Large *a*-*b* Anisotropy of the Expansivity Anomaly at T_c in Untwinned $YBa_2Cu_3O_{7-\delta}$

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The response of the $YBa_2Cu_3O_{7-\delta}$ lattice to superconducting order is studied using an ultrahigh-resolution capacitance dilatometer. The onset of superconductivity is accompanied by highly anisotropic jumps of the expansivities in the *a*-*b* plane. This leads to a reduction of the orthorhombic splitting below T_c, which suggests that superconductivity favors a symmetric ($b=a$) CuO_2 plane. Little effect is seen along the *c* axis. Superconducting fluctuations are for the first time clearly observed in the lattice expansion.

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There is a great deal of interest in studying the coupling of superconductivity to the structural parameters in $YBa_2Cu_3O_{7-\delta}$, as the numerous structural studies using x-ray [1-5] and neutron diffraction [6-9] demonstrate. These methods, however, usually suffer from insufficient resolution to observe the very small effects due to superconductivity, and this has led to many contradictory results. Detailed information about the temperature dependence of the structure provides important clues about the nature of superconductivity in these materials. In general, the crystal structure of a superconductor adjusts itself below T_c in order to minimize the total free energy of the lattice and the superconducting electrons. The onset of these adjusting strains results in second-order jumps of the expansivity at T_c, which, together with the specific-heat discontinuity, provide information about the uniaxial pressure dependence of T_c. The lattice parameters are also expected to show fluctuation effects near T_c similar to specific-heat fluctuations [10], but this has not been demonstrated. Modern dilatometers are several orders of magnitude more sensitive than either x-ray or neutron diffraction and can be very useful for studying these effects. In a previous dilatometric investigation of twinned $YBa_2Cu_3O_{7-\delta}$ crystals, we showed that the expansivity jumps at the onset of superconductivity occur only within the *a*-*b* plane and that the positive hydrostatic dT_c/dp is due almost entirely to the uniaxial pressure components within the *a*-*b* plane [11]. This has been confirmed by recent anisotropic pressure measurements [12].

In this Letter we present ultrahigh-resolution thermal-expansion data from 5 to 300 K of untwinned $YBa_2Cu_3O_{7-\delta}$ crystals. It will be shown that a very large anisotropy exists within the *a*-*b* plane, which suggests that a nondistorted CuO_2 plane ($b\approx a$) is favorable for superconductivity.

$YBa_2Cu_3O_{7-\delta}$ crystals were grown in a Y_2O_3-stabilized ZrO_2 crucible and were subsequently detwinned under uniaxial pressure (≈ 0.1 GPa) at 400 K in flowing O_2. Further details are given in Ref. [13]. dc magnetic-shielding measurements showed a sharp superconducting transition at 90.9 K with $\Delta T_c = 0.7$ K for the presently discussed crystal. The dimensions were $1.9\times1.2\times0.13$ mm^3 ($a\times b\times c$). Two pieces stacked on top of each other were used for measurements along the *c* axis. All crystals appeared to be single domain, except for small regions at several corners. The expansivity was measured with the same capacitance dilatometer described previously [11]. Data were taken every 0.1 K with a length resolution of $\approx 10^{-11}$ m. To obtain reproducible and smooth data at T_c, the temperature was cycled several times up and down between 70 and 110 K. The anomalies were identical for both heating and cooling, as expected for a second-order transition.

The relative thermal expansion $\varepsilon = \Delta L(T)/L(5\text{ K})$ and corresponding expansivities $\alpha = d\ln L(T)/dT$ of all three axes are presented in Figs. 1(a) and 1(b). The *c* axis has the largest expansion followed by the *a* and then the *b* axes. $\alpha_a(T)$ and $\alpha_c(T)$ both exhibit normal temperature dependences. In contrast, $\alpha_b(T)$ behaves anomalously, being negative between 5 and 60 K and then increasing almost linearly from 60 to 300 K, where $\alpha_b \approx \alpha_a$. The relative length changes between 5 and 300 K are 1.90 ± 0.05, 1.23 ± 0.1, and 3.7 ± 0.3 (all $\times10^{-3}$) for the *a*, *b*, and *c* axis, respectively. Also evident in Fig. 1(b) are anomalies of the expansivity in the vicinity of T_c, of which an expanded view, obtained by subtracting a linear fit above T_c from the data, is presented in Fig. 1(c). Both jumps in α_a and α_b have nearly identical shapes and magnitudes [14], but they have opposite signs: $\Delta\alpha_a = \alpha_S - \alpha_N = (-8.95\pm1)\times10^{-7}$ K^{-1} and $\Delta\alpha_b = (10.5\pm1)\times10^{-7}$ K^{-1}. No jump of α_c is observed within the experimental resolution ($\pm5\times10^{-8}$ K^{-1}); however, a slope change $\Delta(d\alpha_c/dT) = -2.2\times10^{-8}$ K^{-2} is found, in qualitative agreement with our previous measurements on twinned crystals [11]. Two other crystals showed essen-

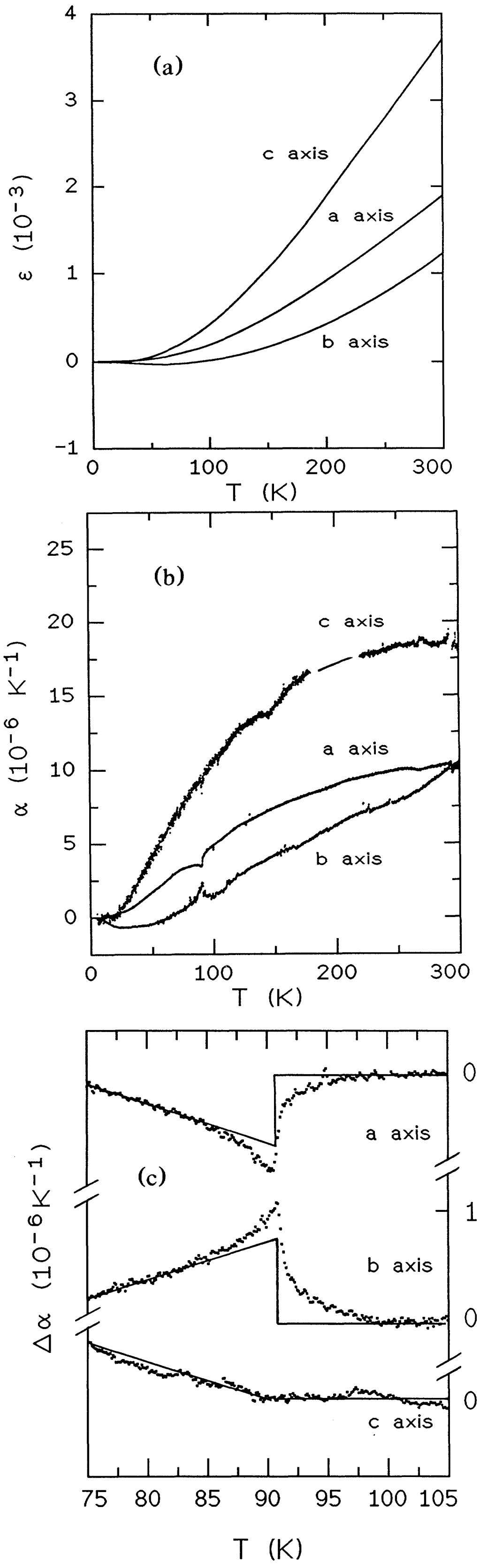

FIG. 1. Temperature dependence of (a) relative thermal expansion $\varepsilon=[L(T)-L(5\ \mathrm{K})]/L(5\ \mathrm{K})$, (b) thermal expansivities, and (c) expanded view of the change in expansivities $\Delta\alpha$ near the transition temperature obtained by subtracting a linear fit above T_c from the data (all three curves have the same vertical scale). Significant deviations from mean-field behavior [indicated by solid lines in (c)] occur for both jumps and most likely result from superconducting fluctuations.

tially identical expansion behavior. Both exhibited the same anisotropy of the expansivity jumps ($\Delta\alpha_a \approx -\Delta\alpha_b$), although the size of the anomalies varied by about 30%.

The magnitudes of the relative length changes between 5 and 300 K agree well with the diffraction studies from the literature [1,2,5,6], demonstrating that the crystal is macroscopically untwinned. The anomalous *b*-axis expansion is not observed in twinned samples; however, x-ray investigations of untwinned samples show similar effects [3,5], suggesting that the presence of twins interferes with the natural expansion of $YBa_2Cu_3O_7$. The negative expansion of the *b* axis may be due to large temperature-dependent transverse vibrations of O_{chain}. Interestingly, the *b* axis of $YBa_2Cu_3O_8$, which has double chains and does not twin, also exhibits this anomalous behavior [15].

Turning to the anomalies at T_c, the striking features are the magnitude of the anomalies, which are about an order of magnitude larger than what is observed in twinned and polycrystalline samples [11,16], and the large anisotropy within the *a*-*b* plane. We attribute these effects solely to superconductivity and have no evidence for the additional structural transitions proposed in Ref. [5]. Superconductivity couples strongly to the orthorhombic strain $(b-a)$ as shown in Fig. 2. $b-a$ changes slope at T_c so as to slightly reduce $b-a$ from its normal-state value. A much larger anomaly in $b-a$ has previously been seen with x-ray diffraction [1], although more recent studies have failed to observe such an anomaly [2]. The error bars of these measurements were, however, too large to resolve the presently observed effect.

The expansivity jumps deviate significantly from mean-field behavior [Fig. 1(c)] as is indicated by the solid lines. The shape is very similar to specific heat curves of "good" samples where the deviation has been attributed to superconducting fluctuations due to extremely short coherence lengths [17]. Due to the similarity of shape and the thermodynamic ties of the expansivity with the specific heat [10,11,16], we attribute the sharp peaks in Fig. 1(c) also to superconducting fluctuations. These fluctuations must also be intimately related to the lattice fluctuations seen in recent extended x-ray-absorption fine-structure studies [18], in which two slightly separated potential wells were found for the apex oxygen atom. Near T_c the site separation was found to decrease by 0.02 Å, which is qualitatively consistent with the presently observed shrinkage of the *b* axis.

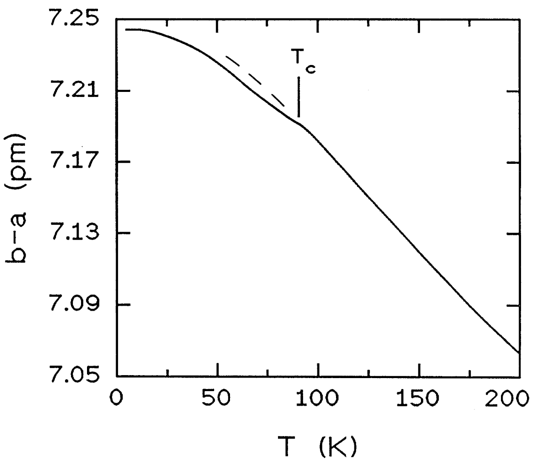

FIG. 2. Temperature dependence of the orthorhombic distortion $(b-a)$. Evident at T_c is a change of slope, which reduces the distortion in the superconducting state slightly below that of the normal state (extrapolated value indicated by the dashed line). a- and b-lattice parameters were taken to equal 3.82 and 3.89 Å at 300 K, respectively.

The magnitudes of the expansivity jumps can be used to calculate the first-order uniaxial-pressure dependence of T_c via the Ehrenfest relationship: $dT_c/dp_i = \Delta\alpha_i V_m / \Delta C_p T_c^{-1}$ [11]. We find (assuming $\Delta C_p T_c^{-1} = 50$ mJ mol^{-1} K^{-2}) $dT_c/dp_a = -1.9$ K GPa^{-1}, $dT_c/dp_b = +2.2$ K GPa^{-1}, and $dT_c/dp_c \approx 0$ K GPa^{-1}. Thus, T_c is expected to increase for uniaxial pressure along the b axis, to decrease for uniaxial pressure along the a axis, and to be insensitive to c-axis uniaxial pressure. For hydrostatic pressure, the a- and b-uniaxial-pressure dependences largely cancel each other, leaving a small positive pressure dependence ($dT_c/dp \approx 0.3$ K GPa^{-1}). This value is consistent with both our previous measurements [11,16] and actual pressure experiments [19]. It should be stressed that these uniaxial effects are an order of magnitude larger than what would be expected from the isotropic-hydrostatic case, and that any realistic theory of dT_c/dp must take into account these large anisotropies.

The above anisotropy is essentially reproduced also for the uniaxial strain dependences of T_c,

$$\frac{dT_c}{d\varepsilon_i} = \sum_j C_{ij} \frac{dT_c}{dp_j} ,$$

where C_{ij} are the components of the elastic tensor and a positive ε_i corresponds to a shortening of the ith axis [10,11]. Using C_{ij} values from Reichardt *et al.* [20] and the above dT_c/dp_i, we find $dT_c/d\varepsilon_a = -217$ K, $dT_c/d\varepsilon_b = 316$ K, and $dT_c/d\varepsilon_c = 30$ K.

In conclusion, in $YBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0$) the response of the lattice to superconducting order results in a nearly volume-preserving distortion in the a-b plane. A tetragonal lattice appears favorable for superconductivity. Physically this may be related to maximizing the electronic density of states near the Fermi surface [21]. The lattice expansion shows clear signs of fluctuation behavior near T_c. Calculated (from the expansion anomalies at T_c) uniaxial-pressure dependences provide the first clear evidence that dT_c/dp_i and $dT_c/d\varepsilon_i$ are extremely anisotropic and this should be considered by models for dT_c/dp. Pressure-induced charge transfer [22,23] is an unlikely explanation of these effects. Although the largest charge transfer is expected for c-axis changes, as suggested by O-doping studies [24], we see very little effect along the c axis for optimally doped crystals. Indeed, no driving force from charge transfer is expected, since T_c is already at its maximum value [25]. On the other hand, for oxygen-deficient crystals a large expansivity anomaly (i.e., pressure effect) occurs along the c axis and a charge-transfer mechanism may dominate [26].

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[1] P. M. Horn, D. T. Keane, G. A. Held, J. L. Jordan-Sweet, D. L. Kaiser, F. Holtzberg, and T. M. Rice, Phys. Rev. Lett. **59**, 2772 (1987).

[2] H. You, J. D. Axe, X. B. Kan, S. Hashimoto, S. C. Moss, J. Z. Liu, G. W. Crabtree, and D. J. Lam, Phys. Rev. B **38**, 9213 (1988).

[3] A. Simon, J. Köhler, H. Borrman, B. Gegenheimer, and R. Kremer, J. Solid State Chem. **77**, 200 (1988).

[4] D. Dernbach and K. Ehses, Ferroelectrics **105**, 63 (1990).

[5] H. You, U. Welp, and Y. Fang, Phys. Rev. B **43**, 3660 (1991).

[6] J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournier, Europhys. Lett. **3**, 1301 (1987).

[7] M. Francois, A. Junod, K. Yvon, P. Fischer, J. J. Capponi, P. Strobel, M. Marezio, and A. W. Hewat, Physica (Amsterdam) **153-155C**, 962 (1988).

[8] H. You, R. K. McMullan, J. D. Axe, D. E. Cox, J. Z. Liu, G. W. Crabtree, and D. J. Lam, Solid State Chem. **64**, 739 (1987).

[9] G. H. Kwei, A. C. Larson, W. L. Hults, and J. L. Smith, Physica (Amsterdam) **169C**, 217 (1990).

[10] A. J. Millis and K. M. Rabe, Phys. Rev. B **38**, 8908 (1988).

[11] C. Meingast, B. Blank, H. Bürkle, B. Obst, T. Wolf, and H. Wühl, Phys. Rev. B **41**, 11 299 (1990).

[12] G. L. Belenky *et al.* (unpublished).

[13] A. Zepold, M. Dürrler, H. P. Geserich, A. Erb, and G. Müller-Vogt, Physica (Amsterdam) **177C**, 151 (1990).

[14] The magnitudes include the fluctuations since specific heat jumps are usually also quoted in this fashion.

[15] O. V. Alexandrov, M. Francois, T. Graf, and K. Yvon, Physica (Amsterdam) **170C**, 56 (1990).

[16] C. Meingast, R. Ahrens, B. Blank, H. Bürkle, B. Rudolph, and H. Wühl, Physica (Amsterdam) **173C**, 309 (1991).

[17] S. E. Inderhess, M. B. Salamon, N. Goldenfeld, J. P. Rice, B. G. Pazol, D. M. Ginsberg, J. Z. Liu, and G. W. Crabtree, Phys. Rev. Lett. **60**, 1178 (1988).

[18] Y. J. Mustre de Leon, S. D. Conradson, I. Batistic, and A. R. Bishop, Phys. Rev. Lett. **65**, 1675 (1990).
[19] R. Wijngaarden and R. Griessen, in *Studies of High Temperature Superconductors,* edited by A. Narlikar (Nova Science, New York, 1990).
[20] W. Reichardt, L. Pintschovius, B. Hennion, and F. Collin, Supercond. Sci. Technol. **1**, 173 (1988). Here we have assumed that $C_{11}=C_{22}$ and $C_{12}=C_{13}=C_{23}$ since a complete set of elastic constants is unknown to us. The *a-b* anisotropy of C_{ij} is small and is not expected to change these results significantly.
[21] This is similar to *A*-15 and Chevrel superconductors, where the highest T_c also occurs in the phases with highest crystal symmetry.
[22] E. Kaldis, P. Fischer, A. W. Hewat, E. A. Hewat, J. Karpinski, and S. Rusiecki, Physica (Amsterdam) **159C**, 668 (1989).
[23] J. D. Jorgensen, S. Pei, P. Lightfoot, D. G. Hinks, B. W. Veal, B. Dabrowski, A. P. Paulikas, R. Kleb, and I. D. Brown, Physica (Amsterdam) **171C**, 93 (1990).
[24] R. J. Cava, B. Batlogg, K. M. Rabe, E. A. Rietman, P. K. Gallagher, and L. W. Rupp, Jr., Physica (Amsterdam) **156C**, 523 (1988).
[25] J. B. Torrance, A. Bezinge, A. I. Nazzal, and S. S. P. Parkin, Physica (Amsterdam) **162-164C**, 291 (1989).
[26] O. Kraut *et al.* (unpublished).