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Short communication

Single crystal X-ray characterization of the incommensurate modulation in the high T_c superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.

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Résumé.— Nous avons étudié la modulation incommensurable du composé $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ par diffraction des rayons X sur monocristaux. Des réflexions satellites d'ordre 1 et 2 et de vecteurs d'onde $\mathbf{q}_1 = (0, 0.211, 1)$ et $\mathbf{q}_2 = 2\mathbf{q}_1$ ont été mesurées. La modulation a une période de 25.59 Å selon b . Une analyse préliminaire des intensités des satellites indique que la modulation comporte des composantes displacives prédominantes polarisées selon b et c . Aucune évolution n'est observée à basse température. Les monocristaux présentent systématiquement une importante mosaïque.

Abstract.— We have studied the incommensurate modulation in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ by single crystal X-ray diffraction. First and second order satellite reflections with wave vectors $\mathbf{q}_1 = (0, 0.211, 1)$ and $\mathbf{q}_2 = 2\mathbf{q}_1$ have been measured. The period of the modulation along b is 25.59 Å. A preliminary analysis of the satellite intensities indicates that the modulation involves strong displacive components polarized along b and c . No low-temperature changes have been observed. The single crystals exhibit a large systematic mosaicity.

Since the discovery of the bismuth based high T_c superconductors Bi–Sr–Cu–O [1] and Bi–Sr–Cu–O [2, 3, 4] a number of electron diffraction studies have revealed the existence of a basic subcell with supplementary superstructure or modulation effects [5–8]. Although high resolution electron microscopy (HREM) imaging has been able to give a deep insight into the nature of the incommensurate modulation in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [5–8], X-ray studies can provide complementary information from macroscopic single crystals. In this paper we

report on the photographic and diffractometer study of single crystals of nominal composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. First and second order satellite reflections have been measured and their intensity distribution indicates that the modulation is essentially displacive with displacements in the (b, c) plane. No detectable changes are observed upon cooling to 13 K.

The samples were prepared from a mixture of Bi_2O_3 , SrCO_3 , CaCO_3 and CuO in the

cation ratio 2:2:1:2, fired in a platinum crucible at 900°C for 2 hours, cooled to 800°C at a rate of 5°C/hour and finally furnace-cooled to room temperature. Single crystals separated from the melt were found to be superconductors with zero resistance at 90 K [9]. No chemical analysis was performed.

Results and discussion.

Several plate-like crystals suitable for X-ray diffraction were selected (less than 0.1 mm thick). Precession photographs (MoK α radiation) of various reciprocal lattice planes ($hk0$), ($h0l$), ($0kl$), (hkl) were taken. All crystals investigated (eight) showed ($hk0$) and ($0kl$) diffraction patterns similar to those of figure 1. They can be indexed using a body-centered tetragonal sublattice (cell parameters $a = b = 3.82 \text{ \AA}$, $c = 30.8 \text{ \AA}$). This c parameter agrees with that of the Bi $_2$ Sr $_2$ CaCu $_2$ O $_8$ compound built from double CuO $_2$ sheets. To comply with the current use and the possible existence of a small orthorhombic distortion we shall use an equivalent face-centered unit cell with $a = b = 5.40 \text{ \AA}$, $c = 30.8 \text{ \AA}$ (rotated by 45° with respect to the small unit cell). Furthermore the photographs of figure 1 reveal additional satellite reflections which are incommensurate in the (a^* , b^*) plane. Actually they can be divided into two sets of satellite reflections defined by wave-vectors of the type $\mathbf{q}_1 = (0, 0.21, 1)$ and $\mathbf{q}_2 = (0.21, 0, 1)$ respectively. The origin of the two sets of satellite reflections resides in the existence of domains where the modulation runs along either a or b directions. This is substantiated by (i) variations in the relative intensities of the two sets of satellite reflections for different crystals, (ii) the observation of single domains by electron diffraction [5 – 8], (iii) the observation of twin domains and twist boundaries by high resolution electron microscopy [7, 8, 10]. It is therefore sufficient to consider a single direction of modulation with for instance $\mathbf{q}_1 = (0, 0.21, 1)$. A large number of first-order, several second-order and some third-order satellite reflections are visible in the highly-exposed photographs of figure 1. Actually some of the apparent first-order satellite reflections in the ($h, k, 0$) pattern (Fig. 1a) are due to contamination from the $l = \pm 1$ layers because of the large mosaic spread of the crystal. This effect is clearly seen in the ($0, k, l$) pattern (Fig. 1b) and it appears to be systematic and

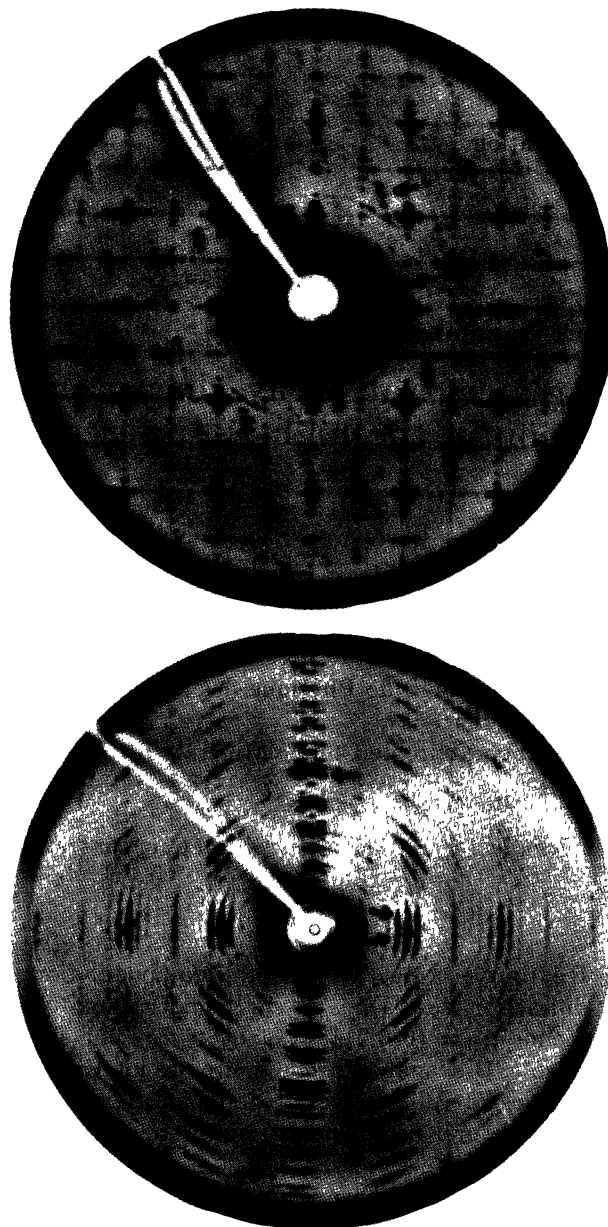


Fig. 1.— (a) ($h, k, 0$) precession photograph (MoK α , precession angle 25°, 50 kV, 150 mA, exposure time 15 hrs). Arrows point to additional reflections from a second crystal. Some satellite and main reflections are located in upper and lower layers but are visible because of a large mosaic spread ; (b) ($h, 0, l$) precession photograph. The upper and lower halves correspond primarily to reflection by the upper and lower faces of the crystal because of the strong absorption. The arrows point to satellites of the ($0, 0, l$) reflections. Same experimental conditions as in (a).

intrinsic for macroscopic crystals of typical size $0.5 \times 0.5 \times 0.1 \text{ mm}^3$. Moreover this mosaic spread, which amounts to several degrees, is probably related to the fact that the two faces of the platy crystals, which have a good optical quality, are systematically not parallel to each other and

form a wedge whose angle is of the order of 6° . This accounts for the unusual $(0kl)$ pattern of figure 1b where the upper and lower halves are strikingly different. Because of the strong absorption they are produced primarily by diffraction from the "upper" and "lower" faces of the crystals. Since the crystal was oriented with respect to one of the faces, the "upper" one, then the lower part of the photograph and especially the lower $(00l)$ reflections and their accompanying satellites are misoriented. The macroscopic mosaicity is probably related to microscopic bendings of microcrystals as previously observed by electron microscopy [11].

To obtain more quantitative data about the nature of the modulation and its possible temperature dependence we then carried out a diffractometer study on one of the crystals. We used a three-circle diffractometer operated in the normal-beam, lifting detector geometry. The MoK_α radiation from a rotating-anode generator was selected by a singly-curved graphite monochromator. The sample was cooled in a closed-cycle helium refrigerator. The symmetry of the sublattice was found to be tetragonal within experimental accuracy, with lattice parameters $a = b = 5.400(5) \text{ \AA}$, $c = 30.86(2) \text{ \AA}$ at room temperature and $a = b = 5.400(5) \text{ \AA}$, $c = 30.53(2) \text{ \AA}$ at $T \simeq 13 \text{ K}$. The strong anisotropy of the thermal contraction (no measurable temperature effect in the basal plane, given our limited accuracy) reflects the weak interlayer bonding of the Bi-based compounds. Using second-order satellite reflections we could refine the incommensurate component of the modulation wave-vector which is found to be $q_b = 0.211 \pm 0.002$ (see for instance Fig. 2). This corresponds to a wavelength $\Lambda = (4.74 \pm 0.05) \times 5.400 = 25.59 \pm 0.27 \text{ \AA}$ in the b direction. There is no detectable change in the position of the satellite reflections and therefore in the value of Λ upon cooling the sample down to $T \simeq 13 \text{ K}$.

In spite of high-resolution lattice imaging by electron microscopy experiments [5–8, 11, 12] there is still no definite understanding of the nature of the incommensurate modulation and several models have been proposed. It was suggested for instance that the Bi layers are composed of alternating "Bi-concentrated bands" and "Bi-deficient bands" where, in the latter, Sr atoms replace Bi atoms [5, 6]. This can be described as a modulation of concentration.

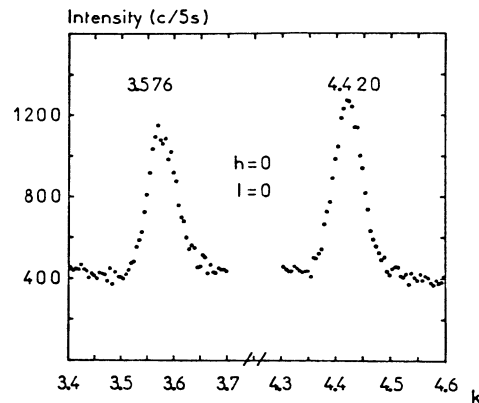


Fig. 2.— Scan of second-order satellite reflections $(0, 4 \pm 2q_b, 0)$ in the b^* direction. Several such scans were used for the determination of $q_b = 0.211 \pm 0.002$ (the position of each peak is indicated).

Furthermore, lattice distortions of large amplitude are observed in the lattice images and they take the form of modulations in the Bi-O layers along c together with tilts of the perovskite building blocks in the b direction [6, 7]. Misfits between the lattice constants of the BiO and perovskite units [12] or the presence of additional oxygen atoms in the Bi-O layers [7] were put forward to explain these effects. Our photographic data and the measurement of satellite reflection intensities in various zones and directions of reciprocal space can help distinguish between the above models.

First we note that diffractometer scans of first and second-order satellite reflections confirm that they correspond to wave vectors of the type $\mathbf{q}_1 = (0, q_b, \pm 1)$ and $\mathbf{q}_2 = 2\mathbf{q}_1$, respectively. This is shown in figure 3 for some $(0, q_b, l)$ and $(2, 2 + 2q_b, l)$ satellite reflections. The existence of this c^* component means that, in the (b, c) plane, the modulation pattern is face-centered or, in other words, there is a phase shift of π for the modulation for a translation of $c/2$. This

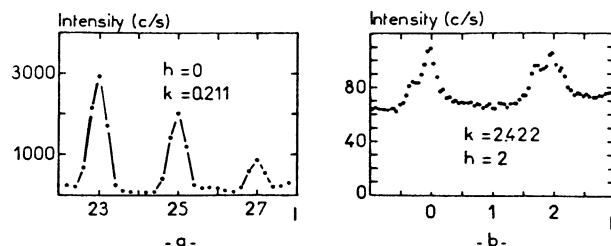


Fig. 3.— (a) Scan of first-order satellite reflections of indices $h = 0$ and $k = q_b$ in the c^* direction. Satellite reflections appear at odd l indices. (b) Scan of second-order satellite reflections of indices $h = 2$ and $k = 2 + 2q_b$ in the c^* direction. Satellite reflections appear at even l indices.

result is in agreement with the HREM images [5 – 8, 11, 12].

It is quite remarkable that satellites of the $(h, 0, 0)$ main reflections are absent or extremely weak. These satellite reflections can be expressed (h, nq_b, n) where $q_b = 0.211$ and n corresponds to the order of the satellite reflection ($\pm 1, \pm 2, \dots$). For instance, the intensity ratio of the first-order satellite to main reflection for $(2, 0, 0)$ is found to be $I(2, 0.211, \pm 1) / I(2, 0, 0) = 2 \times 10^{-3}$. In contrast, satellite reflections associated with $(0, k, 0)$ main reflections are strong and high-order ones (second and sometimes third-orders) are easily observed in figure 1a. Thus, in the case of the $(0, 2, 0)$, which is equivalent to the $(2, 0, 0)$, we obtain $I(0, 2.211, \pm 1) / I(0, 2, 0) = 0.12$. The absence or weakness of (h, nq_b, n) satellite reflections appears to rule out the existence of a modulation of concentration (such as that mentioned above for the Bi-O layers) because, in this case, the intensity of the satellite reflections would be the same around the $(h, 0, 0)$ and $(0, k, 0)$ main reflections. Actually for such a modulation the satellite intensity should be periodic in reciprocal space except for the decrease of the atomic scattering factors with $|\mathbf{q}|$. Furthermore, the absence of the $(h, nq_b, \pm n)$ satellite reflections, which is verified even for relatively large wave vectors (i.e. around the $(8, 0, 0)$ main re-

flection), indicates that the displacements have negligible components in the a direction. This can be deduced from the fact that the structure factors of satellite reflections associated with a displacement \mathbf{u} are proportional to the Bessel function $J_n(\mathbf{q} \cdot \mathbf{u})$ where \mathbf{q} is the corresponding wave vector and n is the order of the satellite (for small displacements $J_n(\mathbf{q} \cdot \mathbf{u})$ approximates to $(\mathbf{q} \cdot \mathbf{u})^n / 2^n n!$). Therefore a displacement component in a given direction gives rise to satellite reflections whose intensity is maximum when \mathbf{q} and \mathbf{u} are parallel and increases with $|\mathbf{q}|$. Accordingly, satellite reflections around the $(h, 0, 0)$ main Bragg peaks should be visible and increase in intensity with h if appreciable displacements occurred along a . We thus conclude that the displacements are primarily polarized in the (b, c) plane. This is in agreement with the HREM lattice imaging where the major lattice distortions are observed in this plane, as noted above [5, 6]. Along these lines one expects the intensity ratio of the satellite to main reflections to increase with both k and l indices. To verify this behaviour we have measured the intensity of several reflections in the b^* and c^* directions. The corresponding ratios are given in table Ia for the $(0, k, 0)$ reflections and their satellites. However these values have the same order of magnitude and thus the expected increase with k is not clearly observed. In table Ib we give the values of the measured intensi-

	$I(0, k - 0.211, -1) / I(0, k, 0)$	$I(0, k + 0.211, -1) / I(0, k, 0)$
$k = 2$	0.035	0.068
$k = 4$	0.050	0.069
$k = 6$	0.024	0.068
$k = 8$	satellite too weak	0.060

(a)

	$I(0, 0, l)$	$I(0, \pm 0.211, l - 1)$		$I(0, 0, l)$	$I(0, \pm 0.211, l - 1)$
$l = 6$	1225c/s	129c/s	$l = 18$	1145c/s	194c/s
$l = 8$	26336c/s	1026c/s	$l = 20$	26950c/s	9518c/s
$l = 10$	29225c/s	253c/s	$l = 22$	4712c/s	1414c/s
$l = 12$	32660c/s	172c/s	$l = 24$	147c/s	2733c/s
$l = 14$	300c/s	3055c/s	$l = 26$	3572c/s	1839c/s
$l = 16$	17917c/s	3776c/s	$l = 28$	4514c/s	713c/s

(b)

Table I.— (a) Ratio of the intensity of the satellite reflections $(0, k \pm q_b, -1)$ to the main reflections $(0, k, 0)$ for $k = 2, 4, 6$ and 8 . (b) Measured intensities of the main reflections $(0, 0, l)$ and the related satellite reflections $(0, \pm q_b, l - 1)$ for l running from $l = 6$ to $l = 28$.

ties (in counts/s.) for the $(0,0,l)$ main reflections and the associated satellites. First one notes large and rapid variations of the intensity of the main reflections with l which makes the comparison between main and satellite reflections difficult. Second we observe some strong satellite reflection intensities for large l values ($l = 19$ to 25) but again there is no marked and clear increase with respect to the main reflections. These observations are puzzling as they would in fact support the existence of a modulation of concentration, which was ruled out previously. Possible origins for this apparent contradiction may be found in the combined effects of (i) the complex nature of the modulation where several types of atoms (from the Bi-O layers and the perovskite-related blocks) undergo displacements with different polarizations and magnitudes and (ii) the very large amplitude of the displacements (HREM imaging suggests

that they can reach 20% of the lattice spacing [6]) which implies that the approximate expression for the Bessel functions does not hold and the exact value must be used. This means that, for instance, the intensity of first-order satellite reflections will go through a relative maximum, then decreases ($J_1(\mathbf{q}\cdot\mathbf{u})$ has a maximum for $\mathbf{q}\cdot\mathbf{u} \simeq 1.84$). It shows that a quantitative structural determination of the modulation will require a difficult and very careful study beginning with the data collection (large and apparently intrinsic mosaic spread, strong X-ray absorption, $\mu = 676 \text{ cm}^{-1}$ for $\text{MoK}\alpha$) and taking account of the combination of large displacements with a probably strong non-harmonicity.

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