Experimental investigation of the pairing state of high-temperature superconductors

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To address the issue of the pairing state in high-temperature superconductors, four different experimental investigations have been carried out on a *single* high-quality, untwinned single crystal of $LuBa_2Cu_3O_{7-\delta}$. These include measurements of the specific heat in magnetic fields, both near the transition temperature and at low temperatures, investigations of the angular dependence of the transverse magnetic moment in the nonlinear Meissner regime, and the measurement of microwave properties leading to the temperature dependences of the penetration depth and the surface resistance at low temperatures. Some of the results raise questions relating to the existence of a pairing state with line nodes in the energy gap, whereas others appear to be consistent with this picture. The results taken together suggest that studies of the pairing state be examined critically for possible alternative explanations. [S0163-1829(96)09134-5]

I. INTRODUCTION

The mechanism underlying high-temperature superconductivity, although the subject of a great deal of scientific investigation over the ten years since the discovery of this phenomenon, is still an unresolved matter. The related question of the identification of the symmetry of the pairing state has attracted considerable interest because knowledge of this symmetry may serve to narrow the choice of potential mechanisms.[1,2] In particular the unambiguous observation of d-wave, rather than s-wave symmetry would argue strongly for antiferromagnetic spin fluctuations mediating the electron-electron pairing interaction rather than a conventional mechanism based on a variant of electron-phonon coupling. Moreover s-wave symmetry would not be consistent with such a spin-dependent coupling. A d-wave pairing state would result in the superconducting gap exhibiting nodes, i.e., vanishing at certain positions on the Fermi surface, in stark contrast with the situation in conventional superconductors. The presence of such nodes would result in quasiparticle excitations existing down to zero temperature. Such excitations should in principle be detectable in a number of experiments, and indeed the results of a number of measurements have in fact been interpreted in such a manner. These include studies of the temperature dependence of the superconducting penetration depth well below the transition temperature,[3] microwave surface impedance measurements,[4] angle-resolved photoemission studies,[5] and some specific-heat studies.[6] Studies of the Knight shift, nuclear relaxation, and inelastic neutron scattering can also be described within the d-wave phenomenology.[7] The d-wave pairing state also brings about unique effects associated with the phase of the superconducting order parameter.[8] A number of Josephson junction experiments in several geometries[9–13] can be interpreted in the context of the d-wave picture, and observation of the paramagnetic Meissner effect, or Wohlleben effect[14] has been interpreted in that context.[15] On the other hand, there are additional results from other efforts, including neutron scattering,[16] penetration depth in the $Nd_{2-x}Ce_xCuO_4$ cuprate,[17] c-axis Josephson tunneling,[18] one grain-boundary tunneling study,[19] and the nonlinear Meissner effect,[20] which do not support the d-wave picture.

The experimental situation, which is a result of utilizing different samples, makes it difficult to arrive at a definitive conclusion regarding the pairing state. Although there are many results which have been interpreted as evidence of d-wave pairing, one must assert that this evidence is not incontestable. Each investigation must be scrutinized to determine whether there are subtle sources of systematic error in the measurements, consequences derived from the complexity of the materials not taken into account in the analysis, or unusual features of a specific compound. Any of these could lead to erroneous conclusions on one side or other of the s-wave vs d-wave controversy. Material effects such as disorder, impurities, and oxygen deficiency can have important effects on the data. Although a given set of measurements can be interpreted as evidence for a certain pairing state, even for a well-conceived study there may be alternative explanations for data which in most instances have not been examined critically, or tested as exhaustively as some preferred hypothesis. As a consequence no single experiment can be taken to be ''proof'' of the character of the pairing state.

In this work we report on a series of different pairing state

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studies on a *single* well-characterized, ''high quality'' $LuBa_2Cu_3O_{7-\delta}$ untwinned single-crystal sample. Details of sample characterization have been given elsewhere.[20] The work reported here includes measurements of the specific heat near T_c and in magnetic fields applied along the principal axes of the crystal in fields up to 6 T,[21] the low-temperature specific heat in zero field and in applied fields up to 8 T in the a-b plane, the angular-dependent transverse magnetic moment in the nonlinear Meissner regime,[22] and the temperature dependence of the penetration depth below 10 K and associated microwave surface impedance. Each set of measurements addresses the pairing state issue in a unique way. The specific-heat measurements in zero field near T_c in zero field attest to sample quality. The measurements in a magnetic field near T_c raise questions as to the location of the superconducting charge carriers within the crystal structure, and the existence of an inherent anisotropy in the superconductivity. The low-temperature specific heat is sensitive to the presence of gap excitations. The measurements of the transverse Meissner effect, penetration depth, and microwave surface impedance have a direct bearing on the s- vs d-wave problem. When taken together, the results of these experiments, obtained from one crystal, suggest that the hypothesis of a pure d-wave state may not be an appropriate description. Some of the investigations are consistent with the d-wave picture whereas others are not, raising the possibility that experiments on one side or other of d-wave pairing controversy may involve some other physical interpretation. The work highlights the care that must be taken in designing, performing, and analyzing experiments directed at elucidating the symmetry of the pairing state.

II. SPECIFIC-HEAT MEASUREMENTS NEAR T_c

The results of measurements of the specific heat of single crystals of high-temperature superconductors in magnetic fields have several implications relating to the pairing state. First we consider measurements with a magnetic field applied along different crystallographic directions at temperatures near T_c.[23] Such studies can serve to demonstrate the fundamental anisotropy of the superconductivity not only in the a-b plane relative to the c direction, but in the a-b plane itself. This has serious implications for the suitability of models which assume tetragonal symmetry or a two-dimensional (2D) square lattice geometry. Second, certain aspects of the field dependence of the specific heat at low temperatures have been interpreted as evidence of a d-wave state, as was done in Ref. 6. This issue will be considered in Sec. III.

In our measurements we employed ac calorimetry to obtain the specific heat of the $LuBa_2Cu_3O_{7-\delta}$ crystal as a function of temperature near T_c, and in applied magnetic fields up to 6 T. A detailed thermodynamic analysis of this data, with the magnetic field along the c axis, has been published elsewhere.[24] For the present purposes, Fig. 1 displays the temperature variations of specific heat measured with no applied magnetic field and with a field of 6.0 T along each of the three principle crystallographic directions. The sharp specific-heat anomaly at zero field becomes a small and broad hump at 89 K with an applied field of 6 T along the c axis. This suppression is much more pronounced than the largest previously reported,[25] and is larger than that obtained with the field along the a or b axes. This is an indication of the *predominantly* (not exclusively) 2D nature of the superconductivity in these compounds.

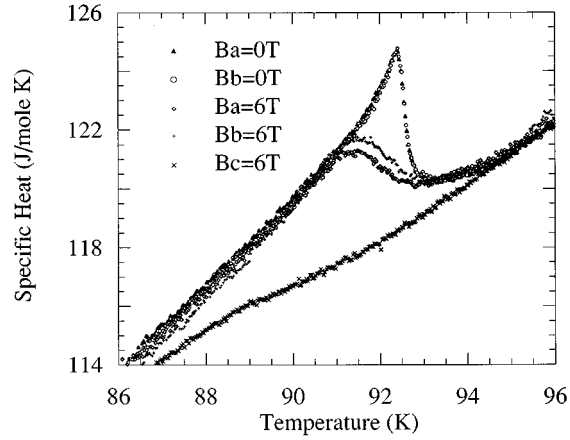

FIG. 1. Specific heat vs temperature for a $LuBa_2Cu_3O_{7-\delta}$ single crystal. The curves with suppressed anomalies are those taken in the presence of a 6 T field oriented along particular directions. The largest suppression occurs for a magnetic field applied along the crystalline c axis.

The specific heat clearly differs for the case of an applied magnetic field along the a axis as compared to the b axis, the suppression of the anomaly near T_c being smaller with the field along the b axis. The difference between the results of the two sets of measurements falls outside of the error, which is given by the scatter in the data of any experimental run. The most likely explanation of these observations is that the charge carriers existing in the CuO chains (along the b axis) contribute significantly to the superconducting properties of the crystal. Fields applied along the a axis induce currents in the b-c plane, which flow in part along the chain direction, whereas fields applied along the b axis induce currents in the a-c plane which flow in part perpendicular to the chain direction. There is further evidence of this anisotropy in infrared reflectivity studies,[24] and in c-axis Josephson tunneling measurements[25] which imply significant anisotropy in the superelectron densities and penetration depths between the a and b directions.

The difference between the specific heat measured with the fields along the a and b directions can be quantified by looking at the entropy difference apparent in the two data sets. The normalized entropy difference near the transition is calculated using

$$\frac{\int_{T_1}^{T_2} dT[C_p(H_b=6\mathrm{T})-C_p(H_a=6\mathrm{T})]/T}{\int_{T_1}^{T_2} dT[C_p(H=0\mathrm{T})-C_p(H_a=6\mathrm{T})]/T}=0.22. \qquad (1)$$

Here $T_1=90.7$ K and $T_2=93.0$ K. $C_p(H=0\ \mathrm{T})$, $C_p(H_a=6\ \mathrm{T})$, and $C_p(H_b=6\ \mathrm{T})$ are the temperature-dependent specific-heat data taken in zero magnetic field and in an applied field of 6 T along the a and b axis, respectively. The orthorhombic structure of the CuO_2 planes, and the resultant ratio $b/a=1.019$, may cause some of the observed thermodynamic

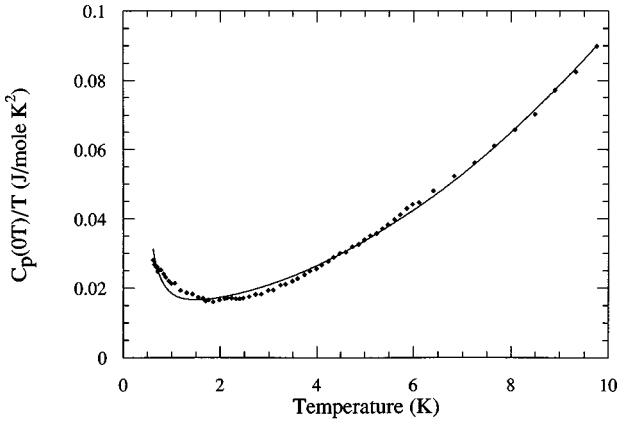

FIG. 2. Plot of C_p/T vs T in zero field for the crystal of Fig. 1. The experimental data are represented by the solid triangles. The fit is represented by the solid line.

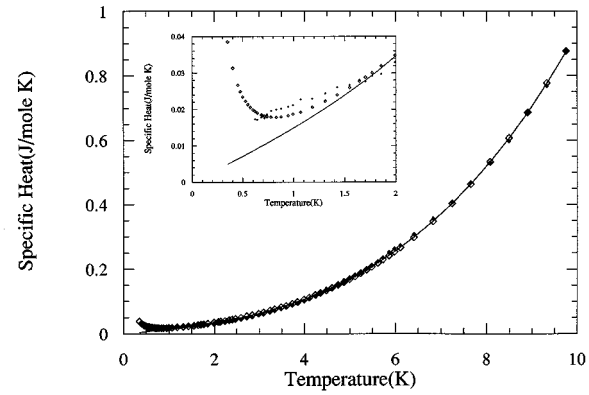

FIG. 3. Plot of C_p vs T in zero field of the crystal of Fig. 1. The hollow diamonds are a fit including the Schottky anomaly. The solid line is a fit without it. The open circles are the data. The inset shows details at the lowest temperatures.

anisotropy. However, given the closeness of this ratio to unity, it is unlikely that all of the observed 22% additional reduction in the entropy for fields applied along the b axis is due to this structural anisotropy. Thus, the thermodynamic properties in the a-b plane of the 1:2:3 compounds possess an additional anisotropy, beyond the obvious one seen between the c axis and the a-b plane.

The above result has implications for d-wave theories of superconductivity in the cuprates, in particular for the $YBa_2Cu_3O_{7-\delta}$ family of compounds, i.e., the 123 compounds, whose members all possess chains. Since the CuO chains appear to directly participate in the superconducting properties, the question of the suitability of a model which only considers effects in the CuO_2 sheets in square 2D model, such as those leading to a d-wave pairing state would seem to be open to question. Recently a model has been proposed[26] that directly addresses the role of chains in supercurrent response, and implies an explanation not involving d-wave pairing for Josephson tunneling studies of the 123 compounds which measure phase differences, and which have been interpreted as evidence of d-wave pairing.

III. LOW-TEMPERATURE SPECIFIC HEAT

The measurement of the low-temperature specific heat is a key experiment in the description of the superconducting state. Work of this nature done in 1954 on Sn provided conclusive evidence of the superconducting gap. Thus, high-quality specific heat data has been sought to explain the cuprates. The zero-field specific-heat data from the $LuBa_2Cu_3O_{7-\delta}$ crystal is shown in Fig. 2, along with a generic fit to the data using the following expression:

$$C_p/T = \gamma_0 + B_3{*}T^2 + B_{-2}{*}T^{-3}. \tag{2}$$

Equation (2) is used by most researchers to fit to low-temperature specific-heat data of high-T_c compounds. The various fitting parameters represent the normal electronic, the phonon, and the Schottky contributions to the specific heat, respectively. The values of the fitting parameters for Fig. 2 are γ_0=13.6 mJ/K^2, B_3=0.8 mJ/K^4, and B_{-2}=0.8 mJ/K. A few things are apparent from an inspection of the fitting curve and its relationship to the data. The low-temperature upturn, which is believed to owe its existence to some kind of magnetic ordering phenomenon, is not well approximated by the $1/T^2$ term. The peak is visibly broadened relative to the Schottky fitting form. This visual characteristic is independent of the fitting window. This is consistent with the bulk of the published data in the high-T_c superconductors, as was pointed out in Ref. 27. A nonzero linear term does exist. The presence of the T^3 term captures the essence of the data quite nicely above 2.0 K.

Numerical values must be found for the coefficients of the fitting expression. The values of the coefficients are sensitive to the size of the temperature window being utilized. The low-temperature upturn seen in a C_p/T plot is in fact not an upturn when a C vs T plot is examined. This is seen in Fig. 3. The inset of the figure provides a view of the low-temperature behavior, along with fits with and without a Schottky term. There is no upturn at all in the data. It was found that excellent fits to the data could be achieved with only two parameters, the normal electronic and Debye terms, excluding the Schottky term. The parameters found using this approach are given in Table I. The sizes of the fitting windows in Kelvin form the columns and the coefficient values are the rows. The best fit, as determined by a normalized value of χ^2, was found for the fitting window restricted to an 8 K upper temperature. This is consistent with the breakdown of the Debye approximation at higher temperatures. The inclusion of the Schottky term results in reduction in magnitude of the linear term. In the fitting window, 0.6 to 8 K, the magnitude of the linear term is reduced by 6%. This effect is fitting window dependent. This result calls attention to the difficulty of fitting data of this type with many terms. Careful examination of the relevance of the various fitting terms within the fitting windows is necessary before any conclusions can be drawn.

This idea becomes more apparent when the connection between the *d-wave* issue and the low-temperature specific heat in zero field is considered. The presence of line nodes as in a *d-wave* pairing state will result in a T^2 term in the specific heat at low temperatures. Such a term was added to the fitting expression. No improvement in the fit, as measured by χ^2, was found in any temperature window that in-

cluded the data at the lowest temperatures. As seen previously, the fits to the data with only linear and Debye terms generate a linear term of magnitude greater than 10 mJ/K^2, a value larger than found recently by other workers in the field.[6] However, unexpected behaviors of the various fitting parameters emerged as the temperature window was adjusted. (See Table II.) If a T^2 term is added to the fit, and all the data are considered from 0.6 K, nothing dramatic happens. The linear and Debye terms are unchanged and the coefficient of the T^2 term is below the resolution of the experiment. If the fitting window is restricted to temperatures above 2 K a more puzzling result emerges. The magnitude of the T^2 coefficient increases to nearly 2 mJ/K^3 and the linear term decreases to around 8 mJ/K^2. These values are closer to what has been reported in one of the more recent experiments with a similarly restricted temperature window, though the linear term is still quite large.[6] The inset of Fig. 3 shows that something is going on at the lowest temperatures. This behavior is not explained by any current models. It should be pointed out that a T^2 term should become more important as T approaches 0 K, especially relative to the Debye term. So the questions remain. Why does the inclusion of data at lower temperatures affect the T^2 term so strongly? Is this an extrinsic effect, or has some physics been missed because the specific-heat data on small single crystals is not of sufficient quality at low temperatures? Perhaps measurements in large magnetic fields can shed some light on this matter.

Low-temperature specific-heat measurements on the 123 compounds, in applied magnetic fields greater than 1 T, have been the subject of a recent paper.[6] These measurements were interpreted as providing evidence for a *d-wave* pairing state based on the theory of Volovik.[28] A similar study was also carried out on the $LuBa_2Cu_3O_{7-\delta}$ single crystal. The magnetic field was applied in the a-b plane. This is not an ideal geometry for observation of the *d-wave* effects. However, if the large linear term were due to Cu^{2+} moments, it should be seen in a Schottky anomaly at a higher temperature and should be independent of field orientation. In Fig. 4 we display the low-temperature specific heat in fields of 4 and 8 T, applied in the a-b plane, as well as a fit to both data sets using the expression, $C_p = \gamma(H)*T + B_3*T^3$. The parameter $\gamma(H)$ is assumed to be field dependent and B_3 is assumed to be field independent. Each data set was assumed to have the same value of B_3. This is in keeping with the standard convention. The Debye term was found by fitting one data set to the above expression in the temperature range 4–to 8 K. The resulting B_3 was then used to fit the other data set similarly. It was found that the results were independent of the choice of parameters for the first data set. The value of $\gamma(H)$ was found to be field independent, with a value of 13.4 mJ/mole K^2, within the error of the measurements. The lack of a Schottky anomaly at a few Kelvin in a field of 8 T is puzzling in the presence of the large zero-field linear term.

TABLE I. Parameters of the fit to the data for the low-temperature specific heat.

	0.6–6 K	0.6–8 K	0.6–10 K
γ_0 (mJ/mole K^2)	12.8	13.3	14.2
B_3 (mJ/mole K^4)	0.85	0.83	0.79

TABLE II. Parameters of the fit to the data which includes a T^2 term (B_2).

	0.6–10 K	2–10 K
γ_0 (mJ/mole K^2)	13.1	7.96
B_2 (mJ/mole K^3)	0.36	2.0
B_3 (mJ/mole K^4)	0.76	0.64

To reiterate the findings, there is no strong evidence for *d-wave* superconductivity in the specific heat in zero-field. The relevant T^2 term is seen only if a partial data set is examined. If all the data from 0.6 K is considered, a large linear term is seen and no evidence is found for a Schottky term in a field of 8 T, in apparent contradiction to the prevailing ideas about the presence of a large linear term in zero field. The inclusion of the various appropriate fitting terms was shown to be problematic and temperature window driven. This work shows the need for further specific-heat studies on high-quality *single* crystals to resolve the matter.

IV. MEASUREMENTS OF THE ANGULAR DEPENDENCE OF THE TRANSVERSE MAGNETIC MOMENT IN THE NONLINEAR MEISSNER REGIME

The supercurrent response to a magnetic field will deviate from linearity at low temperatures when the supercurrent velocity becomes comparable to a critical velocity $v_c = \Delta(\mathbf{k})/v_F$, where v_F is the Fermi velocity and $\Delta(\mathbf{k})$ is the energy gap. When this critical velocity is reached there will be a quasiparticle current persisting to zero temperature, which reduces the supercurrent response. An earlier experiment probing this nonlinear Meissner effect in terms of the field-dependent penetration depth in the Meissner state was carried out on twinned Y-Ba-Cu-O crystals. The results were interpreted with the framework of an s-wave order parameter.[29] A more recent penetration depth experiment[30] has been interpreted in terms of d wave, but the parameter values required seem unreasonable.

An angular dependence of the energy gap in k space will

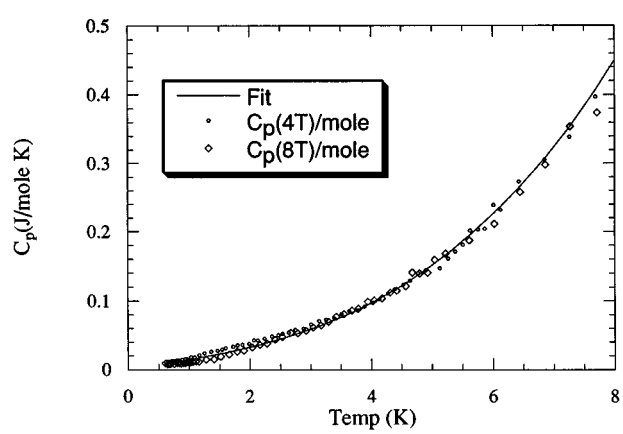

FIG. 4. Plot of C_p vs T under applied magnetic fields of at 4 and 8 T applied along the a-b plane.

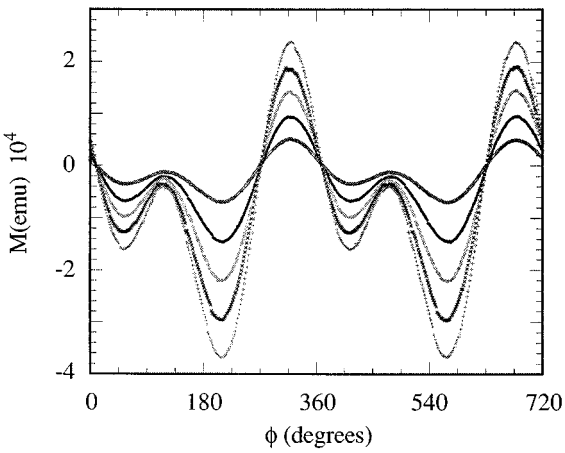

FIG. 5. Transverse magnetic moment as a function of angle for rotations in the basal plane at 2 K for various fields. The rotation angle is the inclination of the crystal's *a* axis with respect to direction of the applied field. The values of the field are 50, 100, 150, 200, and 250 G. The amplitude of the signal increases with field.

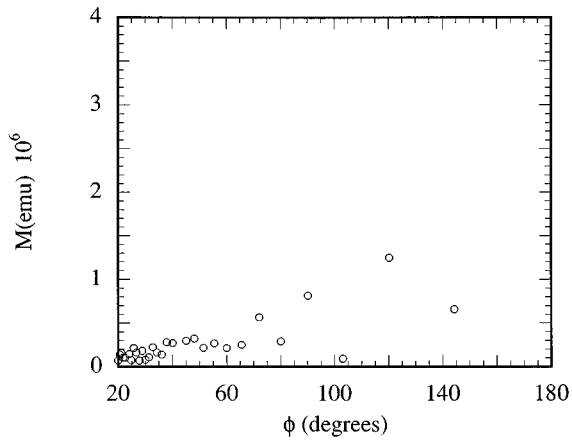

FIG. 6. Amplitudes of various harmonics for an FFT analysis of data taken at 300 G and 2 K. The amplitude of the harmonic with angular period π is off scale, at about 6×10^{-5} emu.

result in an angle-dependent supercurrent in the a-b plane and a transverse magnetic moment.[31] If the order parameter exhibits d-wave symmetry, the transverse magnetic moment will have fourfold symmetry with respect to rotation about the $c$axis, while it will vanish in the isotropic case. The calculation can be generalized to the cases of anisotropic s-wave or $s+id$-wave pairing in which there can be fourfold symmetric responses, but with reduced amplitude.[32] The nonlinear regime is defined by a crossover temperature or a crossover field. For the particular $LuBa_2Cu_3O_{7-\delta}$ crystal the crossover field has been estimated as 10 G at a temperature of a few K. The crossover field and temperature are approximately linearly related to each other.

The transverse magnetic moment was measured in the nonlinear regime at fixed magnetic field as a function of temperature, and at fixed temperature as a function of magnetic field using a superconducting susceptometer equipped with a sample holder which permitted rotation of the crystal about an axis perpendicular to the applied field direction. The magnetic signal was obtained with a superconducting quantum interference device coil with its axis at right angles to both these directions. The crystal was zero-field cooled, with the crystal's a axis along the solenoid axis, to the temperature at which the data was 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 was then acquired as a function of angle in the basal plane with the crystal rotated about its c axis. After each measurement, 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. After this, 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 magnetic moment data, at 2 K, as a function of field and angle in the basal plane, are shown in Fig. 5. The data consist of five runs starting at 50 G, 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 periodicity's 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 magnetic moment 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. 6. The dots represent the absolute values of the complex Fourier coefficients corresponding to angles smaller than 180°. The 180° and 360° coefficients are of course much larger, and are therefore not shown, since they would be off the scale. One can see that the dot corresponding to the $\pi/2$ component falls in a continuum with the other higher-order components. This suggests that this component arises in about the same manner as the others, i.e., it is a harmonic of the dominant 2π and π components.

To confirm this and to further analyze the results, we note that the trapped flux and demagnetization factor signals and their harmonics are proportional to the field H, while the putative signal from the nonlinear Meissner effect is quadratic in H (Refs. 31 and 32) at low temperatures. To extract the nonlinear part, i.e., the $\pi/2$ component, we fit our experimental result for this component to the sum of a linear and a quadratic term in H. As expected, the dominant signal is linear. The remaining signal (i.e., the $\pi/2$ signal in absolute value, minus the linear part in the field) is an upper bound to any experimental signal corresponding to nonlinear effects, and it is plotted as the symbols in Fig. 7. It is an upper bound because it is derived from the absolute value of the Fourier component: there is an assumption in this analysis that the phase of the signal is fully consistent with theory.

These experimental results are plotted in Fig. 7 together with the theoretical curve. The theoretical values were computed using material parameters appropriate to $YBa_2Cu_3O_{7-\delta}$.[33] It should be emphasized that very conser-

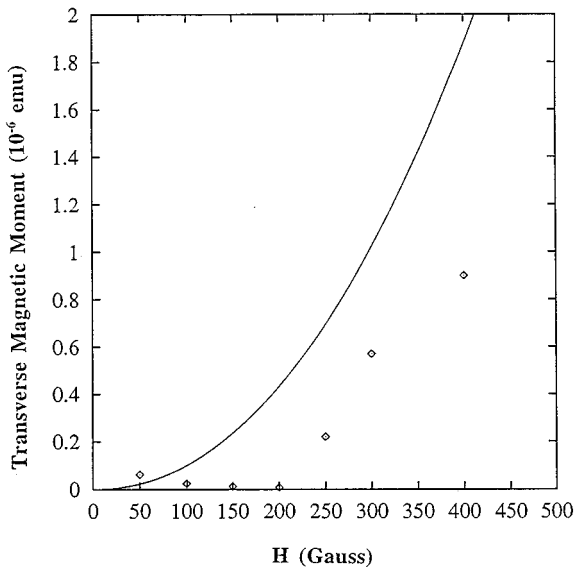

FIG. 7. Fourier amplitude of the magnetization at the angular period of $\pi/2$, as a function of magnetic field at a temperature of 2 K. The solid line is a numerical evaluation based on the theory described in Ref. 32.

vative assumptions were made in choosing these parameters. In particular, the value of the penetration depth λ was taken to be equal to λ_{ab}, without including *any* corrections from the much larger λ_c corresponding to return currents in the c direction. The latter would have led to much larger theoretical estimates.[20] Thus, even though the experimental results in Fig. 6 are upper bounds and the theoretical values lower bounds, one still finds that the experimental signal is consistent with the ''noise,'' and is too small to arise from nonlinear effects. Finally, we find that the phase, found with the real and imaginary parts of the FFT analysis, of the signal at $\pi/2$ is consistent with the signal itself being generated as a higher harmonic of the diamagnetic response.

In summary, the angular dependence of the in-plane, off-axis magnetization of the single crystal of $LuBa_2Cu_3O_{7-\delta}$ was measured. 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, the conclusion is that no nodes are being observed in the superconducting energy gap. The 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.[32]

V. MICROWAVE SURFACE IMPEDANCE

Microwave surface impedance measurements were carried out in a specially designed, high-sensitivity Nb cavity based on a technique introduced by one of authors.[34] The surface resistance is measured from the temperature-dependent Q using $R_s(T)=\Gamma[Q^{-1}(T)-Q_b^{-1}(T)]$ and the

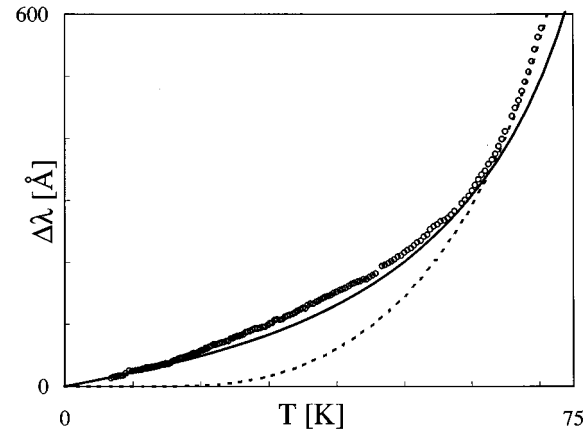

FIG. 8. Low-temperature dependence of the ab-plane penetration depth. Also shown are comparisons to weak-coupling d-wave (solid line) and isotropic s-wave (dotted line) calculations.

penetration depth using $\Delta\lambda(T)=(2\xi/f_0)[f(T)-f_b(T)]$, where ξ is a geometric factor and Q_b is the background Q(nearly 10^8) of the empty cavity.

At low temperature the $\lambda_{ab}(T)$ data displayed in Fig. 8 show a polynomial temperature dependence with a leading linear term. The data are very similar to data on Y-Ba-Cu-O crystals[3,35,36] and new results on Bi-Sr-Ca-Cu-O.[37] It is evident that the λ vs T data do not show the exponential dependence $\Delta\lambda\sim(T_c/T)^{1/2}\exp(-\Delta/k_BT)$ expected at low temperature for an isotropic s-wave superconductor. Comparison to weak-coupling d-wave and isotropic s-wave calculations as shown in Fig. 8 demonstrate that the d-wave calculation[37] describes the data quite well at low temperature. For the $d_{x^2-y^2}$ order parameter a gap $\Delta(\theta)=\Delta_d(T)\cos(2\theta)$ was used. Note that since the penetration depth measurements are insensitive to the phase of the order parameter, an extended s-wave state with a $|\cos(2\theta)|$ dependence would give the same results as the $d_{x^2-y^2}$ state.

The weak-coupling model gives for the low-temperature slope $d[\Delta\lambda_{ab}(T)]/dT=\lambda_{ab}(0)\ln(2)/\Delta_d(0)$ for a $d_{x^2-y^2}$ order parameter.[38] The experimental slope of 2.1 Å/K along with the weak-coupling gap value $\Delta_d(0)=2.16k_BT_c$ gives a value $\lambda_{ab}=600$ Å. This is somewhat lower than has been obtained for Y-Ba-Cu-O. The use of a higher gap value (for the 123 compounds values between 2 and $4k_BT_c$ have been suggested) would lead to a higher value of $\lambda(0)$ obtained from the fit.

At high temperatures the data differ significantly from the weak-coupling d-wave model. However it should be noted that addition of scattering and strong-coupling effects may lead to improved agreement of the data with d-wave models, although additional input parameters would need to be determined.[35] We note also that the high-temperature data are better described by a mean-field temperature dependence $(T_c-T)^{-1/2}$ rather than a 3D X-Y behavior $(T_c-T)^{-1/3}$. This result is consistent with the results of recent radio-frequency measurements on high-quality films.[39]

The superconducting surface resistance $R_s(T)$ shows a characteristic peak (see Fig. 9) which is also observed in Y-Ba-Cu-O and has been attributed to a rise of the quasiparticle scattering time.[4] In Lu-Ba-Cu-O it is very pronounced and sharp. The size (roughly 250 $\mu\Omega$) and position of the

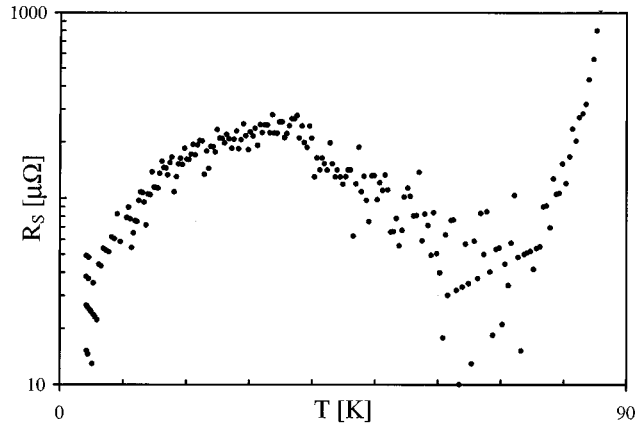

FIG. 9. Low-temperature dependence of the surface resistance $R_s(T)$.

peak with the maximum at 35 K is comparable with Y-Ba-Cu-O data obtained by some of us[35] and others.[4,36]

An important prediction for any superconducting state with nodes is the presence of a finite residual conductivity due to elastic scattering.[40,41] Its value depends on the particular pairing state, and, if determined experimentally could help to identify the type of pairing present. Unfortunately because of the very small sample size, the experimental uncertainty in our present measurement is higher than the expected residual value of a few $\mu\Omega$, so that further conclusions regarding the residual conductivity are not possible.

Overall the Lu-Ba-Cu-O crystal has all the features found in very high-quality Y-Ba-Cu-O crystals, and which have been demonstrated recently in Bi-Sr-Ca-Cu-O crystals also. This suggests a common behavior of the density of states in all of these materials. While the low-temperature penetration depth is in good agreement with an order parameter with nodes in the gap such as a d-wave order parameter or and extended s-wave state, the high-temperature behavior and the surface resistance point to the need for better understanding of scattering, coupling strength and fluctuations.

VI. DISCUSSION

We have presented the results of two heat-capacity studies of different types, an investigation of the angular dependence of the transverse magnetization in the nonlinear regime, and a study of the penetration depth and microwave surface resistance, all carried out on the *same* single crystal of $LuBa_2C_3O_{7-\delta}$. This particular crystal was untwinned, as determined by precision x-ray diffraction, and exhibited an extremely narrow superconducting transition. The specific heat results near T_c in a magnetic field demonstrate an inherent anisotropy in the supercurrent response of the 123 compound which raises questions as to the inherent validity of models which treat such systems as two-dimensional objects with square symmetry. The analysis of the specific-heat results at low temperatures in a magnetic field is in disagreement with the analysis of similar measurements made by the Stanford group which purport to demonstrate d-wave pairing. The nonlinear Meissner effect studies also do not support d-wave pairing. Only the microwave impedance studies at low temperatures yield results for the penetration depth which are consistent in detail with d-wave pairing. The shift in the penetration depth at low temperatures is linear in temperature. The surface resistance falls to small values with decreasing temperature. Unfortunately the predicted residual resistance for d-wave pairing and the resistance the sample is approaching in the $T\rightarrow 0$ limit are both below the experimental resolution. As a consequence, this measurement does not conclusively reveal the nature of the pairing state either.

The observation of a linear temperature dependence for the penetration depth at low temperatures either implies d-wave pairing, or it could follow from another explanation, such as the one in which it is a signature of collective modes in an s-wave superconductor.[42,43] If the microwave results mean that the pairing is d wave, then there must be systematic errors in *both* the low-temperature specific-heat and nonlinear Meissner effect studies.

An alternative scenario which might be argued is that the data for $\Delta\lambda$ in Fig. 9 are actually quadratic at the lowest temperatures, and fit a straight line only within the range 10 K$<T<$40 K. This form is *qualitatively* the behavior expected in a d-wave system with impurities. We do not believe that this is as good a representation of the data as a linear dependence at the lowest temperatures, but present this as a ''straw man'' to argue against the possibility that impurities are responsible for the null results for d wave in the nonlinear Meissner effect measurement. The idea is that impurity scattering, presumably the presence of which is indicated in this interpretation of the microwave data would smear the nodal features enough to wash out the nonlinear Meissner signal. Then a ''dirty'' d-wave scenario might provide a consistent view of all of our results. However, this is not the case. The question of impurities was quantitatively studied in Ref. 32, where it was shown that the impurity concentration required to reduce the transverse magnetic moment signal at low temperatures by a factor of 2 is large enough that it would produce quadratic behavior in $\Delta\lambda$ (Ref. 44) extending all the way up to 40 K. This is a much greater range of quadratic behavior than the 10 K range which *might* be read from the data. Thus even if our Meissner results were interpreted as evidence of impurity scattering, the associated range of quadratic behavior in $\Delta\lambda$ would be much greater than even this generous interpretation. The associated impurity level would also be expected to degrade the transition temperature by about 10 K. For our sample the observed degradation in T_c is much less than 1%. Hence both sets of observations lead to the conclusion that this ''strawman'' scenario involving ''dirty'' d-wave behavior fails quantitatively and the contradiction between the apparent agreement of the microwave data with d-wave theory, and the rest of our transverse magnetic moment results remains.

The high-temperature specific-heat studies in a magnetic field imply the existence of a fundamental in-plane anisotropy in the superconductivity which is not contained in any of the simple d-wave models, but which must be dealt with quantitatively in any detailed theory of superconductivity in these materials. The role of the chains, and the possibility of internal order-parameter phase shifts between chains and planes may be a non-d-wave explanation of the Josephson tunneling studies which are interpreted as evidence of d-wave superconductivity. Clearly it would be desirable to

repeat all of the pairing state experiments on chain-free materials such as the Hg superconductors, as they, in principle, would lay to rest the issue of the chains.

The issue of the existence of *d-wave* superconductivity in the 123 compounds was derived from the contention that antiferromagnetic excitations must play a role in the superconductivity. The evidence for such excitations in these compounds is strong. However, its direct association with superconductivity is not as fully established. If a pairing mechanism not involving exchange of antiferromagnetic excitations, or one involving such excitations, but compatible with a symmetry other than *d* wave, could be established, then the issue of the pairing state being *d* wave would be less significant.

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