Transverse Magnetization Study of the Pairing State of the High-T_c Superconductor $LuBa_2Cu_3O_{7-\delta}$

J. Buan, Branko P. Stojkovic, N. E. Israeloff,* A. M. Goldman, C. C. Huang, and Oriol T. Valls
Center for the Science and Application of Superconductivity and School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455

J. Z. Liu and Robert Shelton
Department of Physics, University of California, Davis, California 95616
(Received 9 December 1993)

The angular dependence of the in-plane transverse magnetization of an untwinned single crystal of $LuBa_2Cu_3O_{7-\delta}$ has been studied in the Meissner state as a function of temperature and magnetic field. The amplitude of the Fourier component of the signal with angular period $\pi/2$ has been found to be smaller than the theoretical prediction for a d-wave pairing state. The results are consistent with isotropic pairing, but they do not rule out nodeless anisotropic pairing states.

PACS numbers: 74.25.Ha, 74.72.Jt, 74.90.+n

An important unsolved problem in condensed matter physics is that of the mechanism of high-temperature superconductivity, and the associated question of the identification of the symmetry of the pairing state. Although many different pairing state symmetries are possible [1], not all are compatible with the complete range of suggested mechanisms. Recently there has been serious consideration of pairing in a d-wave rather than in an s-wave state [2–4]. This has come in part from the realization that models of superconductivity involving antiferromagnetic spin fluctuations may require such a state. The experimental findings relating to the pairing symmetry are quite disparate in that one can find experiments which support either s-wave or d-wave pairing. Although many recent studies appear consistent with nodes in the energy gap [5–12], these studies are also consistent with an anisotropic s-wave state [13], or with $s+id$ pairing [14]. Other recent measurements of temperature dependent phenomena, such as microwave determinations of $\lambda(T)$ [15], and neutron scattering and specific heat studies [16], do not support either the d-wave or the anisotropic pairing pictures. Measurements of various Josephson tunneling geometries, which should provide information on the phase of the order parameter, also yield conflicting results. The study of the field dependence of the critical current in dc SQUIDS is consistent with the phase anisotropy of a $d_{x^2-y^2}$ state [17], whereas the investigation of c-axis Josephson tunneling of studies agrees with an s-wave state [18,19]. Recently reported thermodynamic anisotropy in the a-b plane should be considered in interpreting the dc SQUID results [20]. Since accounting for all of the subtleties of even nominally simple measurements in a rigorous manner requires much work, the question of the nature of the pairing state in the high-T_c superconductors must be considered to be unanswered.

In this Letter, we report the results of a study of the supercurrent response to determine the symmetry of the pairing state of a high quality single crystal of $LuBa_2Cu_3O_{7-\delta}$. This approach, suggested by Yip and Sauls [21], and based on ideas attributable to Bardeen [22], can detect the presence of nodes in the superconducting energy gap through the measurement of the angular dependence of the in-plane, off-axis magnetization of the crystal in the Meissner state. The anisotropy of the response, and thus of the magnetization, will be determined by any anisotropy in the magnitude of the gap and the location of any nodes that might be present on the Fermi surface. The latter are characteristic of unconventional pairing states. If there are nodal lines in the gap in momentum space, the response will deviate from linearity at low temperature when the supercurrent velocity becomes comparable to a critical velocity $v_c=\Delta(\hat{\mathbf{k}})/v_F$, where v_F is the Fermi velocity and $\Delta(\hat{\mathbf{k}})$ is the energy gap. When the critical velocity is reached, there will be a quasiparticle current persisting to zero temperature, which in turn will reduce the supercurrent response. An analysis of our measurements as discussed below suggests that there are no nodes in the gap, eliminating the pure d-wave pairing state as a possibility. However, pairing state anisotropy, such as that of an $s+id$ state, is not ruled out by our results.

The transverse magnetization measurements, as a function of both temperature and applied magnetic field, were made using a superconducting susceptometer equipped with a special sample holder which permitted rotation about an axis *perpendicular* to the field direction. The crystal was positioned so that the applied magnetic field was in the a-b plane. The measurements were taken in the third orthogonal direction relative to the axis of rotation and the applied field. The crystal's orientation relative to the field was controlled by a computer driven stepper motor. This motor changed the angle of orientation, *in situ*, by driving a long shaft that actuated a worm gear, on which the sample was mounted.

In order to understand the measurements, we first review the calculation of the transverse component $\mathbf{M}_{tr}$ of the magnetic moment $\mathbf{M}=(1/2c)\int(\mathbf{r}\times\mathbf{j}_s)d\mathbf{r}$. The effect

0031-9007/94/72(16)/2632(4)$06.00

of a possible d-wave pairing state on $\mathbf{M}_{tr}$ can be calculated as a function of H and T using the method of Ref. [21]. Consider a superconducting crystal with its a-b (x-y) plane parallel to a magnetic field $\mathbf{H}$. Assuming a cylindrical Fermi surface and defining the velocity field $\mathbf{v}=\nabla\phi/2+(e/c)\mathbf{A}$, one obtains $\mathbf{M}_{tr}$ from the supercurrent density $\mathbf{j}_s$:

$$\mathbf{j}_s=-\rho e\left\{\mathbf{v}+\int(d\theta/2\pi)\hat{\mathbf{k}}\int(d\xi/v_f)[f(E+\sigma)-f(E-\sigma)]\right\}, \tag{1}$$

where $E=[\xi^2+|\Delta(\hat{\mathbf{k}})|^2]^{1/2}$, $\sigma=\mathbf{v}_F\cdot\mathbf{v}$ is the shift in quasiparticle energy due to the superflow, $\mathbf{v}_F=v_F\hat{\mathbf{k}}$ is the quasiparticle velocity on the Fermi surface, and a factor of the effective mass has been absorbed into the definition of $\mathbf{v}$, following Ref. [21]. The total carrier density is ρ and f is the Fermi function. Equation (1) must be solved numerically together with Maxwell's equations. We use the natural boundary conditions $\partial\mathbf{v}/\partial z|_{z=0}=\partial\mathbf{v}/\partial z|_{z=d}=(e/c)\mathbf{H}$, where d is the thickness of the crystal. Assuming the order parameter possesses d-wave symmetry, i.e., $\Delta(\hat{\mathbf{k}})=\Delta_0(\hat{k}_x^2-\hat{k}_y^2)$, it follows that, for low temperatures, $\mathbf{M}_{tr}$ has a fourfold symmetry in the x-y plane, while it vanishes identically for the isotropic case. There should be a similar signature in the effective penetration depth λ [21]. The same considerations apply to anisotropic s-wave or $s+id$ pairing [14].

In the anisotropic case one can define a crossover temperature $\tilde{T}(H)$ [or alternatively a crossover field $\tilde{H}(T)$] above (below) which $\mathbf{M}_{tr}$ decreases rapidly. It follows from Eq. (1) and Ref. [21] that $\tilde{T}\approx\Delta_0(H/H_a)$, where H_a is a *characteristic* field given by $H_a\approx\phi_0/2\pi\sqrt{2}\xi\lambda$ [alternatively $\tilde{H}=H_a(T/\Delta_0)$]. As noted in Ref. [21], $\mathbf{M}_{tr}$ can be observed only for $T<\tilde{T}\ll T_c$. On the other hand, the predicted linear behavior of $\lambda(H\to 0,T)$ should only be seen for $\tilde{T}<T\ll T_c$ ($H<\tilde{H}\ll H_a$). The low magnetic field dependence of $\mathbf{M}_{tr}$ is also different, i.e., $\mathbf{M}_{tr}\approx H^\alpha$ with $\alpha\to 2$ for $T<\tilde{T}$ and $\alpha\to 3$ for $T>\tilde{T}$.

We now turn to the measurements, which were performed on a small, untwinned, single crystal (a:b:c $=1.2$:0.9:0.07 mm) of $LuBa_2Cu_3O_{7-\delta}$. Since twin boundaries and other imperfections could mask any effect, the issue of crystal quality is of paramount importance. This topic was addressed through detailed x-ray diffraction and specific heat studies, shown in Fig. 1 [20,23]. The x-ray diffraction analysis of the crystal was carried out using a diffractometer. The orthorhombic nature of the $LuBa_2Cu_3O_{7-\delta}$ single crystal allowed for identification of twinning in the crystal by constructing a map of an off-axis reciprocal space point of the form hkl, with h and k not equal. No twinning was identified by this procedure [20]. The presence of twin boundaries in the crystal would be detected by the presence of a peak at the position of the + in inset (a) of Fig. 1. The anomaly in the specific heat found at the transition temperature in zero applied magnetic field is sharper and larger than any reported in the literature for either single crystal or polycrystalline samples [23].

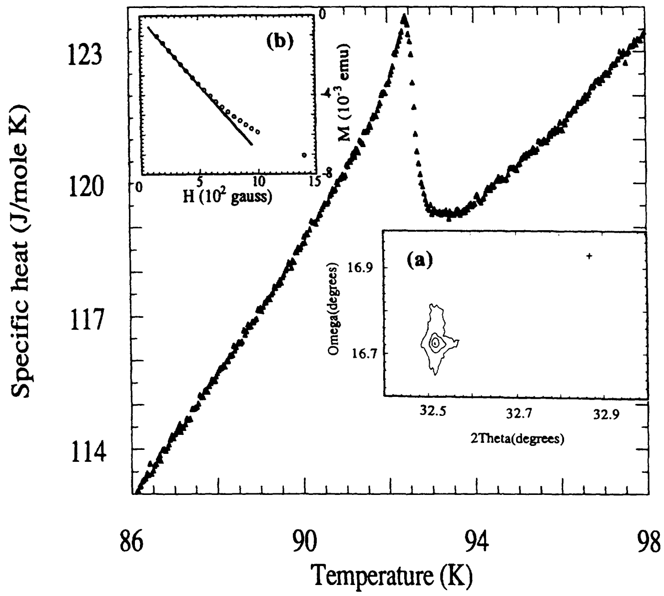

FIG. 1. Specific heat data as a function of temperature, in zero applied magnetic field, of the untwinned $LuBa_2Cu_3O_{7-\delta}$ crystal studied in this work. See Ref. [23] for details. Inset (a): Reciprocal space map of the [013] peak of the single crystal, as determined by x-ray diffraction. The four constant intensity contours correspond to 475, 335, 50, and 5 counts/sec with the background less than 2 counts/sec. If the crystal were twinned, a second diffraction peak would appear at the position denoted by a +. Inset (b): Longitudinal magnetization vs field at $T=2$ K.

The interpretation of the supercurrent response requires that the applied field H be well into the Meissner regime, so as to avoid the nucleation of vortices. In other words, the applied field must be below the field of first flux entry. Thus, the field dependence of the magnetization was investigated using a superconducting susceptometer. It was determined that for fields applied parallel to the a-b plane, at a temperature of 2 K, the first deviation from linearity in the magnetization for this crystal was found at fields ≥ 500 G as shown in inset (b) of Fig. 1. Therefore, to be safely within the Meissner regime, $\mathbf{M}_{tr}$ was studied in fields below 300 G.

The use of relatively low fields necessitated that the measurements be carried out at the low temperatures to satisfy the condition $T<\tilde{T}$. The value of $\tilde{T}$ can be estimated using parameters given for the extensively studied compound, $YBa_2Cu_3O_{7-\delta}$ [24–26], which is isostructural with $LuBa_2Cu_3O_{7-\delta}$. The appropriate values for ξ and λ used in the isotropic theory [21] must be inferred [27]. It is clear that the relevant coherence length is ξ_{ab}, for which we take the value to be 15 Å [25]. The choice of λ is not so obvious. The signal measured in this experiment is sensitive to the volume fraction of the sample in which the field penetrates and currents exist. The

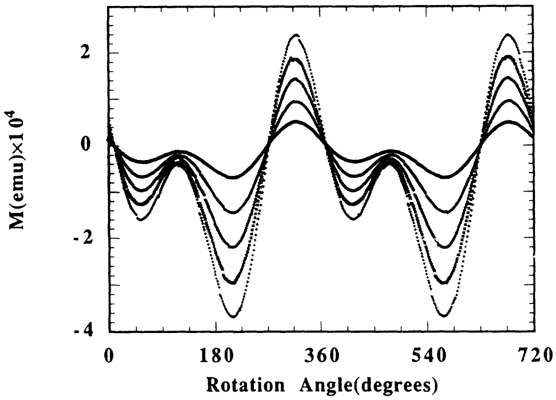

FIG. 2. Transverse magnetization as a function of angle for rotations in the basal plane, at $T=2$ K for various fields. The rotation angle is the inclination of the crystal's a axis with respect to the direction of the applied field. The values of the field are 50, 100, 150, 200, and 250 G. The amplitude of the signal increases with field.

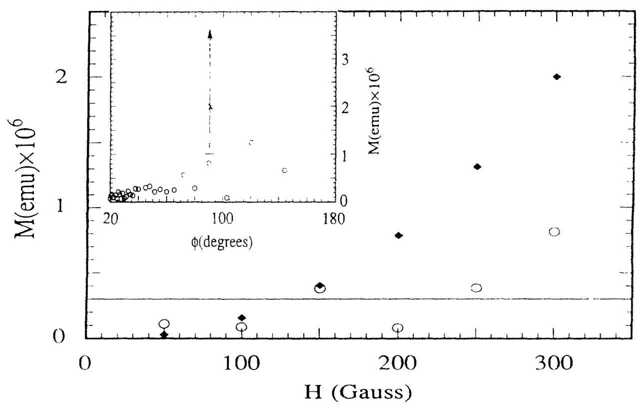

FIG. 3. Fourier amplitude of the magnetization at the angular period of $\pi/2$, as a function of field. The symbols ♦ and ○ represent the theoretical predictions and the experimental results, respectively. The horizontal line indicates the resolution of the measurement. Inset: Amplitudes of various harmonics as determined from the FFT analysis. The theoretical prediction of 2×10^{-6} emu, computed using $\lambda_c=1$ μm and $\xi_{ab}=15$ Å as indicated in the text, is denoted by an ×. The vertical line is the spread of results obtained from using the full range of parameters reported in the literature. The lower limit of the vertical line is the lowest *possible* prediction. The end of the arrow extends to more than 10^{-4} emu. Amplitude of the harmonic with angular period π is off scale and is about 6×10^{-5} emu.

effective value of λ must be taken as a weighted average of λ_c and λ_{ab}, with the weights being proportional to the volumes of the sample in which the currents flow, along the c axis and in the a-b plane, respectively. The relative weight of λ_c to λ_{ab} contributing to λ is proportional to the product $(c/a)\lambda_c/\lambda_{ab}$. The aspect ratio of our crystal, c/a, of about 0.1, implies that the influence of λ_c cannot be neglected. With $\lambda_{ab}=1700$ Å [24] and $\lambda_c=1$ μm [26], we calculate an effective $\lambda=4000$ Å. Thus, $H_a \approx 3000$ G and $\tilde{T}\approx 10$ K at an applied field of 100 G.

The transverse magnetization $\mathbf{M}_{\rm tr}$ was measured at fixed magnetic field as a function of temperature, and at fixed temperature as a function of magnetic field. The crystal was zero-field cooled, and the crystal's a axis along the solenoid axis, to the temperature at which the data were to be taken. Then, the field was ramped to the starting value (for the runs at fixed temperature this was 50 G). The magnetization data were then acquired as a function of angle in the basal plane. After each measurement of the magnetization, the sample was rotated by 1.44°. A total of 501 data points were taken in every data set, resulting in two full rotations of the sample. Then, the field was increased to the next value, or the temperature was changed with the field being fixed. In this way, a grid of data in the H-T plane was generated.

Transverse magnetization data, at 2 K, as a function of field and angle in the basal plane, are shown in Fig. 2. The data consist of five runs starting at 50 G and ending at 250 G, with the field incremented by 50 G for each data set. Each data set can then be fit by the sum of only two sinusoidal contributions with angular periodicities of π and 2π. These periodicities are consistent with the signals being generated only by the standard geometric demagnetization factor and trapped flux, respectively. Both signals have a linear field dependence. The quality of the fit suggests that the signature in the transverse magnetization of a d-wave pairing state, a component with an angular period of $\pi/2$, is at best very small. Indeed the magnitude of such a signal, as discussed below, is predicted to be only about 1% of the amplitude of the largest visible periodicity, the one occurring at an angular period of π. As a consequence another approach to analyzing the data was employed.

To search for a signal with a $\pi/2$ periodicity, a fast Fourier transform (FFT) analysis was undertaken. The Fourier coefficients, for data taken at 300 G and 2 K, are shown in Fig. 3, along with the theoretically predicted signal, denoted by an ×, obtained by numerical solution of Eq. (1). Its value was estimated using parameters given for $YBa_2Cu_3O_{7-\delta}$ [24–26]. The amplitude of the $\mathbf{M}_{\rm tr}$ signal at $H=300$ G should approach 2.0×10^{-6} emu at $T\approx 2$ K, a value which is above the resolution of the susceptometer by an order of magnitude. It should be emphasized that the values of parameters utilized for the theoretical prediction of the size of the d-wave signature are on the conservative side. If we consider the full range of values for both λ_c (7000 Å to 3 μm [26]) and ξ_{ab} (15 to $\sim$40 Å [25]) reported in the literature, we obtain the signal range indicated by the vertical line in Fig. 3. If we followed the less conservative procedure used to estimate the magnetic torque in Ref. [21], then the expected signal would be about 2 orders of magnitude larger than our estimate.

The temperature and field dependences of the signal at $\pi/2$ provide important corroborating information. We find that the signal of interest, at $\pi/2$, has roughly the same field dependence as all the other higher harmonics, close to linear. This is inconsistent with the numerically obtained theoretical prediction of an $H^{2.3}$ dependence at 2 K for a system with line nodes (see Fig. 3). Similarly, the temperature dependence of the $\pi/2$ signal may be examined. We have done this at 250 G, where the expected signal is well above the noise, and find that it is approximately temperature independent, whereas theoretically [21] it should decrease with temperature. Finally, we find that the phase of the signal at $\pi/2$ is consistent with the signal itself being generated as a higher harmonic of the diamagnetic response.

The calculation of $\mathbf{M}_{tr}$ outlined above can be repeated for an $s+id$ pairing state. In this instance the experimental results are compatible with this mixed symmetry. If one assumes that the entire $\pi/2$ amplitude is due to the signal from the gap anisotropy, then the magnitude of the s-wave component of the gap will be at least 10% of the maximum gap. The actual percentage of s wave is likely to be higher because the signal at angular period $\pi/2$ is actually a mixture of the anisotropic response due to the d-wave or $s+id$ pairing and higher harmonic contributions from the signals at angular periods π and 2π.

In summary, we have measured the angular dependence of the in-plane, off-axis magnetization of a $LuBa_2Cu_3O_{7-\delta}$ single crystal. The amplitude of the Fourier component with angular period $\pi/2$ is found to be smaller than theoretical expectations for a pure d-wave pairing state. Furthermore, the field and temperature dependences, as well as the phase, of the signal are consistent with it being generated as a higher harmonic of the signals at angular period π and 2π. As a consequence, we conclude that there are no nodes in the superconducting energy gap. Our results are consistent with either isotropic pairing, nodeless s-wave anisotropic pairing, or $s+id$ pairing in which a lower limit on the magnitude of the s-wave component of the gap is at least 10% of the maximum gap. They do not rule out the model in which there are low-lying localized states near a d-wave node [28].

We acknowledge the contribution of M. Tuominen to the design of early versions of the rotating sample holder. We would like to thank A. Basovich, R. Joynt, R. Klemm, J. Sauls, D. J. Scalapino, G. Spalding, and D. VanHarlingen for useful discussions. This work was supported in part by the Air Force Office of Scientific Research under Grants No. F49620-93-1-0076 (Minnesota) and No. F49620-92-J-0514 (California), and by the Minnesota Supercomputer Institute. One of us (B.P.S.) wishes to acknowledge the support of the U.S. Department of Education.

*Present address: Physics Department, Northeastern University, Boston, MA 02115.

[1] C. Gros, R. Joynt, and T. M. Rice, Z. Phys. B **68**, 425 (1987); M. Sigrist and T. M. Rice, J. Phys. Soc. Jpn. **61**, 4283 (1992).
[2] N. E. Bickers, D. J. Scalapino, and R. T. Scalettar, Int. J. Mod. Phys. B **1**, 687 (1987).
[3] P. Monthoux and D. Pines, Phys. Rev. B **47**, 6069 (1993).
[4] W.-M. Que and B. Kirczenow, Z. Phys. B **73**, 425 (1989).
[5] S. E. Stupp and D. M. Ginsberg, *Physical Properties of High Temperature Superconductors I and II*, edited by D. M. Ginsberg (World Scientific, Teaneck, NJ, 1991).
[6] S. E. Barrett *et al.*, Phys. Rev. Lett. **66**, 108 (1991); J. A. Martindale *et al.*, Phys. Rev. B **47**, 9155 (1993).
[7] R. C. Yu, M. B. Salamon, and W. C. Lee, Phys. Rev. Lett. **69**, 1431 (1992).
[8] S. L. Cooper and M. V. Klein, Comments Condens. Matter Phys. **15**, 99 (1990).
[9] W. N. Hardy *et al.*, Phys. Rev. Lett. **70**, 3999 (1993).
[10] D. A. Bonn *et al.*, Phys. Rev. B **47**, 11 314 (1993).
[11] J. E. Sonier *et al.*, Phys. Rev. Lett. **72**, 744 (1994).
[12] Z.-X. Shen *et al.*, Phys. Rev. Lett. **70**, 1553 (1993).
[13] See, for example, S. Chakravarty, A. Sudbø, P. W. Anderson, and S. Strong, Science **261**, 337 (1993).
[14] See, for example, G. Kotliar, Phys. Rev. B **37**, 3664 (1988); Q. P. Li, B. E. C. Koltenbah, and R. Joynt, Phys. Rev. B **48**, 437 (1993).
[15] N. Klein *et al.*, Phys. Rev. Lett. **71**, 3355 (1993).
[16] T. E. Mason, G. Aeppli, S. M. Hayden, A. P. Ramirez, and H. A. Mook, Phys. Rev. Lett. **71**, 919 (1993).
[17] D. A. Wollman *et al.*, Phys. Rev. Lett. **72**, 2134 (1994).
[18] P. Chaudhari and Shawn-Yu Liu, Phys. Rev. Lett. **72**, 1084 (1994).
[19] A. G. Sun, D. A. Gajewski, M. B. Maple, and R. C. Dynes, University of California, San Diego (private communication).
[20] J. Buan *et al.*, Phys. Rev. B (to be published).
[21] S. K. Yip and J. A. Sauls, Phys. Rev. Lett. **69**, 2264 (1992).
[22] J. Bardeen, Phys. Rev. Lett. **1**, 399 (1958).
[23] B. Zhou *et al.*, Phys. Rev. B **47**, 11 631 (1993).
[24] D. R. Harshman and A. P. Mills, Phys. Rev. B **45**, 10 684 (1992).
[25] A. Kapitulnik, M. R. Beasley, C. Castellani, and C. DiCastro, Phys. Rev. B **37**, 537 (1988).
[26] C. Strombos, doctoral dissertation, Ecole Normale Superieure, Paris, 1993, unpublished.
[27] The theory of Ref. [21] is concerned with an infinite planar sample for which the relevant lengths are ξ_{ab} and λ_{ab}. In a finite crystal the response to a magnetic field in the a-b plane involves current loops which are closed by flows along c. The value of λ which governs the magnitude of the current response must therefore include a contribution from λ_c.
[28] P. A. Lee, Phys. Rev. Lett. **71**, 1887 (1993).