Slope discontinuity and fluctuation of lattice expansion near T_c in untwinned $YBa_2Cu_3O_{7-\delta}$ single crystals

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The thermal lattice expansion of untwinned $YBa_2Cu_3O_{7-\delta}$ single crystals is measured from 10 to 300 K with a high-resolution x-ray-diffraction technique on beam-line X22B at the National Synchrotron Light Source. All the unit-cell parameters (a, b, c, and volume) show unexpectedly large slope discontinuities near T_c and possible strong fluctuations over a wide temperature region ($80 < T < 120$ K). Possible implications for the nature of the superconducting mechanism are discussed.

Since the discovery of the $YBa_2Cu_3O_{7-\delta}$ superconductor there have been several measurements of the lattice constants on powder samples by x-ray diffraction,[1,2] by neutron diffraction,[3] and by dilatometric measurements,[4] or on twinned single crystals by x-ray diffraction.[5] A common aspect in all of these studies is that the measurements probably have been affected by the presence of twin boundaries. In addition, the measurements done on pellet samples[1,4] are possibly affected by grain boundaries. A recent study of the time-dependent measurements of the lattice constants using pellet samples[6] shows a noticeable difference in the kinetic behavior from the measurements on single crystals[7] due to the grain boundary stress.

The thermal expansion of the cell parameters $\alpha_x = (1/x)(dx/dT)$ ($x = a$, b, c, and v) is in general a consequence of the anharmonicity of the lattice vibrations. However, when a transition such as the superconducting transition[8] whose order parameter is coupled to the lattice strain occurs, the lattice expansion is expected to show a discontinuity and fluctuation effects. In a theoretical study[8] the discontinuity and fluctuations of lattice expansions at T_c for the cuprate superconductors have been explicitly calculated from the electronic specific heat discontinuity.[9,10] The predicted discontinuity was too small to be seen within the accuracy of the previous measurements and motivated us to perform more accurate measurements. In this communication we present high-resolution synchrotron x-ray measurements on *untwinned* single crystals where the accuracy far exceeds that in all the previous measurements.

Single crystals of $YBa_2Cu_3O_{7-\delta}$ grown by a solid-state sintering method were selected by visual examination and by magnetization measurements for subsequent detwinning. The selected crystals were annealed under a uniaxial pressure at 400 °C overnight with a sufficient oxygen flow.[11] Some crystals become 99% or more single-domain samples after the detwinning process and often have excellent mosaic distributions suitable for high-resolution x-ray scattering measurements. The mosaic width of the sample crystal is 0.017° or better in all three directions and the size is about $1.2\times1.0\times0.4$ mm^3. The sample crystal shows an excellent superconducting transition at 92.3 K with a transition width of 0.2 K in SQUID measurements.

The diffraction experiments were performed at X22B beamline, National Synchrotron Light Source. A cylindrical mirror and a horizontally reflecting Ge(111) monochromator were used to focus the x-ray beam and to select $\lambda = 1.6653$ Å. The divergence of the incoming x-ray beam was 0.1 mrad. A Ge(220) analyzer was used to match with the scattering angles of the pseudocubic (200) reflections of $YBa_2Cu_3O_{7-\delta}$ for a high momentum resolution. The resulting resolution was $\sim 5\times10^{-4}$ Å^{-1}.

The sample was reoriented at each temperature with the same statistics as for the radial scans. The small amount of translation did not affect the measurements due to the use of an analyzer crystal which defines momentum of the outgoing x rays not the sample position relative to the slits. Only one reflection [(200),(020),(006)] for each axis was used to find the peak positions because we found counting longer (200) reflection gives us better accuracy in both absolute and relative angles than scanning (200) and (400). The (400) is normally broader due to dispersion of x rays and much weaker in intensity. The essential feature, i.e., the large slope discontinuity and anomaly at T_c, has been reproduced in two other samples with another displex cryostat and with Mo $K\alpha_1$ radiation in complete transmission measurements. A complete detail for several samples will be presented in a future paper. The line shape of the x-ray scans are very sensitive to the sample homogeneity at least for the part of the sample radiated by x rays. The width of the radial scan indicates that the dispersion in oxygen content should be less than 0.03 oxygens per unit cell (see the cited Ref. 5).

The a, b, and c lattice constants were measured independently on warming. Occasional cooling scans to check the reproducibility showed no sign of hysteresis. Special care was taken to ensure the thermal equilibrium and to avoid any change in the wavelength of the incoming x rays due to the monochromator or the electron orbit during the measurements. The temperature stability was better than 0.1 K over the temperature range of this study. Typical mosaic and radial scans of the x-ray reflections are shown in Fig. 1. It should be noted that the FWHM of our radial (θ-2θ) scan is about seven times narrower than that of powder measurements[1] and three times narrower than the previous measurements on twinned single crystals.[5] The peaks were fit with a pseudo-Voigt function[12] and a standard nonlinear fitting routine.

The expansion of a, b, and c lattice constants are shown in Fig. 2. The a, b, and c lattice constants show the nearly linear temperature dependences near 300 K as expected from the quasiharmonic approximation.[13] The expansion rates, $\alpha_x = 1.4$, 0.9, 1.9, and 4.2×10^{-5} for $x = a$, b, c, and v, respectively. The overall thermal expansion of the b axis is smallest and it is presumably due to the bridging oxygens in the chain sites. The b and c axes clearly show the discontinuity in the expansion and the deviation from the smooth guide to the eye around T_c. This behavior is less pronounced in the a axis due to the rapid change of the expansion. The discontinuities in expansion rates, $\Delta\alpha_x$ for the temperature range of 80 to 120 K are approximately 4, 2, 12, and 18×10^{-6} for $x = a$, b, c, and v, respectively. The b axis shows the discontinuity and deviation most clearly because α_b is nearly zero for this temperature range. Below the superconducting transition temperature the lattice constants behave quite differently. The c axis continuously contracts down to 10 K while the b axis shows *expansion* (negative thermal expansion) from 80 to 10 K. The a axis

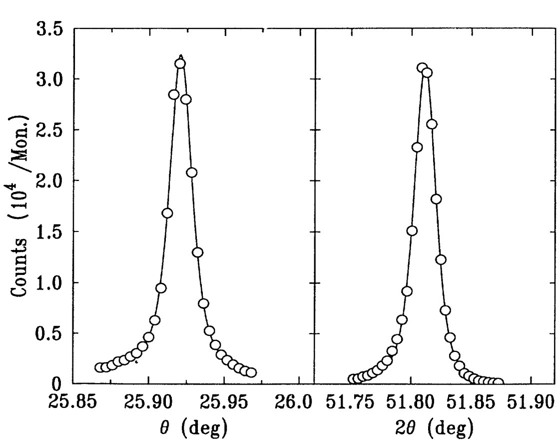

FIG. 1. The typical mosaic and radial scans of the (200) reflection. The solid lines are the best fit by the pseudo-Voigt function.

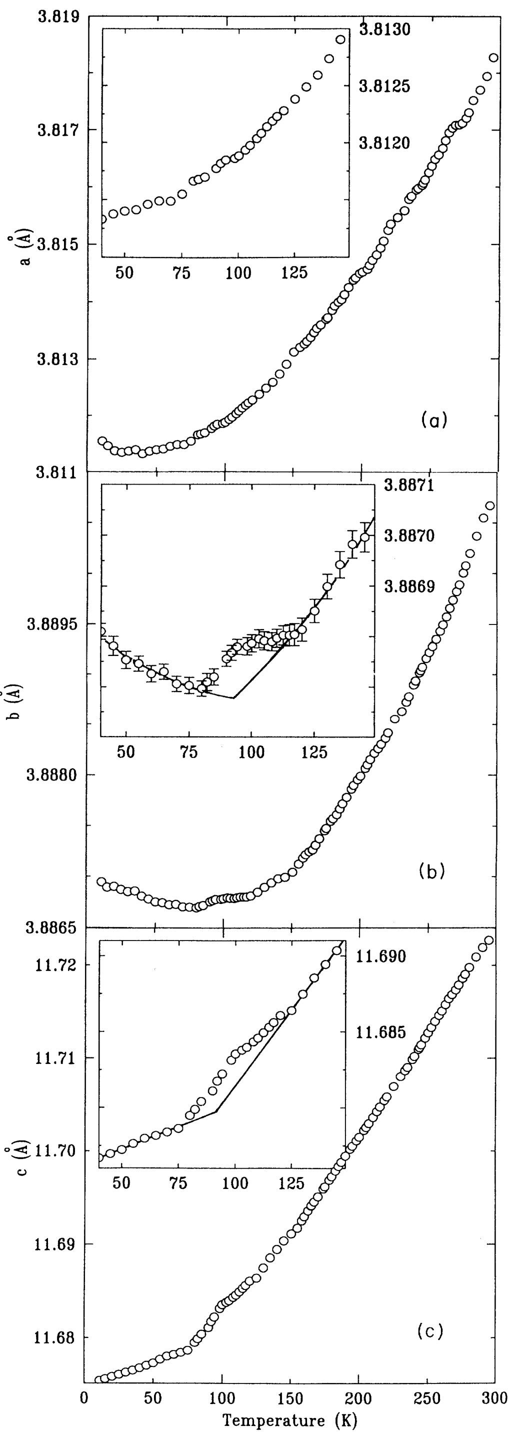

FIG. 2. The expansion of a, b, and c lattice constants are shown in (a), (b), and (c), respectively. The details near the superconducting transition temperature are shown in the insets. The solid lines are guides for the eye and the deviations are very clearly seen for b and c axes and less clearly in the a axis.

contracts down to 35 K and shows the negative thermal expansion below 35 K. However the net effect, the volume of the unit cell, smoothly approaches zero thermal expansion as expected.[13] The negative thermal expansion of b axis below the superconducting transition temperature is unexpected. The most likely explanation of the negative expansion is the unbending of the buckled Cu-O bonds. The neutron crystallographic study shows a significantly larger thermal ellipsoid of oxygens in the b-axis bridge sites of the Cu-O_2 planes than in a-axis bridge sites indicating that it may be easier to bend or unbend the Cu-O bonds along the b axis than along the a axis.[14] The unbending of the buckled oxygen bonding has also been suggested by recent channeling measurements.[15] Below 35 K the a axis also shows negative thermal expansion indicating that the unbending also occur. The unbending may result from the interaction between charge carriers and phonon modes associated with the buckled Cu-O bonds.[16]

The anomaly in orthorhombicity previously identified as evidence for anisotropic pairing[1] is about six times smaller in our measurements.[17] Nevertheless, the orthorhombicity shows a small deviation around the superconducting transition temperature. This small anomaly might well result from the difference between c_{11} and c_{22}.[17]

Figure 3 shows the temperature dependence of the unit cell volume near the superconducting transition temperature. Three aspects seen in Fig. 3 (also shown in the a, b, and c axes individually) will be discussed. (i) The slope of expansion shows a very large jump from $T<80$ to $T>120$ K as shown by the solid lines. (ii) For the transition temperature range of 80 K $<T<$ 120 K there is a slight but clear expansion of the unit cell volume above the solid lines. (iii) The transition region stretches 20 to 30 K above the superconducting transition temperature (the crossing point of the two solid lines) while it reaches only 10 K down below.

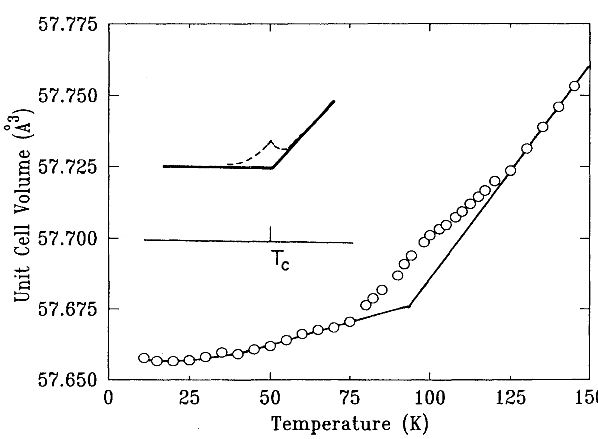

FIG. 3. The unit cell volume expansion measurements between 10 and 300 K. The solid lines are approximate extrapolations from $T<80$ K and $T>120$ K. The inset is the predicted behavior of the lattice expansion reproduced from Ref. 8.

The jump in relative expansion, $\Delta\alpha_v$, estimated by extrapolating (solid lines) above and below the transition region (80 K $<T<$ 120 K) is approximately 1.8×10^{-5} which is about 50 times larger than the estimates[8] (3.6×10^{-7}) based only on the electronic specific heat jump[9,10] at the superconducting transition. It therefore appears that the discontinuity observed in our measurements is not only caused by the electronic contribution. There are two possible explanations for the unexpected large slope discontinuity. The observed behavior can be due to three consecutive structural transitions at $\sim$120 K, near T_c, and $\sim$80 K. Or there is one structural transition associated with the superconducting transition with strong fluctuation effects associated with it. Since the lattice expansion is a result of lattice fluctuations (e.g., thermal fluctuations induce thermal expansion), our straightforward interpretation of the anomalous expansion above the solid line is "fluctuation." In other words, a structural anomaly such as condensation of soft phonon modes (rotation, breathing, and/or Jahn-Teller type distortions) concurrently occurs with the superconducting transition.

As an inset of Fig. 3, the theoretically predicted behavior of the lattice expansion[8] was reproduced for discussion. The solid line is a mean-field result and the dashed line is the expected behavior when the effect of the fluctuations is included. Since mean-field results do not depend on the nature of the order parameter as long as the order parameter is coupled to the lattice strain, the striking resemblance of the predicted behavior to the data enforces our conclusion that the deviation from the extrapolation seen in our measurements is due to the lattice fluctuations. In addition the fluctuations disappear around 80 K where the 3D to coupled 2D crossover has been observed.[18] Therefore, it appears that the structural fluctuations seen in our measurements are strongly affected by the dimensional crossover indicating that the correlation lengths of the fluctuations might be similar to that of superconducting order parameter.

Since the fluctuations of the lattice would strongly scatter ultrasound, anomalous behavior in ultrasonic measurements are also expected.[19–21] Strong absorption anomalies in the temperature range of 80 to 120 K observed in two independent measurements present additional strong support for the lattice fluctuations.[20,21] The strong lattice fluctuations are also consistent with the anomalous lattice vibrations seen in channeling experiments[15,22] and with the smearing of the coherence peak in a recent NMR study.[23]

In recent electron energy loss measurements[24] and in infrared measurements[25] non-BCS behavior of $YBa_2Cu_3O_{7-\delta}$ has been reported. A very large in-plane superconducting gap of $\sim8\ kT_c$ (Refs. 24 and 25) was observed and the population of pairs and gaplike features[24] were observed at temperatures as high as 116 K. Based on these observations, we cautiously relate the strong fluctuation effects seen in our measurements at similar temperatures to the formation of the superconducting pairs. The strong fluctuations may result from the distortion of the lattice by the superconducting pairs well above T_c. Such strong lattice distortions by the pair formation has been expected for bipolaronic superconductivity.[26,27] Since the theories for the bipolaronic superconductivity do not have any quantitative predictions on the lattice expansion, relating our observation to the theories remains speculative. Our observations also need to be examined by other theoretical models predicting subtle structural distortions such as the twitch transition,[28] dynamic Jahn-Teller coupling,[29] and percolative superconductivity.[30]

In conclusion the expansion rates of the unit cell parameters show the discontinuities and possible fluctuations around T_c qualitatively consistent with the theory[8] but their unexpectedly large magnitudes suggest a structural transition or instability in addition to the superconducting transition. It appears that phonons with short correlation lengths (possibly similar to the superconducting correlation length) are concurrently populated near the superconducting transition temperature. Our observations are unexpected in a BCS momentum space pairing.

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