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A new aspect of the structural modulation in crystal $Bi_2Sr_2CaCu_2O_y$

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Abstract. Scans by means of x-ray diffraction of both the fundamental and the modulation-related reflections in the b^*c^* reciprocal plane were carried out for a highly oriented $Bi_2Sr_2CaCu_2O_y$ crystal with sufficiently small intrinsic mosaicity. In addition to the satellites, modulation-related additional reflections which are incompatible with the generally accepted $Bbmb$ symmetry were recorded for up to the second order. For the first time, it was found that, for this high-quality single crystal, the position distribution of the modulation-related reflections arranged around each fundamental reflection could not be translated between the $00l$ (l even, from two to 30) and the $0k0$ (k even, from zero to six) Bragg reflections, if the weak additional reflections were taken into account. We suggest that there may exist different extinction rules on the b^* and c^* axes for the modulation-related additional reflections.

1. Introduction

It is well known that due to the micaceous growth habit, $Bi_2Sr_2CaCu_2O_y$ crystals usually exhibit intergrowth defects, twins and more frequently considerable mosaic spread. Existence of these defects has compounded the studies on characterizing the real structure as well as probing the intrinsic physical properties of this compound. It is generally accepted that $Bi_2Sr_2CaCu_2O_y$ has an average crystal structure of $Bbmb$ symmetry with $a \approx b = 5.4$ Å and $c = 30.8$ Å, and it is also noted that this compound has an incommensurate modulation described usually by a wavevector $\boldsymbol{q}^* = \delta \boldsymbol{b}^* + \boldsymbol{c}^*$ ($\delta \approx 0.21$) [1–4]. Due to the existence of the superstructure, though great effort has been devoted in the past several years, a consensus on the intensity distribution of the modulation-related reflections arranged around the Bragg reflections has not been reached, since additional reflections incompatible with the $Bbmb$ Bravais lattice were frequently observed in many diffraction patterns [5–13]. Whether the modulation-related additional reflections are intrinsic to the $Bi_2Sr_2CaCu_2O_y$ crystals or not and, if the answer is affirmative, their features in the reciprocal space have been the most controversial points. These points may originate from the following factors: first, $Bi_2Sr_2CaCu_2O_y$ crystal samples with different quality have been used [12]; second, different areas in the b^*c^* reciprocal plane have been focused on by different researchers, such as the position distribution of the modulation-related reflections centred around the $00l$ or the $0k0$ fundamental reflections [8, 12, 13]. In this paper, by using

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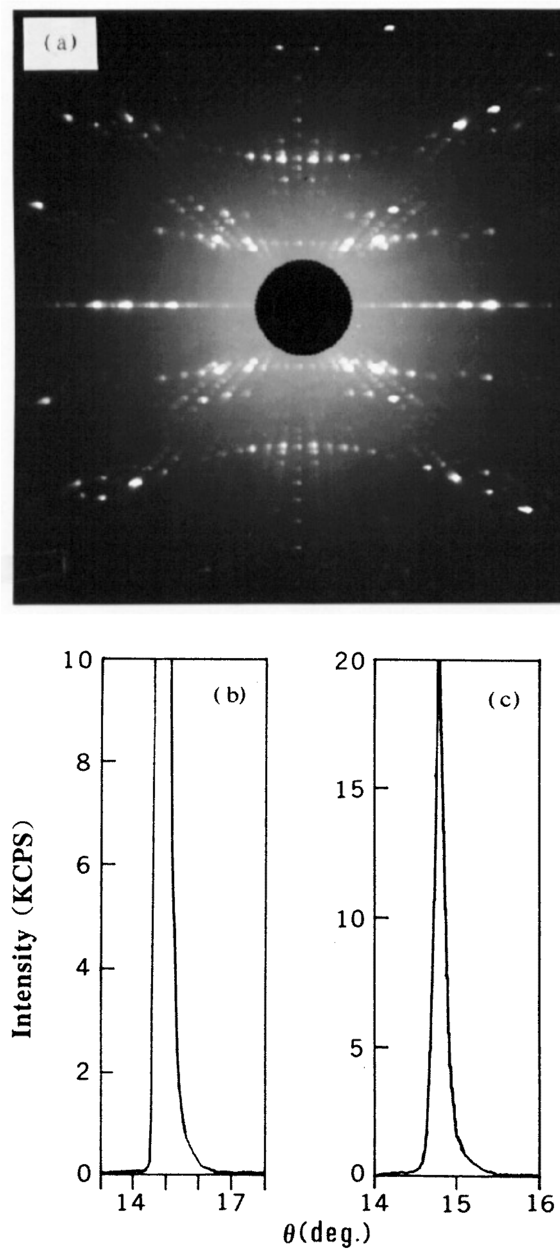

Figure 1. An x-ray back-reflection Laue photograph (a) and x-ray θ-scan RCs of the $00\underline{10}$ fundamental reflection of the $Bi_2Sr_2CaCu_2O_y$ crystal sheet to be used. The curve (b) or (c) is recorded with 40 kV voltage and 50 mA current or 20 kV and 10 mA applied to the x-ray rotating anode.

a highly oriented $Bi_2Sr_2CaCu_2O_y$ crystal sheet of sufficiently small intrinsic mosaicity, relatively comprehensive x-ray diffraction scans of the modulation-related reflections near both the $00l$ and the $0k0$ fundamental reflections have been conducted. The appearance and

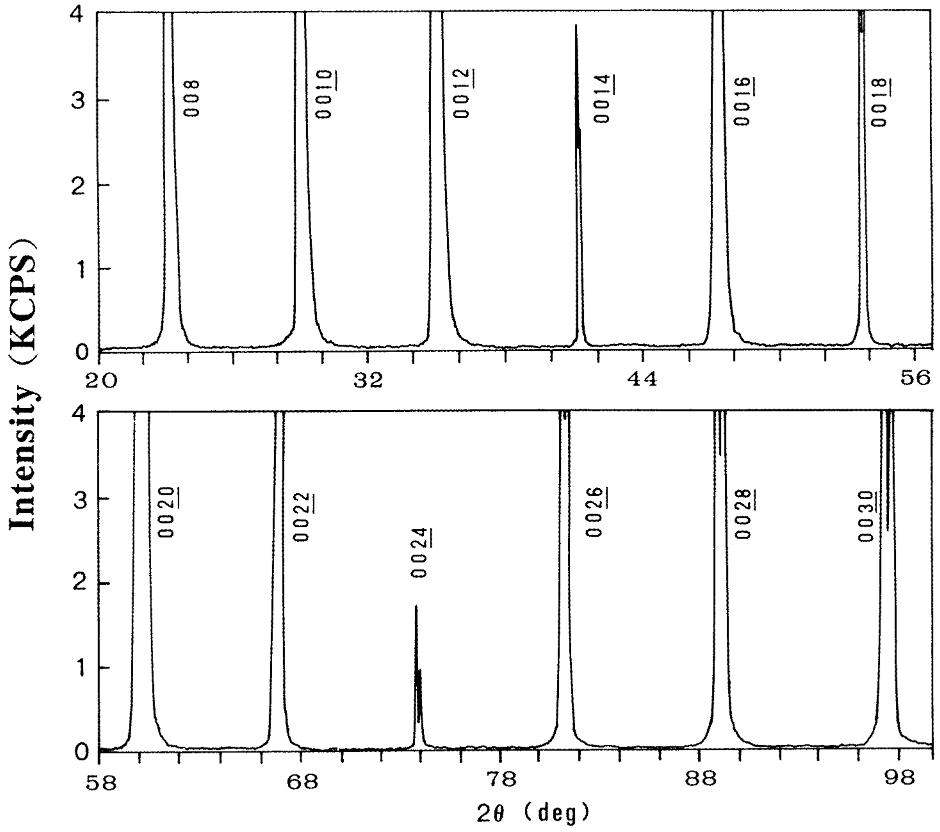

Figure 2. An x-ray l scan of the $00l$ fundamental reflections.

broadening along the c^* direction of the modulation-related additional reflections has been confirmed and a new feature of these reflections has been clearly observed.

2. Experimental details

The growth of the $Bi_2Sr_2CaCu_2O_y$ single crystal has been described in detail elsewhere [14]. The selected crystal sheet to be used in this experiment, with dimensions of $2 \times 1 \times 0.02$ mm^3 ($a \times b \times c$), was found to be superconductive at 83 K. X-ray diffraction studies were performed on a high-resolution rotating-anode diffractometer (D/max-γA, Rigaku) with graphite-monochromatized Cu Kα radiation. For the x-ray diffraction measured in transmission [15], a divergence slit (DS) of $1/6°$ was used. All the diffraction data were collected by carefully adjusting the b^*c^* plane of the crystal right into the x-ray scattering plane. The back-reflection Laue photograph of the crystal was taken by an x-ray source of Cu radiation with point focus, a distance between the sample and the film of 30 mm and the incident beam along the c axis of the single crystal.

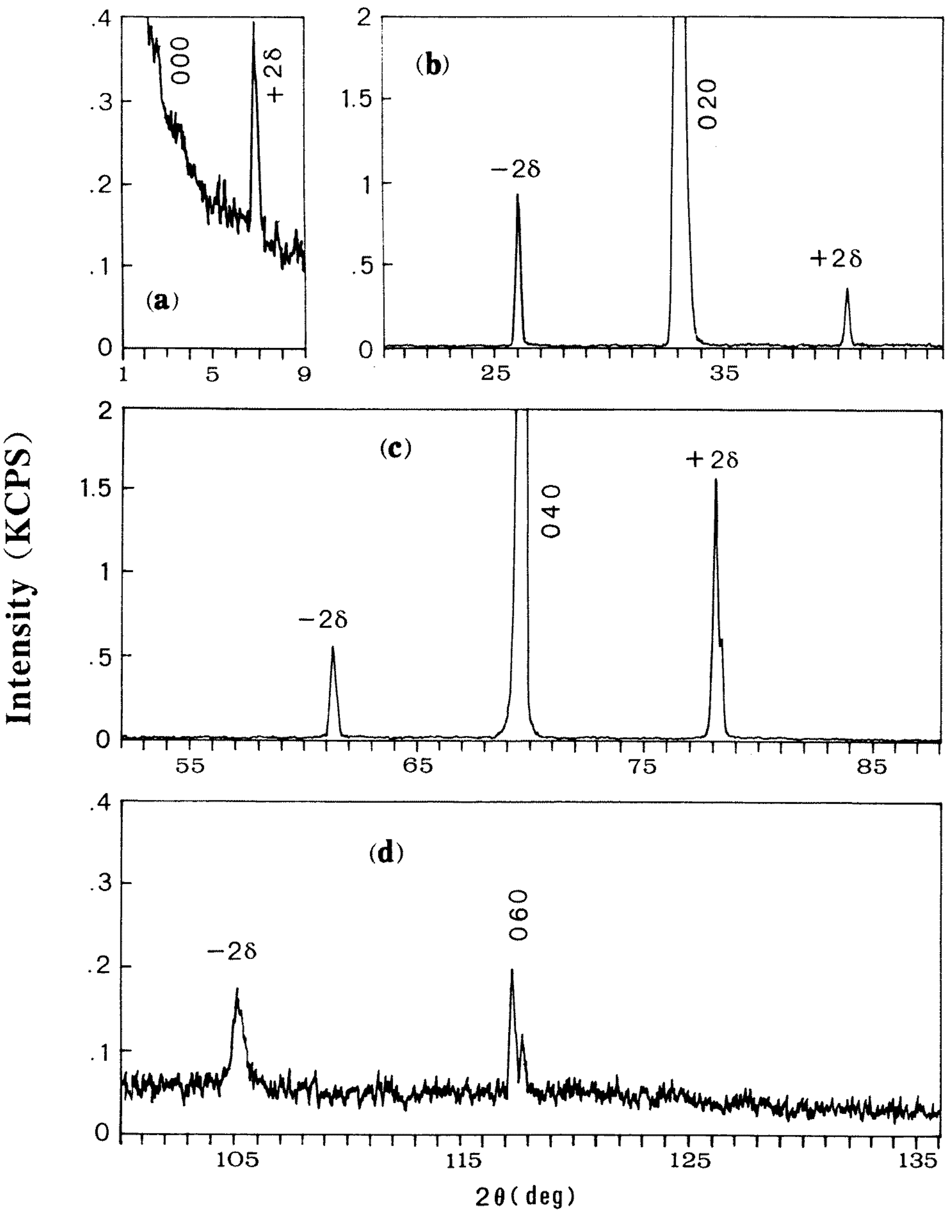

Figure 3. X-ray k scans of the 000 (a), (020) (b), 040 (c) and 060 (d) reflections; $+2\delta$ or -2δ indicates one of the second-order satellites of each main reflection.

3. Results and discussion

Figure 1 shows the x-ray Laue back-reflection photograph (a) and the x-ray θ-scan rocking curves (RCs) of the $00\underline{10}$ fundamental reflection (b, c) of the selected single-crystal sheet. Figure 1(b) was collected with higher power applied to the x-ray rotating anode compared with (c). From figure 1, it is certain the crystal sheet is highly oriented with only one large

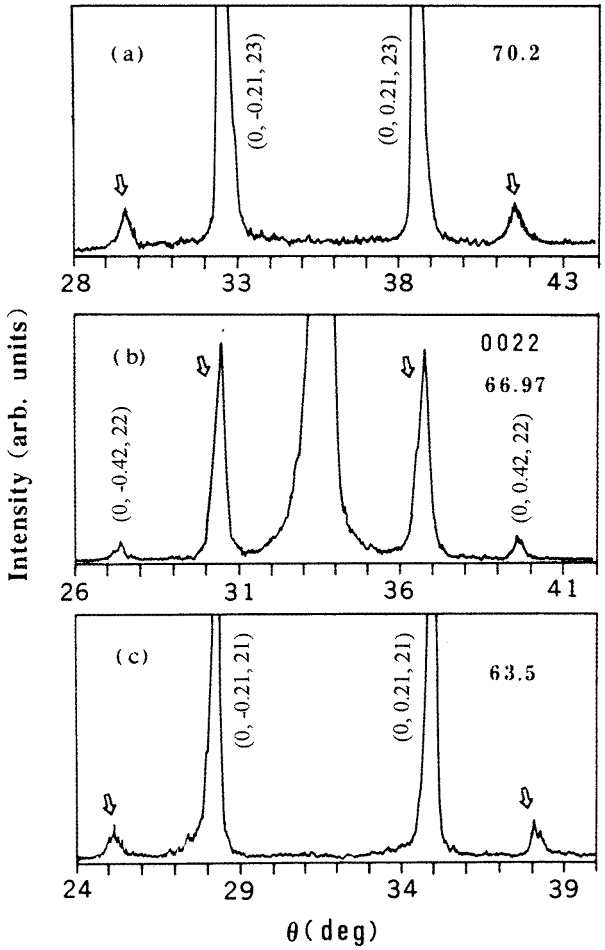

Figure 4. X-ray θ-scan RCs measured in reflection with the fixed Bragg angle as indicated in each panel: 70.2° (a), 66.97° (b) and 63.5° (c). Apart from the satellites (indexed) near the 00$\underline{22}$ Bragg reflection, additional reflections incompatible with the *Bbmb* symmetry were recorded and are indicated by open arrows.

single block. The full width at half maximum (FWHM) shown in figure 1(c) indicates the crystal is of sufficiently small intrinsic mosaicity, of about 0.15°.

Figure 2 is an x-ray l scan of the 00l fundamental reflections. It was noted that only reflections with even l appeared in the diffraction pattern. All the odd reflections violating the *Bbmb* symmetry and frequently observed for relatively poorly oriented $Bi_1Sr_2CaCu_2O_y$ crystals are systematically absent from this diffraction pattern [12] and this is also true for the reflections shown in Bragg angles between 3 and 20° and 100 and 140°, which have been omitted from figure 2. Double peaks appearing at high Bragg angles for each reflection were attributed to the Cu Kα_1 and Cu Kα_2 splitting. The pattern shown in figure 2 is in good agreement with the results presented by Johnson *et al* [12] for their good quality sample and confirms that only the even reflections in the 00l scan are fundamental to the $Bi_2Sr_2CaCu_2O_y$ crystals.

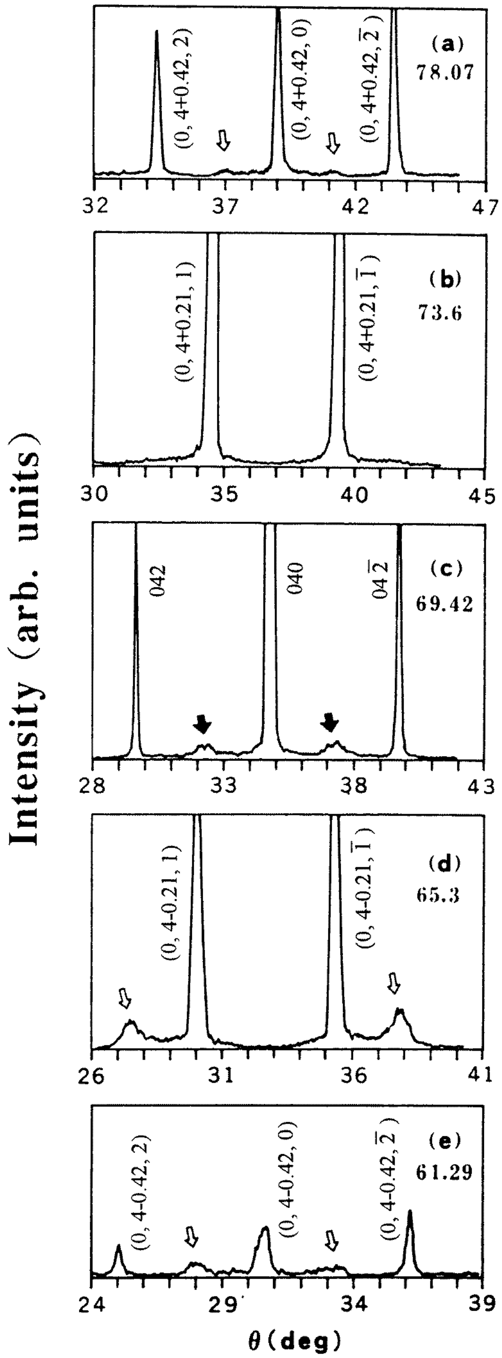

Figure 5. X-ray θ-scan RCs measured in transmission for a map of reflections near 040. Each curve was collected with the fixed Bragg angle as shown in each panel: 78.07° (a), 73.6° (b), 69.42° (c), 65.3° (d) and 61.29° (e). The Bragg reflection and the satellites compatible with the *Bbmb* symmetry are indexed and the additional reflections are denoted by arrows.

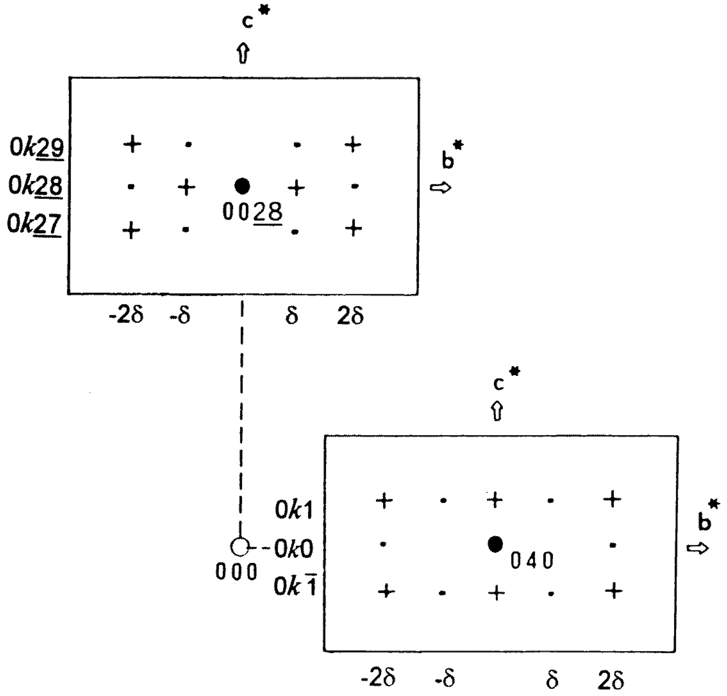

Figure 6. A schematic position distribution of reflections centred around the 00l and 0k0 Bragg reflections and within one unit cell in the b^*c^* reciprocal plane. Additional reflections scanned at the forbidden positions are indicated with '+' and the satellites are denoted by '·'.

Figure 3 gives x-ray k scans of the 0k0 fundamental reflections measured in transmission. Satellites near each fundamental reflection (indexed with $k = 0, 2, 4$ and 6) and residing on the b^* axis were also recorded and indicated by $+2\delta$ and -2δ according to Fischer *et al* [8]. Reflections shown in figure 3(a) and (d) were recorded for the first time, to our knowledge. The x-ray diffraction pattern shown in each panel confirms that the modulation-related additional reflections residing on the b^* axis, which could be indexed as $(0, k\pm\delta, 0)$, are absent and therefore are not intrinsic to the $Bi_2Sr_2CaCu_2O_y$ structure [8, 13].

Patterns shown in figure 4 are a set of x-ray θ-scan RCs measured in reflection with the 2θ angles fixed at 70.2, 66.97 and 63.5°. These have detected the position distribution of reflections centred around the $00\underline{22}$ fundamental reflection. Each curve was recorded almost parallel to the b^* direction. It is found that apart from the reflections which have been indexed according to the B-centred Bravais lattice and the matching satellites with wavevector $\boldsymbol{q}^* = \delta\boldsymbol{b}^* + \boldsymbol{c}^*$, modulation-related additional reflections also appeared and are denoted by open arrows. Reflections near some other 00l main reflections showed almost the same patterns. The position distribution of the modulation-related reflections near $00\underline{22}$ reflected by figure 4 is very similar to that near $00\underline{20}$ observed by Johnson *et al* for their good quality sample and confirms that the additional reflections around the 00l Bragg reflections are intrinsic to the $Bi_2Sr_2CaCu_2O_y$ crystals.

To give a full description of the additional reflections, the position distribution of the modulation-related reflections near the 0k0 Bragg reflections has also been scanned. Figure 5 is also a set of x-ray θ-scan RCs measured in transmission with the Bragg angles fixed at the values indicated in each panel. Each curve was recorded almost parallel to the c^* axis. This figure has mapped the position distribution of reflections centred around the 040 fundamental reflection. All the weak reflections denoted by the open and solid arrows are the additional reflections and the other peaks (indexed) shown in the patterns are compatible with the *Bbmb* Bravais lattice symmetry. It is clear that all the modulation-related additional reflections are broadened along the c^* direction, which was also observed by other authors [5, 9, 11]. In figure 5(c), the three strong peaks are the Bragg reflections and can be indexed as 042, 040 and $04\bar{2}$ from left to right. The two weak spots denoted by the solid arrows possibly also result from the superstructure and could be considered as modulation-related additional reflections, since they are weak and diffuse along the c^* direction. Figure 5 further confirms that the additional reflections on the b^* axis $(0, 4 \pm 0.21, 0)$ are absent.

According to the results presented in figures 2–5, the satellites and the modulation-related additional reflections centred around each $00l$ or $0k0$ (l, k, even numbers) Bragg reflection, within a unit cell in reciprocal space, are typically shown by the position distribution of reflections near the $00\underline{28}$ or 040 main reflection presented in figure 6. In the figure, it is surprisingly found that the distribution of these modulation-relatted reflections near the $00l$ and $0k0$ fundamental reflections cannot be translated into each other, if the weak additional modulation-related reflections (denoted by '+') are taken into account. The *Bbmb* matching sattellites are indicated by '·'. This strongly suggests that there may exist different extinction rules for the modulation-related reflections on the two different axes. Clarification of this new feature is surely indispensable to further understand the nature of the additional reflections in the $Bi_2Sr_2CaCu_2O_y$ compound.

4. Conclusions

In summary, high-resolution x-ray diffraction measurements of the position distribution near both the $00l$ and $0k0$ Bragg reflections in the b^*c^* reciprocal plane have been performed on a high-quality $Bi_2Sr_2CaCu_2O_y$ crystal sheet. This confirmed that the presence of modulation-related additional reflections is intrinsic to the $Bi_2Sr_2CaCu_2O_y$ bulk crystals. Aside from the broadening solely along the c^* direction, a new feature of the modulation-related additional reflections has been observed, which suggests that the distinction rules for the modulation-related additional reflections on the b^* and c^* axes may be different.

Acknowledgments

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