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ATOMIC STRUCTURE OF GRAIN BOUNDARIES AND SURFACES IN YBA[SUB]2 CU[SUB]3 0[SUB]7-DELTA AND LABACACU[SUB]3 O[SUB]7-DELTA

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December 1988

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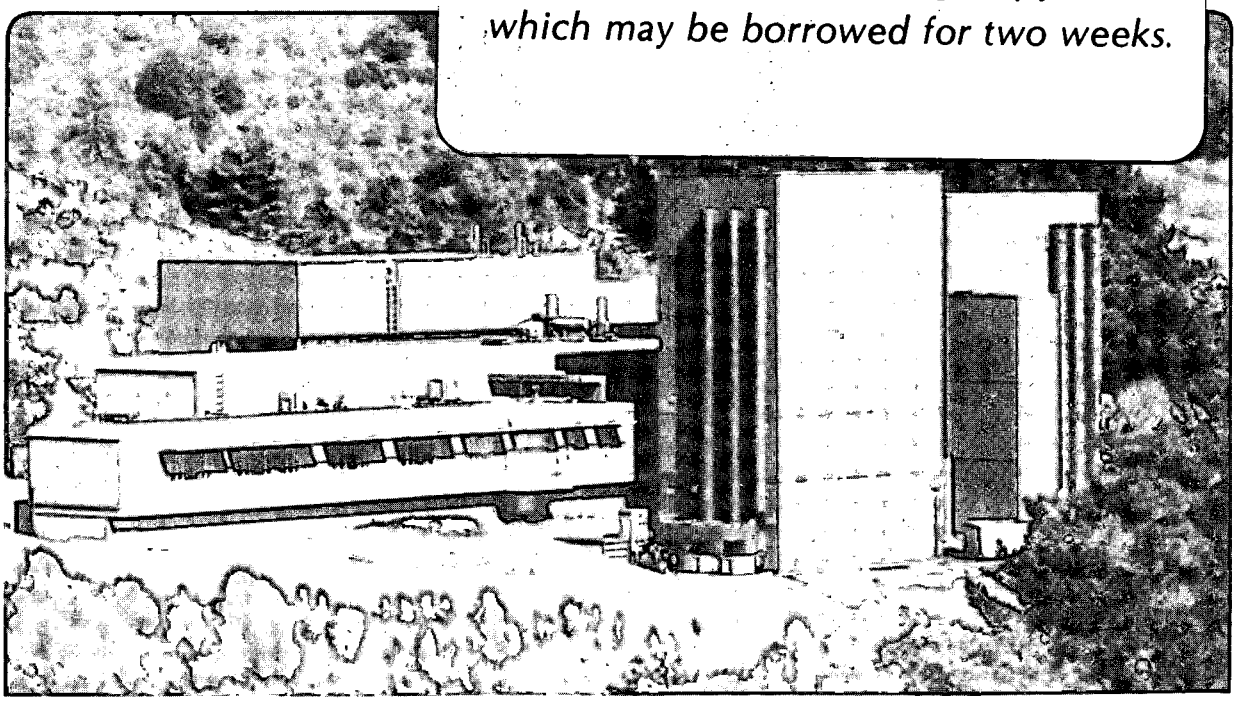

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Atomic Structure of Grain Boundaries and Surfaces in $YBa_2Cu_3O_{7-\delta}$ and $LaBaCaCu_3O_{7-\delta}$

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ATOMIC STRUCTURE OF GRAIN BOUNDARIES AND SURFACES IN $YBa_2Cu_3O_{7-\delta}$ and $LaBaCaCu_3O_{7-\delta}$

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ABSTRACT

High resolution electron microscopy (HREM) studies of grain boundaries and fractured surfaces in both the tetragonal and orthorhombic phases of dense (>90%) $YBa_2Cu_3O_{7-\delta}$ and tetragonal $LaBaCaCu_3O_{7-\delta}$ have been conducted. Grain boundaries in polycrystalline $YBa_2Cu_3O_{7-\delta}$ are found to be frequently parallel to a (001) plane of one of the adjacent grains, with a structure similar to that of the (001) surface of fractured $YBa_2Cu_3O_{7-\delta}$. Matching of experimental and calculated images shows that the outermost surface layer in this compound is a deformed BaO layer. Both grain boundaries and fractured surfaces in $LaBaCaCu_3O_{7-\delta}$ show no such tendency for preferential orientation of the interface plane. Results indicate that the low critical currents observed in sintered materials are caused by textured grain growth in combination with the atomic structure of the grain boundary plane, and the intercalation of off-stoichiometric species near the grain boundary. This work is partly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Dept. of Energy under contract No. DE-AC03-76SF00098.

INTRODUCTION

Phase contrast techniques of high resolution electron microscopy provide a direct image of the atomic structure of most materials under carefully-controlled experimental conditions. This technique has been successfully applied to the analysis of perfect crystals of $YBa_2Cu_3O_{7-\delta}$, yielding excellent agreement with x-ray and neutron scattering data. However, the strength of the technique is its spatial localization, in particular as applied to the analysis of defects in materials. To date, applications of high resolution electron microscopy to the analysis of defects in $YBa_2Cu_3O_{7-\delta}$ have been limited. The first class of defects to be studied were stacking disorders involving the c-planes [1-3]. These are very often created at room temperature or during post-sintering heat treatment [2], e.g. annealing at 450°C, and are exaggerated by some preparation techniques [4]. Because most of these planar defects are formed by an intercalation of Cu and O atoms from the surface [2], the resultant strains cause lattice deformations. Careful studies showed that in properly-prepared bulk $YBa_2Cu_3O_{7-\delta}$ the number of planar defects is very low. Evidently in any study of grain boundaries it is very important that the specimens be carefully prepared and screened against the introduction of artificial planar defects. Other defects which are observed in $YBa_2Cu_3O_{7-\delta}$ polycrystalline materials are: antiphase boundaries, [001] 90° rotation twins and several types of dislocations. These are summarized in [3].

The study of grain boundaries in these materials is becoming increasingly more important [5-6]. It is well known that grain boundaries are sources of problems in many ceramic materials: they affect mechanical properties such as creep, electronic properties such as ionic conduction in ß Na alumina [7-8] and magnetic response such as magnetostriction which can impair soft magnetic properties [9]. Similarly, it should be expected that grain boundaries might affect superconductivity, and any discontinuity in electronic conduction across the boundary plane might account for the relatively poor critical currents observed in sintered specimens. Evidence shows that sintered polycrystalline $YBa_2Cu_3O_{7-\delta}$ with random grain-to-grain orientation exhibits much lower

critical currents than single crystals, typically 10^3 versus 10^6 Amp/cm^2. This is surprising because the material can be densified up to 94%, and the anistropy of the critical current (10) can only account for a relative small drop in J_c due to random grain misorientation. A possible explanation, the existence of an amorphous phase at the grain boundaries, was reported by Nakahara et al [11]. However in all of our investigations no amorphous layer was observed and is therefore ruled out as the only cause of the low critical currents. Detailed high resolution electron microscopy of the grain boundaries was initiated in order to investigate whether the atomic structure at the interface can be the reason for the low critical currents observed in polycrystalline material.

Recently it was reported that $LaBaCaCu_3O_{7-\delta}$ has a T_c of 80 K when it is annealed in oxygen at 400° [12]. This material differs from $YBaCu_3O_{7-\delta}$ in its oxygen ordering [13-16]. Although the total oxygen content is similar, no transformation to orthorhombic symmetry is observed; the material retains tetragonal symmetry. Electron diffraction on the compositions $LaBaCaCu_3O_{6.5}$ and $LaBaCaCu_3O_{6.85}$ showed the presence of a superstructure which can be described with a 4a, 4b, 2c and 2a, 2b, 2c [15-17] unit cell respectively, where a, b and c are the axes of the simple unit cell of tetragonal $LaBaCaCu_3O_{7-\delta}$.

In the series $LaBaACu_3O_{7-\delta}$ where A can be either Ba, Sr, or Ca, the low temperature structure (δ close to 0) changes from orthorhombic symmetry for Ba to tetragonal symmetry for Sr and Ca. No superstructure is observed for the Sr compound. It is suggested by Zandbergen *et al* [14] that in this series the oxygen ordering changes from chains in one direction (Ba) to intersecting chains in two directions (Ca) the last resulting in an octahedrally square planar structure.

It is reported that $LaBaCaCu_3O_{6.85}$ [13] and $LaBaSrCu_3O_{6.85}$ [16] cleave very differently from $YBa2Cu_3O_{7-\delta}$. The preferred cleavage planes of $YBa2Cu_3O_{7-\delta}$ compounds are (001). For the other compounds, no preferred plane of cleavage is observed. In this paper the low energy cleavage and grain boundary planes of both $LaBaCaCu_3O_{7-\delta}$ and

$YBa2Cu_3O_{7-\delta}$ are studied and compared The effect of interfacial plane on transport properties in polycrystalline materials is also discussed, and in particular the importance of the atomic structure at the interface is addressed.

EXPERIMENTAL PROCEDURES

Sample Preparation

Samples were prepared by preheating $YBa_2Cu_3O_{7-\delta}$ at 850°C for approximately 6 hours then sintering for 2 to 48 hours at 950°C into pellet form. Subsequent annealing at 450°C was carried out for several days to ensure complete uptake of oxygen . Specimens representing both the tetragonal phase (before oxygen annealing) and the orthorhombic phase (after oxygen annealing) were prepared for electron microscopy by dry grinding to 10-80μm thickness using 320 mesh paper, followed by ion beam thinning using an Ar beam at 4kV and an incident angle of 12-15° in a liquid nitrogen cooled stage. To prevent reaction of the samples [4] they were left in the vacuum of the ion milling equipment until they could be transferred into the electron microscope.

Electron Microscopy

High resolution electron microscopy was carried out in a JEOL JEM 200CX electron microscope, equipped with a top entry ±10° double-tilt goniometer operating at 200 kV, a JEOL 4000 EX, with top entry ±20° double-tilt lift goniometer operating at 400 kV, and the Berkeley Atomic Resolution Microscope [18] equipped with a ± 40° biaxial, double-tilt goniometer operating at 1000 kV.

EXPERIMENTAL RESULTS

Electron microscopy studies of $YBa_2Cu_3O_{7-\delta}$ and like compounds are difficult because of their instability against the formation of planar stacking faults [4] that increase the c-axis by 15%. Comparisons between simulated images [3,19] and experimental ones

indicate that the disruptive planar defect is a $(CuO)_2$ double layer. *Ex-situ* heating experiments have shown [2] that these defects initiate at internal and exposed surfaces, and are formed by insertion of an extra CuO layer at the site of the original CuO layer between the two BaO layers [1] in the "perfect" structure. An example of the defect is shown in Figure 1. Note that insertion of the extra layer only takes place along the original CuO layer, perpendicular to the c-axis.

$YBa_2Cu_3O_{7-\delta}$

A large number of grain boundaries show the interface of one of the grains to be a low energy (001) plane with the appearance of being formed by impingement of grain upon grain. Figure 2 shows a typical example of a tri-grain junction in the tetragonal phase $YBa_2Cu_3O_{7-\delta}$ material. In none of the specimens investigated was any amorphous phase found to be present at the grain boundaries.

Figure 3 shows another grain boundary in tetragonal $YBa_2Cu_3O_{7-\delta}$. Close inspection of the image reveals that there is an incomplete unit cell, defined here as an intact block of the six-layer sequence CuO_2-BaO-CuO-BaO-CuO_2, bordering the grain boundary. The image furthermore reveals, after careful processing, that the interface terminates at a BaO layer. A similar termination of the lattice is observed for surfaces obtained by fracturing $YBa_2Cu_3O_{7-\delta}$, as can be seen in figure 4, and is also reported by Bursill *et al.* [20] This is consistent with the results of XPS measurements of Halbritter *et al* [21], which show the (001) surface to be a BaO_2 plane.

In material sintered at 950°C for 48 hours and annealed at 450°C for 48 hours, both in an oxygen flow, it was observed that near some of the grain boundaries many $(CuO)_2$ double layers were present as shown in Figure 5. This indicates that prolonged annealing encourages the intercalation phenomenon. Regions of both very high and very low defect density were found near grain boundaries, indicating that the boundaries play an essential

role in the transport of material necessary for the intercalation process. This is expected because of enhanced diffusion along grain boundaries relative to that within the matrix.

$LaBaCaCu_3O_{7-\delta}$

$LaBaCaCu_3O_{7-\delta}$, like $YBa_2Cu_3O_{7-\delta}$, exhibits stacking faults due to the insertion of extra Cu and O leading to $(CuO)_2$ double layers. However, it appeared in this investigation that the rate of deterioration by this intercalation process is considerably slower for $LaBaCaCu_3O_{7-\delta}$. The two compounds also differed significantly in their grain boundary structure. Whereas polycrystalline $YBa_2Cu_3O_{7-\delta}$ preferred a very large fraction of (001) grain boundary planes, $LaBaCaCu_3O_{7-\delta}$ exhibited (001) grain boundary planes far less frequently. An example of a typical tri-grain junction in a crushed sample is given in Figure 6. Note that there is also no preferential (001) orientation of the grain boundaries in this sample.

When a (001) crystal plane is exposed in $LaBaCaCu_3O_{7-\delta}$, the atomic structure at the surface is different from that in $YBa_2Cu_3O_{7-\delta}$. As shown schematically in figure 7, the surface is a CuO layer, and not a BaO layer as in $YBa_2Cu_3O_{7-\delta}$. The exact composition of this surface layer is difficult to establish by inspection of the high resolution image, but the relative intensities of the black dots in the image suggest that the composition could be simply CuO, but also CuO_x.

Another defect observed with high density in the $LaBaCaCu_3O_{7-\delta}$ samples was the [100] 90° rotation twin. Across the twin boundary a **c** axis continues as either an **a** or a **b** axis. Such defects are also found in $YBa_2Cu_3O_{7-\delta}$ but only when prepared at temperatures below 850°C [22].

DISCUSSION

The above results show that the atomic stacking sequence in perfect $YBa_2Cu_3O_{7-\delta}$ is terminated abruptly at those grain boundaries with (001) orientation in such a way that an

incomplete unit cell is left at the interface.[23,27] The structural block observed here, i.e. CuO_2-BaO-CuO-BaO_x, will have different superconducting properties than the perfect 1-2-3 phase, and in fact may be completely insulating. Since the correlation length of Cooper pairs along the **c** axis is approximately 0.6 nm [25], such an insulating layer of 1nm thickness can have a strong negative effect on superconduction, especially because it is so abundant. More than 90% of the grain boundaries observed in these materials were parallel to (001) planes of one of the adjacent grains. For $LaBaCaCu_3O_{7-\delta}$ only a small portion of all grain boundaries are parallel to (001). The correlation length of the Cooper pairs perpendicular to the **c** axis is approximately 2.5 nm and even greater in other directions [25]. Therefore it is expected that tunneling of the Cooper pairs across the grain boundary would be relatively easy and this material might be expected to show better superconducting critical currents.

Nagahara *et al* [11] investigated materials of 1-2-3 phase with small and large grain sizes. They observed that the large-grain material had a plate-like character with a preference for (001) interfaces and interfacial facets, whereas the small-grain material had no distinct faceting. They also found that the small-grain material sustained a considerably higher critical current. This is in conflict with their assumption that an amorphous phase is present at all grain boundaries. However it agrees very well with our model, since in the small-grain material the number of problematic (001) interfaces at the grain boundaries will be much less. Also the observation by Jin *et al* [26] that **c**-axis aligned polycrystalline material has a much higher critical current is in agreement with our model. In this case the grain boundaries will join either two non-conducting (001) interfaces perpendicular to their common **c** axis, or two conducting (001) interfaces in a direction closely parallel to their common **c** axis.

Intercalation of extra CuO layers is found to take place in both compounds even at room temperature and is enhanced progressively at increasing temperatures. This intercalation occurs only along the CuO planes, viz. normal to the **c** axis, and is

consequently restricted by diffusion of Cu and O from the surface. Investigation of dense orthorhombic material, sintered and annealed for several days, showed that the intercalation can also take place along those CuO planes intersecting grain boundaries (see figure 3). When the grain interface is a (001) plane, intercalation from that grain boundary obviously cannot occur, and this is observed experimentally. Although the volume fraction of grain-boundary intercalated material might be small when it does occur, the effect on the critical current will be large, since the affected material is concentrated at grain boundaries.

Due to the expansion of the c axis caused by the extra CuO layer (~15%), partial intercalation will lead to local lattice bending [2,24]. This lattice distortion causes difficulties in image interpretation, but it also might have a significant effect on superconducting properties. Kapitulnik *et al* [27] report that structurally-modified 1-2-3 phase in which every CuO layer is replaced by a $(CuO)_2$ double layer, in a sense the extreme of the intercalation behavior observed here, leads to the compound $YBa_2Cu_4O_{8-\delta}$ which has a T_c of approximately 80 K. But Bordet *et al.* [28] report that $Y_2Ba_2Cu_7O_{15-\delta}$, which has every second CuO layer replaced by a $(CuO)_2$ double layer, has a T_c of 40K, showing that a mixture of single and double layers does not necessarily interpolate to a T_c value between those for a pure single CuO layer material and pure $(CuO)_2$ double-layer material. Unfortunately, partial intercalation and its concomitant lattice distortion might cause strong decreases in the critical temperature and current. One possible cause for poorer superconducting properties in the locally intercalated regions is the detailed structure of the core of the distortion observed at high spatial resolution. At the termination of the intercalated layer there is a bifurcation of the original CuO layer into the two layers comprising the $(CuO)_2$ double layer.

It is instructive to compare $LaBaCaCu_3O_{7-\delta}$ with $YBaCaCu_3O_{7-\delta}$ not only because of their grain boundary structures, but also for their twinning behavior. Since $LaBaCaCu_3O_{7-\delta}$ is tetragonal, no (110) mirror twins of the type found in $YBaCu_3O_{7-\delta}$ are observed. These twins cannot be avoided in $YBaCu_3O_{7-\delta}$ because of the transformation

from tetragonal to orthorhombic structures. Consequently, the influence of these twin boundaries in $YBa_2Cu_3O_{7-\delta}$ can be determined from a direct comparison with the pinning properties of $LaBaCaCu_3O_{7-\delta}$. Moreover, another type of twin observed in $LaBaCaCu_3O_{7-\delta}$ can possibly be used to create pinning centers. This twin is a [100] 90° rotation twin, also observed in $YBa_2Cu_3O_{7-\delta}$ when it is fired at temperatures below 850°C. With decreasing temperatures the twin density in this compound decreases [22]. It is reported that the higher twin density is favored because the difference between the **c** axis and three times the **a** axis becomes progressively less at lower temperatures, increasing the strain energy of the twinned material. The c/a ratio for $LaBaCaCu_3O_{7-\delta}$ is very close to 3 explaining the preferential occurrence of twins in this material. From the results observed in $YBa_2Cu_3O_{7-\delta}$ it is expected that lowering the sintering temperature might enhance twin formation in $LaBaCaCu_3O_{7-\delta}$. Furthermore, by cycling between two temperatures, it might be possible to create intergrowths of regions with low and high [100] 90° rotation twin density, thereby producing microstructural regions with a strong flux-pinning capacity.

CONCLUSIONS

The low critical current in polycrystalline $YBa_2Cu_3O_{7-\delta}$ is attributed to the structure and frequent occurrence of low-energy (001) interfaces at grain boundaries, as well as the intercalation of extra CuO planes along those CuO planes that intersect grain boundaries. Since both phenomena are inherently associated with the chemical bonding configurations of bulk $YBa_2Cu_3O_{7-\delta}$, the critical current cannot be improved significantly by grain boundary engineering alone. By contrast, $LaBaCaCu_3O_{7-\delta}$ shows no preference for faceted (001) grain boundary planes; consequently, higher critical currents are expected for this material. However, the absence of twin boundaries in tetragonal $LaBaCaCu_3O_{7-\delta}$ provides fewer pinning sites which could adversely affect J_c. At the moment investigations on these characteristics are being carried out.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Example of planar defects in $YBa_2Cu_3O_{7-\delta}$ viewed along [010]. The defects are formed by intercalation of Cu and O, creating a $(CuO)_2$ double layer. Depending upon the shift (a/2 or b/2) across the layers, two different images are obtained for the same defect as shown here. The figure shows (a) the digitized image, averaged over 10 unit cells along the **a** axis, (b) the calculated image, (c) the image without any image processing and (d) the model used for the image calculations. More details on the image calculations are given in ref [1]. XBB 881-479.

Figure 2. Tri-grain junction observed in tetragonal $YBa_2Cu_3O_{7-\delta}$ and typical for this material. No amorphous phase is observed at the grain boundaries. The two large grain boundaries are parallel to the (001) planes of one of the adjacent grains. About 90% of the grain boundaries show this configuration. XBB 870-10597.

Figure 3. Micrographs showing (a) the structure of the (001) interface at the grain boundary, and (b) and (c) the same image after processing by averaging over a repetition period characteristic of the top and bottom grain respectively. At the interface a CuO_2-BaO-CuO-BaO_x block is present, probably leading to an insulating layer. XBB 8711-4633.

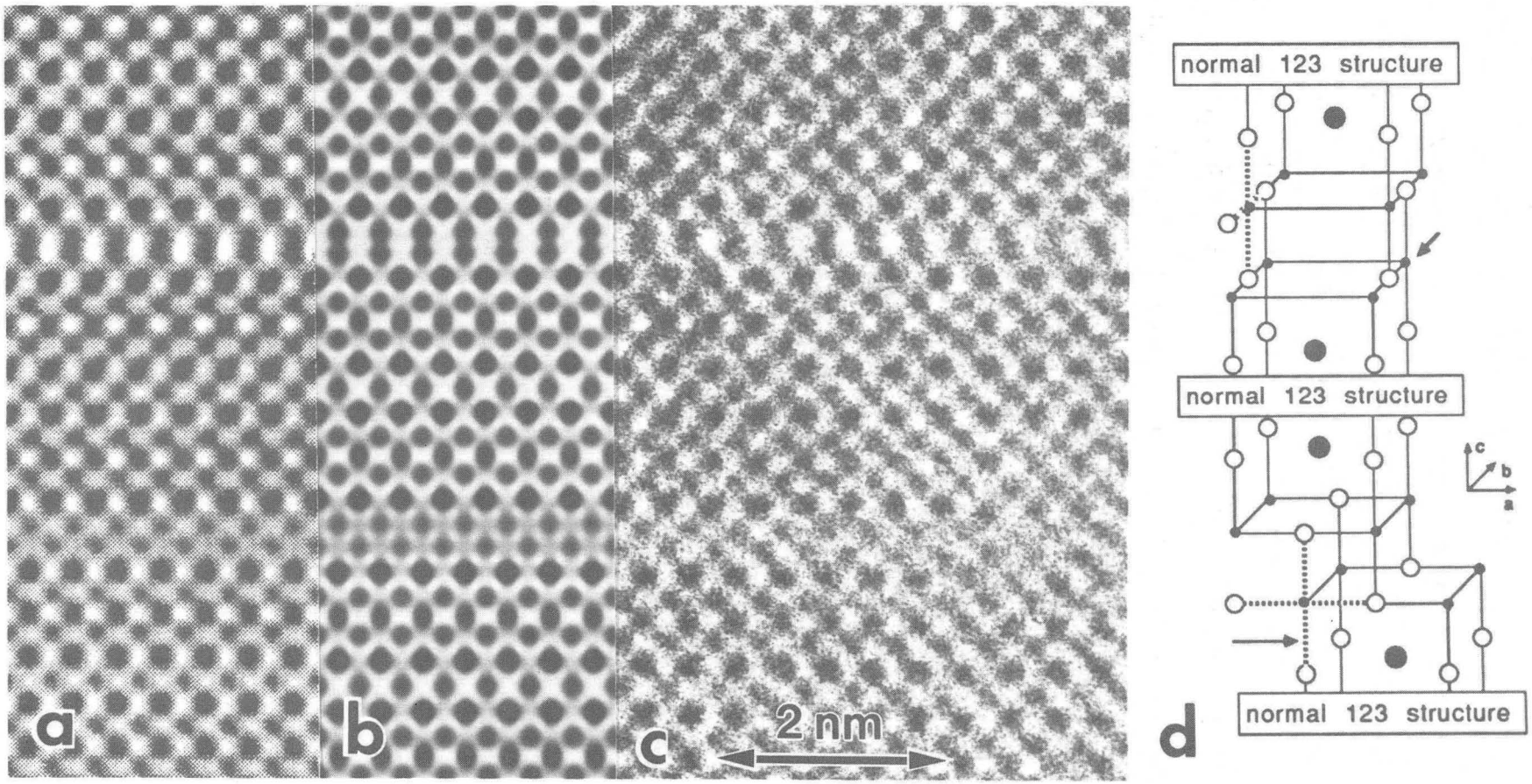
Figure 4. The surface of a fractured crystal from a polycrystalline sample of $YBa_2Cu_3O_{7-\delta}$. The atomic structure at the surface is similar to that of the grain interface shown in Figure 3. XBB 870-10603.

Figure 5. Micrograph of a grain boundary in dense $YBa_2Cu_3O_{7-\delta}$, which has been sintered at 950°C and annealed at 450°C, both treatments conducted for 48 hours in oxygen. The upper grain is approximately 10° off of an exact [110] orientation and the lower grain exactly in the [100] zone. The lower grain has only $(CuO)_2$ double layers in the region shown. Note the continuous bending of the (001) layers over the whole region. Furthermore the grain boundary shows a stepped interface with the [100] grain, whereas the other grain has grown into the steps to complete impingement. The grain boundary remains straight in spite of the severe lattice bending and 15% expansion caused by the intercalation. XBB 888-7815.

Figure 6. Tri-grain junction in air-quenched (from 950°C) $LaBaCaCu_3O_{7-\delta}$. No amorphous material is seen at the grain boundaries. The grain boundary planes have high crystallographic indices relative to the lattices of the adjacent grains. XBB 8812-11401.

Figure 7. [100] high resolution micrograph showing a fractured surface in $LaBaCaCu_3O_{7-\delta}$ obtained by grinding. Note the peculiar image at the surface. This suggests that at the [001] step on the (001) surface, Cu atoms are absent , allowing the Ba atoms shift towards the Cu sites. Further away from the step, the contrast of the atomic columns is reduced, indicating either a smaller amount of Ba or more likely, the presence of Cu at the surface. This step is schematically represented in the right hand side of the figure. XBB 8812-11400.

Figure 8. Micrograph of a [100] 90° rotation twin observed frequently in specimens of $LaBaCaCu_3O_{7-\delta}$. XBB 8812-11399 .



XBB 881-479

Figure 1

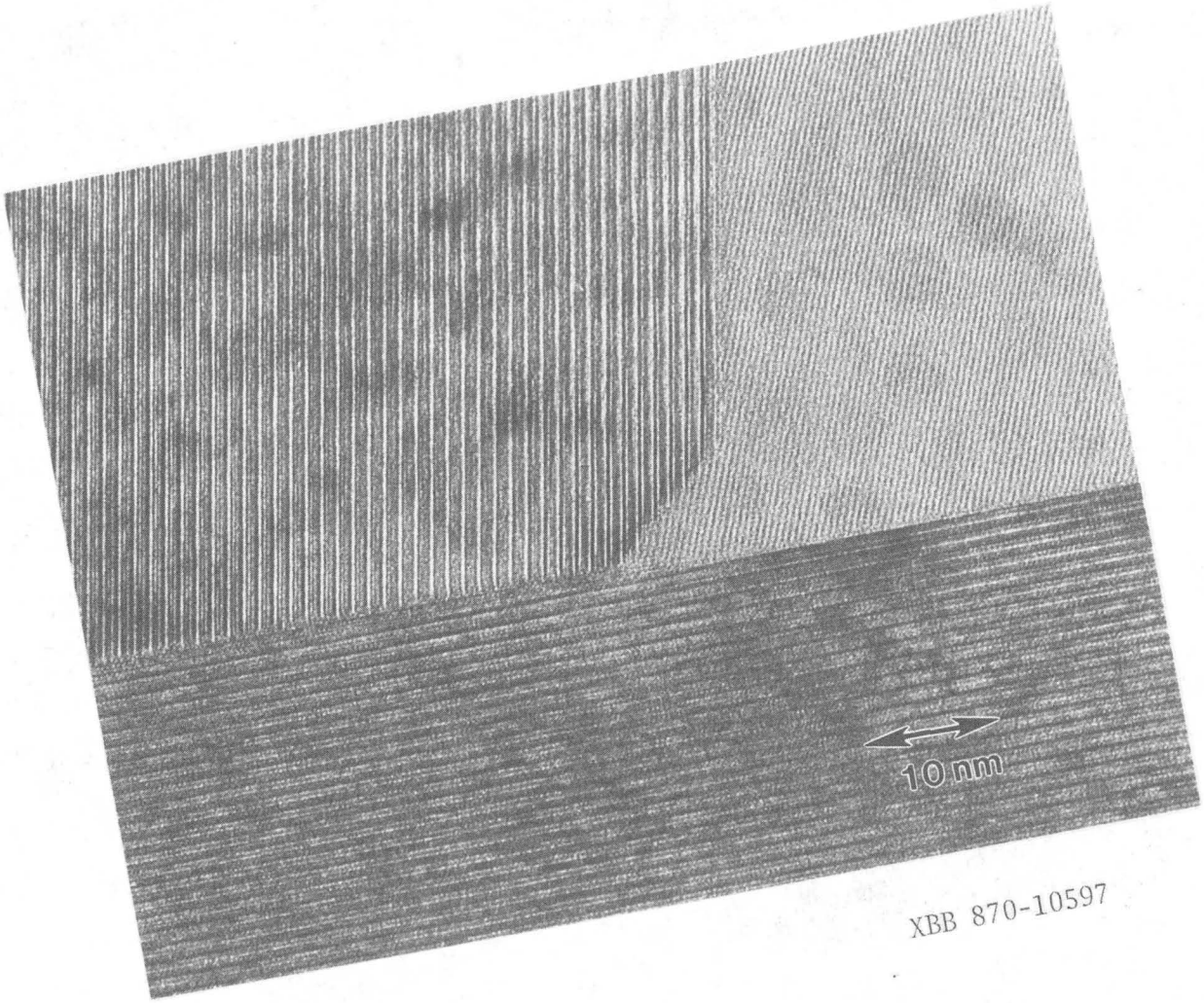


Figure 2

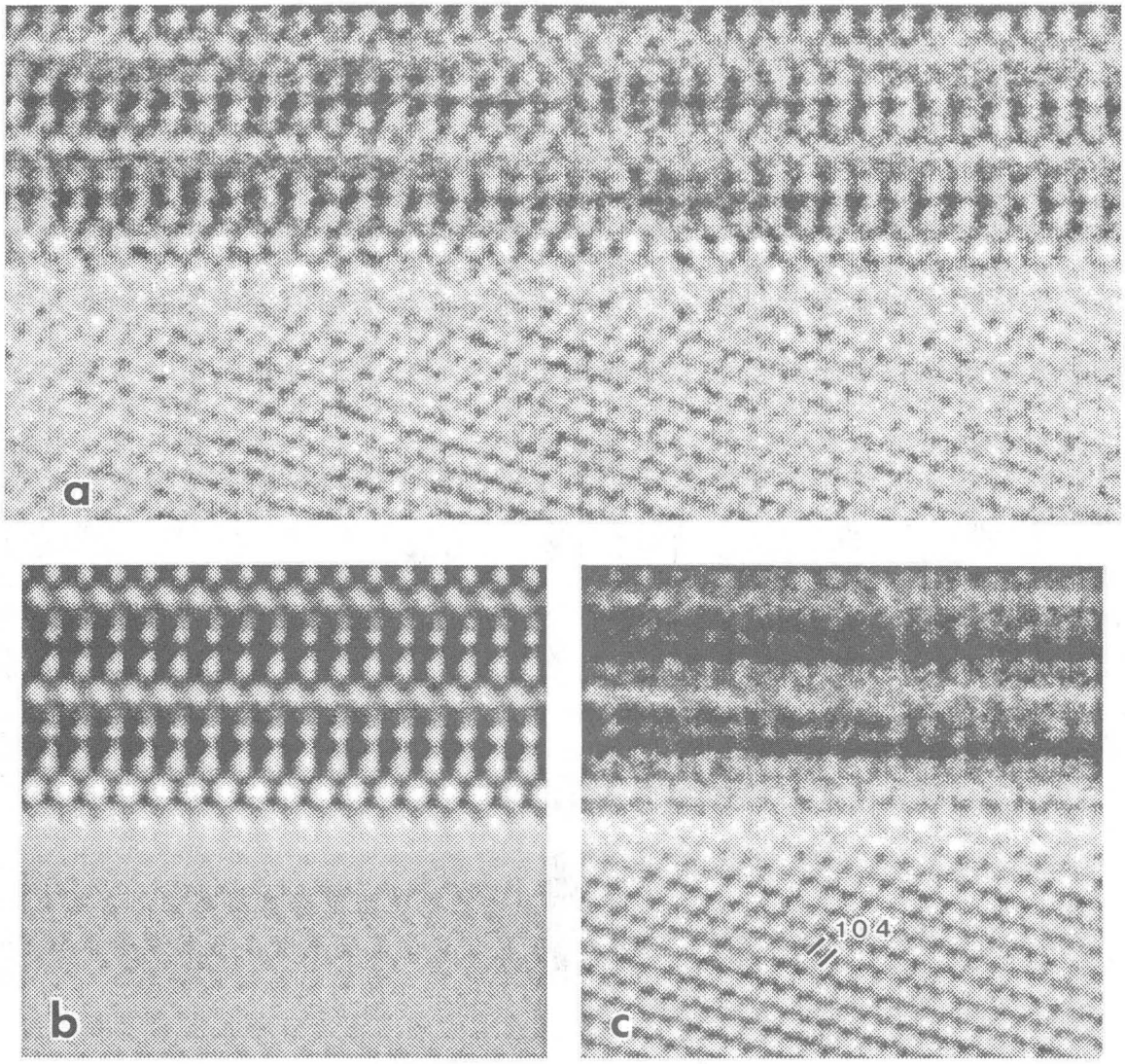


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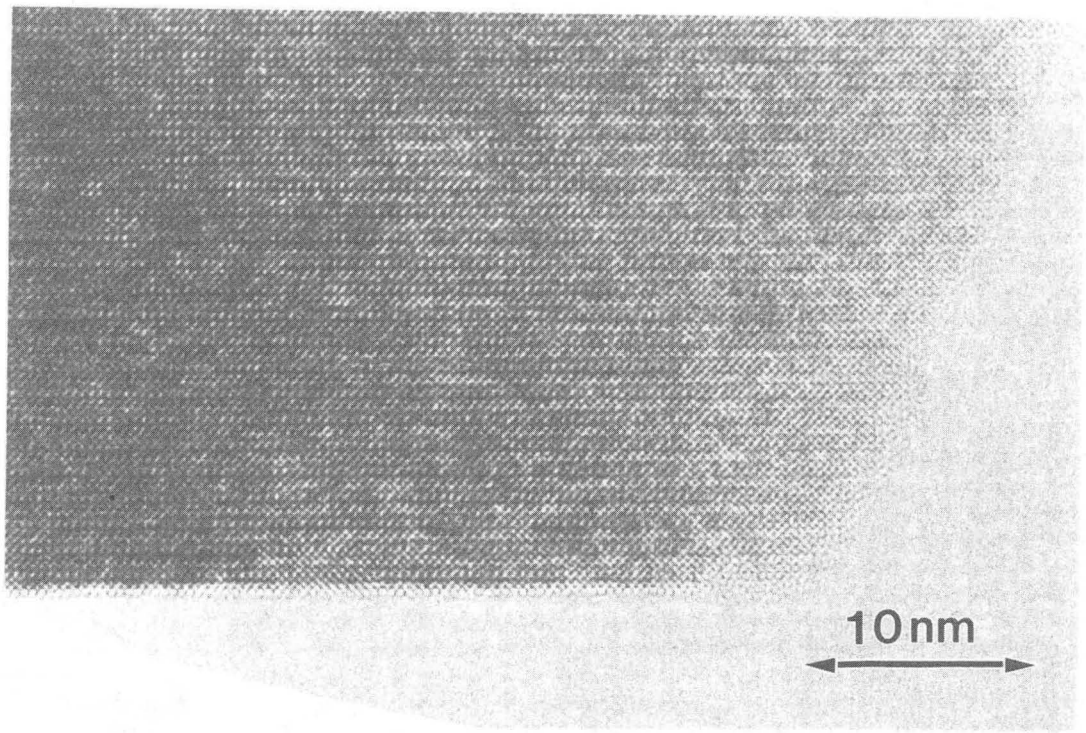
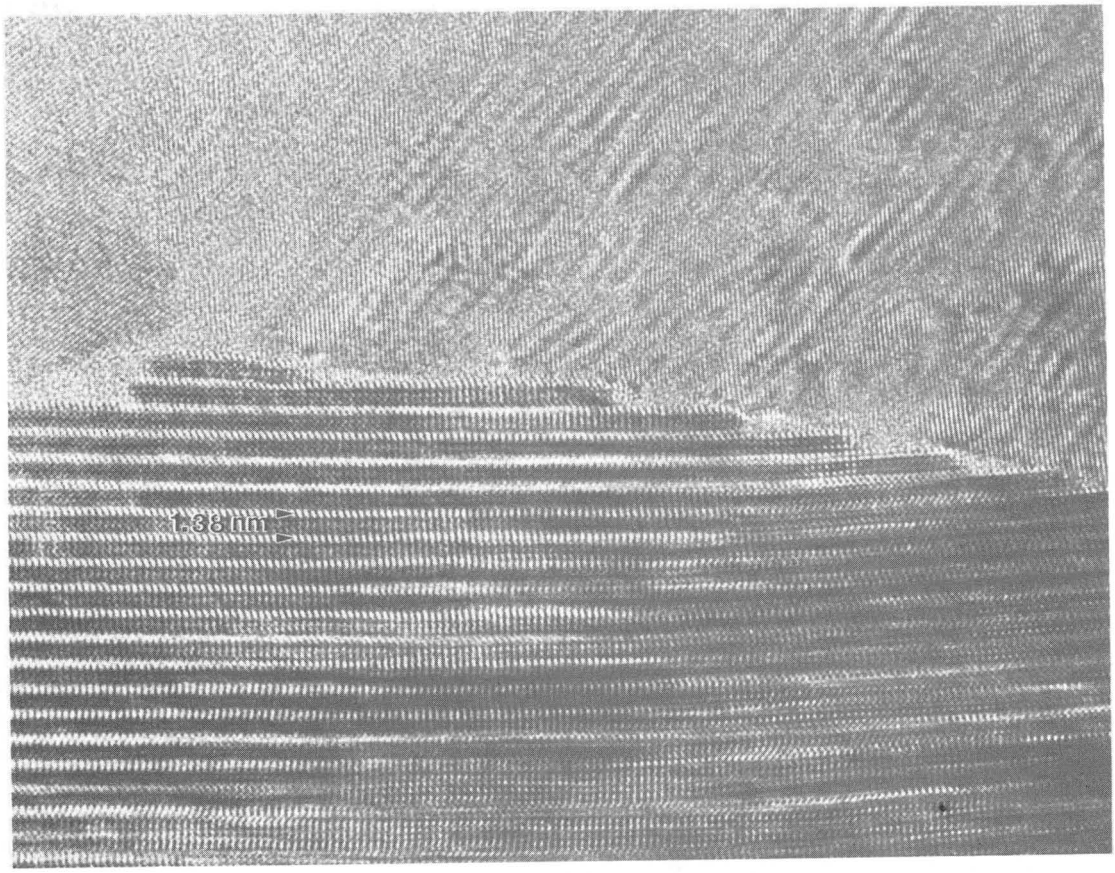
Figure 3



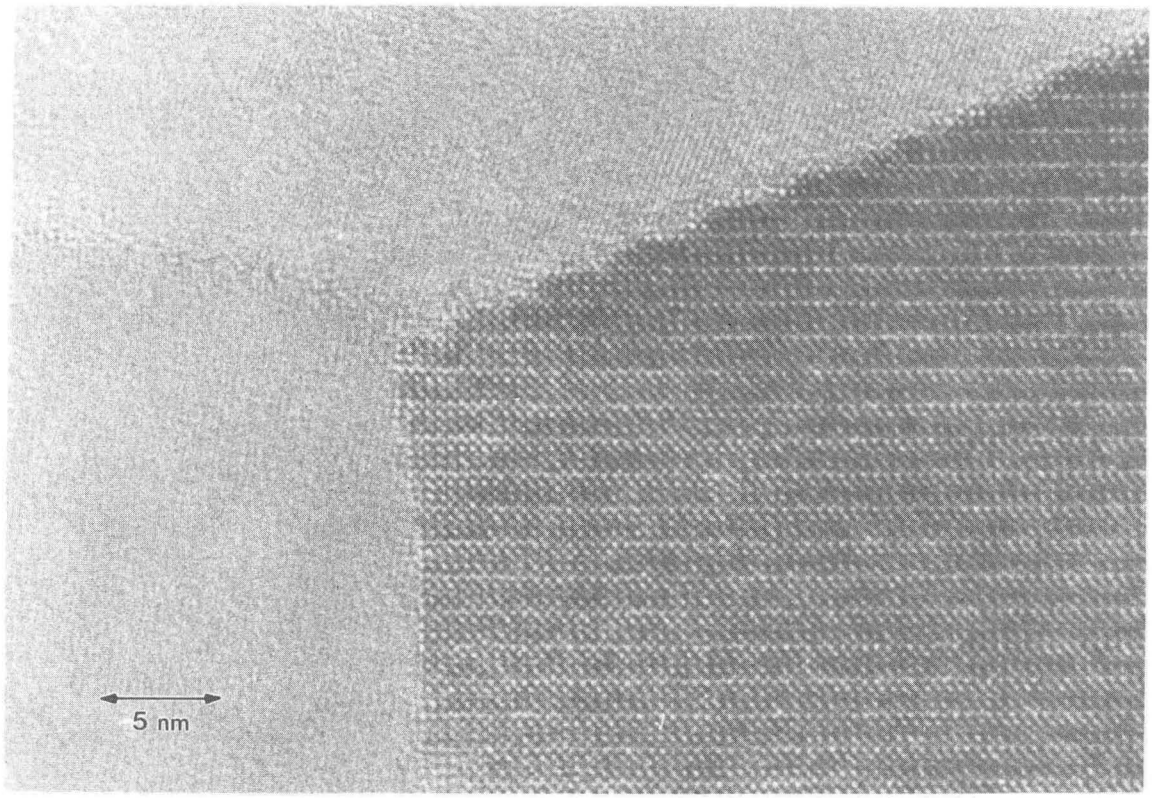
XBB 870-10603

Figure 4



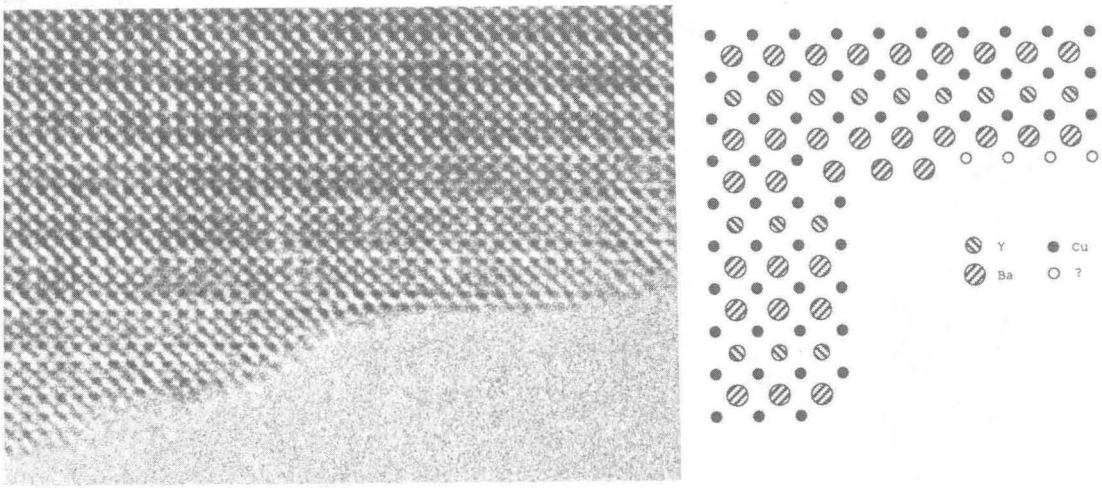
XBB 888-7815

Figure 5



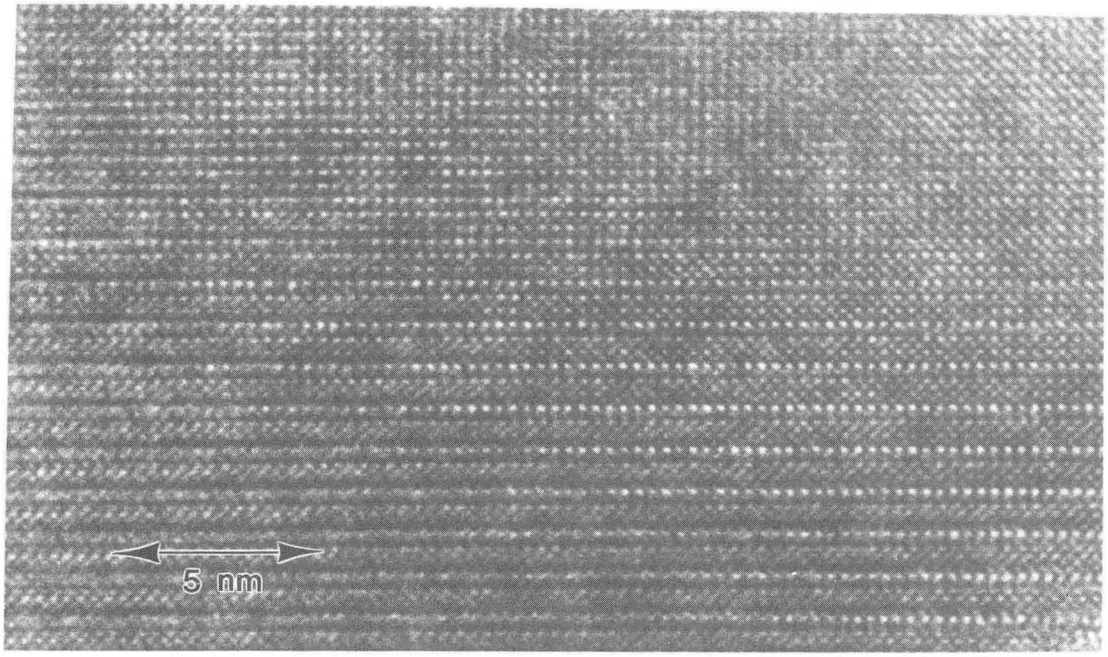
XBB 8812-11401

Figure 6



XBB 8812-11400

Figure 7



XBB 8812-11399

Figure 8

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