First Order Phase Transition at the Irreversibility Line of $Bi_2Sr_2CaCu_2O_{8+\delta}$

H. Pastoriza, M. F. Goffman, A. Arribére,* and F. de la Cruz
Comisión Nacional de Energía Atómica, Centro Atómico Bariloche, 8400 San Carlos de Bariloche, Argentina

(Received 16 December 1993)

Magnetization and susceptibility measurements show a first order phase transition in the magnetic flux structure at the irreversibility line of $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals, in the field range $0 < H < 360$ Oe. The resistivity in the c direction drops 5 orders of magnitude in less that 0.1 K, and there is a discontinuous change in the magnetization at the same temperature. The change in magnetization together with the Clausius-Clapeyron equation gives a variation of entropy of $0.06k_B$ per vortex layer, at the transition. Above 360 Oe the irreversibility line has the known frequency dependence.

PACS numbers: 74.60.Ge, 74.40.+k, 74.72.Hs

Transport measurements [1–4] in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) and $YBa_2Cu_3O_{7-y}$ (YBCO) at high fields have shown that a three dimensional vortex structure makes a second order phase transition from a noncoherent state to a superconducting phase coherent state at low temperatures [5,6]. Whether this transition coincides with the irreversibility line $T_I(H)$ that separates the reversible from the nonreversible magnetic behavior is yet the subject of controversy.

While the above mentioned results describe the experimental data over a large range of fields and temperatures for dirty samples of YBCO, the appearance of a first order phase transition [2,7] in clean samples has shown the importance of disorder in the thermodynamic properties of that material.

The second order phase transition in YBCO seems to be coincident with the dc irreversibility line $T_I(H)$ defined as the merger of the field cooling (FC) and zero field cooling (ZFC) magnetizations. However, the experimental situation in BSCCO is less clear. Although resistivity measurements at high fields [7] have provided convincing results on the existence of a second order phase transition, there is no clear evidence of its relation with $T_I(H)$, as determined by dc magnetization measurements. In particular, it has been shown [8,9] that for fields higher than 400 Oe the dc irreversibility line, with the applied field in the c direction, lays well above the temperature where the resistivity in the c direction goes to zero, in agreement with previous sugestions [10,11].

A remarkable result of Refs. [8,9] is that $T_I(H)$ becomes frequency independent for $H < 400$ Oe, suggesting the existence of a phase transition in the low field and high temperature region of the phase diagram. This possibility has received strong support after the neutron diffraction experiments by Cubitt *et al.* [12], where the diffracted intensity from a vortex lattice is shown to disappear suddenly on the melting line at $T_I(H)$.

The experimental results for BSCCO [8–11] support the theoretical picture proposed by Glazman and Koshelev [13], who studied the effect of thermal fluctuations in layered superconductors. In their model there is a crossover field,

$$B_{\rm cr} \approx \frac{4\Phi_0}{\gamma^2 d^2}, \tag{1}$$

where Φ_0 is the flux quantum, γ the anisotropy ratio, and d the interlayer spacing. For $B > B_{\rm cr}$ the thermal fluctuations behave quasi-two-dimensionally. At a temperature $T_M(H)$ the superconducting order in the field direction is destroyed. However, the long range order of the lattice in the a-b planes remains up to a higher temperature. For $B < B_{\rm cr}$ the thermal fluctuations produce a melting of the vortex lattice, leading to a 3D vortex liquid with long range correlation in the direction of the field. At higher temperatures the correlation in the c direction is finally lost and the vortices become quasi-2D. On the other hand the effect of structural disorder in the possible phase transitions has not been taken into account in Ref. [13].

The results of Refs. [8,9,12] suggest the possibility of a melting phase transition at the irreversibility line $T_I(H)$. Thus, it is important to test this hypothesis and, if true, determine whether the transition is of first or second order. To do this we studied the frequency dependence of $T_I(H)$ for $H < 600$ Oe in a range of frequencies from 3 Hz up to 100 kHz with the dc field H parallel to c and an ac field perpendicular to it. The ac susceptibility shows that for $H > 360$ Oe the linear response is associated with a thermally activated process inducing a dissipation peak that lies above or below the dc irreversibility line, depending on frequency [8,14]. The frequency dependence of the dissipation peak disappears for $H < 360$ Oe. When the data are analyzed using the simple skin effect model, it shows that the resistivity in the c direction drops at least 5 orders of magnitude in less than 0.1 K, at the same fields and temperatures where neutron diffraction detects the sudden disappearance of the intensity of the lattice diffraction pattern [12].

The change of the ac susceptibility at $T_I(H)$ for fields below 360 Oe is found to be abrupt and frequency and amplitude independent, suggesting that the low field irreversibility line in BSCCO represents a first order ther-

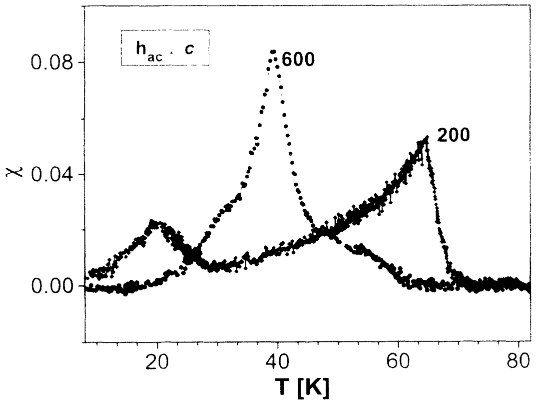

FIG. 1. Dissipative component of the ac susceptibility in the linear regime with the ac field parallel to the Cu-O planes as a function of temperature, for selected fields. The measurement frequency was 12 Hz. The numbers indicate the applied dc field parallel to the c axis.

modynamic transition, similar to that found [2,7] in clean YBCO samples. This is strongly supported by what we believe is the first thermodynamic proof of the order of the transition. That is, through careful dc magnetization measurements we have measured an abrupt change in magnetization associated with the phase transition.

The measurements were performed in high quality single crystals of BSCCO with $T_C = 89.5$ K, grown and characterized as described in Ref. [15]. The samples were typically slabs of $1 \times 1 \times 0.01$ mm^3.

The dc magnetization data were obtained using a SQUID magnetometer in a custom-made cryostat. In the experiments the field was applied in the c direction and the change in magnetic flux recorded as a function of temperature at constant magnetic field, without moving the sample. Details on the experimental setup can be found elsewhere [16].

The ac susceptibility was obtained using two complementary techniques for low and high frequencies. Above 200 Hz a conventional mutual inductance setup and a lock-in amplifier were used. In the range 1–1000 Hz the measurements were carried out using a SQUID as an amplifier. Details can be found in Ref. [8]. In all the ac measurements the ac field was perpendicular to the dc field, that is, parallel to the Cu-O planes.

Shown in Fig. 1 are typical data of the in-phase component, χ'', of the ac susceptibility as a function of temperature for two different dc fields. The ac field has a frequency of 12 Hz and an amplitude of 50 mOe. At this amplitude the ac response is found [8] to be linear in the whole range of temperatures and fields. The qualitative change of the shape of the dissipation peak when the field is increased is evident. At low fields and high temperatures the peak is asymmetric, quite sharp in the high temperature side, indicating that the effective shielding currents are switched in a narrow range of temperatures, as confirmed by a rapid change in the out of phase component χ', not shown in the figure. At higher fields the peak becomes more symmetric. Within the picture of Glazman and Koshelev [13] the low field peak corresponds to the establishment [8–11] of a coherent state in the c direction. On the other hand, it should be noticed that in the low field regime the energy dissipation is not totally quenched until a lower temperature, where a smaller and frequency dependent peak is detected [8]. The origin of this dissipation peak is the subject of current investigation.

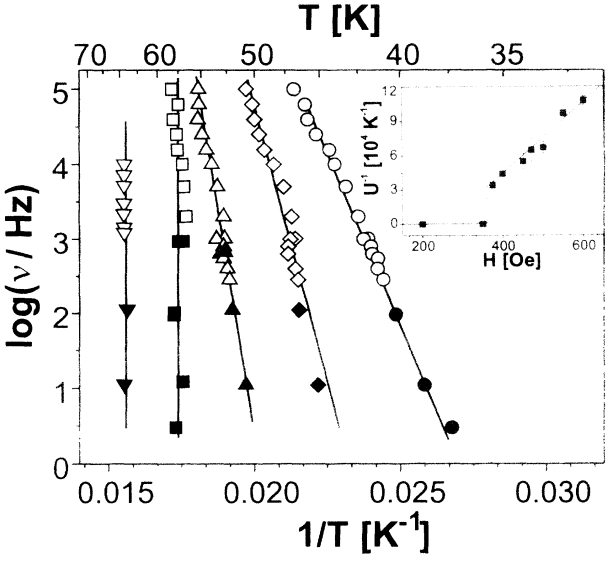

FIG. 2. Arrhenius plot for the measurement frequency vs temperature of the peak in χ'' for different applied fields. Open symbols are obtained using a conventional mutual inductance technique and full symbols using the SQUID as amplifier. Inset: Inverse of the activation energy as a function of the applied field.

In Fig. 2, we show an Arrhenius plot of the measuring frequency as a function of the temperature where the dissipation peak is observed for different applied fields. Considering that the ac response is in the linear regime we could associate the dissipation peak to a matching of the skin depth δ to some characteristic dimension of the sample $D = \delta = \sqrt{\rho(T)c^2/2\pi\omega}$, where $\rho(T)$ and ω are the resistivity and measuring frequency, respectively. We see from Fig. 2 that while at $H = 400$ Oe, the change in resistivity to match a change in frequency of 4 orders of magnitude occurs when the temperature changes 5 K; at 200 Oe the matching for an equivalent change in frequency requires a variation of temperature of less than 30 mK (close to the experimental error in the temperature measurement). This result obviously shows that the sudden change of the susceptibility in the low field range cannot be explained by a skin depth description. This is also seen in Fig. 2, where the activation energy, given by the slope of the straight lines, increases monotonically when decreasing field until a divergence in a very narrow range of fields is detected (between 375 and 350 Oe). The

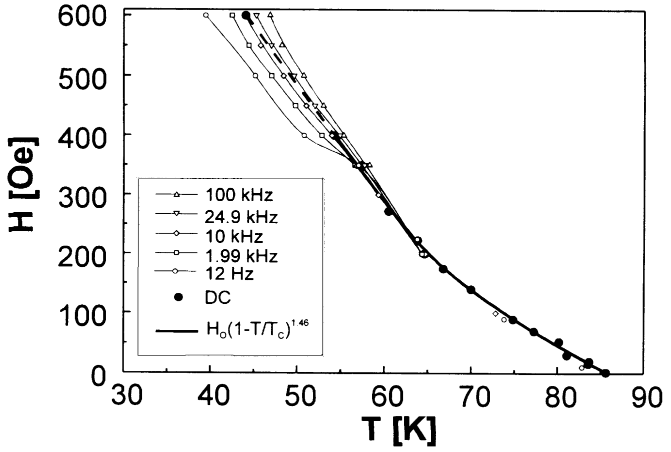

FIG. 3. Low field phase diagram of $Bi_2Sr_2CaCu_2O_{8+\delta}$. Closed circles: $T_I(H)$ from dc magnetization. Open symbols: Peak temperature in χ'' for selected frequencies. Thin lines represent constant resistance contours.

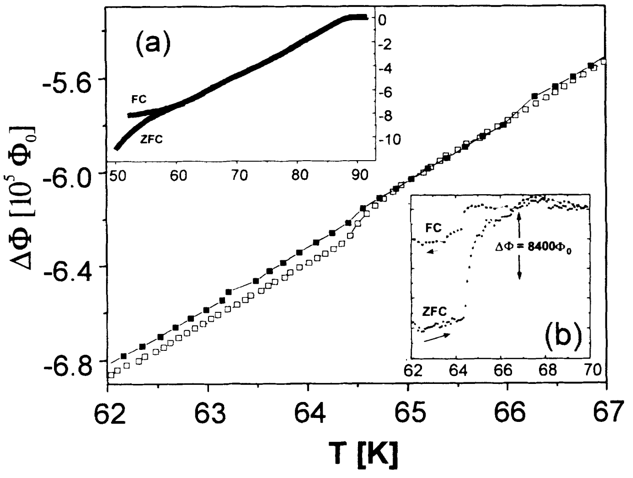

FIG. 4. Expanded view of ZFC and FC flux expulsions in a region of temperatures close to the irreversibility line, for an applied field of 223 Oe. The lines corresponds to linear fitting of the data. Inset (a) shows the ZFC and FC magnetizations up to T_c. Inset (b) shows the difference between the data and the linear fit of the equilibrium magnetization close above T_I.

inverse of the activation energy as a function of field is plotted in the inset of Fig. 2. We see then that above 360 Oe a thermally activated process is responsible for the temperature dependence of the resistivity, while the discontinuous divergence of the activation energy for smaller fields indicates the presence of a new phenomenon.

In the H-T diagram shown in Fig. 3 we have plotted the temperatures where the dissipation peak is detected for different fields, at some selected frequencies. The data corresponding to the irreversibility line as measured by dc magnetization [16] are also shown in the same figure. The frequency dependence of the position of the dissipation peaks for $H > 360$ Oe is evident. The thin solid lines drawn in the figure correspond to contours of constant resistance. The coincidence between the temperature where the dissipation peak is detected and that of the dc irreversibility line is clearly seen for $H < 360$ Oe. This is particularly relevant since the SQUID measurements probe the currents flowing in the a-b planes with an effective frequency at least 2 orders of magnitude smaller than the minimum frequency used in the ac measurements. It is interesting to point out the strong similarity between the contours of constant resistance and those reported in Ref. [17] for YBCO. However, there is a difference that reflects the importance of the laminar structure of the BSCCO compound. The first order phase transition in YBCO is manifested through the behavior of the resistance in the a-b planes and in BSCCO, through that in the c direction. In YBCO the long range order in the c direction is established well above the transition [18,19], while in BSCCO long range order is established at the first order phase transition.

Within the frame of the previous discussion there is a remarkable similarity [10,11] between the phase diagram of the superconducting BSCCO single crystals and that predicted in Ref. [13] for laminar structures. Using expression (1) with $B_{cr} = 360$ Oe and taking $d = 15$ Å we obtain $\gamma = 154$, a reasonable value among those reported in the literature [20]. In this sense the crossover field would determine the simultaneous 2D-3D crossover and the appearance of a first order transition at $T_I(H)$.

Although the transport properties and the neutron diffraction results provide strong evidence of the existence of a first order phase transition, there is no thermodynamic proof that such a transition takes place either in YBCO or in BSCCO. A first order phase transition requires a latent heat and a finite discontinuity in the sample magnetic moment. Careful dc magnetization measurements at the temperature where the departure between the ZFC and FC magnetization takes place has allowed the observation of a jump in the equilibrium magnetization, at the low field irreversibility line. This jump disappears above 360 Oe, where $T_I(H)$ becomes frequency dependent.

Figure 4 shows the change in magnetic flux in ZFC and FC experiments at the irreversibility line for a field of 223 Oe. In the inset (a) the FC and ZFC data are plotted in a wider range of temperature. In inset (b) we depicted the data after substracting the linear fit of the equilibrium magnetization close above T_I. The results of Fig. 4 show that the change in the number of vortices [21] at the melting transition is of the order of $8400\Phi_0$ over a total of 4×10^7 Φ_0. The experimental data shown in Fig. 4 were obtained in our thickest available sample of 2×10^{-4} cm^3. Measurements in thinner samples show the same anomaly in $\Delta\Phi$ at $T_I(H)$, although less evident than that shown in the figure.

One interesting feature that can be observed in Fig. 4 is that simultaneously with the melting transition a finite critical current appears, as is reasonable to expect in a first order phase transition from a liquid vortex state to a solid structure. The contribution of the critical current to the flux jump is discounted, taking the flux jump corresponding to the average of the ZFC and FC values, as indicated by the line between arrows.

Although the precision of the experimental data is not good enough to provide the temperature and field variation of the jump of the discontinuity of the magnetization we can use the Clausius-Clapeyron equation

$$-\frac{1}{4\pi}\frac{dH}{dT}=\frac{\Delta S}{\Delta BV} \tag{2}$$

to estimate the change in entropy ΔS at the transition. This value corresponds to $\Delta S=(6\times10^{-2})k_B$ per vortex per layer, in fairly good agreement with recent Monte Carlo simulations of the melting transition by Hetzel *et al.* [22].

Before summarizing the results it is convenient to mention the open question left by the presence of the small frequency dependent peak shown in Fig. 1 at around 20 K. Its main features have been already discussed [8]. Although it is difficult to suggest its origin we point out that it takes place at the lowest temperature where the ac ZFC and FC shielding coincide [23]. Below this temperature the FC shielding is larger than the ZFC [23]. This unusual manifestation of the critical state at low temperatures has been attributed [23] to the two dimensional character of the vortex structure, induced by a nonuniform current distribution. Whatever the cause of the dissipation peak, it coincides with a corresponding increase of the shielding capability of the order of 8% of the total [8]. Whether this decrease of resistance is the result of the establishment of a true long range order in all crystalline directions is the subject of present investigation.

In conclusion, we have presented ac susceptibility measurements in a broad range of frequencies and careful magnetization measurements in BSCCO single crystals. We have found clear evidence that the irreversibility line below 360 Oe is a true phase transition of first order. The change in entropy has been estimated from the change of magnetization and the slope of the irreversibility line. Contrary to what is observed in YBCO the first order phase transition in BSCCO coincides with a change from a 3D behavior at low temperatures to a 2D system with a high electrical resistance in the *c* direction. The first order phase transition defines a line in the *H*-*T* diagram ending at 360 Oe where the transition becomes continuous. This field coincides with the crossover field [13] above which the system becomes more sensitive to disorder due to its two dimensional character, suppressing the first order transition.

We want to acknowledge J. Luzuriaga for a critical reading of the manuscript. This work was partially supported by Fundación Antorchas and CONICET (PID 33650092). H.P., M.F.G., and A.A. hold fellowships from CONICET, Argentina.

---

* Deceased.

[1] H. Safar *et al.*, Phys. Rev. Lett. **68**, 2672 (1992).
[2] W. K. Kwok *et al.*, Phys. Rev. Lett. **69**, 3370 (1992).
[3] R. H. Koch *et al.*, Phys. Rev. Lett. **63**, 1511 (1989).
[4] T. K. Worthington *et al.*, Cryogenics **30**, 417 (1990).
[5] D. S. Fisher, M. P. A. Fisher, and D. A. Huse, Phys. Rev. B **43**, 130 (1991).
[6] G. Blatter *et al.*, Rev. Mod. Phys. (to be published).
[7] H. Safar *et al.*, Phys. Rev. Lett. **69**, 824 (1992).
[8] A. Arribére *et al.*, Phys. Rev. B **48**, 7248 (1993).
[9] F. de la Cruz *et al.*, in Proceedings of the 20th International Conference of Low Temperature Physics, Oregon, 1993 (to be published).
[10] C. Durán *et al.*, Phys. Rev. B **44**, 7737 (1991).
[11] J. Yazyi *et al.*, Physica (Amsterdam) **184C**, 254 (1991).
[12] R. Cubitt *et al.*, Nature (London) **325**, 407 (1993).
[13] L. I. Glazman and A. E. Koshelev, Phys. Rev. B **43**, 2835 (1991).
[14] H. Pastoriza *et al.*, in Proceedings of the 20th International Conference of Low Temperature Physics (Ref. [9]).
[15] D. B. Mitzi *et al.*, Phys. Rev. B **41**, 6564 (1990). We thank D. B. Mitzi and A. Kapitulnik for providing the single crystals used in this experiment.
[16] H. Pastoriza *et al.*, Phys. Rev. B **46**, 9278 (1992).
[17] H. Safar *et al.*, Phys. Rev. Lett. **70**, 3800 (1993).
[18] D. Lopez *et al.*, in Proceedings of the 20th International Conference of Low Temperature Physics (Ref. [9]).
[19] F. de la Cruz, D. Lopez, and G. Nieva, Philos. Mag. (to be published).
[20] J. C. Martinez *et al.*, Phys. Rev. Lett. **69**, 2276 (1992).
[21] The sample filling factor was estimated through measurements of the total flux expulsion in the Meissner state.
[22] R. E. Hetzel, A. Sudbø, and D. A. Huse, Phys. Rev. Lett. **69**, 518 (1992). Following the arguments presented in this reference and using the parameters of BSCCO the field studied there corresponds roughly to 150 Oe.
[23] E. Rodríguez *et al.*, Phys. Rev. Lett. **71**, 3375 (1993).