Orthorhombic Distortion at the Superconducting Transition in $YBa_2Cu_3O_7$: Evidence for Anisotropic Pairing

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We report the results of a high-resolution x-ray scattering study of the structure of $YBa_2Cu_3O_7$ as a function of temperature. We find that there is an anomaly in the orthorhombic splitting, $b-a$, near the superconducting transition, whereas there is little or no anomaly in the unit-cell volume. Our results suggest that the superconducting wave function has a uniaxial anisotropy within the a-b plane.

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Empirical characterization of the symmetry of the superconducting wave function in the new oxide superconductors[1-3] is essential to the understanding of the electron pairing mechanism. Traditionally, the symmetries of superconducting wave functions have been determined indirectly from the temperature dependence of thermodynamic quantities which depend on the excitation of quasiparticles above the superconducting gap; wave functions which have orbital angular momentum $l>0$ may have nodal points or lines in the gap, allowing for low-energy excitations.[4] Unfortunately, in the present case, the possible existence of low-lying excitations not related to superconductivity makes the interpretation of thermodynamic measurements difficult.[5,6] Furthermore, s-symmetry wave functions with states in the gap have been proposed.[7] In this Letter we present an alternative approach. Specifically, we show that anisotropy in the superconducting wave function can be inferred by characterizing the structural response of the lattice to the development of superconducting order. Such a method was proposed by Joynt and Rice[8] for the case of a highly symmetric crystal (e.g., cubic) undergoing a transition to a lower-symmetry superconducting state. In the present case the lower orthorhombic symmetry of the normal phase rules out a symmetry change at the superconducting transition. Nonetheless, it is useful to study the lattice strain that occurs as superconducting order develops. Surprisingly, our data on $YBa_2Cu_3O_7$ imply a large anisotropy within the basal a-b plane. The implication of our results as to the form of the superconducting state will be discussed below after the presentation of the data.

Our experiments were carried out on powder samples of $YBa_2Cu_3O_7$. Details of the sample preparation are published elsewhere.[9] Briefly, $YBa_2Cu_3O_7$ was synthesized from mixtures of $BaCO_3$, CuO, and Y_2O_3. Pellets of the mixtures were fired at 950 °C in flowing O_2 for 16 h and slowly cooled (50 °C/h) to 400 °C. During the firing the sample was mounted on a platinum sheet on top of powder of the same mixture. The resulting material was single phase and had a relatively sharp superconducting transition ($\simeq 1$ K wide) at 91 K as characterized by resistivity and magnetic susceptibility measurements.

The sample was mounted inside a helium-gas–filled beryllium cell which was attached to the cold finger of a closed-cycle Displex cryostat. The temperature stability was about ± 0.01 K over the course of typical scans which were up to 10 h in duration. High-resolution x-ray scattering was carried out with utilization of Cu $K\alpha$ x-rays from a rotating-anode x-ray generator. The x rays were collimated and analyzed with perfect Ge(111) crystals yielding a nondispersive longitudinal resolution of 4×10^{-4} Å^{-1}. The scattering was carried out in reflection geometry from a pellet which was large compared to the size of the beam ($\simeq 1\times10$ mm).

Typical x-ray scans are illustrated in Fig. 1. Data near the nondispersive condition $Q=2k_i \sin\Theta \approx 2$ Å^{-1} (where Q is the momentum transfer, k_i is the Cu $K\alpha$ wave vector, and Θ is the scattering angle) were fitted by single Lorentzian line shapes. Data for $Q \gtrsim 4$ Å^{-1} were fitted by the sum of two Lorentzians to account for the Cu $K\alpha_1$-$K\alpha_2$ splitting. The solid lines through the data are best-fit curves. As a result of the accidental coincidence $c/3 \approx b$, the (103) and the (110) peaks overlap while the (006) and (020) peaks nearly overlap.

A few features of the data are worth noting: Firstly, the x-ray peaks are broader than our instrumental resolution. We find that the peak widths vary approximately linearly with Q, suggesting a distribution of lattice spacings as the origin of the disorder. The measured strain corresponds to about 0.05% in the c direction and about twice this in the a-b plane. Strains this small could easily be the result of a slight distribution in oxygen concentration throughout the sample. Also, some of the broad-

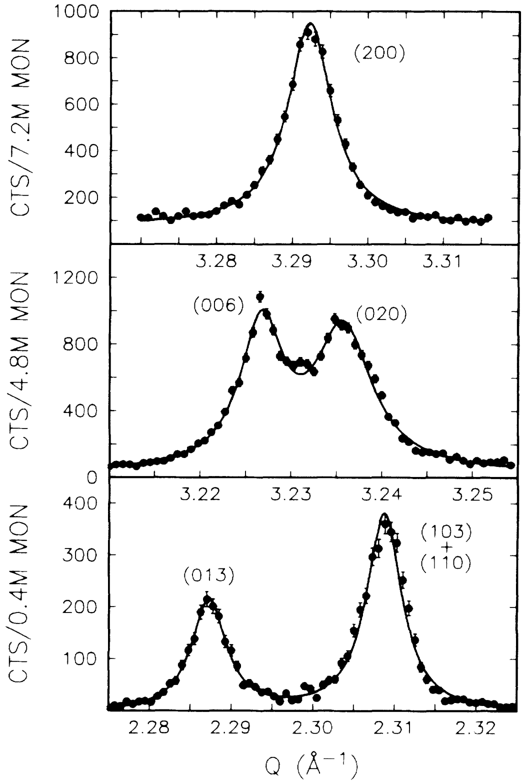

FIG. 1. Scattered x-ray intensity vs momentum transfer Q ($=2k_i \sin\Theta$) at typical room-temperature Bragg peaks. 1M MON corresponds to approximately 220 s. Solid lines through the data are Lorentzian best-fit curves.

ening of the peaks in the a-b plane could be due to twinning. However, it should be noted that in our material the peak widths suggest that the twins are on average at least 2000 Å apart. Thus, twinning cannot be playing a major role in the determination of the superconducting properties. Secondly, we observed that the peak widths and line shapes remain relatively constant as a function of temperature. We have, therefore, no evidence of temperature-induced nonequilibrium strains or incipient structural transitions.

Our data are consistent with the orthorhombic structure reported elsewhere.[10-13] At room temperature we find $a=3.8166$ Å, $b=3.8836$ Å, $c=11.6838$ Å. The absolute uncertainty in these numbers is about ± 0.0005 Å. Our lattice constants differ by about 0.003 Å from those reported elsewhere,[13] presumably because of slight differences in the sample preparation. The temperature dependence of the lattice constants was determined by our fitting the peaks at various temperatures with fixed

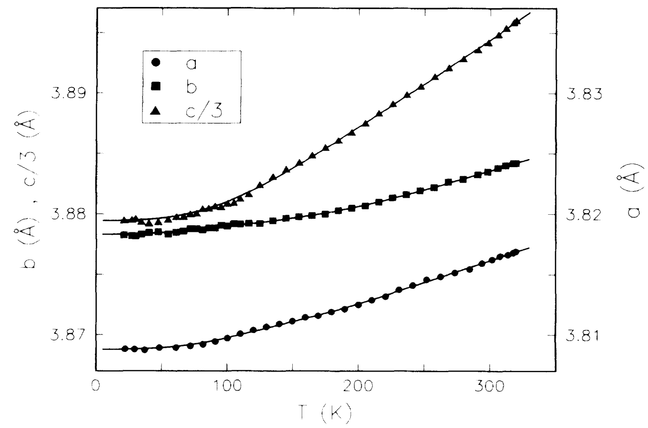

FIG. 2. Temperature dependence of the lattice constants a,b,c. Solid lines are cubic-smoothing-spline fits to the data.

line shapes. The statistical error (relative uncertainty) in this procedure corresponds to about 7×10^{-5} Å.

Our results are illustrated in Figs. 2 and 3 where we show the temperature dependence of the lattice constants, the unit-cell volume V ($=a\times b\times c$), the in-plane area ($=a\times b$), and the orthorhombic distortion $b-a$. The data were taken over a period of about two months during which time the temperature was cycled from 10 to 300 K numerous times. Within the scatter, the data are completely reproducible and we find no evidence for thermal hysteresis. For comparison, we show the results of a high-resolution neutron-scattering experiment.[13] The neutron data have been scaled by about 0.003 Å to agree with our room-temperature data. The overall agreement between the two experiments is excellent.

It is clear from Fig. 3 that there is anomalous behavior in the temperature dependence of the orthorhombic distortion $b-a$ near the superconducting transition. On the other hand, there is no obvious anomaly in the unit-cell volume or in the in-plane area. Given the uncertainties in the nonsuperconducting component of the temperature dependence of the lattice constants, it is possible that the superconductivity induces a small distortion ($\lesssim 2\times10^{-4}$) in the unit-cell volume. Nonetheless, the anomaly in $b-a$ is at least this large, suggesting that b and a respond quite differently to the development of superconducting order.

To understand this observation, consider the additional free-energy gain from condensation into a superconducting state, $F_s(a,b,c)$. In general, F_s is a function of all three lattice parameters, but in view of the highly anisotropic electronic structure it is reasonable to neglect the dependence of the c parameter. Therefore, we expand F_s about the normal-state lattice parameter (a_0,b_0,c_0) as

$$F_s(a,b,c)=F_s(a_0,b_0,c_0)+F_s\left[\frac{\partial \ln F_s}{\partial \ln a}\frac{\delta a}{a}+\frac{\partial \ln F_s}{\partial \ln b}\frac{\delta b}{b}\right]+\dots \quad (1)$$

The restoring force opposing any change in lattice parameters is determined by the elastic free energy

$$F_{\mathrm{el}}=\frac{c_{11}}{2}\left(\frac{\delta a}{a}\right)^2+\frac{c_{22}}{2}\left(\frac{\delta b}{b}\right)^2+\frac{c_{33}}{2}\left(\frac{\delta c}{c}\right)^2+c_{12}\frac{\delta a\,\delta b}{ab}+c_{23}\frac{\delta b\,\delta c}{bc}+c_{13}\frac{\delta a\,\delta c}{ac}. \tag{2}$$

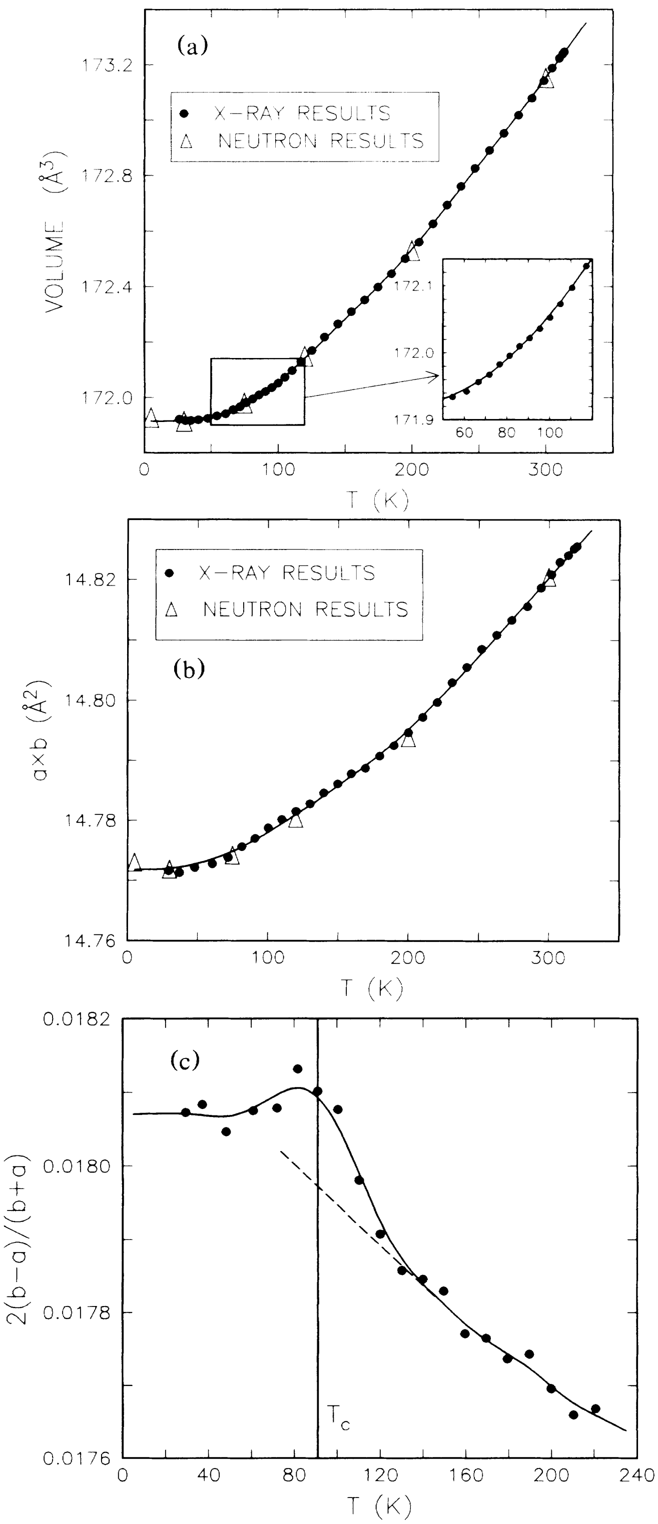

FIG. 3. Temperature dependence of (a) the unit-cell volume ($=a\times b\times c$), (b) the in-plane area ($a\times b$), and (c) the orthorhombic strain. Solid lines are cubic-smoothing-spline fits to the data. High-resolution neutron-scattering results (Ref. 13) shown as triangles have been normalized to the present data at room temperature. Inset in (a): Expanded view of the volume in the vicinity of the transition temperature.

In view of the approximately tetragonal structure, we can assume the elastic moduli $c_{11}\approx c_{22}$ and $c_{13}\approx c_{23}$ [i.e., $(c_{11}-c_{22})/(c_{11}+c_{22})\ll 1$ and $(c_{13}-c_{23})/(c_{13}+c_{23})\ll 1$]. Minimization of the total free energy then gives the result

$$\frac{\partial \ln F_s}{\partial \ln b}-\frac{\partial \ln F_s}{\partial \ln a}=\frac{(c_{11}-c_{12})}{F_s}\left(\frac{\delta a}{a}-\frac{\delta b}{b}\right). \tag{3}$$

Therefore, if the a and b derivatives are equal, no anomaly is expected in $b-a$. {Actually, if calculated more accurately, since the elastic constants are orthorhombic, a small anomaly $[\simeq(c_{11}-c_{22})/(c_{11}+c_{22})]$ is expected in $b-a$. Estimates based on the room-temperature thermal expansion suggest that the $b-a$ anomaly should be less than 15% of the anomaly in $b+a$.} Therefore the observation of an anomaly in $b-a$ but not in $b+a$ requires a large difference between the derivatives $\partial \ln F_s/\partial \ln b$ and $\partial \ln F_s/\partial \ln a$.

Such a large difference is difficult to reconcile with an essentially isotropic or even a d-wave superconducting state originating in the layers of fivefold-coordinated Cu atoms uncoupled from the chains since in these layers the deviations from a square lattice of Cu atoms are very small ($\simeq 10^{-2}$). Instead it suggests that either (a) the superconductivity originates in the layers containing chains of Cu atoms along the b direction, or at least is strongly coupled to the chains, or (b) the superconducting state in the square layers has essentially axial symmetry. If we look at the symmetry classifications given by Sigrist and Rice,[14] this restricts us to p-wave (or odd-parity) states or possibly to an even-parity Γ_1 state in which there is a special interference between d- and s-wave states. This latter possibility cannot be ruled out. Nonetheless, it is clear that these results pose a problem for all theories which predict either isotropic s-wave or d-wave superconductivity originating in the square Cu layers uncoupled from the Cu chains.

Lastly, as regards the magnitude and form of the anomaly, a rough estimate from Eq. (3) gives a value of $\simeq 10^{-4}$, in accord with experiment. Mean-field theory predicts a kink in $b-a$ as a function of T at T_c. The data in Fig. 3 suggest some evidence of a critical behavior but a definite analysis is not possible from these data.

It is worth noting that an ultrasound study of sintered pellets of $YaB_2Cu_3O_7$ shows a discontinuity in the slope of the sound velocity v_s at the superconducting transition.[15] The magnitude of the discontinuity was far larger than estimated within an isotropic model, from the measured dT_c/dP. However, as noted here, the superconducting order parameter couples primarily to the orthorhombic strain $b-a$, which depends only weakly on the hydrostatic pressure. Thus the large slope discontinuity in v_s provides additional evidence for a nonisotropic superconducting wave function.

In conclusion, we have observed the structural consequences of the development of superconducting order in $YBa_2Cu_3O_7$. It should be stressed that the measured coupling of the superconductivity to the lattice does *not* imply a phonon mechanism for electron pairing. Indeed, the observed anisotropy in the structural response is difficult to reconcile with an essentially isotropic BCS wave function.

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