by direct C_p measurements by Fisher *et al.*[8]

Comparison with C_p

To make a direct comparison with specific-heat results via Eq. (1), the curvature of the $G(H)-G(0)$-vs-T curve was determined. Figure 5 illustrates results calculated by selecting seven consecutive temperature data points, least-squares fitting these to a parabola, and evaluating the specific heat. To get to the next C_p point, the highest-temperature $G(H)-G(0)$ datum is dropped from the group and one is added at the low-temperature end. Other methods of evaluating the curvature give similar results. For Tl (2:2:2:3) at $H=2$ T, $C(0)-C(H)$ shows a peak of 4 mJ/cm^2 K at 115 K followed by random oscillations about zero below 110 K. For Tl (2:2:1:2) results at $H=2$ T show a peak of 3 mJ/cm^3 K at 100 K, followed by random oscillations about zero. A 5-T curve for Tl (2:2:2:3) presented elsewhere[11] shows a peak of 6 mJ/cm^3 K about 10 K wide, centered at 116 K. Fisher *et al.* have presented direct measurements of $C(0)-C(H)$ for $H=7$ T and find a broad peak running from 115 to 90 K having a maximum of about 4 mJ/cm^3 K. Hence, the free-energy plots and the C_p measurements both show $C(0)-C(H)$ close to zero below 90 K with a peak on the order of 5 mJ/cm^3 K high for $H=5$ T at T_c.

Upper critical field

As pointed out by Malozemoff and co-workers,[5] the definition of the upper critical field H_{c2} may depend on the method of measurement, because there are giant flux creep phenomena involved. Here we have chosen static magnetization to define H_{c2} vs T, where the equilibrium flux expulsion is measured over periods of hours and in both field-increasing and field-decreasing sequences to assure thermodynamic equilibrium. Above 1 T, the equilibrium times are easily less than normal measuring times. For Tl (2:2:2:3), a linear extrapolation of the M-vs-T curve to $M=0$ gives transition temperatures of 116.7, 116.4, 116.9, 116.6, and 116.9 K for 1, 2, 3, 4, and 5 T, respectively. If the first deviation of M from the normal-state line is used to define the transition, then temperatures of 119.2, 121.0, 120.3, 121, and 119.6 K are found for 1, 2, 3, 4, and 5 T, respectively. Within the accuracy of the measurement, both definitions give vertical straight lines so dH_{c2}/dT must be larger than 20 T/K.

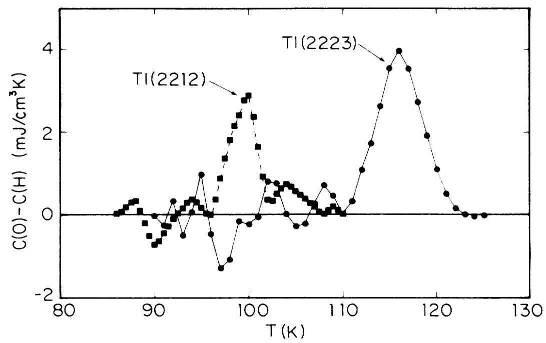

FIG. 5. Specific heat calculated from the curvature of the free-energy curves for both Tl (2:2:2:3) and Tl (2:2:1:2) at $H=2$ T.

CONCLUSIONS

In the vortex state of both Tl (2:2:1:2) and Tl (2:2:2:3), there is a wide temperature and magnetic field range where the magnetization is thermodynamically reversible. The Gibbs free-energy differences, $G(H)-G(0)$, are found to undergo a gradual slope change just below T_c and become linear again below T/T_c of about 0.9. This means that the change in electronic specific heat, $C(0)-C(H)$, has a bump just below T_c, and then below $T/T_c=0.9$ the specific heat is independent of field within the accuracy of these data.

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