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Effect of structural instability between 80 and 300 K on superconductivity of $YBa_2Cu_3O_x$

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The lattice parameters of $YBa_2Cu_3O_x$ have been carefully measured by x-ray polycrystalline diffraction between 80 and 300 K. As a function of temperature, they reveal a large variation above T_c, which is mainly attributed to a few abrupt changes near certain temperatures rather than thermal expansion. Such structure instability, accompanied with the appearance of internal friction peaks and elastic softening, is related to oxygen content x. The instability near 120 K was found to be related to the superconductivity at 90 K.

With a great many active studies on the high-T_c superconducting oxide $YBa_2Cu_3O_x$, it is certain that the resistivity, lattice parameters, and so on, are susceptible to oxygen content.[1-3] Neutron powder diffraction analysis shows that only O(1) sited on the Cu-O chains decreases correspondently with the decrease of oxygen content, while other sites remain fully occupied.[3,4] Nevertheless, the transition temperature T_c is nearly unchanged as x changes from 7.0 to 6.8, then drops rapidly within the small decrement of oxygen content.[1,2] Thus, it has been proposed that the one-dimensional (1D) Cu-O chains are not essential to the superconductivity.[5] X-ray and neutron diffractions show that the crystal structure of oxide $YBa_2Cu_3O_x$ is a triple perovskitelike structure. In such a distorted perovskite-based superconducting oxide there are a few anomalies on the lattice parameters as a function of temperature. Those anomalous jumps of the lattice parameter at several temperatures lead to the appearance of internal friction peaks and ferroelastic hysteresis.[6,7] The anomalous behavior, which Wang *et al.* refer to as phase-transition-like behavior, may be related to high-T_c superconductivity.[6,8] In this report, it is confirmed that there exists crystal structural instability above T_c, and it is related to the oxygen content as well as to high-T_c superconductivity. The characteristic of structural instability is also studied.

The samples prepared by a standard powder metallurgical method[6] have the composition $YBa_2Cu_3O_x$, $x=7.0-6.98$. They were sliced and divided into several groups. Each group of specimens was placed in a vacuum furnace at varying temperatures between 360 and 520 °C for 24 h, and then gradually cooled. The oxygen content x was evaluated by comparing the lattice parameters and resistivity at room temperature with those of Cava.[1] X-ray diffraction patterns and a narrow superconducting transition width indicate that the treated samples exhibit a fairly homogeneous phase with less inherent stress than those samples treated by quenching from higher temperature to room temperature or liquid-nitrogen temperature.

X-ray polycrystalline diffraction data $2\theta_B$ (θ_B, Bragg angle) have been recorded on a Rigaku diffractometer; the resistivity was measured by a four-probe configuration, internal friction by a Marx three-component composite oscillator, and the Stress-strain curve by a tensile test, for each group of samples (with different x) between 80 and 300 K. The curves of resistivity versus temperature for the samples with various oxygen content are shown in Fig. 1. The superconducting transition temperature T_c is still about 90 K as x drops to 6.8.

The average gradient of lattice parameters a and b as a function of temperature, which is defined as $\Delta b/\Delta T=(b_{300\,\mathrm{K}}-b_{80\,\mathrm{K}})/(300\ \mathrm{K}-80\ \mathrm{K})$ and same for $\Delta a/\Delta T$, is shown in Fig. 2. It is clear that the curve of $\Delta b/\Delta T$ or $\Delta a/\Delta T$ vs x exhibits a steplike change rather than a linear one just as T_c does.[1,2] At $x=7.0-6.8$, the value $\Delta b/\Delta T$ or $\Delta a/\Delta T$, which coincides with the results of neutron powder diffraction,[9] is the largest and then decreases as the oxygen content decreases. Even though the structure symmetry turns tetragonal, the value is still larger than that of the dashed line (shown in Fig. 2), the thermal expansion coefficient, which will be explained in the next paragraph.

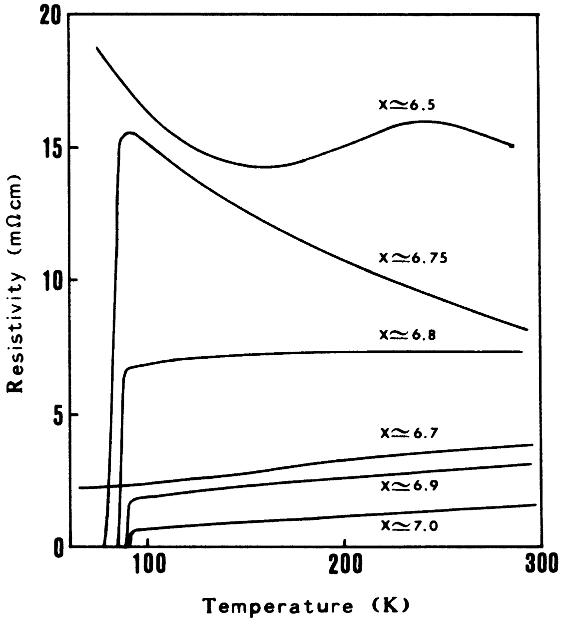

FIG. 1. Resistivity vs temperature with various oxygen content x.

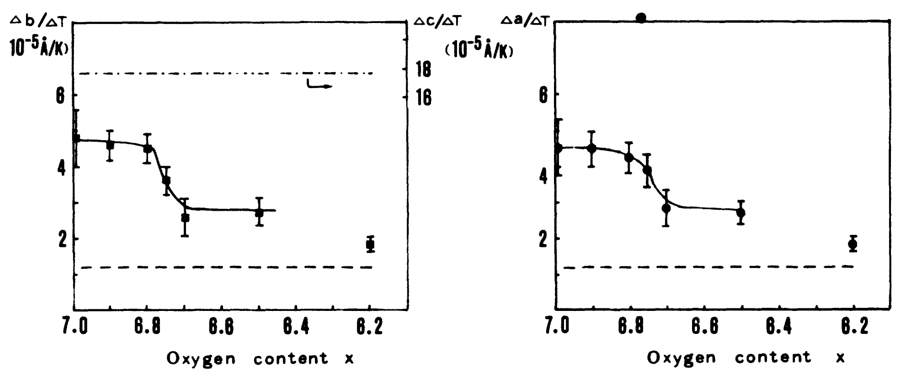

FIG. 2. $\Delta b/\Delta T$ and $\Delta a/\Delta T$, the average gradient of the lattice parameters b and a, vs oxygen content x. The dashed line indicates thermal expansion coefficient along the b or a axis, and the dashed-dotted line indicates that along the c axis.

The curves of lattice parameter b with different x versus temperatures between 80 and 300 K are shown in Fig. 3. There are a few small abrupt changes on the curves, but no change of structure symmetry was observed. Those abrupt changes or jumps of lattice parameters, which only occur above superconducting transition temperature T_c, induce the appearance of internal friction peaks (Fig. 4) and ferroelastic hysteresis (Fig. 5) near corresponding temperatures (120, 160, and 220 K). An internal friction measurement is more sensitive than x-ray diffraction in verifying such small variation of crystal structure. The occurrence of both the internal friction peaks accompanied by the minima of Young's modulus (Fig. 4) and the ferroelastic hysteresis (Fig. 5) indicates that there exists a mobile interface between two coexistent "phases" with different lattice constants and an elastic softening near the jump temperature.[6] Because the measurements were carried out with polycrystalline samples, the minima of Young's modulus near phase-transition temperature is much less obvious than that with a single crystal. As we know, the ferroelastic hysteresis appears near the temperature at which a certain elastic constant shows softening in shape memory alloys[10] and even in ferroelastic oxides. Thus, it also indicates the existence of elastic softening.

As the oxygen content decreases there are less such

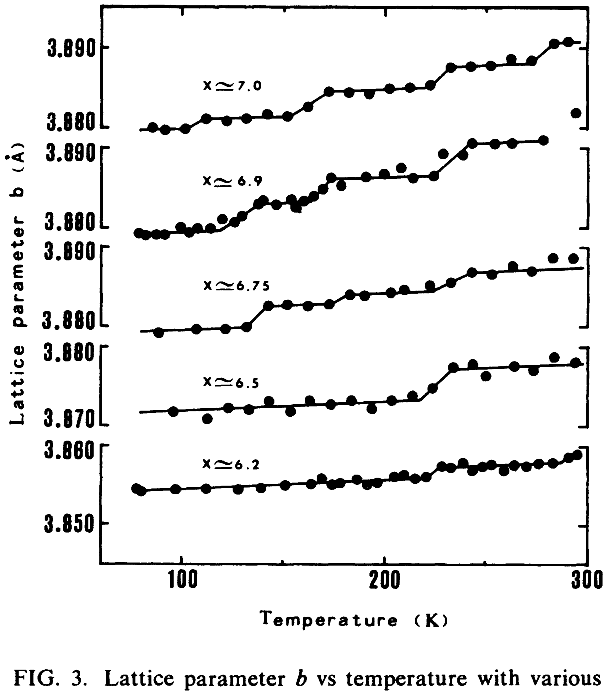

FIG. 3. Lattice parameter b vs temperature with various x. There are a few small abrupt changes near certain temperatures on the curves.

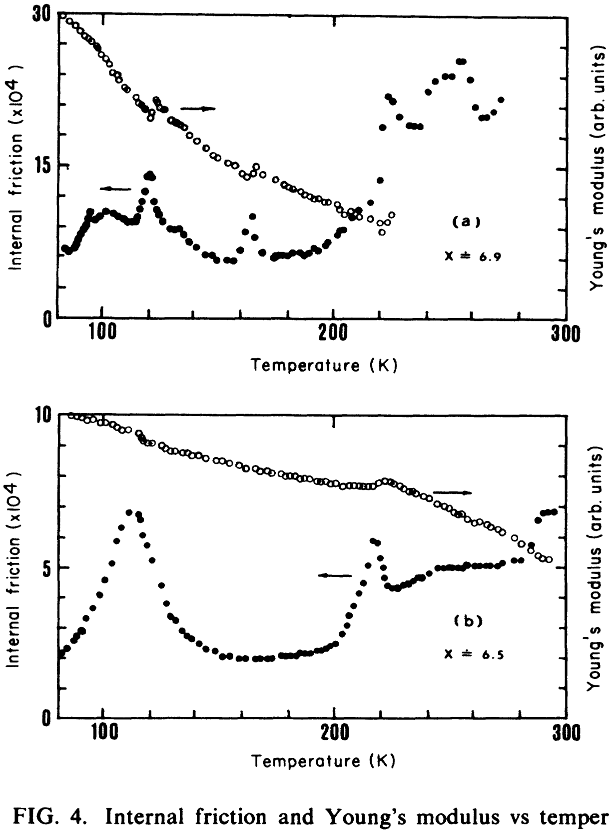

FIG. 4. Internal friction and Young's modulus vs temperature for the samples with (a) oxygen content $x \simeq 6.9$; (b) $x \simeq 6.5$.

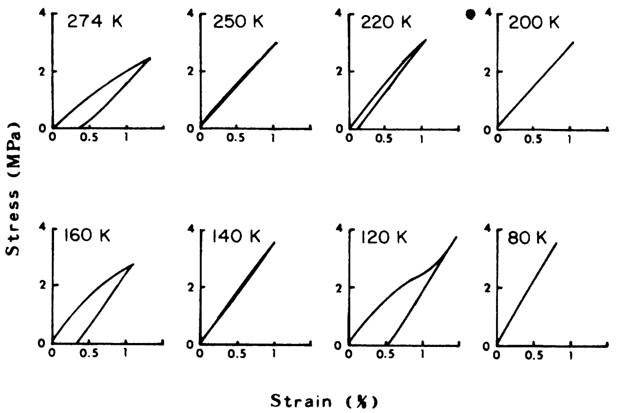

FIG. 5. Stress-strain curves at different measurement temperatures for the sample with $x \simeq 6.9$. The ferroelastic loops occur near 274, 220, 160, and 120 K.

jump points as well as internal friction peaks between 80 and 300 K, resulting in the decrease of $\Delta b/\Delta T$ and $\Delta a/\Delta T$. The curves of lattice parameter b versus temperature beyond the jump regions show a linear variation with a constant slope which is just the thermal expansion coefficient (dashed line in Fig. 2). The thermal expansion coefficient, which has no obvious change with varying x, is much smaller than the average gradient of lattice parameters above T_c. Neutron powder diffraction also indicates that the average gradient of lattice parameters above T_c is much larger than that below T_c.[9] Thus, it is certain that there are structural instabilities in $YBa_2Cu_3O_x$ above T_c for both the orthorhombic and tetragonal phases, and the large average gradient of lattice parameters is mainly due to a series of small abrupt changes of lattice parameters.

There is a relaxation internal friction peak near 100 K (Fig. 4) for varying oxygen content, but it is not the case discussed above since it can be shifted by altering the measurement frequency.

It is interesting that the abrupt change of lattice parameters as well as the corresponding internal friction peak, Young's modulus minimum, and ferroelastic hysteresis, always exist near 120 K for the sample with transition temperature T_c at 90 K (Figs. 3 and 4). Furthermore, they disappear for a possibly lower T_c ($T_c < 77$ K) or nonsuperconducting tetragonal phase. But the abrupt change of lattice parameters and internal friction peak near 220 K always exist for both orthorhombic and tetragonal phases. When the specimen with $T_c < 77$ K was annealed in an oxygen atmosphere, the abrupt change of lattice parameters and internal friction peak near 120 K would turn up again as long as T_c reaches 90 K. Therefore, the abrupt change of lattice parameters near 120 K is considered to be closely connected to the superconductivity at 90 K.

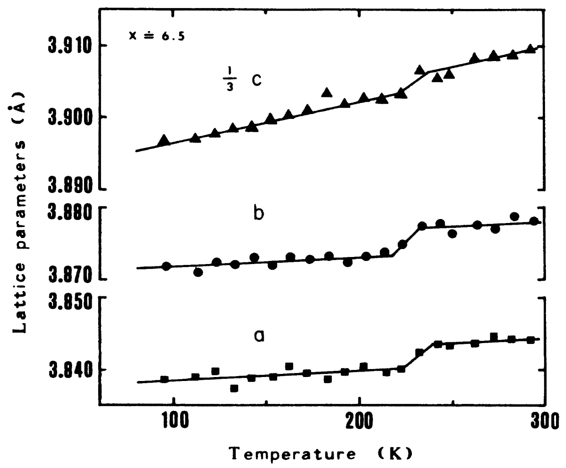

FIG. 6. Lattice parameters a, b, and $\frac{1}{3}$ c vs temperature for the samples with oxygen content $x \simeq 6.5$. The curves show the same tendency of abrupt changes for a, b, and c.

The average gradients $\Delta a/\Delta T$ and $\Delta b/\Delta T$, as well as the variations of lattice parameters a, b, and c at jump points, have the same trend (Fig. 6). Therefore, the abrupt change of lattice parameters might not mainly result from the transfer of partial oxygen atom from the O(1) site to the O(5) site (on the a axis) within Cu(1) layer (between Ba and Ba). Since the abrupt change is associated with lattice parameters, a, b, and c, it is speculated that the simultaneous abrupt changes of lattice parameters are probably due to an alternative rotation or distortion of the octahedron (or the so-called pyramid), which is similar to the case of $LiNbO_3$.[11] The octahedron containing Cu(2) (between Y and Ba) and its neighboring oxygen atoms (see the sketch in Ref. 12) exists not only in orthorhombic phase but also in tetragonal phase.[4] Thus, some jumps of the lattice parameter, e.g., near 220 K, occur in both the orthorhombic and tetragonal phases. But the jump near 120 K occurs only in the orthorhombic phase with T_c at 90 K. Such rotation or distortion of the octahedron is often associated with the softening of a certain optical phonon[13,14] which may be coupled with the softening of the acoustic phonon and is favorable to high-T_c superconductivity.

In summary, there exists a distinct structure instability in the distorted perovskite-based superconducting oxide $YBa_2Cu_3O_x$ above T_c. The structure instability is affected by the oxygen content. The structure instability near 120 K is favorable to superconductivity at 90 K.

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