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A study of $Bi_2Sr_2CaCu_2O_\delta$ superconducting crystals by diffuse scattering measurement

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Abstract. Although the crystal structures of the Bi-based high-T_c superconductor, which is distinguished by incommensurate modulations, were solved several years ago, their implications for superconductivity are as yet uncertain. This indicates that the deviation from the average structure also should be considered; this may play an important role in the superconductivity. For this purpose the contour maps of the scattering intensity in the b^*–c^* plane for $Bi_2Sr_2CaCu_2O_\delta$ single crystals have been observed by both ordinary x-ray and synchrotron radiation. The characteristic feature was obtained in the experiments; that is, the intensity distribution around both the Bragg reflection and its satellites show a strong asymmetry. Both of them are elongated along the c axis, especially the satellites, connecting each other and almost forming a rod shape, which reveals the origin of the presence of the incompatible satellite reflections. This indicates that the structure has a strong two-dimensional feature, which is coincident with the two-dimensional characteristics of physical transportation. Our observation also confirms the previous results that the modulated wavevector is $\boldsymbol{q} = q_2\boldsymbol{b}^* + \boldsymbol{c}^*$ ($q_2 = 2.0 \sim 2.1$).

1. Introduction

Since the observation of superconductivity at 20 K by Michel *et al* for the BiSrCuO system [1], it has been identified that there are three Bi-based cuprates with the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ with $n = 1$, 2 and 3, T_c being 10, 85 and 110 K [2], respectively. These three crystal structures are basically similar. The perovskite-related slabs $SrO(CuO_2Ca)_{n-1}CuO_2SrO$ with different numbers of CuO_2Ca slabs stacked along the c axis are separated by BiO double layers. The c parameters are about 24.6, 30.8 and 37.1 Å for $n = 1$, 2 and 3 respectively. All three Bi phases possess an incommensurate modulation along the b axis ($b \approx 5.4$ Å) with a period $\sim 4.72b$. Among these three Bi-based cuprates, the $Bi_2Sr_2CaCu_2O_\delta$ superconductor has attracted much attention because of two factors: compared with the $Bi_2Sr_2Ca_2Cu_3O_y$ superconductor its structure is more stable, and its superconducting transition temperature T_c is above liquid nitrogen temperature. There have been a number of studies on the average structure. Tarascon *et al* [3] have determined the three-dimensional structure of a $Bi_4(Sr, Ca)_6Cu_4O_{16+x}$ single crystal by x-ray diffraction. Kan and Moss [4] and Petricek *et al* [5] have determined the crystal structure of nominal composition $Bi_2Sr_2CaCu_2O_\delta$ with the aid of four-dimensional analysis. Now the crystal structure of $Bi_2Sr_2CaCu_2O_\delta$ including modulation structure is well established. In general,

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it is believed that the incommensurate modulation structure, which is one of the characteristic structural features, is formed by the periodic arrangement of Bi-concentrated bands in the BiO layers. However, to date, the implications of the structure for superconductivity are uncertain.

On the other hand, experimental results of ultrasonic [6, 7], internal friction [8, 9], positron annihilation [10, 11] and specific heat [12, 13] measurements have shown that there are anomalous changes, deviations from the expected values, when the temperature decreases. Phillips [14] pointed out that these anomalies can be largely explained when account is taken of the real material properties of the cuprates and other new oxide superconductors. Furthermore, dramatic differences in the intrinsic flux pinning of the various compounds also suggests that the crystal structure, including both the 'ideal' features of the structure and the presence of defects, can play an important role. When exploring the origin of high T_c, the deviation from the average structure also should be considered. In fact, in the normal state the resistivity measurement shows a strongly two-dimensional feature, i.e. the measured resistivity along the c axis $\rho_c(T)$ is generally 10^2–10^3 times larger than $\rho_{ab}(T)$, and shows a semiconductive temperature dependence ($\mathrm{d}\rho/\mathrm{d}T < 0$) [15]. In the $Bi_2Sr_2CaCu_2O_\delta$ system, it has been shown [16, 17] that a Kosteritz–Thouless (KT) type transition, manifested by the spontaneous creation of thermally induced free vortex–antivortex pairs, occurs just below T_c, confirming this system to be of two-dimensional type over a large temperature range. In our previous papers, it was revealed [18, 19] that the $Bi_2Sr_2CaCu_2O_\delta$ single crystal is a stacking layer structure with a two-dimensional lattice by the study of the x-ray diffraction patterns using both Laue photography and the crystal rotation method. For further study of the structural characteristic feature and the deviation from the average structure, in this paper, the contour maps of the scattering intensity in the b^*–c^* plane for $Bi_2Sr_2CaCu_2O_\delta$ single crystal were observed by both ordinary x-ray and synchrotron radiation.

2. Experimental details

Single crystals of $Bi_2Sr_2CaCu_2O_\delta$ phase were grown from Bi-rich melts by a normal directional solidification method with the atomic ratio 2.4 Bi : 2.0 Sr : 1.0 Ca : 20 Cu. The a.c. susceptibility measurements showed that the superconducting transition temperatures of the specimens are $T_c \sim 81$ K and transition width $\Delta T_c \sim 1.5$ K. After careful examination by x-ray Laue photography, several perfect single crystals with different sizes were selected for the diffuse scattering analysis of the ordinary x-ray and synchrotron radiations.

Although the synchrotron radiation can give high intensity, high resolution and more information about the detail of the structure, there is a possibility of damaging the sample during the experiment. Ensuring the correction of the results, an ordinary x-ray diffractometer was used. The ordinary x-ray and synchrotron radiation measurements were carried out for several crystal on a Rigaku four-circle diffractometer (AFC-5) with a rotating-anode x-ray generator (RU-200), Cu Kα radiation with a graphite monochromator ($\lambda = 1.5405$ Å), and at the BL-10A station in the Photon Factory, KEK, with $\lambda = 1.04611$ Å, respectively. In this work, the two results coincide well. The unit cell obtained by a least-squares fit from 18 centred reflections in the ordinary x-ray four-circle diffractometer shows the single crystal belongs to the orthorhombic system with lattice parameters $a = 5.417(1)$, $b = 5.410(1)$, and $c = 30.883(8)$ Å. The contour maps of the scattering intensity were obtained by a diffuse-scattering-measurement (DSM) technique. In the technique, a sample can be aligned on the diffractometer in Bragg reflection geometry with its special reciprocal plane by four-circle equipment, and a linear scan along an axis can be performed by

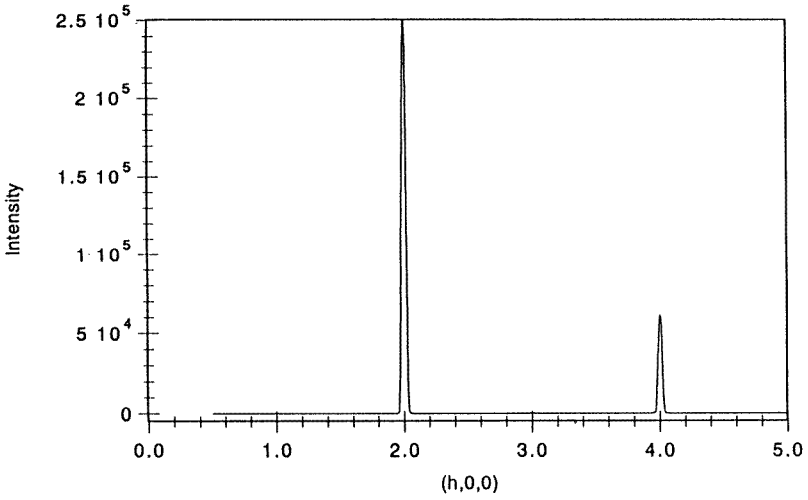
measuring the intensity step by step. It is therefore possible to map out the intensity distribution of the scattered x-rays in an area of reciprocal space by grid scan. For the ordinary x-ray diffraction, horizontal and vertical receiving divergent slits of $1/2^\circ$ were used. All the measurements were made at room temperature (293 K).

3. Results and discussion

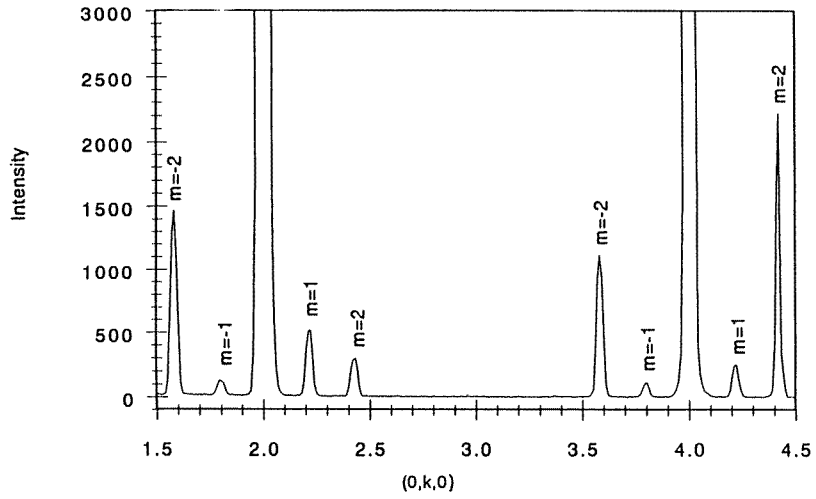
The ordinary x-ray diffraction patterns along each axis direction of the crystal, which coincide with previous reports [20, 21], are illustrated in figure 1. The first- and second-order satellites can be identified in figure 1(b) and (c), which give the wavevector along the b^* direction a $q_b = 0.21$. This corresponds in real space to a period $1/0.21 \approx 4.76b$, or 25.8 Å. It is known that the single crystal of the $Bi_2Sr_2CaCu_2O_\delta$ phase belongs to the orthorhombic system with space group N_{111}^{Bb2b} [4]. According to the extinction rule of the space group, it can be found that the first-order (see figure 1(b)) and second-order (see figure 1(c)) satellites appear at 'unallowed' positions ($h + 1 + m =$ odd). It is believed that the incommensurate wavevector $\boldsymbol{q}$ which describes the position of the satellites varies slightly between samples due to the differences in thermal processing during growth. On the other hand, Kan and Moss [4] suggested another two reasons: one is a randomness in the phase modulation wave from layer to layer with a small deviation from 1.0 of the c^* component of the modulation wavevector and the other is small c axis transverse-zone boundary displacements (in the b direction) of the basic structure weakly correlated along c. In this work, it is suggested that the presence of the incompatible satellite reflections is caused by the diffuse scattering along the c direction, which shows the intrinsic two-dimensional structural feature of the $Bi_2Sr_2CaCu_2O_\delta$ phase (the reason will be shown in context below). Instead of layer to layer, the randomness in the phase modulation is from block to block with a small deviation from 1.0 of the c^* component of the modulation wavevector and displacement of the basic structure along the b direction. Each block, which may be formed by several, or several tens of atomic layers along the c direction of the crystal, is a perfect three-dimensional crystal.

Figure 2 gives the contour map of the scattering intensity in the b^*–c^* plane around the (040) Bragg reflection, which was obtained by synchrotron radiation, of one $Bi_2Sr_2CaCu_2O_\delta$ single crystal. Several noticeable features are found in figure 2. First, the centre positions of the first- and second-order satellites are located at the incommensurate $\boldsymbol{q} = q_2\boldsymbol{b}^* + \boldsymbol{c}^*$ positions ($q_2 = 2.0 \sim 2.1$). Second, the intensity distribution around both the Bragg reflection and its satellites shows a strong asymmetry. Both of them are elongated along the c-axis direction, especially the first-order satellites, connecting each other and almost forming a rod shape. Third, comparing the Bragg reflection, the satellites are obviously broadened along the b-axis direction. These results have also been observed by ordinary x-ray diffraction with several other single crystals. Except a small change in the length of the rod along the c-axis direction, the results have been well confirmed. From figure 2, it can be easily found that the satellites that appeared at 'unallowed' positions in figure 1(b) and (c) are caused by the diffuse scattering of the satellites at 'allowed' positions along the c-axis direction. The crystal extinction condition still coincides with the space group N_{111}^{Bb2b} i.e. the symmetry of the average crystal structure still belongs to the space group N_{111}^{Bb2b}.

The rod-shaped intensity distribution indicates the existence of two-dimensional structure in the $Bi_2Sr_2CaCu_2O_\delta$ single crystal [18]. In other words, there may be stacking layer defects which destroy the c period. Careful checking shows that the length of the rod for Bragg reflection is finite (in figure 2 the length is about $\Delta l \approx 0.76$), which reveals that the stacking layer defects appear every few layers, instead of from layer to layer. This



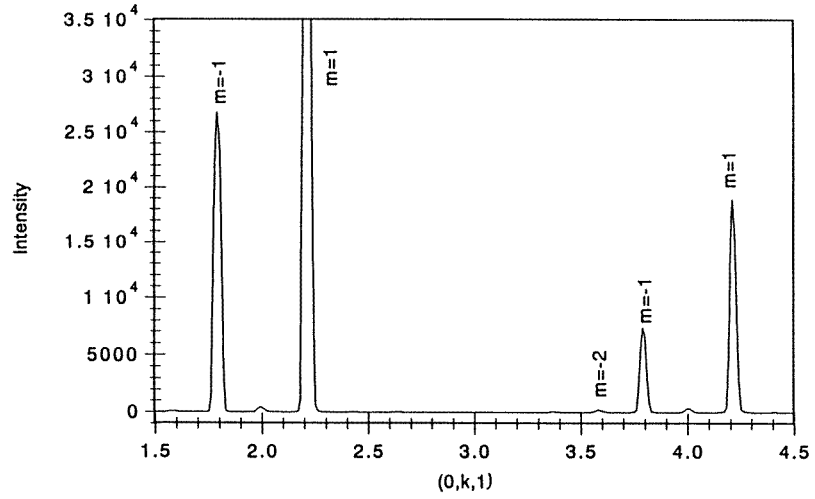
(a)



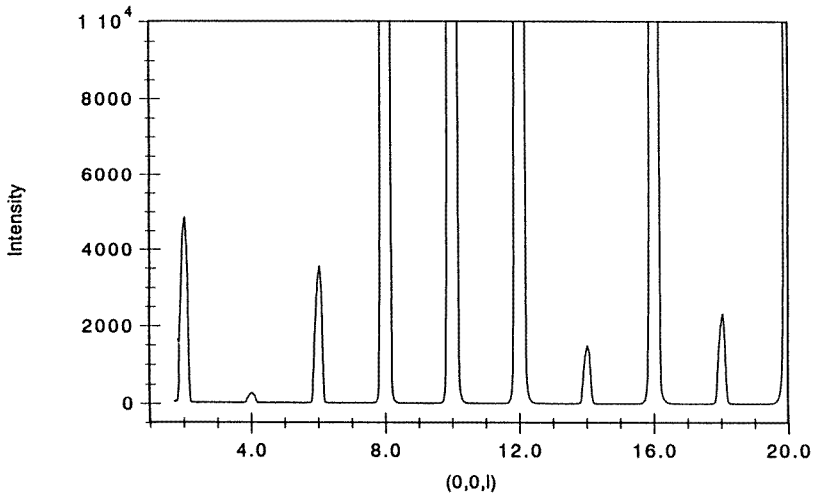
(b)

Figure 1. Linear scans of (a) $(h, 0, 0)$; (b) $(0, k, 0)$; (c) $(0, k, l)$ and (d) $(0, 0, 1)$ with a scanning step $\Delta h = 0.01$, $\Delta k = 0.01$, $\Delta l = 0.01$ and a count-timer constant of 2 s.

can be explained by a two-component system, or composite crystal [22]. In the composite crystal, there are at least two components with interpenetrating but distinct lattices. Since the two lattices coexist in the same crystal, there is a mutual interaction which corresponds to a perturbing potential with the periodicity of the other sublattice. The perturbation causes each of the sublattices to be modulated with a repeat of the perturbing potential, which is a translation period of the second sublattice. As a result, the diffraction pattern of a composite crystal is the superposition of the diffraction patterns of the two sublattices, plus satellite reflections representing the modulations [23, 24]. It is well known that in $Bi_2Sr_2CaCu_2O_\delta$ single crystal the c period is formed by the interval arrangement of two layer components,



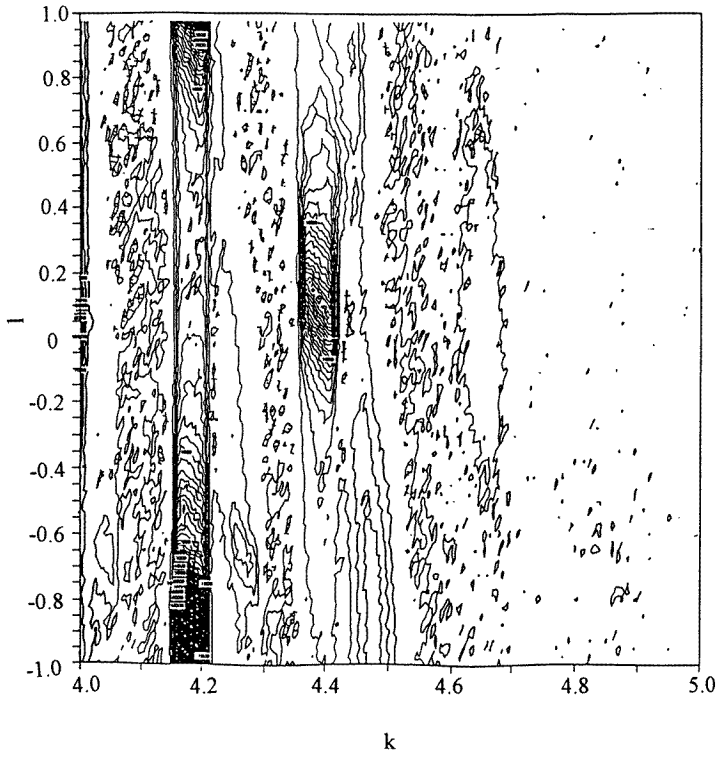
(c)



(d)

Figure 1. (Continued)

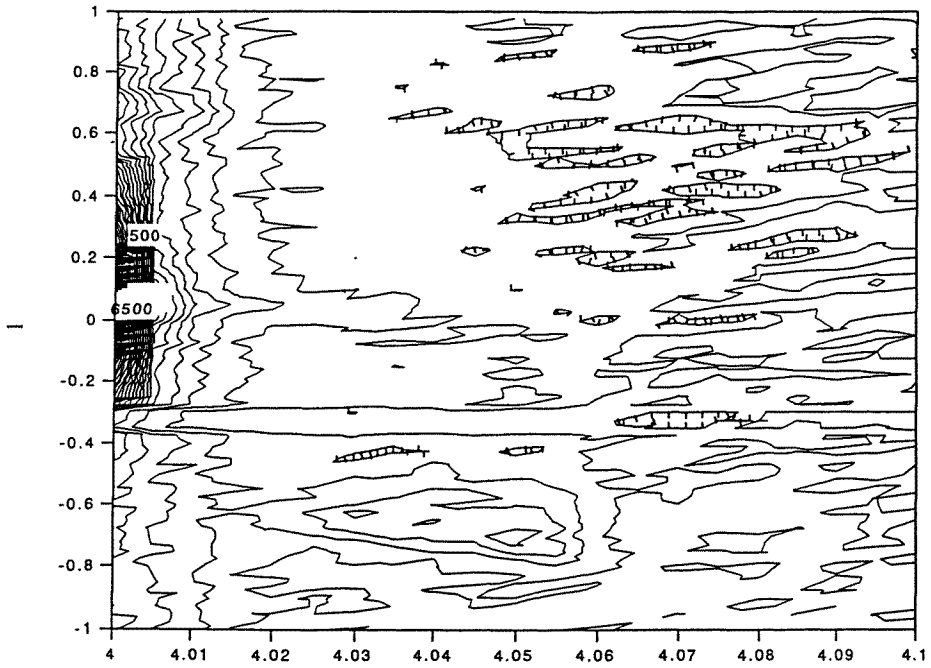
Bi–O layers and the perovskite-related slabs (Sr–Cu–Ca–Cu–Sr). Each layer, or slab, has its own lattice, and the two lattices coexist in the same crystal. In general, it is believed that the perovskite-related slab is stiffer than the Bi–O layers. The weaker Bi–O layers undergo a large modulation to accommodate the structure of the perovskite-related slab. The structure of the Bi–O layers may become seriously distorted and even ill defined. Moreover, the distorted Bi–O layers may destroy the *c* period of the crystal. On the other hand, the structure of the stiff perovskite-related slab may change little and maintains a perfect two-dimensional lattice in the *a–b* plane. This is also the reason for the satellite broadening along the *b*-axis direction while the Bragg reflection shows little broadening, because the satellite reflections correspond to the 'Bi-concentrated' bands while the Bragg reflection



(a)

Figure 2. (a) An iso-intensity contour map of the synchrotron radiation measurement near the (040) peak and (b) a partial amplified contour map. Equal intensity collected on a mesh with $\Delta Q_k = 0.005$ Å^{-1}, $\Delta Q_L = 0.025$ Å^{-1} and a count-timer constant of 3 s.

corresponds to the perovskite-related slabs. Considering the three-dimensional period of the rod-shaped reflection distribution and the finite length of the rod, the crystal structure can be considered as being formed by blocks. Each block may be formed by several, or several tens of atomic layers with a perfect lattice. In figure 2, if we use the length to reduce the width of the rod-shaped Bragg-reflection spot (here we suppose that the width of the rod-shaped Bragg-reflection spot is caused by the instrument), and according to the relation of crystal space and reciprocal space, we can obtain the thickness of the block about $1.5c(\approx 45$ Å), or 21 atomic layers. Budin *et al* [25] have observed the well known intergrowth defects in Bi-based superconductors and found one type of defect concerning mainly the Bi–O sublattice in the structure. The structure of $Bi_2Sr_2CaCu_2O_\delta$ consists of a sequence of lamellae parallel to the c axis. These results indicate that the boundary of the blocks is in the Bi–O layers. The blocks are separated by the distorted Bi–O layers, and the three-dimensional period may be destroyed, and form a two-dimensional layer-like structure. Meanwhile, the layer-like block itself forms a good c period and gives a reflection along the c direction. As a result, a number of defects, such as dislocations and vacancies, will occur in the boundary of the blocks. The distribution of these defects is a periodic one, which may have a strong effect on the electronic properties both in the normal and superconductive states. It is worth mentioning that in the conventional structural determination of a single crystal the structure is



(b)

Figure 2. (Continued)

considered as an ideal three-dimensional one, and the rod-shaped intensity distribution is not considered during the data collection. Therefore, the deviation from the average structure, or the two-dimensional structural characteristic, and periodic stacking-layer defect in the $Bi_2Sr_2CaCu_2O_\delta$ single crystal will be omitted, but these structural features may be helpful for understanding the origin of the high-T_c superconductivity.

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