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Lattice readjustment of $YBa_2Cu_3O_{7-y}$ between 150 and 300 K: a transmission-microscope study

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Abstract. The lattice instability of the high-T_c superconductor $YBa_2Cu_3O_{7-y}$ has been studied at temperatures between 150 and 300 K by transmission electron microscopy. Anomalous changes in the lattice constant c were observed near 170 and 250 K. The axial ratio b/a was found to vary in a range from 1.014 to 1.018 (error: ±0.1%), and a tendency towards a reversible orthorhombic–tetragonal phase transition was observed between 170 and 200 K. Possible explanations are proposed.

Since the discovery of the new high-T_c superconducting system (Wu *et al* 1987), many investigations have been made of their physical properties. In our early work, we found possible structural changes or lattice instability near 250, 160 K and above T_c in Y–Ba–Cu–O and Y–Ba–Cu–Nb–O systems (He *et al* 1987). Similar results were also reported by other groups using different experimental methods (Ewert *et al* 1987, Horie *et al* 1987, Cannelli *et al* 1987, Wang *et al* 1987, Du *et al* 1987, Lagreid and Fossheim 1988). It was believed that some kind of relationships existed between the structural readjustment or lattice instability and the high-T_c superconductivity, which was even more apparent after the 200 K zero-resistivity anomalies were widely observed (Zhao 1987, Bhargava *et al* 1987, Djurek *et al* 1987, Chen *et al* 1987).

In this paper, we present our further studies on such a lattice instability of $YBa_2Cu_3O_{7-y}$ by means of transmission electron microscopy (TEM) between 150 and 300 K. Anomalous changes in the lattice constant c and a tendency towards a reversible orthorhombic–tetragonal phase transition are reported.

Two samples (denoted A and B) were used in this study. They were prepared by different laboratories. Both of them were made by standard ceramic sintering processes. The zero-resistivity temperatures for samples A and B were 85 and 94 K, respectively; and the Meissner effect of sample B was much stronger than that of sample A. However, x-ray diffraction results proved that both were of single-phase perovskite orthorhombic structure. For TEM observations, the samples with some ethyl alcohol were put into an agate mortar for grinding into fine flakes with a size of the order of a micrometre. These were then dispersed in acetone and scooped onto a carbon-coated copper grid. Polycrystalline gold powder was used as a diffraction-pattern standard; it was dispersed on the carbon-coated copper grid by evaporation before the specimen flakes were scooped on. A Hitachi 800 transmission–scanning electron microscope (resolution for

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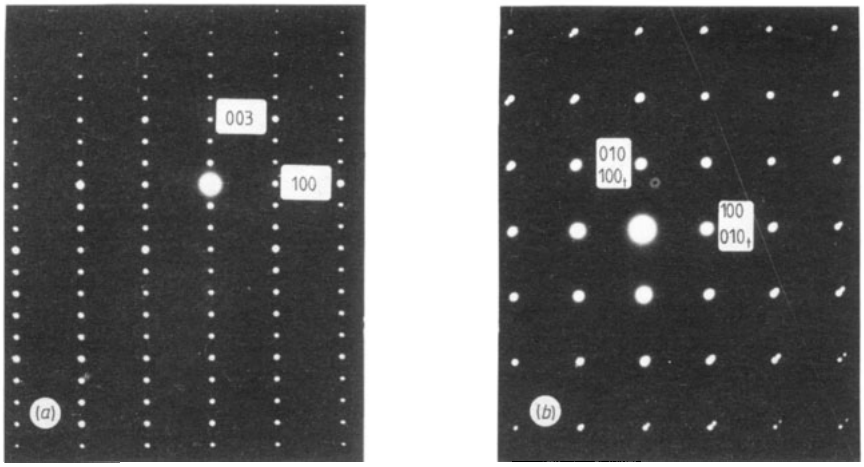

Figure 1. (*a*) Typical SADP of the [100] zone for sample B. (*b*) Typical SADP of the [001] zone for sample B. The orthorhombic structure can be easily recognised by the split spots, which originate from the orthorhombic twins.

TEM: 1.44 Å), operating at 200 kV, was used. The study was conducted during heating, starting from 150 K—the lowest temperature obtainable by using liquid nitrogen. It took at least 15 min for thermal equilibrium at each temperature. Special attention was paid to ensure all conditions were exactly the same during the whole experimental process. Care was also taken to minimise the radiation damage.

A typical selected-area diffraction pattern (SADP) of $YBa_2Cu_3O_{7-y}$ superconductor taken from a number of the fragmented crystals is shown in figure 1. These diffraction patterns proved that all crystals under study were orthorhombic. The two curves in figure 2 show the temperature dependence of the changes of lattice constant c obtained from the electron diffraction patterns. One is for sample A (▼) and the other is for sample B (▽). It can be seen that although the difference in the Meissner effect between samples A and B was remarkable, the two curves in figure 2 are very similar, with two remarkable changes near 170 and 250 K. By using diffraction patterns of gold powder as a standard, the small shifts of the diffraction spots of the single crystals at different temperatures can be clearly distinguished. This ensured that the observed changes of order 10^{-2} in the c axis of both single crystals are real and the results in figure 2 are reproducible and reliable.

The temperature dependence of the variation of the ratio b/a was also obtained from the SADP of twin crystals as shown in figure 1(b). An illustration of the twinned orthorhombic structure is shown in figure 3. There are two methods of measuring the axial ratio b/a. The first one is to measure the splitting angle (2Δ) (see figure 3) which follows the relationship with the orthorhombic cell parameters (a, b) $a/b = 1 - \Delta$, when Δ is small. Since in our case the changes in 2Δ were small, the error would be large. The second method is to measure the distance between diffraction spots (e.g. A and A′, B and B′ in figure 3) directly and repeatedly, then take the average value for further calculation. Using this method, we can make the error as small as $\pm 0.1\%$. Figure 4 shows that the axial ratio b/a obtained from the diffraction patterns of sample B varies from 1.014 to 1.018, and the whole curve seems to decrease slowly with increasing temperature. Possible anomalous changes near 180 and 250 K are also indicated by arrows in figure 4. Since these are near the experimental limit, however, more accurate measurements should be carried out before any definite conclusion can be drawn. It is

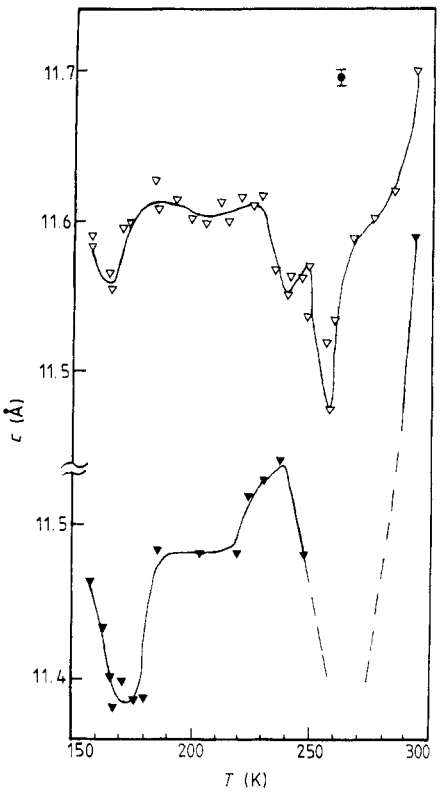

Figure 2. The temperature dependence of the changes of lattice constant c: (▼) for sample A and (▽) for sample B.

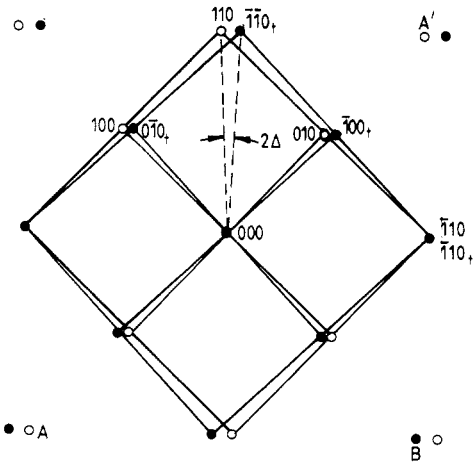

Figure 3. An illustration of the twinned orthorhombic structure.

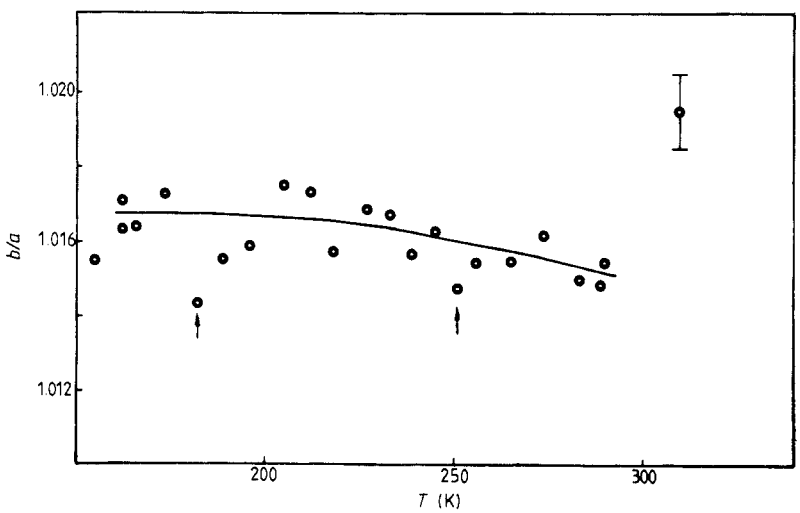

Figure 4. The temperature dependence variation of the axial ratio b/a. Possible anomalous changes are indicated by arrows.

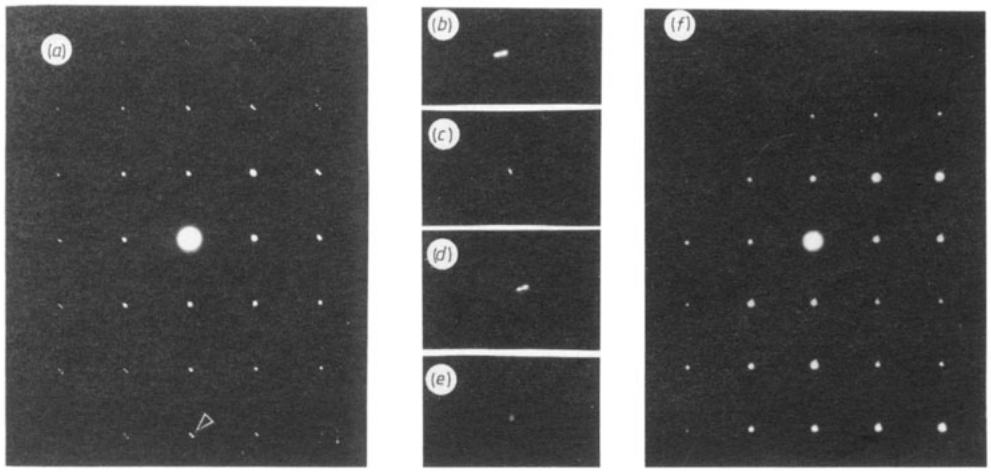

Figure 5. (*a*) Typical electron diffraction pattern along [001] zone taken from a micrometre-sized crystal of sample A at $T = 157$ K, showing the initial orthorhombic structure. The arrowed spot in (*a*) is shown at different temperatures showing a reversible phase transformation process: (*b*) $T = 170$, (*c*) $T = 174$, (*d*) $T = 166$ and (*e*) $T = 203$ K. (*f*) The final tetragonal structure of the same crystal at $T = 219$ K.

worth pointing out that a recent TEM study result from another group also showed similar results for b/a (Yamamoto *et al* 1987). The quoted error was $\pm 0.1\%$, close to our present results.

As mentioned above, in our ultrasonic studies we observed attenuation and velocity anomalies near 160–180 and 240–260 K, which were confirmed by results from different experimental methods at different laboratories. Now the results from our TEM study also show anomalous changes in the lattice constant c near 170 and 250 K and our recent x-ray study gives similar results again (He *et al* 1988). The consistency of all these anomalous changes indicates that there must exist some correlations among them. Furthermore, the new results of lattice constant anomalies in our TEM study reveal that the above phenomena are related closely to the intrinsic lattice instability or structural readjustment. The most reasonable explanation for such instability may be the ordering in the oxygen vacancies. In fact, recent neutron diffraction experiments (Capponi *et al* 1987) and high-resolution TEM studies (Ourmazd and Spencer 1987) seem to show long-range order in the oxygen vacancies near T_c. However, Hirotsu *et al* (1987) found in their TEM study that the ratio b/a of ten different specimen flakes varied from 1.003 to 1.018 at room temperature, which suggests that the distribution of oxygen vacancies is not uniquely specified but varies from place to place. Hence the readjustment of such a distribution, e.g. the ordering of the oxygen vacancies, is necessary for a superconducting transition and it must occur somewhere on approaching T_c from room temperature. Now, we know such processes do occur near 250 and 170 K as indicated by our results showing anomalous changes in the lattice constant c. It is such an ordering movement of oxygen vacancies that causes the lattice instability, leading finally to the high T_c.

The above idea was supported by the observation of a single case reversible orthorhombic–tetragonal phase transition tendency near 170–200 K. The original specimen flake—a micrometre-sized twin crystal taken from sample A—was of orthorhombic structure at room temperature; this was distinguished by the splitting of diffraction spots of the twins. The specimen flake was cooled to 150 K directly and then heated. A typical electron diffraction pattern along the [001] zone is shown in figure 5(*a*); the arrowed spot

Table 1. The temperature dependence of the ratio b/a obtained from the diffraction patterns of figure 5(*a*)–(*e*).

Pattern	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	
T(K)	157	170	174	166	203	291
b/a	1.015	1.009	1.001	1.012	1.002	1.002

from this pattern is enlarged and displayed in figure 5(*b*)–(*e*) for different temperatures, manifesting the tendency towards a reversible phase transformation process. The transformation first appeared at 170–176 K since the splitting of the twin spots disappeared at 176 K when the crystal was heated from low temperature (figure 5(*c*)). Whereas when it was cooled to 166 K again, the twin crystal was recovered (figure 5(*d*)), showing clearly the reversibility of this transformation. The second transformation was observed above 178 K as the crystal was heated again (figure 5(*e*)). Finally it tended to change into a tetragonal phase (figure 5(*f*)). Table 1 gives the ratio b/a of the above micrometre-sized crystal at different temperatures (error: $<\pm 0.2\%$). It shows that in the first heating process the value of b/a changes from 1.015 (T = 157 K) to 1.001 (T = 174 K) and in the second heating process it changes from 1.013 (T = 166 K) to 1.002 (T = 203 K), which suggests that the transformation is nearly a reversible orthorhombic–tetragonal phase transition. Figure 6 gives the temperature dependence of changes in lattice constants b and a obtained from the above diffraction patterns. However, for the high-quality sample B (T_c = 94 K, DC susceptibility better than 30–40%), no such phase transition tendency was observed among four micrometre-sized twin crystals. This is hardly surprising, because it is generally believed that the orthorhombic–tetragonal phase transition for $YBa_2Cu_3O_{7-y}$ occurs above room temperature, for oxygen content $y < 0.3$ (Eatough *et al* 1987). Considering that sample A is a rather poor one with comparatively lower T_c and weaker Meissner effect, its oxygen content must be low. Furthermore, during the experiment, the vacuum pumping and electron irradiation effect, although carefully minimised, might reduce the specimen's oxygen content (say, $y > 0.35$), leading to a reversible phase transition at 170–200 K. Such a low-temperature orthorhombic–tetragonal transition might be an occasional case. However, the observation proves that the oxygen vacancies can move or jump at 170–200 K. Since the tetragonal structure is

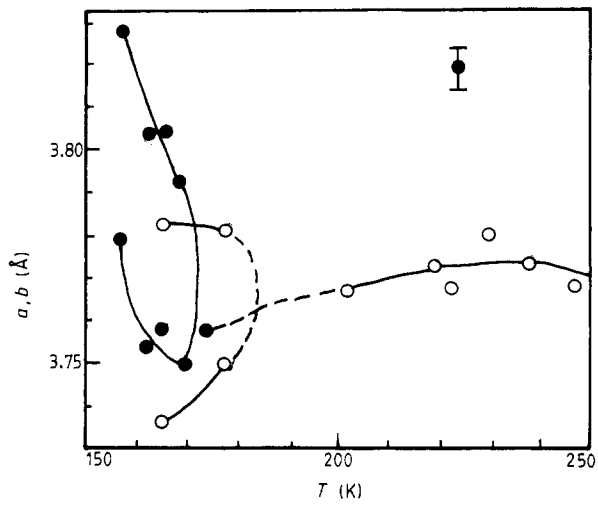

Figure 6. The temperature dependence of changes in lattice constants b and a of sample A. (●) First heating and (○) second heating after cooling from 176 to 166 K.

characterised by disorder of the oxygen in the *a–b* plane, the reversible orthorhombic–tetragonal phase transition tendency around 170–200 K must be essentially caused by the order–disorder transition of the oxygen vacancies (Tendeloo *et al* 1987). Although such a phase transition may occur only occasionally in some rather 'poor' samples, it is evident that the ordering movement or jumping of oxygen vacancies is so active at 170–250 K that it could even lead to a phase transition if suitable conditions were satisfied.

In summary, the following conclusions can be drawn.

(i) By improving experimental methods, reproducible and reliable results of temperature-dependent changes of lattice constant *c* near 170 and 250 K were observed, which is consistent with the results of other experimental methods.

(ii) Such anomalies observed above probably result from intrinsic lattice instability related to the ordering readjustment of the oxygen vacancies. The observed reversible orthorhombic–tetragonal phase transition tendency near 170–200 K provided further evidence of this.

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