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A temperature-dependent study on a superconducting $Bi_2Sr_2CaCu_2O_\delta$ single crystal by x-ray diffraction

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Abstract. The changes of profiles along the *a*, *b* and *c* directions of a $Bi_2Sr_2CaCu_2O_\delta$ single crystal were examined by the x-ray diffraction method over the temperature range from 297 K to 77 K. Splitting of the (0*k*0) and (*h*00) diffraction peaks appeared in the temperature regions from 262 to 222 K and from 226 to 156 K, respectively. Changes of the modulation structure appear in the temperature regions from 207 to 202 K and from 112 to 102 K. Moreover, there is no remarkable change of the (00*l*) diffraction peaks. Below the temperature of 91 K, the (040) diffraction peak obviously begins to broaden.

The lattice instability of Bi-based superconducting ceramic between temperatures $T = 300$ and 4.2 K has drawn much attention. Experimental results of ultrasonic [1–7], internal friction [8–11], positron annihilation [12–14] and specific heat [5, 15, 16] measurements have shown that there are anomalous changes in the temperature region. However, the temperature regions of the anomalous change appearance are not agreed by different authors. It is undoubtedly a product of both the quality, such as the impurity and intergrowth content, of the samples used and the physical experimental method employed. Many papers concerning the observation and characterization in the structure of $Bi_2Sr_2Ca_{n-1}Cu_nO_\delta$ ($n = 1, 2$ and 3) high-temperature superconductors have pointed out that the incommensurate modulation structure [17–25] is one of the characteristic features, which is formed by the periodic arrangement of Bi-concentrated bands in the BiO layers. Reddy and Ramana [1], Wang *et al* [7, 10, 11] and the later authors [5, 6, 12, 13] believed that the anomalous changes are caused by structural changes or phase transition, such as lattice softening, motion of oxygen vacancies in Bi–O layers and lattice distortion. However, Beskrovnyi *et al* [26] have found that the lattice parameters display less pronounced axial anisotropy by x-ray and neutron diffraction methods in the temperature range 8–920 K, which coincides with the results reported by Albouy *et al* [27]. In the x-ray diffraction (XRD) method, Takenaka *et al* [28] have found that both the intensities and the widths of the modulation structure reflections are independent of temperature below room temperature. Coppens *et al* [29] have observed the splitting and recombination of the (0 2 10) reflection of $Bi_2Sr_2CaCu_2O_{8+\delta}$ on cooling. Because only structural changes at two temperatures of 298 K and 170 K have been measured before the superconducting transition temperature T_c, we can hardly find

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the relationship between the anomalous changes and the structural changes. Moreover, the mechanism of the anomalous changes is still unclear. In this work, we have carried out temperature-dependent experiments on single-crystal $Bi_2Sr_2CaCu_2O_\delta$ by means of XRD over the temperature range from 297 K to 77 K. Changes of the profiles along *a*, *b* and *c* directions of the crystal have been examined. We found that the anomalous changes are directly related to the profile changes, which are caused by the phase transition of atomic displacement and a lattice distortion, but not the changes of the lattice constants.

Single crystals of $Bi_2Sr_2CaCu_2O_\delta$ phase were grown from Bi-rich melts by a directional solidification method with the atomic ratio 2.4 Bi:2.0 Sr:1.0 Ca:2.0 Cu [30]. The specimen used for XRD was a large single crystal of about $3.5 \times 1.5 \times 0.01$ mm^3. XRD measurements were performed using a rotating anode x-ray powder diffractometer with

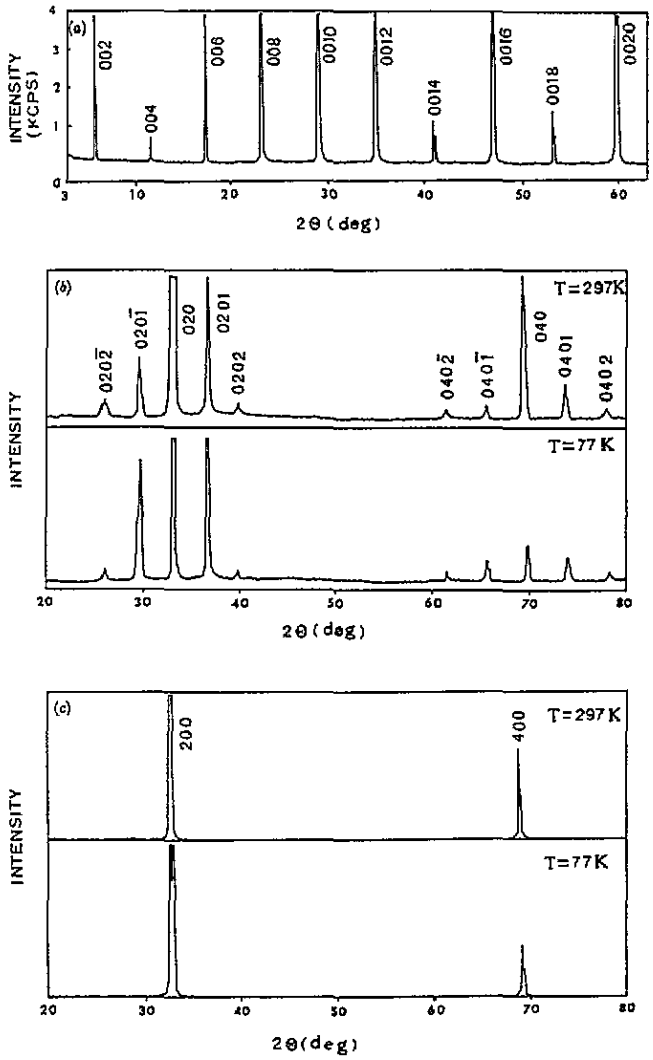

Figure 1. (*a*) The (00*l*) multiple-order diffraction pattern of the single-crystal $Bi_2Sr_2CaCu_2O_\delta$ at room temperature (297 K); (*b*) the (0*k*0) and its satellite spots and (*c*) the (*h*00) XRD patterns of the single crystal at room temperature (297 K) and 77 K respectively.

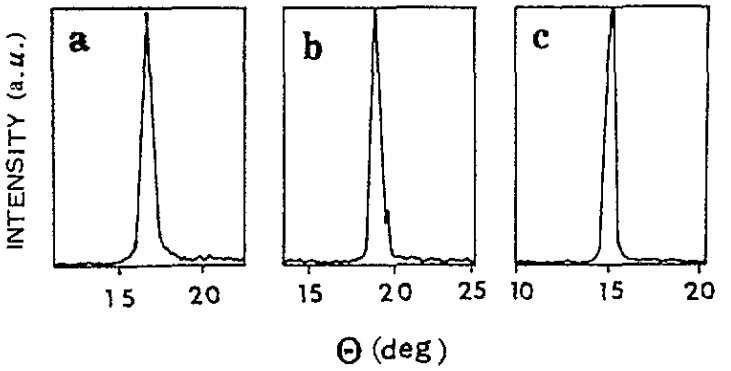

Figure 2. At room temperature (297 K), the rocking curves of the reflections (*a*) (200), (*b*) (020) and (*c*) (0010).

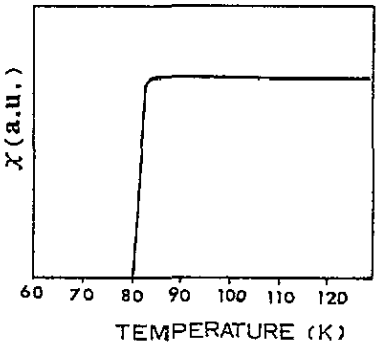

Figure 3. The a.c. susceptibility with respect to the temperature of the single-crystal $Bi_2Sr_2CaCu_2O_\delta$.

a pulse height analyser, type D/max-rA. The x-ray (00*l*) diffraction data of the single crystal $Bi_2Sr_2CaCu_2O_\delta$ were collected in the Bragg–Brentano (BB) geometry with graphite monochromatized Cu Kα radiation. The (h00) and (0k0) XRD data and the modulation period were obtained in a symmetric transmissive geometry with Ni-filtered Cu radiation. In this geometry, the detector at 2θ can only receive the x-ray diffracted by the planes at θ perpendicular to the sample surface normal.

For low-temperature XRD study the crystal was fixed on the cold finger of a liquid nitrogen refrigerator which was mounted on a goniometric head of the x-ray diffractometer allowing fine adjustment. The temperature measurement of the crystal was made by a copper–constantan thermal–electronic couple mounted on the cold finger. The investigation was performed in the symmetric transmissive geometry and at temperatures from 297 K down to 77 K.

Figure 1 shows the XRD patterns along the c, b and a directions of the single crystal at room temperature. Combined with the rocking curve, as shown in figure 2, the diffraction patterns indicate that the specimen is a perfect single crystal of Bi-based 2212 phase with lattice constants $a \simeq b \simeq 5.4$ Å, $c = 30.80$ Å and an incommensurate modulation period $q \simeq 4.8b \simeq 26$ Å along the b direction of the crystal. Moreover, there is no modulation structure along the a and c directions. The a.c. susceptibility with respect to the temperature of the specimen is shown in figure 3, which gives the superconducting transition temperature of $T_c = 81$ K and transition width $\Delta T_c = 1.5$ K.

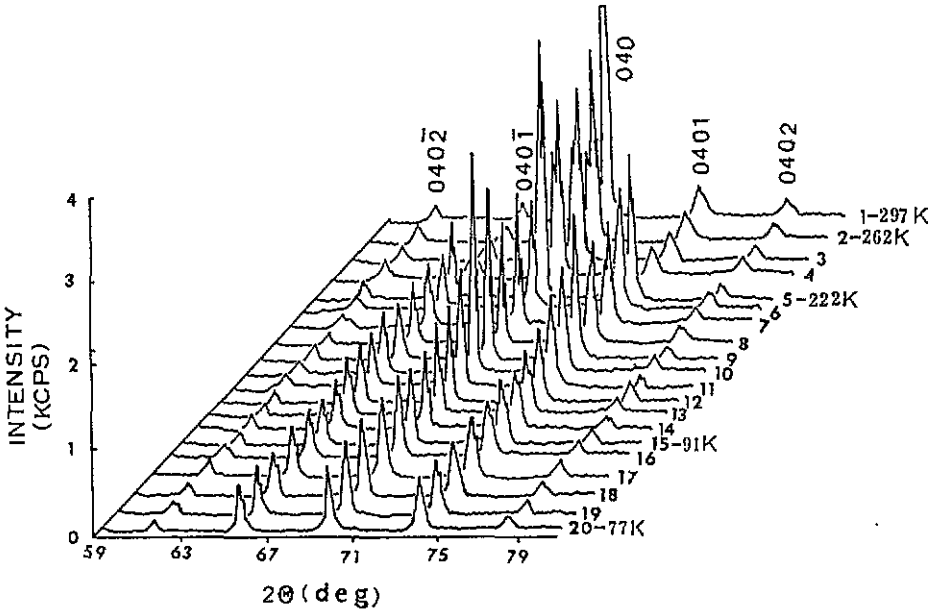

Figure 4. The XRD patterns for (040) and its satellite spots at the following temperatures: 1, 297 K; 2, 262 K; 3, 242 K; 4, 232 K; 5, 222 K; 6, 212 K; 7, 207 K; 8, 202 K; 9, 187 K; 10, 172 K; 11, 142 K; 12, 112 K; 13, 102 K; 14, 96 K; 15, 91 K; 16, 88 K; 17, 85 K; 18, 83 K; 19, 80 K; 20, 77 K.

The single-crystal study in the temperature range from 297 K to 77 K shows that the matrices of the $Bi_2Sr_2CaCu_2O_\delta$ lattice are orthorhombic. The modulation period displays no temperature trend within the experimental uncertainty to some $q = 4.8b$. There is little change of either lattice constant or diffraction intensity along the c direction of the crystal at low temperature except the thermal contraction. These findings confirm the previous single-crystal investigation of the modulation structure between room temperature and low temperature using x-ray and neutron diffraction [26]. Moreover, comparing the profiles along a, b and c directions of the single crystal at room temperature (297 K) with those at the liquid nitrogen temperature of 77 K, it is found that there is no remarkable difference except the diffraction intensity and thermal contraction, as shown in figure 1. However, during the descent process of the temperature, both profiles and intensities of the fundamental reflections ($h00$), ($0k0$) and the satellite reflections ($0k0m$) have undergone dramatic changes apart from the structural changes caused by the thermal contraction. It is suggested that the single crystal has undergone large structural adjustments while descending in temperature from 297 K to 77 K.

The XRD patterns for (040) reflection and its satellite reflections ($040m$) at different temperatures are shown in figure 4. According to the process of the temperature-dependent profile changes of the fundamental reflection (040), the temperature range from room temperature to liquid nitrogen temperature can be divided into three regions. The first one is the temperature region from 262 K to 222 K. In this region, the (040) diffraction peak begins to split into a triplet at the temperature of 262 K. Moreover, the diffraction intensity increases successively and the profile of the reflection (040) continues to change with decreasing temperature. At the temperature of 222 K, the profile of the reflection (040) recombines into a doublet and the intensity becomes very high. Meanwhile, the

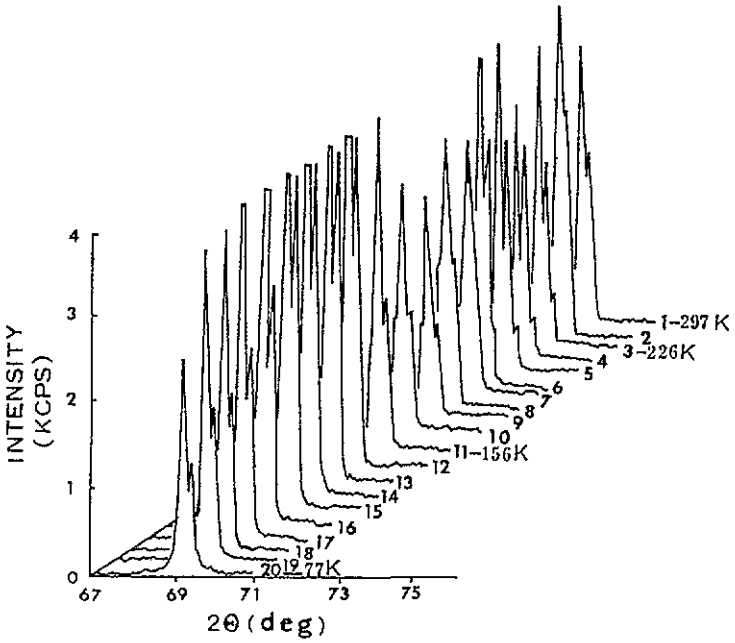

Figure 5. The XRD patterns for (400) at the following temperature: 1, 297 K; 2, 236 K; 3, 226 K; 4, 216 K; 5, 206 K; 6, 196 K; 7, 186 K; 8, 176 K; 9, 166 K; 10, 161 K; 11, 156 K; 12, 151 K; 13, 146 K, 14, 136 K; 15, 131 K; 16, 126 K; 17, 121 K; 18, 116 K; 19, 111 K; 20, 77 K.

profiles of the satellite reflections (040m) ($m = \pm1, \pm2$) are broadened so seriously that the Kα1 and Kα2 lines cannot be separated from the broadened peak. This suggests that the modulation structure is imperfect, or distorted seriously. The second process is over the temperature region from 222 K to 91 K. There is no remarkable change of the profiles in either the (040) reflection or its satellite reflections (040m) ($m = \pm1, \pm2$) except for the intensity. The Kα1 and Kα2 lines of the (040) reflection and its satellite reflections (040m) ($m = \pm1, \pm2$) can be clearly characterized. This shows that both the fundamental lattice and the modulation structure are perfect. Moreover, in this temperature range, the profiles of the satellite reflections (040m) ($m = \pm1, \pm2$) have twice undergone changes in the temperature regions from 207 K to 202 K and 112 K to 102 K. Because the satellite reflection is connected with the double Bi–O layers, the change of the satellite reflection reveals that the structural adjustments mainly appear in the double Bi–O layers. The third process is over the temperature region from 91 K to 77 K. The profile of the (040) diffraction is obviously broadened and the Kα1 and Kα2 lines can hardly be characterized. This suggests that below the temperature of 91 K the lattice distortion becomes very serious and the fundamental lattice becomes imperfect again. Meanwhile, the profiles of the satellite reflections (040m) ($m = \pm1, \pm2$) are still doublets and the Kα1 and Kα2 lines can be characterized clearly. This shows that the modulation structure is still perfect. To sum up, the profile of the fundamental reflection (040) has undergone three changes and the profiles of satellite reflections (040m) ($m = \pm1, \pm2$) have undergone two changes as the temperature is decreased from room temperature to 77 K. Below the temperature of 91 K, the (040) diffraction peak obviously begins to broaden.

Figure 5 shows the XRD patterns of the (400) reflection at different temperatures. From

the XRD patterns, it is found that the (400) peak splits into a triplet in the temperature region from 226 K to 156 K. The (400) peak is obviously broadened at 176 K, which indicates that a transition happens in the crystal structure of $Bi_2Sr_2CaCu_2O_y$ during the process of the temperature change. Below the temperature of 156 K, the profile recombines into a doublet. Moreover, the intensity has undergone a variation from low to high and then to low.

From the results obtained in the experiment, it can be concluded that the crystal has undergone three processes of structural transition above the superconducting transition temperature T_c along the b direction in the temperature regions from 262 K to 222 K, 222 K to 91 K and 91 K to 77 K and one structural transition along the a direction in the temperature region from 226 K to 156 K. We find that the temperature of the splitting and recombination of the profiles just coincides with the one of the anomalous changes for the Bi-based superconductors observed by internal friction [8], positron annihilation [13] and specific heat [16]. This indicates that the anomalous changes are directly related to the profile changes of XRD diffraction, but not the changes of the lattice constants. In figures 4 and 5, the profiles are broadened before they are split, which shows that the single crystal has undergone large structural adjustments. We note that with decreasing temperature, the lattice thermal contraction may cause an atomic displacement. As a result, atomic inhomogenous distribution appears in the crystal structure and causes the splitting and recombination of the profile. Because there is no lattice change along the c direction, it is shown that the structural transitions mainly happen in the ab plane, and can be attributed to the atomic displacement. The structural transition is a phase transition of atomic displacement and lattice distortion. Besides, the broadened profile of the fundamental (040) diffraction appearing at 91 K reveals that the structural transition of the temperature near the superconducting transition temperature is a structural distortion.

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