Reversible magnetization of a strong-pinning superconductor

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Measurements of specific heat and magnetization have been made on the same sample of melt-processed Y-Ba-Cu-O (YBCO). Above the irreversibility line H is constant, and below the irreversibility line B is constant. The free energy and, hence, the reversible magnetization in both the irreversible and reversible region are calculated from the specific heat on this basis. The reversible magnetization and the penetration depth derived from this analysis broadly agree with d-wave theory if the field dependence of $\lambda(0)$ is taken into account and is consistent with other experimental results. A peak in the specific heat at the irreversibility line is not due to the change from C_B to C_H, but is probably due to the entropy associated with the melting transition, although a contribution from the pinning centers cannot be excluded.

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I. INTRODUCTION

Measurements of specific heat as function of magnetic field and temperature can be used to derive the reversible magnetization of a sample. For this to be strictly valid the material must be in thermodynamic equilibrium; in other words, the flux lines must be free to move to their equilibrium positions so there must be no pinning. Normally, the experiments would be done at constant external field, and, if H in the material is equal to the external H, we can derive the entropy $S(H,T)$ directly from the specific heat measurements in the following way.

We define changes in the internal energy U by

$$\delta U = T\delta S + \mu_o \mathbf{H}\,.\,\delta\mathbf{M}. \tag{1}$$

Here $\mathbf{M}$ is the reversible magnetization defined by

$$\mathbf{M} = \mathbf{B}/\mu_o - \mathbf{H}. \tag{2}$$

If we now define the Gibb's free energy as

$$G(H,T) = U - TS - \mu_o \mathbf{H}\,.\,\mathbf{M}, \tag{3}$$

then

$$S = -(\partial G/\partial T)_H. \tag{4}$$

If $\Delta S(H,T)$ is defined as the difference in entropy between the normal and superconducting states, we can integrate Eq. (4) up to a temperature T_o above T_c where $\mathbf{M}=0$ to find the difference in G between the normal and superconducting states, $\Delta G(H,T)$;

$$\Delta G(H,T) = \int_T^{T_o} \Delta S(H,T)dT. \tag{5}$$

At $T_o, \Delta G=0$ because the order parameter is zero and T_o must be above T_c to avoid fluctuation magnetization.

Now

$$\mu_o M = -(\partial G/\partial H)_T. \tag{6}$$

It follows, therefore, that Eq. (5) can be differentiated to give the reversible magnetization M.

The equations for constant H are appropriate to the region above the irreversibility line. Alternatively we can, in principle, do experiments at constant flux density B by surrounding a reversible sample with a layer of Type I material and trapping a fixed number of flux lines in the sample. We will argue below that a strong pinning material cooled in a field is a reasonable approximation to this situation below the irreversibility line and we can use the thermodynamic equations for constant B. Now the measurements give $S(B,T)$. We define the change in internal energy by

$$\delta U = T\delta S + \mathbf{H}\,.\,\boldsymbol{\delta}\mathbf{B} \tag{7}$$

and the Helmholtz free energy to be

$$F = U - TS. \tag{8}$$

Then,

$$S = -(\partial F/\partial T)_B. \tag{9}$$

The difference ΔF between the normal and superconducting states is

$$\Delta F(B,T) = \int_T^{T_o} \Delta S(B,T)dT \tag{10}$$

and

$$H(B,T) = (\partial F/\partial B)_T. \tag{11}$$

From this we can derive M through Eq. (2).

In practice, as we show below, the difference between the specific heats at constant B and constant H is negligible for large κ so that the procedure for constant H can be used in both cases.

II. EXPERIMENTAL METHOD AND RESULTS

In the experiments the sample is first cooled in a field from $T_o=140$ K to 6 K. It is then slowly warmed up to T_o, and the heat input measured as a function of temperature. The original specific heat data have been published separately.[1] The sample was a $7.0\times6.5\times3.3\ \mathrm{mm}^3$ pellet of

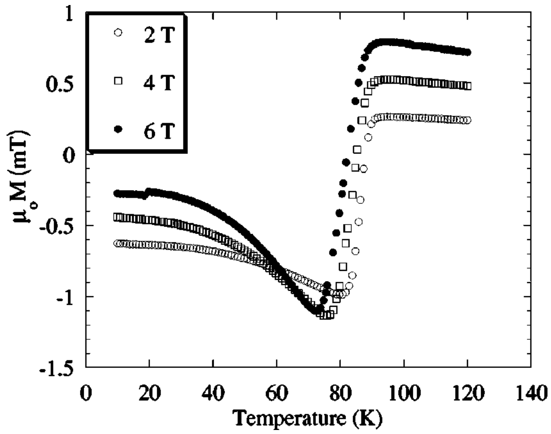

FIG. 1. Magnetization of a bar of melt-processed YBCO at fields of 2, 4, and 6 T. The irreversibility temperature, measured magnetically, is just below the minimum in each case.

melt processed Y-Ba-Cu-O (YBCO) made by top seeded melt growth (TSMG) so that there were no grain boundaries, but there was strong bulk pinning.[2] This was caused by Y-211 particles, which had a strong paramagnetic moment at low temperatures.

In a separate experiment the magnetization of a $6\times2\times2$ mm^3 cylinder cut from the sample was measured with a SQUID magnetometer in a field parallel to the c axis. Figure 1 shows the magnetic moment in fields of 2, 4, and 6 T as the sample was cooled and subsequently heated. The magnetization decreases as expected down to the irreversibility line, but then rises and continues to rise down to 4.2 K. On heating, the magnetization followed the same curve as on cooling. The variation of magnetization in the irreversible region was less than 1 mT compared with an external field of 6 T; therefore, B is constant to within 0.02%. This justifies the use of constant B in the thermodynamic relations. A more detailed discussion of this point is below. The paramagnetic moment above the irreversibility line is due to the Y-211 precipitates plus a small Pauli contribution.

The specific heat was measured as a function of temperature for a series of magnetic fields up to 13 T and the free

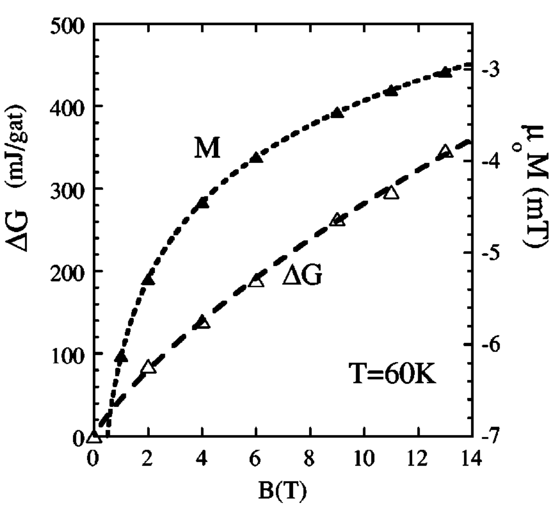

FIG. 2. The experimental free energy, the fitted curve, and the magnetization derived from Eq. (12) at 60 K.

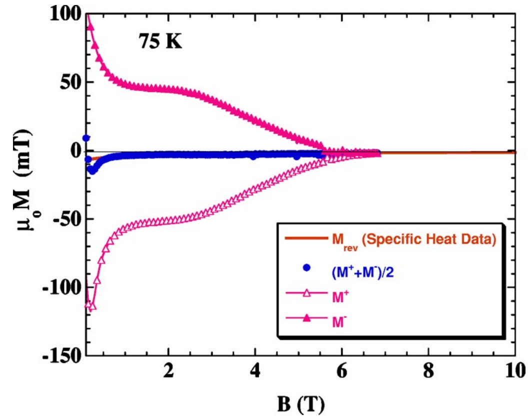

FIG. 3. A comparison of the reversible and irreversible magnetization curves at 75 K.

energy as a function of H calculated from Eq. (4). It was found that a curve of the form $a_1H\ln(a_2H)$, with two fitting parameters a_1 and a_2, gave the best fit. This expression is of the same form as the free energy derived from the magnetization expression given by Hao and Clem,[5] which is

$$\mu_o M = \frac{a\phi_o}{8\pi\lambda^2}\ln\left(\frac{H}{\beta H_{c2}}\right), \tag{12}$$

with a corresponding Gibbs function obtained by integration

$$\Delta G = \frac{a\phi_o H}{8\pi\lambda^2}\left[1-\ln\left(\frac{H}{\beta H_{c2}}\right)\right]. \tag{13}$$

Here λ is the field-independent penetration depth and a and β are approximately field independent with $a=0.77$ and $\beta=1.44$ in the range $0.02<H/H_{c2}<0.3$.

Equation (13) was then used with λ and H_{c2} as fitting parameters to determine the penetration depth and upper critical field. Because H_{c2} appears in the logarithm, the accuracy of its value has little effect on the value of λ.

Figure 2 shows the results for ΔG at a temperature of 60 K and a least squares fit to Eq. (13). The magnetization is from Eq. (12), using the same values of λ and H_{c2}. Similar results were obtained at all temperatures.

Figure 3 shows the complete experimental magnetization

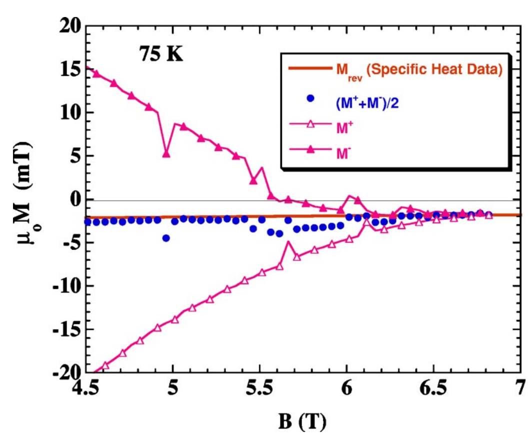

FIG. 4. Magnetization curves near the irreversibility line.

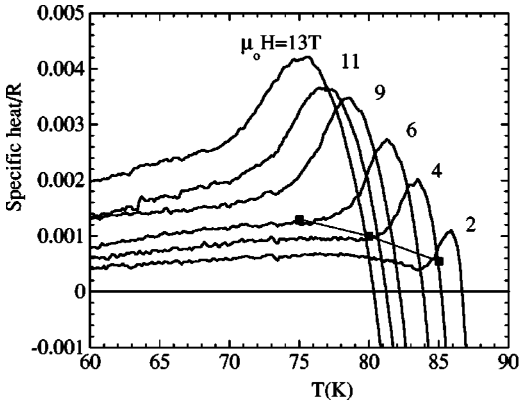

FIG. 5. The difference between the field-cooled specific heat and the zero-field specific heat near the irreversibility line. The squares show the magnetic irreversibility line in the regime where both could be measured.

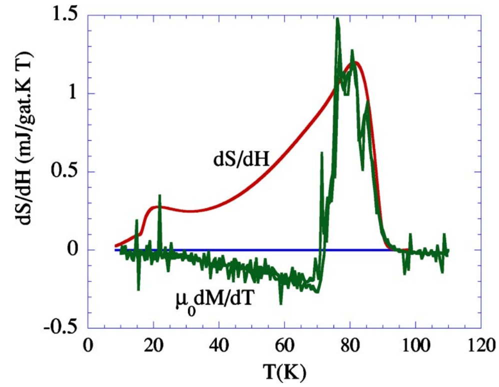

FIG. 6. A comparison of $(\partial S/\partial H)_T$ with $\mu_o(\partial M/\partial T)_H$ at 6 T.

curve for increasing (H^+) and decreasing (H^-) field, the reversible curve derived from the specific heat (discussed in more detail below), and the mean of the increasing and decreasing magnetization at 75 K. On this scale the reversible magnetization is barely visible; thus, Fig. 4 shows the region near the irreversibility line. Above the irreversibility line, the two magnetization curves coincide within experimental error. Were this not the case, at least one set of experiments would be erroneous. Below the irreversibility line the magnetization from specific heats coincides with the means of the increasing and decreasing curves, which at these high fields should give the true reversible magnetization. This gives confidence in the use of specific heat measurements in the irreversible region.

As the field goes through the irreversibility field, the magnetization appears to become noisy, although the noise was repeatable. We believe this is due to the inhomogeneity of the magnet putting the sample around a small hysteresis loop as the sample is moved so that the magnetization appears reversible. However, the signal going into the SQUID is not that of a simple dipole, which confuses the software used to extract the magnetization at low values. The effect is described in Ref. 6. It also means that the irreversibility line measured from the magnetization will be a lower limit as there is still some irreversible flux movement above the field where the magnetization curves coincide. The effect is relevant to Fig. 5 which shows the difference between the field-cooled specific heat and the zero-field specific heat near the irreversibility line. The peaks observed have been seen before and are discussed in more detail in Refs. 7 and 8. The results are shown here to bring out points relevant to the magnetic properties, which will be discussed below. The squares show the point at which the magnetic measurements become reversible, and it can be seen that they coincide with the start of peak in the specific heat. The sharp drop above this peak is due to the suppression by a field of the sharp zero-field peak at T_c.

III. DISCUSSION

We are applying reversible thermodynamics to a very hysteretic system, therefore, we start the discussion with an analysis of the possible errors in this procedure. The effects of pinning will be to distort the lattice from the ideal hexagonal lattice. The flux lines cannot move to restore equilibrium as the sample is cooled, thus, what is measured is the equilibrium magnetization of the lattice in the structure at the irreversibility line, which will be very disordered. However, the pressure on the vortices to rearrange themselves as the temperature is reduced is not great because the *B*-*H* curve of a reversible Type II superconductor is not very dependent on the exact arrangement of the vortices. The difference in magnetization between a square and hexagonal lattice is about 0.1%, and the magnetization of a random melted lattice differs from the hexagonal lattice by less than 2%.[9] In other words, the reversible magnetization is mainly dependent on the mean field *B*, and, therefore, the pinning should not affect the results to within an accuracy of a few percent.

Figure 1 shows that the change in *B* below T_{irr} on cooling in a field is comparable to the reversible magnetization, which might be a problem. The source of an increasing moment on field cooling is the subject of numerous papers, and this is not the place to discuss it in detail. It is clearly not due to the paramagnetic moment of the Y-211 because it begins near the irreversibility line, not at the lower temperature where the Y-211 magnetization becomes significant. Although the paramagnetism and antiferromagnetic transition can be seen in the specific-heat measurements,[1] the local moments will be screened by the pinned flux lines and will not affect the measured magnetization, although at low temperatures the magnetization of the Y-211 is comparable to the 1 mT observed. Figure 1 is very similar to Fig. 1 in Ref. 3, which is the field-cooled magnetization of a YBCO single crystal. Here the moment is attributed to the Koshelev-Larkin mechanism of flux compression.[4] However, this mechanism will only apply in samples at low fields and with a large demagnetizing factor.

In fact, we believe that in our case the moment may be an artifact caused by the movement of the sample in the SQUID magnetometer as the value of the paramagnetic moment depended significantly on the amplitude of the sample movement. However, the results were complex and will be reported separately. This conclusion is reinforced by the observation that although the magnetization below T_{irr} appears reversible in that cooling and heating curves were identical, it does not obey the Maxwell relation

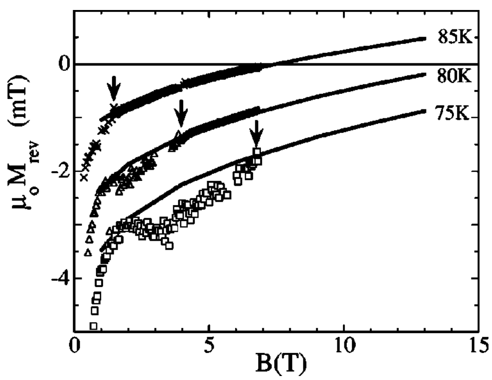

FIG. 7. This shows the reversible magnetization calculated from the specific heat compared with the mean of the increasing and decreasing field magnetization. The arrows show the magnetic irreversibility line. The paramagnetic moment is mainly due to the Y-211 precipitates.

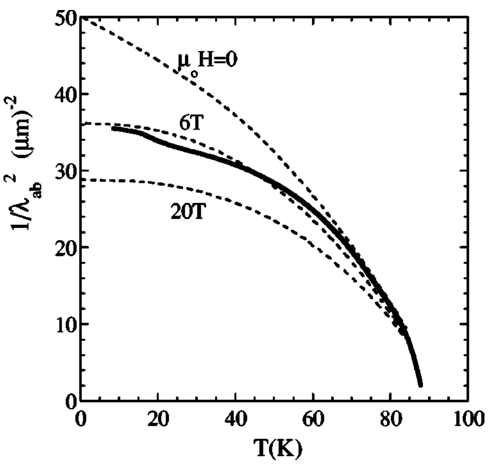

FIG. 8. The solid line shows $(1/\lambda_{ab})^2$ from specific heat measurements.[1] Dotted lines show theoretical curves[16] from *d*-wave theory, with $\lambda_o = 141$ nm in zero field.

$(\partial S/\partial H)_T = (\mu_o \partial M/\partial T)_H$ in contrast to the moment above T_{irr}, which does. This is shown in Fig. 6, which was obtained by fitting a quadratic to the graph of S versus H at fixed T and taking the slope at 6 T. It can be seen that the agreement is good above the irreversibility line, but not below it. This means that the magnetization observed in Fig. 1 below the irreversibility line does not affect the specific heat, which can therefore be used to find the true reversible magnetization.

Another possible source of error is the unpinning of flux lines as the temperature is changed. This will cause dissipation and a temperature rise that would distort the specific heat measurements. In a zero field-cooled sample, where the field is applied at low temperatures, the subsequent rise in temperature leads to the decay of the critical state and dissipation, which totally obscures the reversible heat changes. The changes that occur in the field-cooled sample are not straightforward,[10] but we can put an upper limit on the dissipation as follows.

On cooling the sample, the flux density just inside the surface reduces by $\mu_o M(T)$ the reversible magnetization, producing a critical state penetrating a distance of about $p = M(T)/J_c$ into the sample. On heating the surface flux density rises back to the external value producing a critical state in the opposite direction, which penetrates half as far. If we estimate the loss by the total flux crossing the total current, the loss per unit volume in a sample of radius r is of order $\mu_o M(T)^2\ p/r$. Now the free energies we are measuring are of order $\mu_o M(0)^2$, and the penetration of a few mT into a material of current density 10^4 A/cm is about 0.1 mm, so that although this effect could be important at low fields and also close to the irreversibility line, we expect it to be less than about 5% over the main range of the measurements. (This effect could be measured by comparing the specific heats on heating and cooling, but this was not possible with our present arrangement). A further check that this source of error is small is provided by the observation that the entropy difference measured between zero and above T_c is independent of the applied field.[1]

We have therefore used the specific heat results to calculate the reversible magnetization of YBCO at a number of temperatures; the results are shown in Fig. 7. Here the continuous lines are the specific heat results. The symbols are the mean of the magnetization curves as measured directly by the SQUID in increasing and decreasing fields (the very noisy points at the irreversibility line have been removed).

Below the irreversibility line, the mean of the magnetization curves should give an approximation to the reversible curve, but only under certain conditions. These are that the sample is fully penetrated, the pinning is bulk and not surface, and that the dependence of the critical current density on field can be neglected. In spite of these restrictions the agreement between the specific-heat measurements and the mean magnetization is very good, which gives further confidence that the specific-heat results yield the reversible magnetization in both the reversible and irreversible regimes.

We now consider the values of the penetration depth λ, which we have obtained. (In what follows we have allowed for the fact that there is 33% by volume of normal Y-211 in the material; λ is the value for the YBCO itself.) Figure 8 shows the experimental results for $1/\lambda^2$. Extrapolating to zero temperature gives a value of λ of 165 nm. Direct measurements of $\lambda(0)$ at low fields give the following results: 133 nm from infrared reflectance,[12] 145–116 nm from muon-spin relaxation,[13,14] and 140 nm from grain-aligned powders.[15] A recent paper based on ESR in overdoped material gives a value of 91 nm.[11] We attribute our larger value of $\lambda(0)$ to the recently proposed field dependence of $\lambda(0)$ in *d*-wave superconductors,[16,17] as-our measurements were performed over a range of fields. This is in broad agreement with the high field muon spin resonance measurements of Sonier *et al.*[18] Figure 8 shows our values compared with the theory of Ref. 16, using a value of $\lambda(0)$ at zero field of 141 nm. It can be seen that the variation with temperature follows closely the 6 T curve, which is the average field in our measurements. The absolute value is therefore consistent with other measurements made at low fields. The rather wide range of experimental values of $\lambda(0)$ can be attributed to a number of causes. Measurements can be divided into two classes, those that measure the penetration depth in the Meissner state and those that use the mixed state and the properties of the vortex lattice. There can be several reasons for the spread in values from different techniques in addition to the field dependence of λ. Use of the susceptibility of small particles requires a fairly uniform particle size and orientation, which is not easy to achieve. Surface conditions can affect the results.[19] Muon-spin relaxation relies on the muons sampling the average field, although at least on an atomic scale, this is not the case. Finally variations in crystal quality will lead to different values of $\lambda(0)$.

Finally, we make some remarks about the specific heat as we pass through the irreversibility line as shown in Fig. 5. A number of authors have discussed the peak that is observed and have attributed it to a phase changes in the vortex lattice.[7,8]

One effect that has not been considered previously is that we are changing from a specific heat at constant B to one at constant H; therefore, a step change is expected. The following is an order-of-magnitude calculation to show that the relative difference in specific heats at constant B and H is of order $1/\kappa^2$ and, therefore, too small to be detectable in these experiments or to account for the observed step.

The standard thermodynamic relation is

$$C_H - C_B = (T\,\partial H/\partial T)_B(\partial B/\partial T)_H. \tag{14}$$

Now at high fields,

$$M = (H - H_{c2})/2\kappa^2. \tag{15}$$

We assume

$$H_{c2} = H_{c2}(0)\left(1 - \frac{T}{T_c}\right). \tag{16}$$

Hence,

$$B = \mu_o(H+M) = \mu_o H + \frac{\mu_o H}{2\kappa^2} - \frac{\mu_o H_{c2}(0)}{2\kappa^2}\left(1 - \frac{T}{T_c}\right). \tag{17}$$

This is a reasonable approximation to the B-H curve for a high κ superconductor well above H_{c1}, which allows the relevant differentials to be calculated.

Ignoring numerical factors,

$$\left(\frac{\partial H}{\partial T}\right)_B = -\frac{H_{c2}(0)}{T_c\kappa^2} = -\frac{H_c(0)}{T_c\kappa}, \tag{18}$$

$$\left(\frac{\partial B}{\partial T}\right)_H = \frac{\mu_o H_{c2}(0)}{T_c\kappa^2} = \frac{\mu_o H_c(0)}{T_c\kappa}, \tag{19}$$

$$C_H - C_B = \frac{\mu_o H_c^2(0)}{T_c\kappa^2}. \tag{20}$$

Because the specific heat is of order $\mu_o H_c^2/T_c$, we see that the relative difference in the electronic specific heats of high κ materials is approximately $1/\kappa^2$. This is less than one in 10^4, and two orders of magnitude below the resolution of the experiments. It justifies our integration of the entropy across the irreversibility line, but means that the changes in specific heat as it is crossed cannot be attributed to the difference between C_B and C_H.

However, there is an indication in Fig. 7 of Ref. 20 that the specific heat has a positive step after the first-order transition. A possibility worth exploring further is that there is a contribution to the entropy associated with pinning centers. The entropy contribution of columnar pinning centers to the magnetization above the irreversibility line has been measured in Ref. 21, interpreted with the theory of Ref. 22, and is clearly important. Any strong pinning material will have such a contribution, and the most direct way of measuring the entropy is through the specific heat. The simplest picture is to view a pinning center as creating a two-level state for the flux line in its vicinity, so that the flux line is either in or out of the pinning center. This would lead to a specific heat change of k per pinning center as we go through the temperature at which kT is equal to the pinning energy. In this model, a peak in the specific heat of the size observed would be associated with a pinning center spacing of about 30 atoms. This is plausible if the pinning centers are point defects.

However, although this contribution to the entropy must exist, it is speculative at this stage to attribute the peaks in Fig. 5 to this mechanism. Clearer evidence would come from measurements of the specific heat as a function of pinning center density in a material where the melting transition is not so close to the superconducting transition.

IV. CONCLUSIONS

Measurements of specific heat in a strong pinning superconductor (YBCO) cooled in a field can be used to provide useful data on the reversible magnetization well below the irreversibility line. The curve is continuous with the reversible curve above the irreversibility temperature and close to the mean of the magnetization in increasing and decreasing fields in the irreversible region. The magnetization curve agrees well with the theoretical curve in the London limit at intermediate fields. This gives confidence in the results. The penetration depth can be derived from the magnetization curve and the absolute value is consistent with other measurements if the proposed variation with the magnetic field is taken into account. In addition, the variation with temperature is consistent with the theory of d-wave superconductors. A peak in the specific heat at the irreversibility line is consistent with a second-order phase change. It cannot be attributed to the change from constant B to constant H, but a contribution to the entropy from the pinning centers cannot be excluded.

[1] W. Y. Liang and J. W. Loram, Physica C **404**, 230 (2004).
[2] D. A. Cardwell, Mater. Sci. Eng., B **53**, 1 (1998).
[3] A. I. Rykov, S. Tajima, and F. V. Kursmatsev, Phys. Rev. B **55**, 8557 (1997).
[4] A. E. Koshelv and A. I. Larkin, Phys. Rev. B **52**, 13559 (1995)
[5] Z. Hao and J. R. Clem, Phys. Rev. Lett. **67**, 2371 (1991).
[6] A. Perry and A. M. Campbell, in *Magnetic Susceptibility of Superconductors and Other Spin Systems*, edited by T. Francavilla (Plenum Press, New York, 1991), pp. 567–577.
[7] M. Roulin, A. Junod, and E. Walker, Physica C **296**, 137 (1998).
[8] F. Bouquet, C. Marcenaut, E. Steep, R. Calemczuk, W. K. Kwok, U. Welp, G. W. Crabtree, R. A. Fisher, N. E. Phillips, and A. Schilling, Nature (London) **411**, 448 (2001).
[9] U. Welp, J. A. Fendrich, W. K. Kwok, G. Crabtree, and B. W. Veal, Phys. Rev. Lett. **76**, 4809 (1996).
[10] F. J. Blunt, A. R. Perry, A. M. Campbell, and R. S. Liu, Physica C **175**, 539 (1991).
[11] T. Pereg-Barnea, P. J. Turner, R. Harris, G. K. Mullins, J. S. Bobowski, M. Raudsepp, Ruixing Liang, D. A. Bonn, and W. Hardy, Phys. Rev. B **69**, 184513 (2004).
[12] D. N. Basov, R. Liang, D. A. Bonn, W. N. Hardy, B. Dabrowski, M. Quijada, D. B. Tanner, J. P. Rice, D. M. Ginsberg, and T. Timusk, Phys. Rev. Lett. **74**, 598 (1995).
[13] J. E. Sonier, R. F. Kiefl, J. H. Brewer, D. A. Bonn, J. F. Carolan, K. H. Chow, P. Dosanjh, W. N. Hardy, R. Liang, W. A. MacFarlane, P. Mendels, G. D. Morris, R. T. Riseman, and J. W. Schneider, Phys. Rev. Lett. **72**, 744 (1994).
[14] J. E. Sonier, J. H. Brewer, R. F. Kiefl, G. D. Morris, R. I. Miller, D. A. Bonn, J. Chakhalian, R. H. Heffner, W. N. Hardy, and R. Liang, Phys. Rev. Lett. **83**, 4156 (1999).
[15] C. Panagopoulos, J. R. Cooper, and T. Xiang, Phys. Rev. B **57**, 13422 (1998).
[16] M. H. S. Amin, I. Affleck, and M. Franz, Phys. Rev. B **58**, 5848 (1998); Phys. Rev. Lett. **84**, 5864 (2000).
[17] Yong Wang and A. H. MacDonald, Solid State Commun. **109**, 289 (1998).
[18] J. E. Sonier, J. H. Brewer, R. F. Kiefl, G. D. Morris, R. I. Miller, D. A. Bonn, J. Chakhalian, R. H. Heffner, W. N. Hardy, and R. Liang, Phys. Rev. Lett. **83**, 4156 (1999).
[19] E. Laurman and D. Shoenberg, Proc. R. Soc. London, Ser. A **198**, 560 (1949).
[20] A. Junod, M. Roulin, J.-Y. Genoud, B. Revaz, A. Erb, and E. Walker, Physica C **275**, 245 (1997).
[21] C. J. van der Beek, M. Konczykowski, R. J. Drost, P. H. Kes, N. Chikumoto, and S. Bouffard, Phys. Rev. B **61**, 4259 (2000).
[22] L. N. Bulaevskii, V. M. Vinokur, and M. P. Maley, Phys. Rev. Lett. **77**, 936 (1996).