Phase constitution and thermal expansion of $YBa_2Cu_3O_{7-\delta}$ single crystals

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(Received 21 April 1988)

We present an x-ray diffraction study of $YBa_2Cu_3O_{7-\delta}$ single crystals. High-resolution scans reveal two orthorhombic phases with different lattice constants but a common orientation indicating a phase separation into phases with $\delta \approx 0.0$ and 0.3. Thermal expansions of the unit-cell parameters of both phases measured between 10 and 300 K were fit using a quasiharmonic approximation giving a best-fit Debye temperature of 370 ± 5 K. The measured orthorhombicities were found to change smoothly through the superconducting transition temperature without any anomaly.

It is now well known that the structure of $YBa_2Cu_3O_{7-\delta}$ is an orthorhombic, tripled perovskite with two Cu-O_2 layers and one Cu-O layer in a unit cell.[1] Oxygen ordering of the nominally half-filled Cu-O layer is responsible for the tetragonal-to-orthorhombic phase transition occurring at $\sim 700\,^{\circ}C$.[2] Because of the orthorhombic structure $YBa_2Cu_3O_{7-\delta}$ crystals generally show complicated microstructures including twin boundaries. Several studies[3,4] have focused on the conventional [110] twins and their possible relation to superconducting properties. In our recent study of $YBa_2Cu_3O_{7-\delta}$ single crystals,[4] an unusual domain configuration (previously called "90° twinning")[4] was reported that involved a 90° domain rotation of the *a* and *b* axes about the *c* axis with a boundary parallel to *ab* plane.

At temperatures below the tetragonal-to-orthorhombic phase transition, it has been predicted that the oxygen atoms and vacancies can phase separate into a disordered tetragonal phase and an ordered orthorhombic phase.[5-8] In the present high-resolution x-ray study, we have observed phase segregation within a single crystal with 90° domains and have measured and interpreted the temperature dependence of the unit-cell parameters between 10 and 300 K.

Several single crystals of $YBa_2Cu_3O_{7-\delta}$ were produced by a solid-state sintering method[9] and individually characterized by magnetization measurements. Laue and precession photographs of each single crystal were then obtained with rotating anode x rays. During these characterizations it was found that crystals come predominantly with either 90° domain rotation or [110] twinning. All of the single crystals exhibiting 90° domains show sharp, high transition tempertures, as measured by the dc susceptibility drop, while the crystals with [110] twinning show a wider superconducting transition region. Our observations thereby contradict speculations that [110] twin boundaries may be essential to, or at least enhance, the superconducting properties although they may indeed act as flux pinning centers to enhance the critical current density. Deutscher and Müller have recently proposed[10] that elimination of [110] boundaries normal to the Cu-O and Cu-O_2 planes may in fact improve the superconducting properties.

The magnetization measurement for a single crystal with the 90° domains is shown in Fig. 1(a). The crystal was cooled in zero field to 4.2 K, a field of 10 Oe was applied along the *c* direction of the crystal and the magnetization was measured as the crystal was warmed. The size of the shielding signal was within a factor of 2 of that expected on the basis of the crystal shape, which was ap-

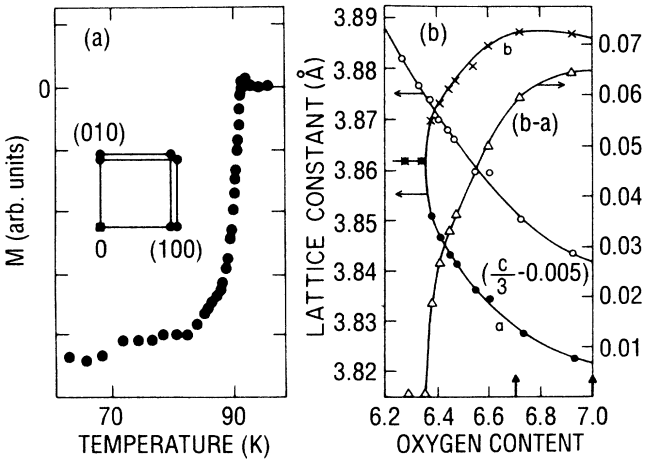

FIG. 1. (a) The magnetization measurement and schematic representation (inset) of the precession photograph for the single crystal used in this study. (b) The lattice constants vs oxygen content for powder samples reproduced from Ref. 12. The oxygen compositions for our two phases (marked by large arrows on the horizontal axis) are deduced by comparing their measured lattice constants, and the difference $b-a$, to this diagram.

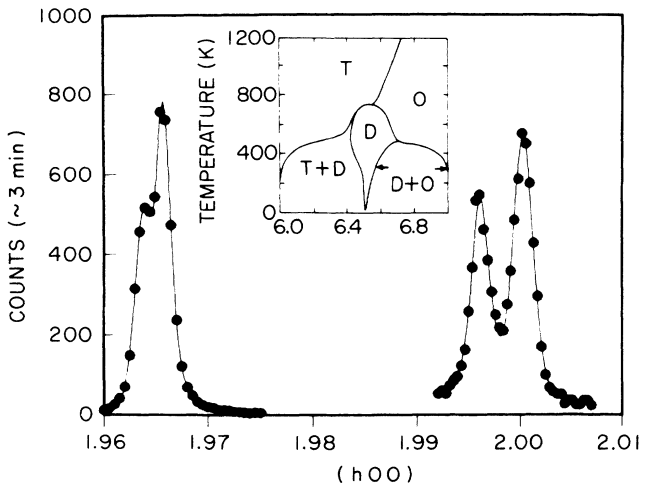

FIG. 2. Integrated radial scans along the [100] direction near a (200) reflection at 300 K (●) where each data point represents the intensity integrated over the mosaic distribution. (200) and (020) reflections appear in the same h scan due to the 90° domain rotation. Each reflection is composed of two split peaks indicating two-phase coexistence and the smooth curve is a profile fit as described in the text. A part of the predicted phase diagram from Ref. 5 is shown as an inset where the two phases are indicated by arrows.

proximately rectangular with a dimension of $0.2\times0.1\times0.05$ mm^3 and a mosaic distribution of 0.2°–0.5° depending on the orientation of the crystal. This single crystal, whose precession photograph [inset in Fig. 1(a)] shows the 90° domain configuration, was used for the diffraction study described below.

The high-resolution x-ray diffraction experiments were carried out with a rotating anode x-ray source using a triple-axis spectrometer with a perfect Ge(111) crystal monochromator at a distance of about one meter from the anode target and a second perfect Ge(111) crystal as the analyzer. In this configuration it was possible to resolve the Cu $K\alpha_1$ radiation and to achieve an in-plane $Q_{\parallel}$ resolution of 3×10^{-4} Å^{-1}. The sample crystal was glued on the tip of quartz fiber, sealed inside a helium-filled Be can, and mounted on a Displex cryostat, which had a temperature stability better than 0.1 K. To avoid complications involved in the convolution of the resolution function with the mosaic distribution of the sample crystal, the diffraction from the entire mosaic spread of the sample was integrated by rocking the crystal while counting with open out-of-plane detector slits. Each scan was then fit with pseudo-Voight line shapes (convolution of Gaussian and Lorentzian functions)[11] to obtain the peak positions.

Integrated radial scans made near a (200) reflection at 300 K are shown in Fig. 2. The integrated radial scans along the [100] direction show peaks at $h=2.000$ (a axis of one domain) and $h=1.965$ (b axis of the other 90° rotated domain). In addition, each peak reflection is actually composed of two split peaks. Since the relative positions of all the peaks measured at several (h00) reflections scale with h, all the reflections are from incoherent domains with different lattice spacings. The lattice constants are $a=3.8219$ and 3.8301, $b=3.8878$ and 3.8917, $c=11.6788$ and 11.7003 for major and minor phases, respectively. The difference in the lattice constants may be explained by postulating different oxygen compositions for the major and minor phases. By comparing the lattice constants for these phases with those measured on powder samples at various oxygen composition [reproduced in Fig. 1(b) from Ref. 12] the compositions for major and minor phases were estimated to be $\delta\approx0.0$ and $\delta\approx0.3$, respectively. In recent experimental studies[12,13] T_c is nearly constant for the compositions between $\delta=0.0$ and 0.3, suggesting two phase coexistence between a structure with $\delta\approx0.0$ and another with $\delta\approx0.3$. This is in agreement with our observation and with a theoretical phase diagram by Wille, Berera, and de Fontaine[5] reproduced as an inset in Fig. 2 where the proposed compositions are indicated by two arrows. The oxygen configuration for the minor phase is likely similar to the structure designated as the $p2mm$ II phase,[5] marked by D in the inset of Fig. 2, in which oxygens form a 2×1 superlattice. The associated scattering at half-integer h values has been seen in recent experimental studies on well-annealed samples[14,15] and also in another of our crystals, examined with lower resolution. (Similar macroscopic segregation into subgrains with different orthorhombicities was also seen in our previous study on a single crystal with [110] twinning.)[4]

X-ray measurements are well suited to thermal expansion determinations particularly when the material is anisotropic and the sample is very small as with $YBa_2Cu_3O_{7-\delta}$. The thermal expansion of solids results from the anharmonicity of the interatomic interaction potentials where the thermal strain tensor, in general, can be expressed within a quasiharmonic approximation[16] as

$$\eta_{ik}(T)=\frac{1}{NV}\sum_{j,l}C^{-1}_{ik,jl}\sum_{K,\lambda}\gamma_{jl,K\lambda}E_{K\lambda}(\omega,T)\,. \tag{1}$$

$C_{ik,jl}$ is the elastic stiffness tensor, $E_{K\lambda}$ is the thermal energy of a phonon mode and, in the Grüneisen approximation, $\gamma_{jl,K\lambda}$ is independent of ω. In the absence of detailed information about the Grüneisen constants it is reasonable to approximate the temperature dependence of Eq. (1) with a function that interpolates properly between the correct low-temperature ($\sim T^4$) and high-temperature ($\sim T$) behavior. The Debye expression for the phonon thermal energy, $f_D(T/\Theta)$,[17] is such a function and the nonvanishing components of the thermal strain may then be approximated by

$$\eta_{ii}(T)=A_i f_D(T/\Theta_i),\quad i=(x,y,z)\,, \tag{2}$$

with a separate effective Debye temperature for each direction.

The (200) and (020) reflections of the sample single crystal were measured in two independent cooling cycles and the (006) reflection was measured in a warming cycle to measure the unit-cell parameters a, b, and c, respectively, with the unit-cell volume given simply by their product. The measured quantities of $[X(T)-X(0)]/X(0)$ for $X=a$, b, c, and v were then best fit to Eq. (2) by allowing Debye temperatures (Θ_i) and prefactors (A_i) to vary and the results are shown in Fig. 3. The effective Debye temperatures found for a, b, c, and v are 418(8), 582(15),

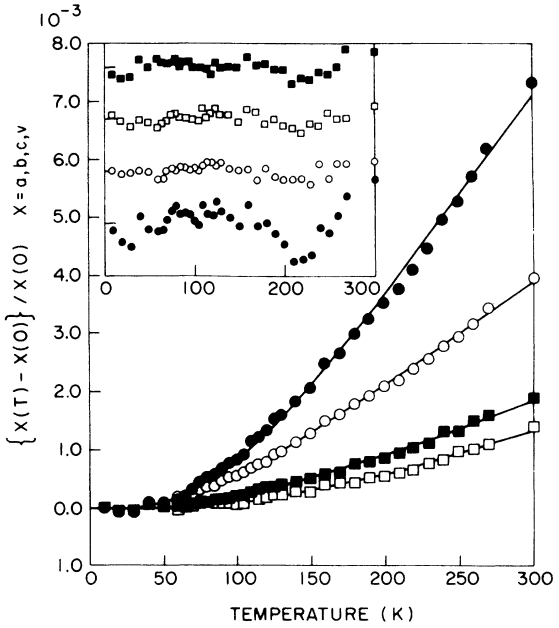

FIG. 3. Temperature dependence of a (□), b (■), c (○), and v (●). $[X(T)-X(0)]/X(0)$, $X=a$, b, c, and v are shown between 10 and 300 K. The differences from the fits to a simple anharmonic theory of thermal expansion (the solid lines) are shown as an inset. Note that similar deviations are independently measured for a, b, and c which sum for the volume, suggesting that the deviations are not due to random statistical errors in the measurements.

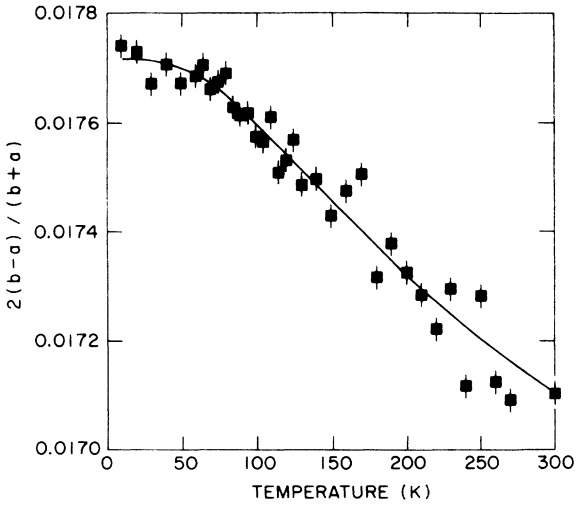

FIG. 4. The temperature dependence of the measured orthorhombicity between 10 and 300 K together with the theoretical curve calculated from the fits for a and b of Fig. 3.

293(5), and 370(5), respectively, and were indistinguishable for major and minor phases.

The deviations of the measured unit-cell parameters from the fit curves are also shown in the inset of Fig. 3. Large deviations of volume from the best fit are clearly seen near 220 K. Similar deviations exist for all independently measured lattice parameters which then add constructively in the volume expansion indicating that the deviation is unlikely to be due to random errors and is indicative of some subtle structural change. Apart from a number of informal reports of anomalies near 240 K, a specific-heat measurement[18] shows a large anomaly at 220 K along with a peak at the superconducting transition. Since this specific-heat anomaly at 220 K was reported to be strongly correlated to the specific heat at the superconducting transition, the phenomenon responsible for the 220-K anomaly might be important for the occurrence of superconductivity in this material.

In a recent article, Horn *et al.*[19] reported that the orthorhombicity has an anomalous temperature dependence at the superconducting transition attributable to the onset of anisotropic pairing. Contrary to their result, such an anomaly has not been observed in our measurements. The orthorhombicity measured in our rotating anode experiments and a smooth orthorhombicity curve (solid line) calculated from the fits to a and b axes of Fig. 3 are shown in Fig. 4. The rotating anode data presented here were repeated at the Cornell High Energy Synchrotron Source. In none of our measurements on the $\delta \approx 0.0$ and $\delta \approx 0.3$ phases was the reported anomaly observed nor has it been seen in our similar studies.[20,21] Recently, it has been suggested that the orthorhombicity anomaly is a sample-dependent effect.[22]

We wish to thank R. M. Fleming and P. Marsh for participating in the CHESS run and for many helpful discussions. The work at the Brookhaven and Argonne National Laboratories was supported by the Department of Energy under Contracts No. DE-AC02-76CH00016 and No. W-31-109-ENG-38, respectively, and the work at Houston was supported by the National Science Foundation (NSF) on DMR-8603662 and by the Texas Center for Superconductivity. The Cornell High Energy Synchrotron Source facility and operation is supported by the NSF Grant No. DMR84-12465.

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$$f_D\left[\frac{T}{\Theta}\right]=\int_0^{T/\Theta}\left\{\frac{4\pi^4}{5}x^3-\frac{3/x}{e^{1/x}-1}+12\ln(1-e^{-1/x})-36x\sum_{n=1}^{\infty}\left[\left[1+\frac{2x}{n}+\frac{2x^2}{n^2}\right]\frac{e^{-n/x}}{n^2}\right]\right\}dx\,.$$

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