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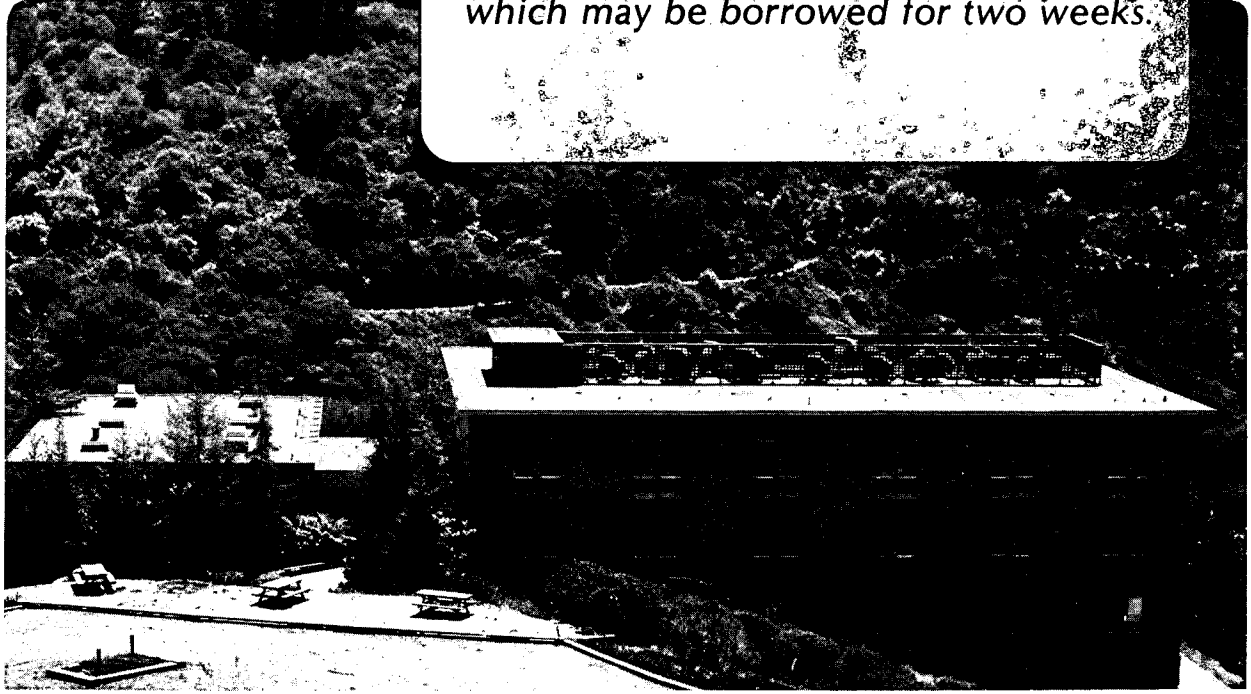
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August 1987

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# Surface Decomposition of Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$

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## Abstract

High resolution electron microscopy has been performed on a number of samples of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  before and after heating at several temperatures between  $20^\circ$  and  $450^\circ\text{C}$ , and in three different atmospheres: oxygen, air and vacuum. By comparison studies of the same crystals it is shown that in all atmospheres the surface decomposes rapidly at temperatures above approximately  $150^\circ\text{C}$ . Below  $150^\circ\text{C}$  the rate of decomposition is much lower; crystals exposed to air for one week show several planar defects indicating the onset of the decomposition. The decomposition reaction proceeds by the insertion of extra  $\text{CuO}$  planes into the original structure resulting in  $(\text{CuO})_2$  double layers between  $\text{BaO}$  planes. This reaction induces large lattice strains at the exposed surfaces, sometimes resulting in fragmentation and spalling.

## 1. Introduction

Previous electron microscopy studies [1-7] of superconducting oxides having the 1-2-3 structure revealed large differences in defect density and defect distribution, even within small single crystals. Samples with relatively small grain sizes were most prone to having both these locally varied concentrations of defects and amorphous surface films. Larger-grained specimens by comparison showed evidence of very clean surfaces, with only occasional amorphous film overlayers. However it was not possible to conclude whether or not all of the observed defects were actually confined to the surfaces of the powder particles, primarily because the preparation of specimens for electron microscopy incorporates a severe crushing and grinding procedure. During observation these ground powders give no clues to discriminate surface from interior structures.

Nevertheless the observed grain size dependence of the defect structures gives reason to suspect that all such defects and amorphous overlayers might be located only on the exterior surfaces of the grains. If so, this would then be consistent with the "epitaxial surface layer" reported by Viegers et al [8].

The purpose of this work is to critically evaluate this effect by determining the thermal stability of superconducting oxide particle surfaces. A number of specimens have been thermally treated at several temperatures and examined before and after these treatments for comparison studies. The results of these experiments are reported here.

## 2. Experimental Procedures

Samples of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  were prepared by heating a pelletized mixture of  $\text{Y}_2\text{Ba}_4\text{O}_7 \cdot x\text{CO}_2$  with known  $x$  and  $\text{CuO}$  at  $920^\circ\text{C}$  overnight [6] and subsequently annealing at  $450^\circ\text{C}$  for two hours. By this preparation method the product always contained more than 95% of the orthorhombic 1-2-3 phase, as determined by X-ray powder diffraction. Annealing at  $450^\circ\text{C}$  and air cooling resulted in a  $T_c$  of about 90 K. The pellet was powdered and cooled quickly from room temperature to 77K with liquid  $\text{N}_2$ . A few droplets of a suspension of the powder were put onto two types of supports: (i) conventional holey carbon films over Cu grids; or (ii) holey  $\text{Si}_3\text{N}_4$  films over Pt grids [9]. The latter type of grid enabled a specific crystal to be studied before and after heating outside of the microscope in a chosen atmosphere.

High resolution electron microscopy was carried out in a JEOL JEM 200CX electron microscope, equipped with a top entry  $\pm 10^\circ$  double-tilt goniometer operating at 200 kV, and the Berkeley Atomic Resolution Microscope [10] equipped with a  $\pm 40^\circ$  biaxial, double-tilt-lift goniometer operating at 1000kV.

After high resolution electron microscopy, those specimens on  $\text{Si}_3\text{N}_4/\text{Pt}$  grids were thermally treated under the following conditions:

- 20°C in air for one week,
- 190°C in air for one hour,
- 450°C in air for one hour,
- 450°C in a sealed quartz tube at  $10^{-4}$  torr for one hour,
- 450°C in flowing oxygen for one hour.

To verify that there were no artifacts induced by either the  $\text{Si}_3\text{N}_4$  or the platinum in the support grids, the following experiment was performed. A few drops of the same suspension described above were put on a glass microscope slide and allowed to dry. Next the small crystals on the slide were gathered, put onto a pellet of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and heated at  $190^\circ\text{C}$  for one hour. These crystals were then mounted on a holey carbon film/Cu grid and investigated by high resolution electron microscopy.

In a parallel study, small wedge-shaped fragments (about 0.5 mm long) were selected after cleaving pieces of the pellet. These fragments were mounted on a Cu grid containing a large 1.5 mm hole in such a way that the thin part of the wedge was centered over the grid hole and fastened in place using a two-component epoxy glue. The entire assembly required heating at  $80^\circ\text{C}$  for two hours to allow the glue to harden (cure). Electron transparent crystals and interfaces located on the thin part of the wedge were then studied by high resolution electron microscopy. The sample was subsequently heated for two hours at  $50^\circ\text{C}$ , one hour at  $120^\circ\text{C}$ , 30 mins at  $180^\circ\text{C}$  and 30 mins at  $200^\circ\text{C}$ . Between each heating cycle, the sample was re-examined using high resolution electron microscopy.

Image calculations were performed using the CEMPAS simulation software developed at the National Center for Electron Microscopy [11]. Images of the "normal" structure were first simulated using the parameters of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [12]. In the calculations the objective lens defocus was varied between 0 and  $-140$  nm and the specimen thickness between 2 and 20 nm. Subsequently simulations were made of two structure models of the planar defects, using a superstructure cell. The "unit cell" dimensions were  $0.382 \times 0.389 \times 6.902$  nm.

### 3. Experimental Results

Exposure to air for one week resulted in the formation of planar defects, ranging in occurrence from a limited amount of defects in some parts of a crystal to no defects at all in other parts. Heating below  $150^\circ\text{C}$  for only one hour did not result in any detectable structural changes.

The results of the heating experiments above approximately  $150^\circ\text{C}$  were all basically the same. The structure was observed to decompose from the relatively perfect 1-2-3 structure to one containing planar defects in varying concentration, up to the point of complete loss of periodicity, i.e. the formation of an amorphous phase. With increasing temperature an increasing rate of decomposition was observed. The reaction front

advanced in directions perpendicular to the c-axis. Samples heated at  $450^\circ$  exhibited complete decomposition of those crystals that were thin in a direction perpendicular to the c-axis, and partial decomposition of those crystals that were thin along the c-axis. Examples are shown in Figures 1 and 2.

No significant differences were observed between crystals heated on  $\text{Si}_3\text{N}_4/\text{Pt}$  grids and those heated on other grids. However, it was very difficult to quantify the degree of decomposition because it depends not only on the thickness and orientation of the crystal but also on its prior thermal history.

An example of the effect of heating at  $180\text{-}200^\circ\text{C}$  is given in Fig. 3. It should be noted that at locations where a single defect is initially observed, new defects appear upon subsequent heating. These defects appear as faults in the regular stacking along the c axis. Figure 3 also shows that the defects move inward perpendicular to the c-axis as they increase in size and density.

Image calculations were obtained and closely compared for two different defect models: (i) a  $(\text{CuO})_2$  double layer, as shown in Figure 4, and (ii) a  $(\text{Cu}_{0.5}\text{O})_2$  double layer, at the same position as the  $(\text{CuO})_2$  double layer shown in Figure 4. The latter structure could result if the oxygen ions in the CuO layer at  $z=0$  were replaced by OH groups ( $z$  is the fractional coordinate along the c axis of the 1-2-3 structure). It was found that only the model with the  $(\text{CuO})_2$  double layer produced calculated images in good agreement with the experimental ones, an example of which is given in Figure 5. The parameters used for the calculated image were: accelerating voltage, 1000 kV; spherical aberration, 2.8 mm; objective aperture,  $6 \text{ nm}^{-1}$ ; defocus spread, 10 nm; beam divergence, 0.6 mrad; defocus, -45 nm; and specimen thickness, 2 nm, agreeing well with the estimated experimental values.

Figure 6 is an image of a cleaved specimen, heated to only  $80^\circ\text{C}$  after cleaving. The image shows that the interface (denoted by white arrows) between the (001) planes of one of the grains and the (116) planes of an adjacent grain is very abrupt and contains no amorphous material. Furthermore it shows that whereas the [100] oriented grain has decomposed up to 30 nm from its thin edge (the thin edge is off to the right in the figure), the [241] oriented grain shows only an amorphous layer of 5 nm from its thin edge. In the region where the [100] grain is amorphous, the position of the grain boundary can still be precisely determined because of the lattice image of the [241] grain. It is expected that this image is

representative of the grain as it was in the bulk. Consequently the destruction of the [100]-oriented crystal must have taken place after the formation of the grain boundary (after the reaction and sintering at 920°C) and before its cooling down below 150°C.

#### 4. Discussion

It is evident from this research that the surface of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is very unstable in oxygen-containing atmospheres at temperatures above 150°C, that the surface becomes progressively less stable at higher temperatures, and that there is a tendency to decompose even at room temperature after longer exposure times.

The observed differences in stability of crystals that are thin along the c-axis compared to those that are thin perpendicular to the c-axis (see Fig. 6) and high resolution images showing defects perpendicular to the c-axis suggest that the destruction of the lattice takes place by a mechanism of incorporation of "extra" ions between c-planes. The insertion of Cu cations and possibly O anions into the 1-2-3 structure was previously indicated by XPS measurements [7], which show a large copper deficiency at the surface. In the present study, comparison between calculated and experimental high resolution images confirms that the inserted ions are Cu ions and the plane of insertion is the CuO plane at  $z=0$ , between the two BaO layers (see Fig. 5). This insertion leads to a double layer of CuO, which requires an expansion of the unit cell by 1/6 its height, assuming all layers along the c-axis to have the same spacing. From Figure 7 the expansion measured directly in the image is  $15\pm 1\%$ . Since the incorporation of these species proceeds only to a limited depth inside the crystal, the exterior shell is exposed to strong stresses, resulting in bending as is shown in Fig. 7, and spallation of small fragments (see Fig. 8) of the 1-2-3 phase. It might be expected that when the material is given enough time to undergo a phase transformation by periodic insertion of extra CuO layers, a superstructure would appear. Indications of such a superstructure having every other CuO layer replaced by a  $(\text{CuO})_2$  double layer can be seen in Figures 6 and 7.

The rate of incorporation of the extra CuO planes is obviously limited by both the mobility of the Cu ion and the availability of oxygen. Consequently electron beam heating of crystals in the vacuum environment of the electron microscope, even above the transition temperature, did not result in decomposition of the surface. The same heating experiment (vacuum environment) performed outside the



microscope is different from the *in-situ* experiment because in the *ex-situ* case a "closed" vacuum is obtained; any oxygen extracted from the sample remains present within the ambient atmosphere for subsequent reaction to form  $\text{CuO}$ . It is clear that once  $\text{Cu}$  and  $\text{O}$  ions are available,  $\text{CuO}$  layer formation will take place. This leads to insertion of extra  $\text{CuO}$  planes adjacent to a large fraction of existing  $\text{CuO}$  planes and ultimately to a collapse of the structure at the surface.

The observation that the surface changes during exposure to air for one week is in agreement with reports [13] that the Meissner effect of a  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound decreases gradually with prolonged exposure to air.

From the present heating experiments it is now known that defect-rich regions deteriorate most rapidly, showing these regions to be less stable than defect-free regions of the material. It is therefore expected that defect-rich regions of the 1-2-3 structure will also decompose quite rapidly at room temperature, when they are exposed to air. The stability of defects under these conditions has not yet been studied. Surface decomposition at room temperature, of the defect-rich regions of the 1-2-3 phase in particular, would induce large differences in the reduction of the Meissner effect, depending upon such specimen parameters as grain size and annealing time. This is indeed observed [13].

There may be significance to the fact that amorphous films were only found to be present on free surfaces, and never at grain boundaries. Figure 6 is an example where the interface between the two grains is very sharp. It must be pointed out however that during this and previous studies it was possible to investigate only a few grain boundaries. A thorough investigation of the location, morphology and composition of amorphous films, including their possible role in the generation of the defects described in this paper, is in progress.

One of the unanswered questions of this research is the temperature range over which surface decomposition occurs, and the temperature treatments that might be prescribed to prevent such decomposition. Some boundary conditions are known however. For example it must be assumed that at about  $920^\circ\text{C}$  the surface is stable; otherwise the formation of the compound would be impossible. Furthermore, the intact appearance of the grain boundaries in Fig. 6, coupled with the decomposed regions that were exposed to the surface, suggest that the decomposition must have taken place after the formation of individual grains.

A temperature treatment suggested by these observations is a rapid quench to below  $150^\circ\text{C}$  followed by oxygen treatment to transform the

material from its non-superconducting tetragonal phase ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  where  $\delta = 0.5$  to  $0.3$ ) to its superconducting orthorhombic phase ( $\delta = 0$ ). Another possible route is the preparation of highly dense materials having only very little free surface of the grains. However it must still be verified that the grain boundaries are stable during thermal treatment at about  $450^\circ\text{C}$  to obtain the orthorhombic configuration with the highest  $T_c$ .

It is clear that a number of other experiments have to be performed to obtain a complete understanding of surface decomposition in these materials. Several of these, namely *in-situ* heating in controlled atmospheres, *ex-situ* heating at  $450^\circ\text{C}$  in dynamic vacuum, thermal treatments in air at temperatures between  $800$  and  $950^\circ\text{C}$ , and the reaction at the interface between  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Cu}$ , are all in progress.

## 6. Conclusions

Several conclusions can be drawn from these experiments. The most obvious is that the surface is unstable, and that any and all processing of superconducting material must take account of this phenomenon. Although there is no direct evidence for similar problems at grain boundaries, it can be expected that at least internal interfaces might show decomposition of the type seen at external surfaces in this study.

Any annealing treatment in the temperature range  $300^\circ\text{C}$  to  $500^\circ\text{C}$  used to introduce oxygen for obtaining a composition with the highest  $T_c$  should be as short as possible. It is still better to use considerably lower temperatures or to find and use other methods of introducing oxygen..

It is noted that in the reports on superconductors with a considerably higher  $T_c$  [14], only a very small fraction of the material is superconducting. It would be very interesting to investigate whether these very high  $T_c$  materials can be correlated with the surface phenomena described in this paper.

### *Acknowledgements*

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### Figure Captions

**Figure 1.** High resolution electron micrograph of [100]-oriented crystal before (a) and after (b) heating in vacuum at  $450^\circ$  for one hour. The 1-2-3 structure, which is evident in (a), is completely absent in the heated sample, even in the thicker regions (not shown here). Note in (a) the very clean and sharp (001) surface (probably the BaO plane) obtained by cleavage. (XBB 877-6390).

**Figure 2.** High resolution electron micrograph of a crystal in [001] orientation before (a) and after (b) heating in oxygen at  $450^\circ$  for one hour. After thermal treatment the image of the 1-2-3 structure appears only in the interior part of the crystal (at bottom of micrograph) in the form of [100] fringes perpendicular to the edge.. (XBB 877-6389).

**Figure 3.** High resolution electron micrographs taken with the JEM 200CX showing a [110]-oriented crystal (a) before heating; (b) after heating at  $180^\circ\text{C}$  for 30 minutes; and (c) after heating at  $200^\circ\text{C}$  for 30 minutes. Due to cleavage of the specimen, a segment (see inset figure a) is partly broken off, exposing a clean surface. Heating at  $180^\circ$  for 30 minutes creates new planar defects extending far into the crystal while previously existing defects propagate further inward from their point of origin at the surface. Heating at  $200^\circ\text{C}$  leads to an even higher number of defects originating at the cleaved surface. (XBB 877-6270).

**Figure 4.** A model of the  $(\text{CuO})_2$  double layer as observed in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and used for the simulated image in figure 5. The model consists of two unit cells of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  shifted over half the b axis. The composition of this model, having each second CuO layer replaced by a  $(\text{CuO})_2$  double layer is  $\text{YBa}_2\text{Cu}_{3.5}\text{O}_{7.5}$ . (XBL 877-3399).

**Figure 5.** Atomic resolution image and inset simulation of the  $(\text{CuO})_2$  double layer in the 1-2-3 phase. Agreement is excellent at the atomic scale of the micrograph. (XBB 877-6268).

**Figure 6.** High resolution image of the interface (along white arrows) between a grain in [100] orientation (bottom) and a grain almost in [241]

orientation (top). The crystal is thinner at the right hand side of the image, with the surface just beyond the edge printed here. Note that the upper grain shows periodic structure extending to the far right side, close to the surface, while the bottom grain shows almost no structure within 30 nm of the surface. Periodic doubling of the c-axis in the bottom grain is also visible, resulting from a replacement of every second CuO layer by a  $(\text{CuO})_2$  double layer. (XBB 877-6391).

**Figure 7** High resolution image of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in  $[210]$  orientation prior to any heat treatment after grinding. The lattice fringes show a regular  $2c$  superstructure close to the surface, along with some structural distortion (bending). (XBB 877-6271).

**Figure 8.** High resolution electron micrograph of the surface of a  $\text{YBa}_2\text{Cu}_3\text{O}_7$  grain in  $[100]$  orientation showing fragmentation (open arrow) of the lattice into very different orientations. Note that across the  $(\text{CuO})_2$  double layers (indicated by bold arrow) the image shifts by half a unit cell. (XBB 877-6269).

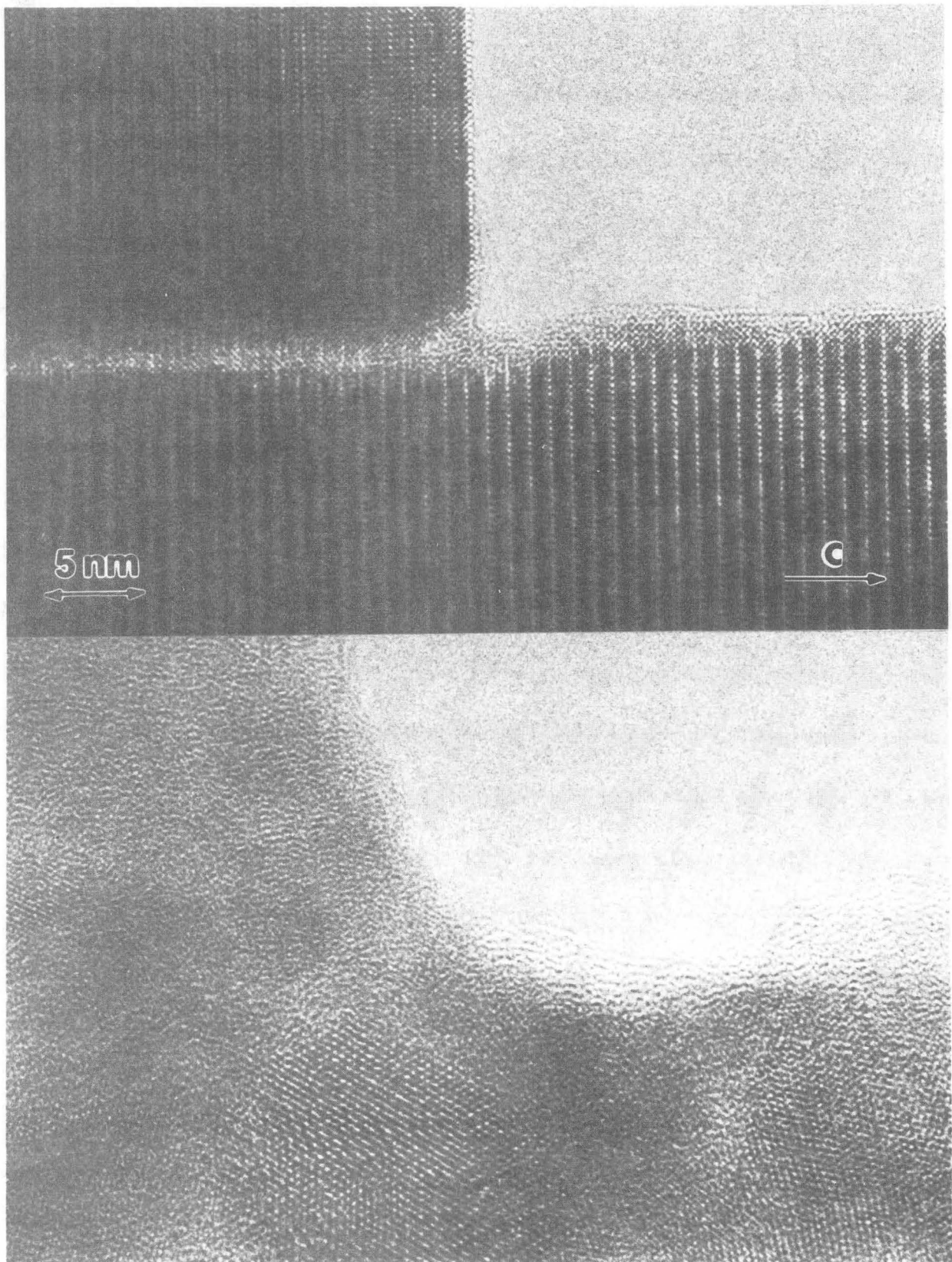


Figure 1

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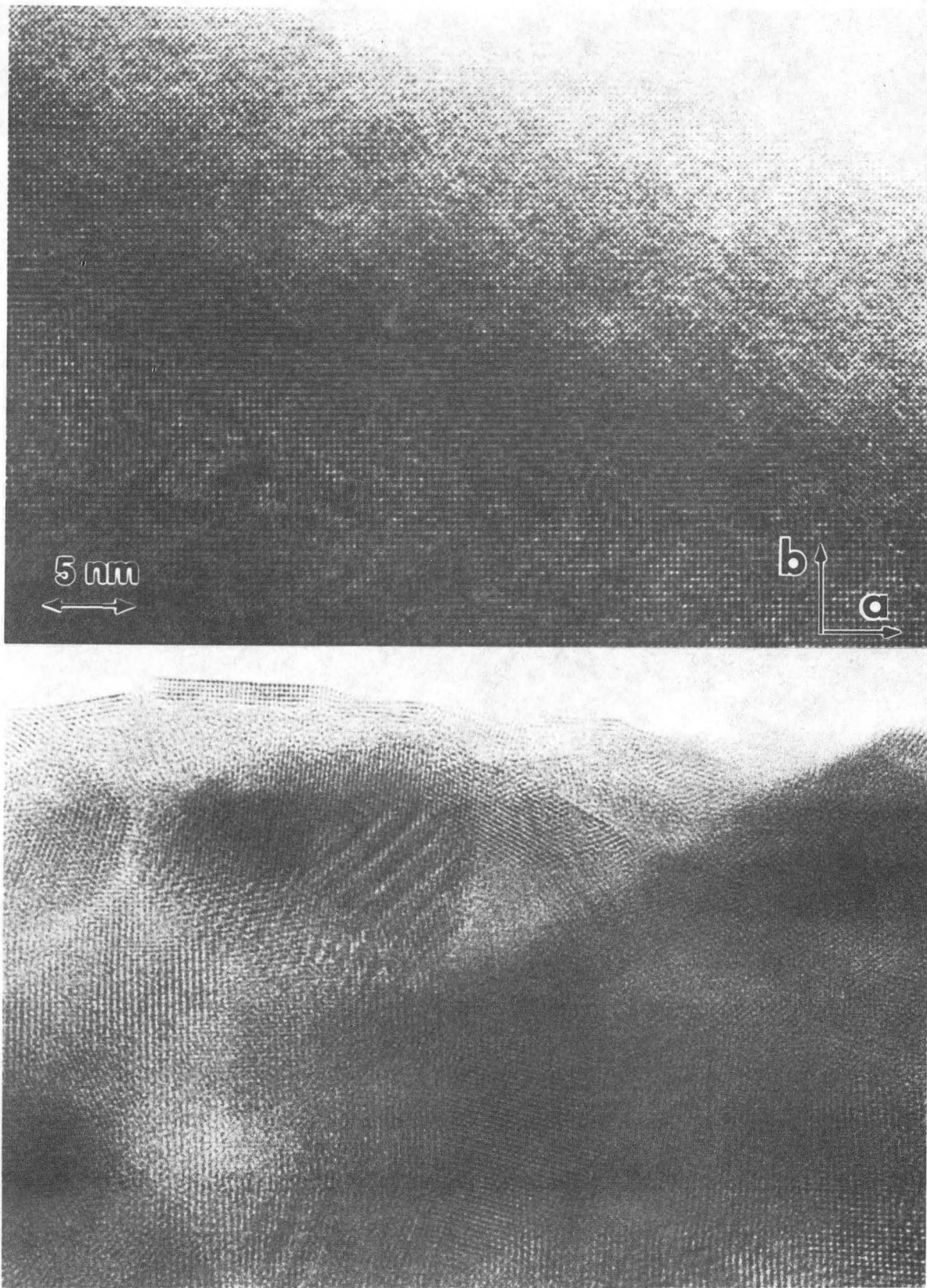


Figure 2

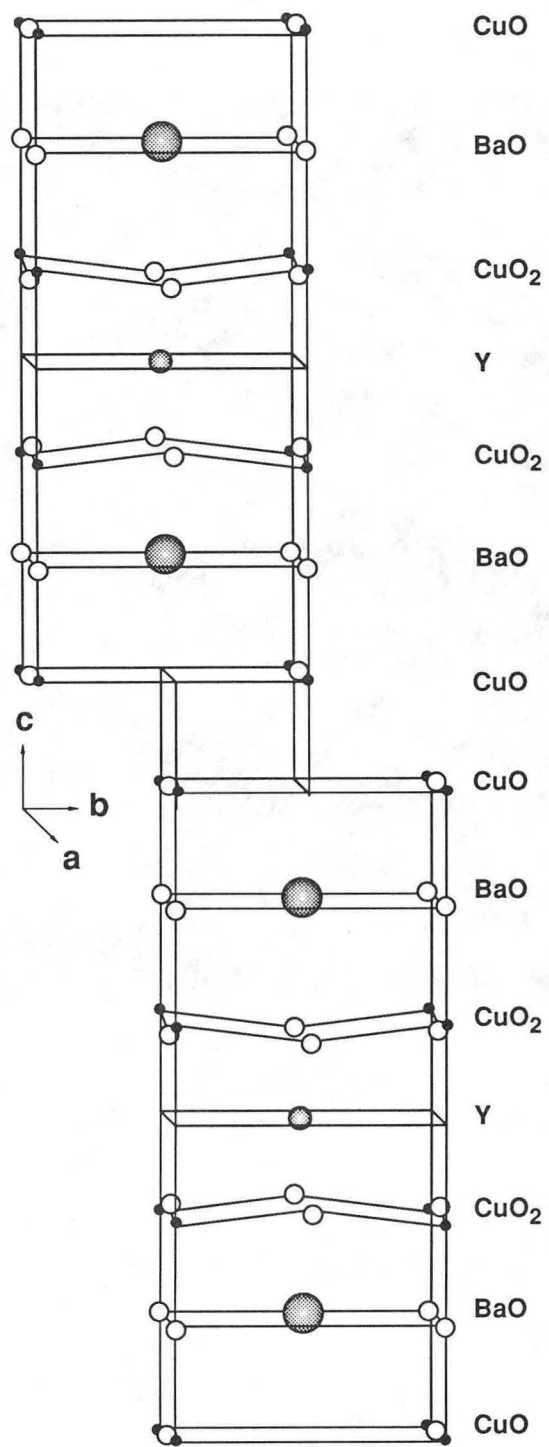
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Figure 3

XBB 877-6270



XBL 877-3399

Figure 4

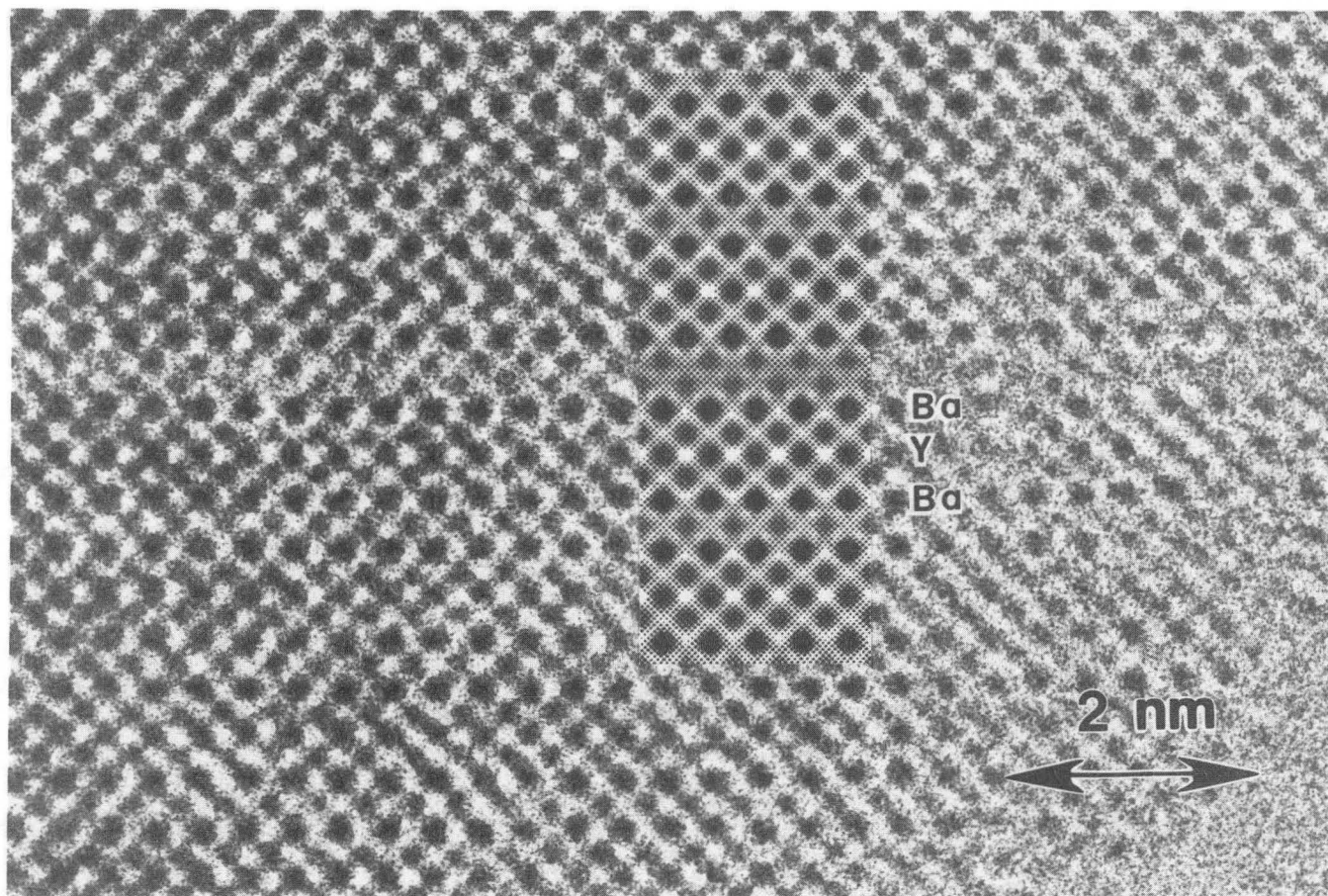
Surface Decomposition of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ 

Figure 5

XBB 877-6268

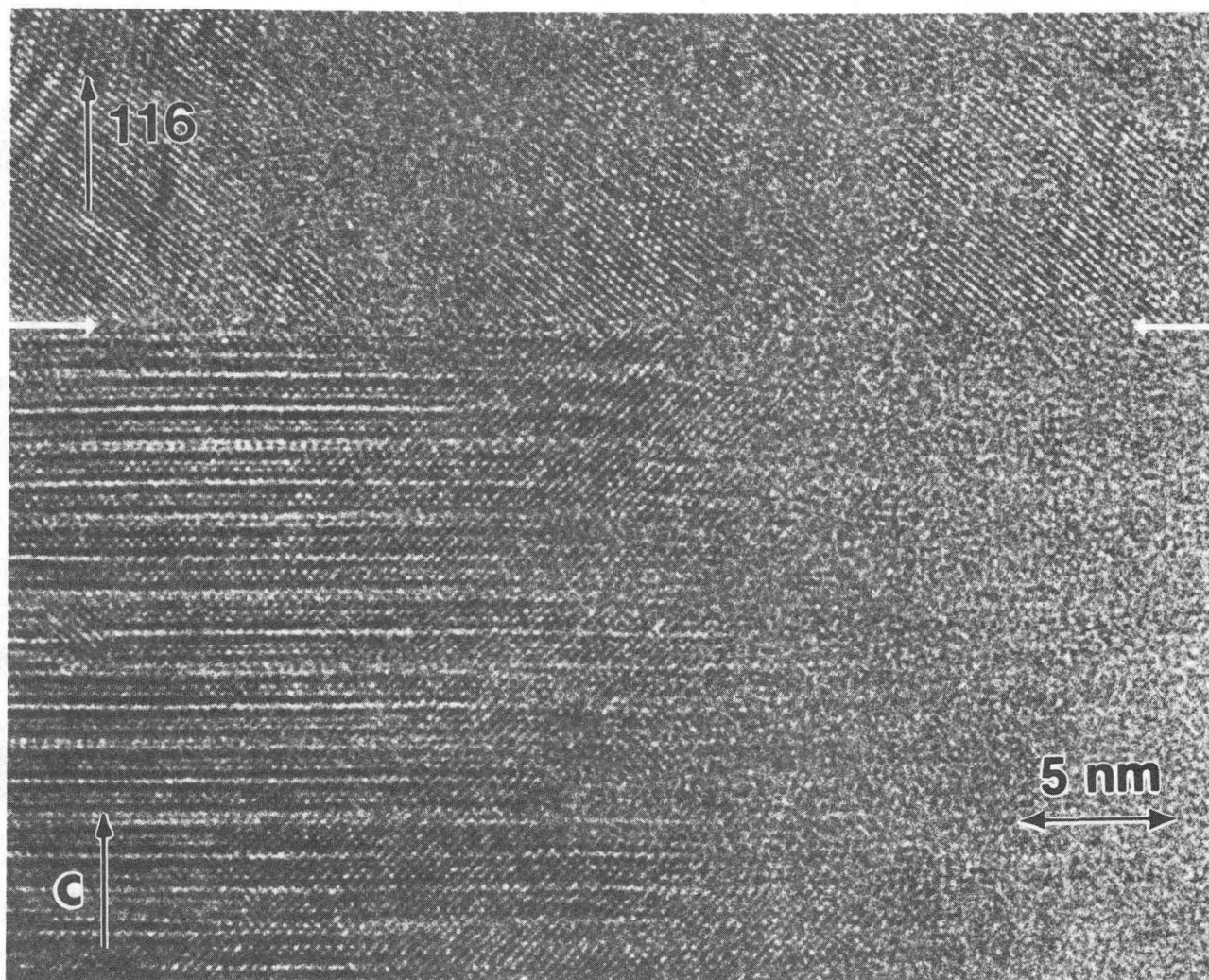


Figure 6

XBB 877-6391

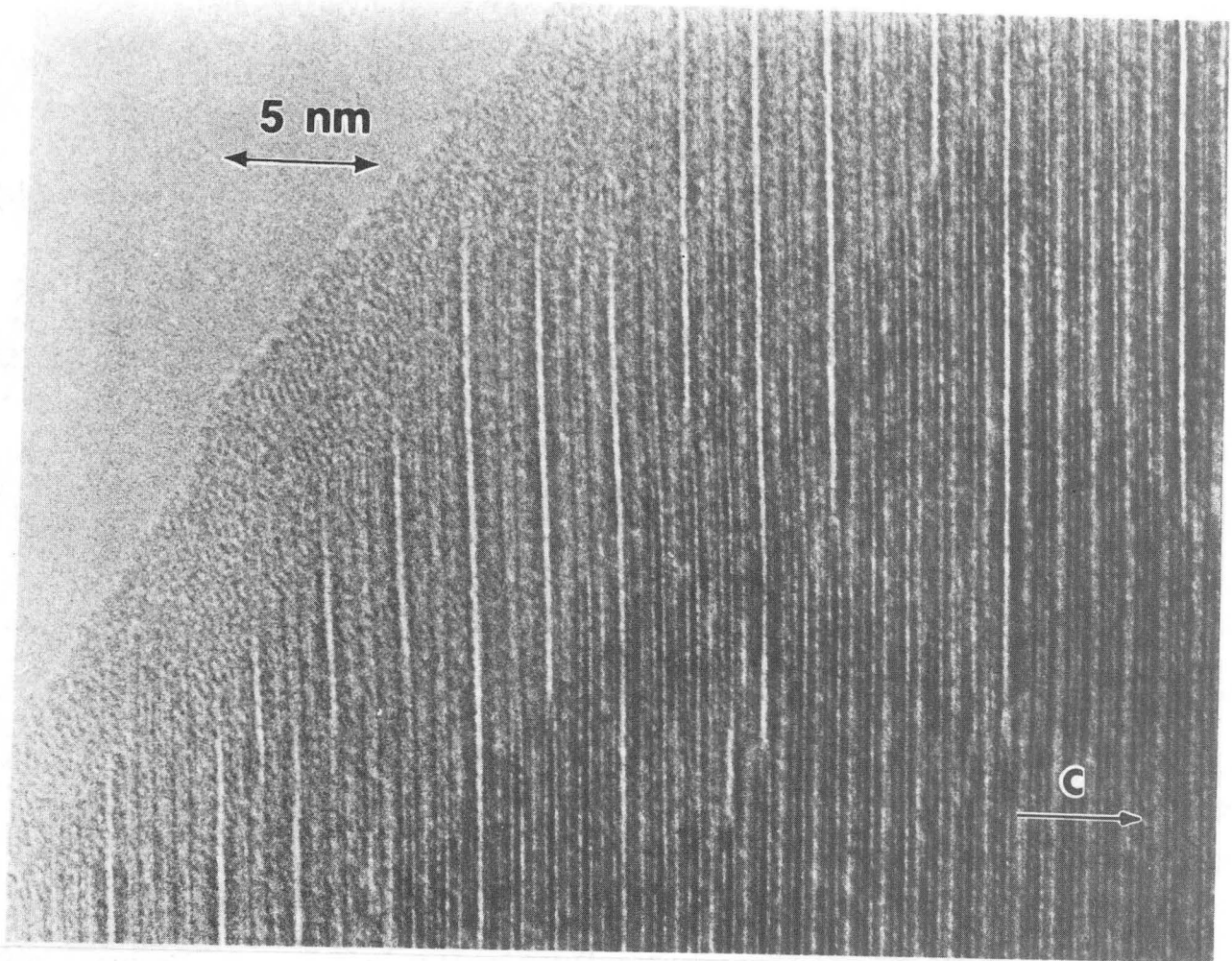


Figure 7

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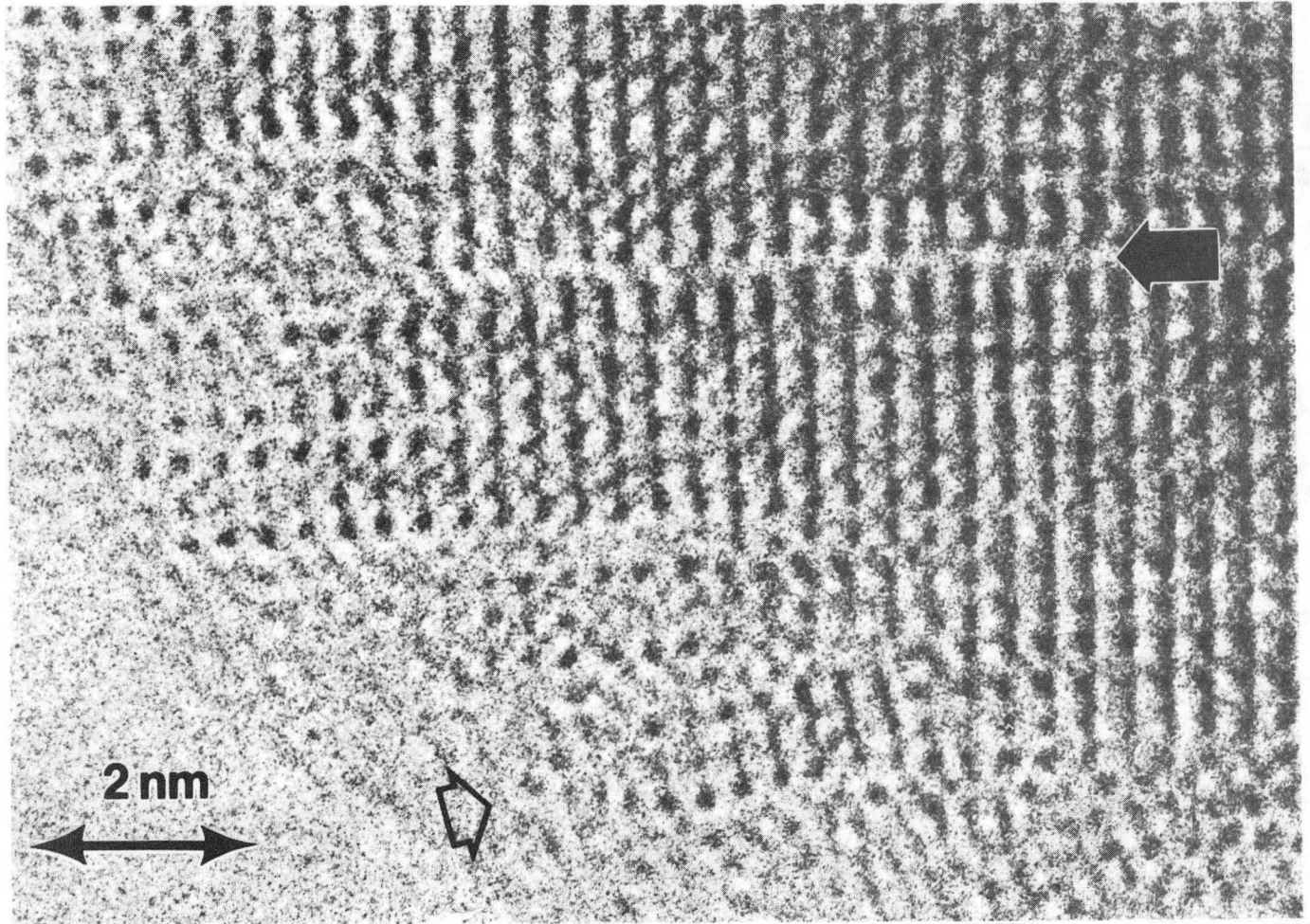


Figure 8

XBB 877-6269

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