RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 1 1 JULY 1988

Microstructure and properties of the ~90-K superconductor $Bi_2Sr_{3-x}Ca_xCu_2O_{8+\delta}$

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(Received 29 February 1988)

Phases with superconducting onset temperatures of 60, 87, and 112 K have been identified in the new superconductor $Bi_2Sr_{3-x}Ca_xCu_2O_{8+\delta}$. The microstructures of two crystal types, one associated with the 87- and 60-K phases, and the other probably with the 112-K phase, have been examined by electron microscopy. The first crystal type has a superlattice structure which is incommensurate for the lower-temperature preparations. The second type of crystal, which forms at higher temperatures, has no superlattice structure.

Beginning with the discovery by Bednorz and Müller[1] of a 30-K transition in $La_{2-x}Ba_xCuO_{4-\delta}$, a rapid series of advances occurred as described by the reports of Wu *et al.*,[2] Tarascon *et al.*,[3] and Zhao *et al.*[4] of an onset temperature greater than 90 K in a multiphase Y-Ba-Cu oxide. Since that exciting period, extensive advances have been made in the physics, chemistry, and applications of $YBa_2Cu_3O_{7-\delta}$, which was quickly identified as the 90-K superconducting phase.[5,6] No materials with T_c higher than around 90 K were, however, found during the last year, although reports of irreproducible higher T_c's have persisted.[7]

In addition, although structures closely related to $YBa_2Cu_3O_{7-\delta}$ were constructed,[8,9] no entirely new high-T_c structures were found till Michel *et al.*[10] reported on a non-rare-earth Bi-Sr-Cu oxide composition, which showed a resistive, possibly superconductive, transition at ~25 K. Studies of the Y-Ba-Sr-Cu oxide[11,12] phase, which has a majority phase structure isomorphous with that of $YBa_2Cu_3O_{7-\delta}$, have indicated the presence of reproducible,[12] high-temperature resistive transitions probably from a minority component. In the last few weeks the field of high-T_c superconductivity was excited by the reports of Maeda[13] and Chu *et al.*[14] on 90-K and higher temperature transitions in new phases in the Bi-Sr-Ca-Cu oxide and Bi-Sr-Ca-Al-Cu oxide systems, respectively.

In this Rapid Communication, we report on details regarding the synthesis of the new Bi-Sr-Ca-Cu oxide system obtained from our studies. In addition, electron diffraction and electron microscope imaging (performed at the National Facility for Electron Microscopy at Arizona State University) of these phases, together with resistivity and magnetometry measurements, are reported and discussed. A structure for the most ordered phase is proposed based on the electron microscopic data.

We have explored a variety of preparative conditions and obtained our best results as follows: Ultrapure (99.999%) Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO powders were rigorously mixed by grinding in a dry box in atomic ratios Bi:Sr:Ca:Cu = 0.8–2.0:1:1:2. A few experiments were carried out with Al in the system in which the Cu:Al ratio was 1.8:0.2. In addition, a few samples were prepared where the nominal Cu component in the above ratio was dropped from 2.0 to 1.5 and 1.0 and in which the Sr-to-Ca ratio was varied between 1.0 and 3.0. Single crystals (ca. 0.3–0.5 mm) were obtained from a 1:1:1:6 nominal composition. The precursor powder was transferred into an alumina boat lined with gold foil and fired in a tube furnace in air. The furnace temperature was carefully controlled by means of two calibrated temperature sensors.

Two sample types (A and B), identified by their powder x-ray diffraction and ac four-probe measured resistive transition onset temperatures (T_{co}), were prepared. Type-A samples were formed by firing the precursor powders at 775 and 800 °C for 12 h, pelletizing to ~10 kbar pressure and then sintering for 6–9 h at 700 °C in air, followed by slow furnace cooling. Type-B samples were prepared by bringing the precursor powder close to the melting temperature, which ranges between 845 and 870 °C as a function of the Bi content. The samples were held at this temperature for times ranging from 1–5 h, rapidly cooled, reground, and refired for another similar period. This is followed by grinding, pelletizing, and a final sinter between 800 and 860 °C for 6–9 h in air. The normalized resistivity (four probe, ac) versus temperature curve for a type-A sample of nominal composition 2:1:1:1.8 containing 0.2 Al and fired at 800 °C is shown in Fig. 1(a). Note that the resistance does not reach the zero level of our system. This is consistent with susceptibility measurements which show that only ~10% volume fraction of the sample is superconducting at 5 K. Two transition onsets, one at 87 K and the other at 60 K, are evident both in the resistivity and the magnetic susceptibility data in all type-A samples. The normalized resistivity versus temperature curve for a type-B sample of nominal composition 1:1:1:2 fired at 850 °C is shown in Fig. 1(b). This sample shows onsets at 112 and 87 K and zero resistance near 65 K. Similar samples, which had been annealed for a longer period of time, show onsets at the same temperature but zero resistance is achieved in the 75–80 K range. The dc magnetization (measured after zero-field cooling using a George Associates Lewis coil force magnetometer in a 30-Oe field) in the 80-140 K range for the same sample as in Fig. 1(b) is shown in Fig. 2. Clear onsets at 112

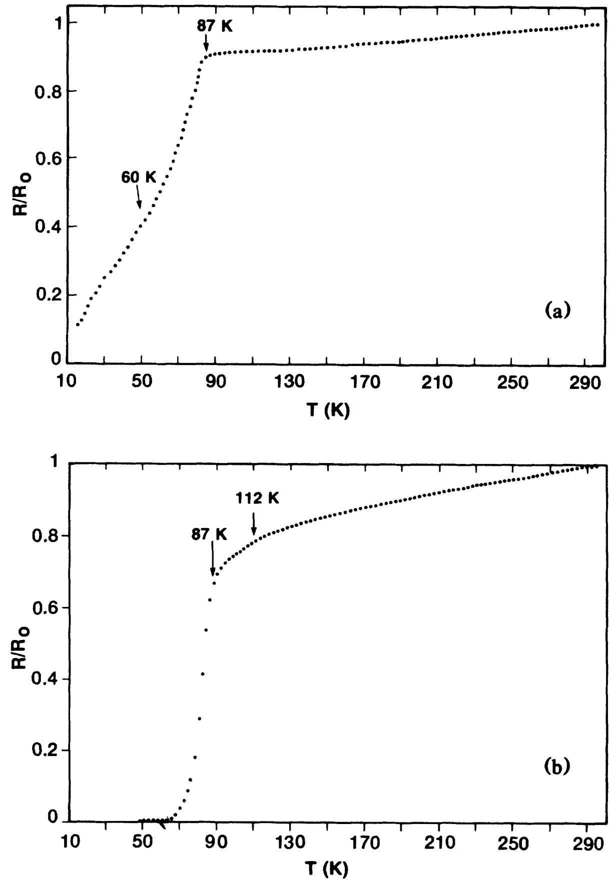

FIG. 1. (a) Normalized resistivity vs temperature for a type-A sample of nominal composition $Bi_2Sr_{1.5}Ca_{0.5}Cu_{1.8}Al_{0.2}O_y$ prepared at 800 °C. (b) Normalized resistivity vs temperature for a type-B sample of nominal composition $Bi_1Sr_1Ca_1Cu_2O_y$ prepared at 845 °C. Measurements in both (a) and (b) were performed using four-probe contacts and 10 mA ac at 100 Hz.

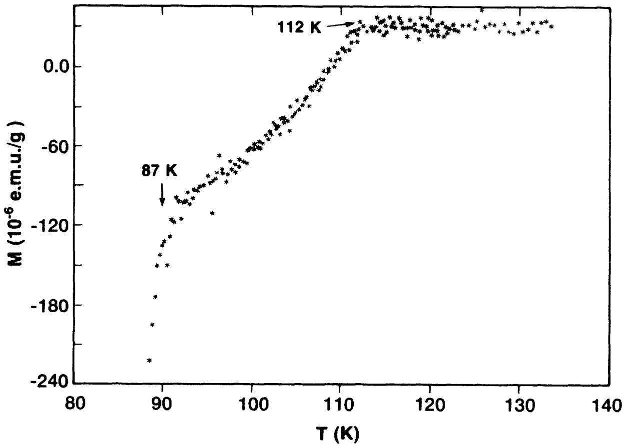

FIG. 2. Magnetic moment (*M*) at 30 Oe magnetic field vs temperature in the 80–140-K range for the same sample as Fig. 1(b), measured after zero-field cooling. The measurement was made down to 5 K where a ≥ 60% volume fraction is superconducting.

and 87 K are also evident in this data consistent with the resistivity results. The diamagnetic transition to a typical volume fraction of 50–70% at 5 K is, however, rather broad in the present type-B samples. The diamagnetic fraction above 100 K is less than 1% in our samples. H_{c1} at 5 K is estimated to be ~1.2 KOe from a magnetization curve. This value is comparable to many of our $YBa_2Cu_3O_{7-\delta}$ samples.

Electron microprobe analyses in the transmission and scanning modes were carried out on representative platelike crystals in both type-A and type-B samples. The results indicated that the composition of most of the crystals is $Bi_2Sr_{3-x}Ca_xCu_2O_y$ (where x is near or equal to 1). This suggests that the crystals of the above composition grow out of a partial flux of a different nominal composition. Some free CuO (~1–5%) was detected in both types of preparations. In addition, a Bi-poor phase was found in samples from a 1:1:1:6 nominal composition. The oxygen content was determined in a type-A sample of nominal starting composition 2:1.5:0.5:2, using its weight loss after reducing the material in an Ar-H_2 atmosphere at temperatures up to 900 °C. From the weight loss, we determined that the oxygen content is 8.04 per formula unit 2:1.5:0.5:2, assuming 5% CuO in the sample.

High-resolution transmission electron microscope (HRTEM) images were obtained using a JEOL 4000EX Microscope (for details of the microscope and sample preparation, see Barry[15]). Both type-A and type-B samples, whose resistivity curves are shown in Figs. 1 and 2, were examined. In addition, we also examined a type-B sample that had been annealed at 850 °C for 9 h.

Two kinds of crystals were found in the type-A and type-B preparations. The first kind of crystal (labeled type 1) has a ×5 superlattice of ~18 or ~25 Å depending on the crystal orientation. The second kind of crystal (labeled type 2) shows a layer structure without a superlattice and a layer spacing of 15.6 Å which has a ×2 modulation. In type-A preparations, the crystals are somewhat disordered. For example, in crystal type 1 the ×5 superlattice is often slightly incommensurate with the sublattice and in crystal type 2, the layers are wavy. In type-B preparations the crystals are better ordered, that is the ×5 superlattice is commensurate in crystal type 1 and the layers are straight in crystal type 2. The former crystals are more abundant in both preparations A and B. Type-2 crystals are still rare though they are more common in samples from preparation B (about ~1% by volume fraction). For this reason it is suggested that the 112-K phase is associated with type-2 crystals.

In Fig. 3 we have an example of a crystal of type 1 with the 18-Å superlattice. Figure 3(a) shows an image with a superlattice of 17.8 Å and a sublattice of 2×1.84 Å from a type-1 crystal obtained from an A-type preparation. Note that the superlattice is approximately ×5 the sublattice but is not exactly commensurate. The diffraction pattern associated with the crystal is shown in Fig. 3(b). The superlattice in the diffraction pattern has a spacing of 18.7 Å and the sublattice has a spacing of 2×2.02 Å. The axis along which the superlattice reflections are seen corresponds to either a or $b \approx 4.0$ Å. The fact that the crystals in preparation A are slightly disordered is reflected in the observation that the spacings given by the image (which

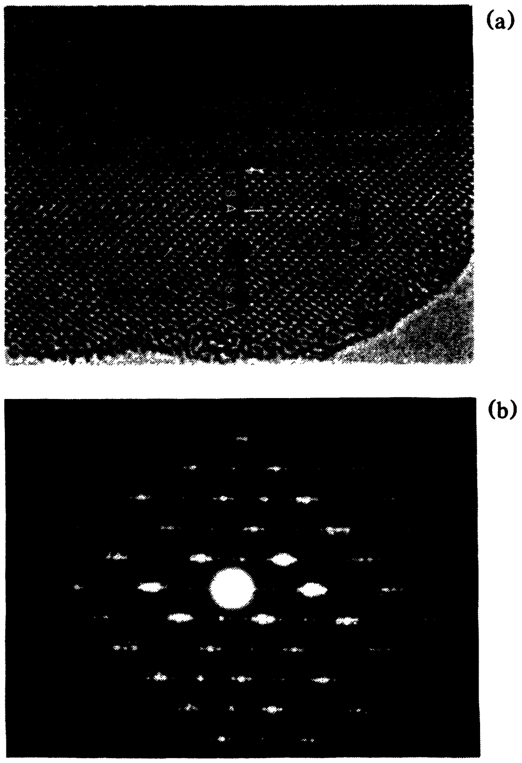

FIG. 3. Lattice image (a) and diffraction pattern (b) of a type-1 crystal with a 18-Å superlattice (see text).

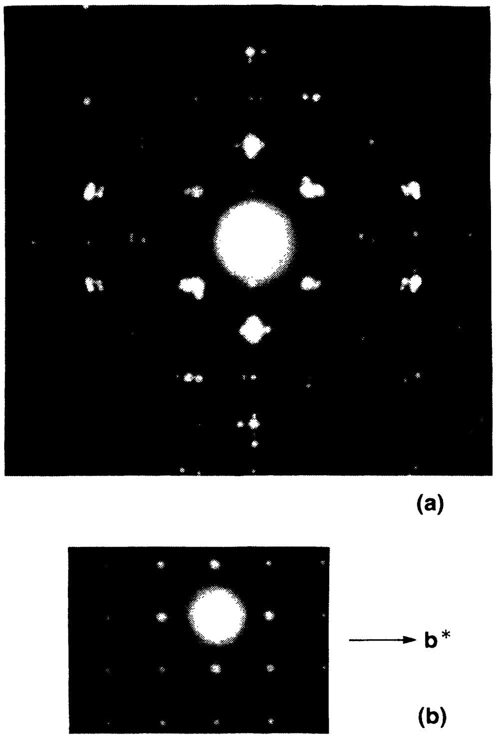

FIG. 4. (a) Electron diffraction pattern of a type-1 crystal obtained from preparation A in the pseudotetragonal (001) basal plane setting. (b) Electron diffraction pattern from a (001) crystal obtained from preparation B.

represents the localized structure) and the spacings given by the diffraction pattern (which represents the average structure), are not the same.

We also have an example of a 25-Å superlattice in a crystal which is oriented in the (110) plane. Crystals of type 1 in the basal plane (001) setting showing a near-tetragonal structure with $a \approx b = 5.39$ Å, have also been obtained from both preparations A and B. The crystals from preparation A, however, unlike those reported by Zhang *et al.*[16] and Chu *et al.*,[14] show a ×5 superlattice along both the a and b directions [Fig. 4(a)]. Crystals obtained from a type-B preparation (in this case using a 1:1:1:6 nominal starting composition), however, show the superlattice structure only along the b axis [Fig. 4(b)]. This suggests that the (001) crystals from our preparation A are stacked on top of each other with the basal plane axes rotated by 90°.

Figures 5 and 6 show crystals of type 2. Figure 5(a) depicts the image of the layer crystal with a layer spacing of 15.4 Å and a lattice spacing perpendicular to the layer of period 3.87 Å. As indicated in Fig. 5(a), a ×2 modulation would double the unit cell perpendicular to the layers. Note that the layers are somewhat wavy due to disorder since the crystal is from a type-A preparation. The diffraction pattern for the crystal in Fig. 5(a) has periodicities of 15.6 and 3.87 Å which are in reasonably good agreement with the image.

Figure 6(a) shows an image of a layered crystal from a type-B preparation with a layer spacing of 15.6 Å (the modulated spacing is 2×15.6 Å) and a periodicity perpendicular to the layers of 2.75 Å. The corresponding diffraction pattern [Fig. 6(b)] has periodicities of 15.6 and 2.72 Å reflecting the greater order in this crystal. Note also that the layers are straight.

If we postulate that the crystals of type 2 have a tetragonal structure with $a = b = 3.88$ Å and $c = 2 \times 15.6$ Å, it is possible to index Fig. 5 as a [100] orientation crystal [i.e., 2×15.6 Å = the (001) spacing and 3.87 Å = the (100) spacing] and it is possible to index Fig. 6 as a [100] orientation crystal where 2×15.6 = the (001) spacing and 2.75 Å is the (110) spacing. The image in Fig. 6(a) was taken at close to optimum defocus at a thin edge of the crystal. So the crystal image at the thin edge should be a structure image that can be intuitively interpreted in terms of a crystal structure—with the heavy black blobs corresponding to Bi-atom positions and the lighter blobs to Sr-, Cu-, and Ca-atom positions. The structure of this crystal (type 2), therefore, appears to be made up of five light atoms sandwiched between bilayers of the heavy Bi atoms. A simulation based on the structure proposed by Subramanian *et al.*[17] indicates that the light atoms consist of a Cu—O double layer separated by 4.9 Å, with a Ca layer in the middle separated from the Cu layer by 2.45 Å. The Sr layers form the outermost layers in the sandwich. The image shows that the Bi layer is separated by 3.6 Å from the Cu layer. Since the type-2 crystal basal plane ($a = b = 3.88$ Å) appears to be related to a type-1 crystal basal plane ($a \simeq b = 5.39$ Å) by a $\times\sqrt{2}$ transfor-

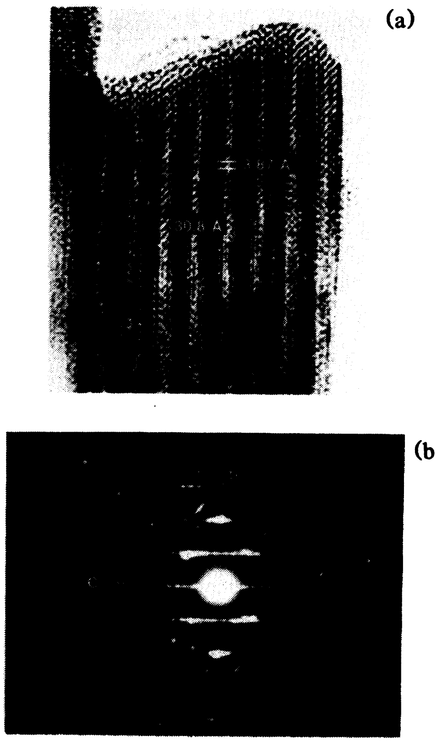

FIG. 5 Lattice image (a) and diffraction pattern (b) of a type-2 crystal in the postulated [100] orientation (see text).

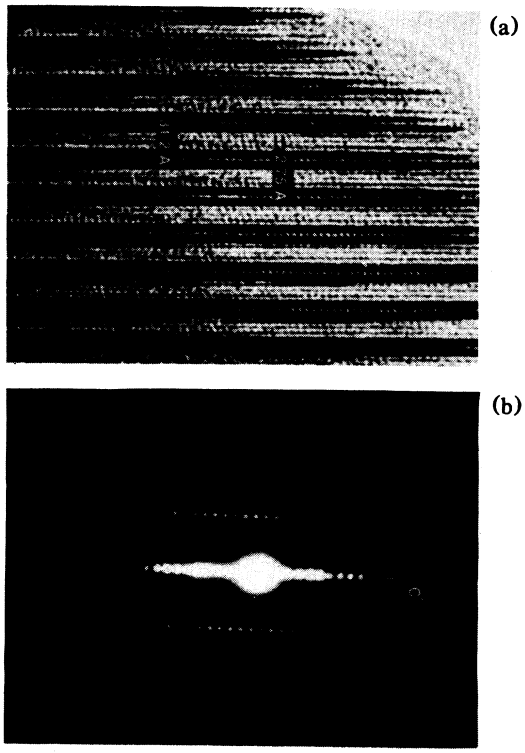

FIG. 6. Lattice image (a) and diffraction pattern (b) of a type-2 crystal in the postulated [110] orientation (see text).

mation to a halved unit cell, one can speculate that the superlattice modulated type-1 structure transforms to the unmodulated type-2 crystal with heat treatment in the 800–850 °-C range. Crystals of type 1 have a T_c in the 70–85-K range while the ordered crystals of type 2 could be associated with the higher-temperature transition. The T_c onset of 60 K seen in a fraction of our type-A samples is presumably associated with the more disordered crystals of type 1.

We would like to thank R. H. Baughman for his enthusiastic support and encouragement of this research, and Bob Antrim and Jordi Marti for the electron microprobe analyses.

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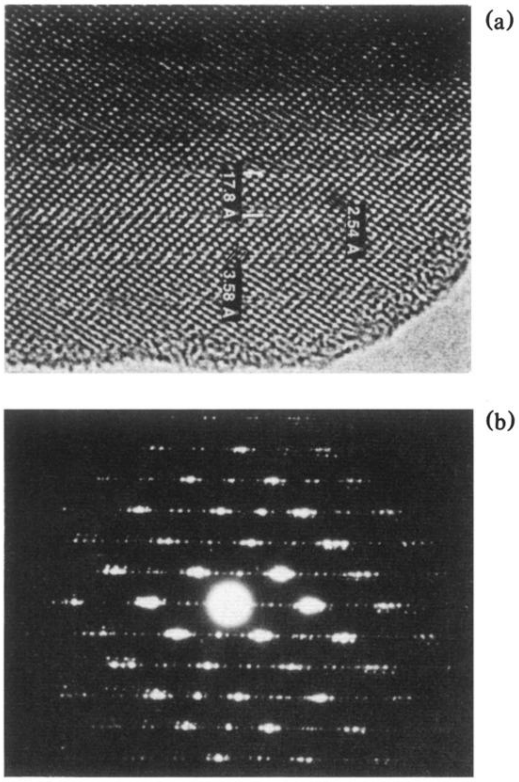

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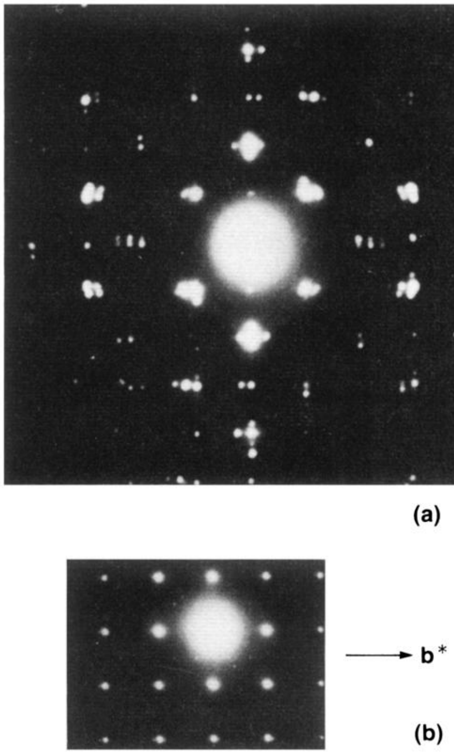

FIG. 4. (a) Electron diffraction pattern of a type-1 crystal obtained from preparation A in the pseudotetragonal (001) basal plane setting. (b) Electron diffraction pattern from a (001) crystal obtained from preparation B.

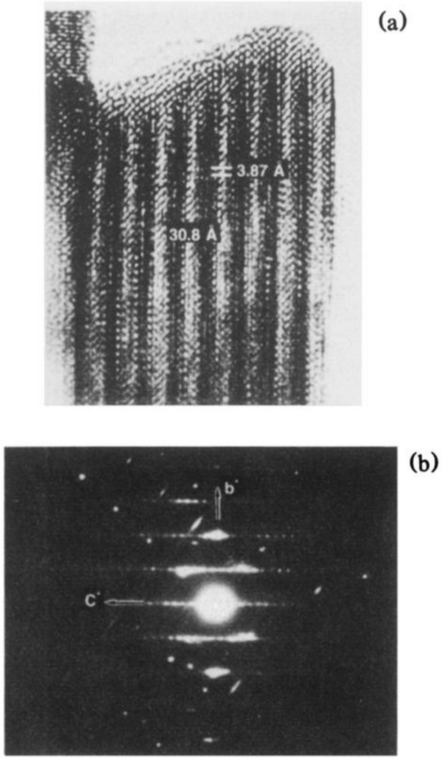

FIG. 5 Lattice image (a) and diffraction pattern (b) of a type-2 crystal in the postulated [100] orientation (see text).

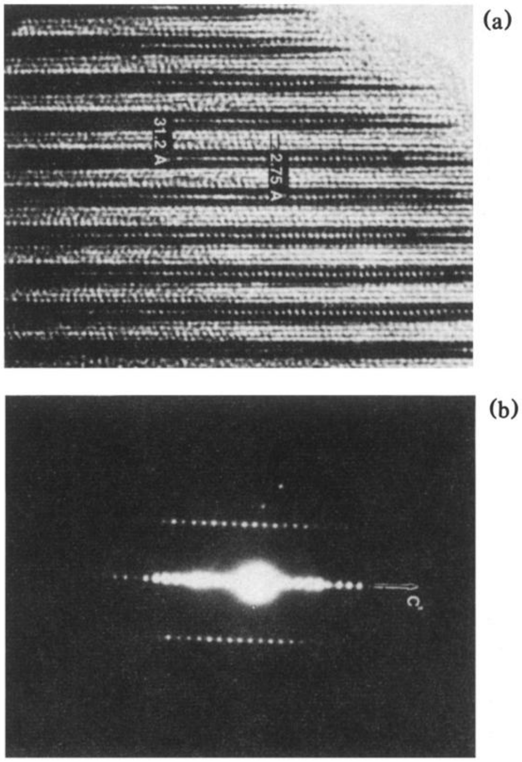

FIG. 6. Lattice image (a) and diffraction pattern (b) of a type-2 crystal in the postulated [110] orientation (see text).