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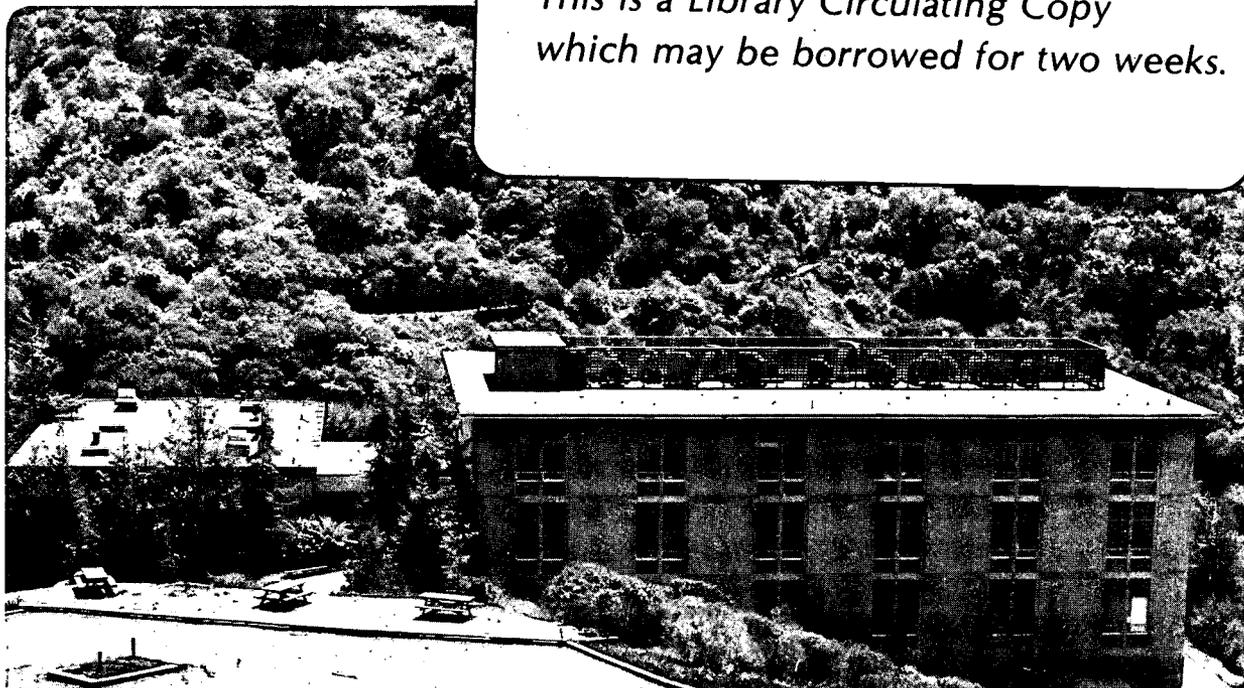
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Sample Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for High Resolution Electron Microscopy

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Abstract

An overview is given of three techniques for preparing thin specimens of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for high resolution electron microscopy: grinding, cleaving, and ion milling. Advantages and disadvantages are described, with particular attention to the artefacts that may be introduced by the different techniques. It is concluded that the most serious problem encountered during high resolution electron microscopy studies is a surface-initiated decomposition leading to the ultimate degradation of the structure. This problem was found to be most pronounced in ion-milled specimens.

Introduction

Specimens for high resolution electron microscopy must be clean, thin, and flat in order to guarantee that phase contrast images can be properly interpreted. Cleanliness is needed to avoid background signals from surface overlayers or oxide films. Sufficiently strong background, even from amorphous layers, can completely disrupt a phase contrast image^[1]. Specimen thickness should be controlled to maintain the image formation process within the linear regime^[2] for accurate interpretation. This requires thicknesses no greater than one extinction distance for primary scattering by the lowest-order Bragg reflection (e.g. copper must be less than 24 nm thick, while aluminum could be 55 nm thick). Finally, flatness is essential if proper orientation is to be preserved over large image areas.

Unfortunately this combination of characteristics induces competition in the

sample preparation process. Thin samples are less likely to remain flat due to bending (or fracture) under the beam, and they are much more susceptible to image artefacts from contamination overlayers that might be introduced by careless handling or exposure to reactive atmospheres. Surface cleaning, often performed by ion milling, can introduce other artefacts due to local damage or heating. Finally, the actual observation of the specimen might also be a source of electron irradiation damage which the microscopist must recognize. Since the objective of any preparation activity is the production of a representative sample, all phases of the process are critical.

These considerations place stringent requirements on the preparation of the new oxide superconductors for examination by high resolution electron microscopy. The materials as a class are brittle, often examined in powder form, notorious for variations in oxygen stoichiometry, and complex in structure. In this paper an overview and comparison of specimen preparation techniques is presented for the specific case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Description of Techniques

Mechanical Grinding

This procedure is both rapid and simple, and a large number of variations are possible. Beginning with a pellet fragment or coarse powder of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound, the material is ground to a fine powder using a hard (e.g. agate) mortar and pestle. Porcelain vessels are not recommended because any surface abrasion can introduce impurities into the powdered sample. After grinding, the powder is suspended in an inert liquid, where particle dispersion can be facilitated by various agitation methods (e.g. ultrasonic). A few droplets of the suspension are then put on a carbon-coated thin film and transferred immediately into the microscope. An example of a dispersion of crystals on a holey carbon film is given in Figure 1.

Variations in this basic procedure are used to give control over the final specimen morphology. For example, if the 1-2-3 compound is partially ground, rapidly cooled in liquid nitrogen, then further ground in the suspension medium, the powders are more flake-like, due to preferential fracture along c planes. This

causes them to settle onto the carbon film with a strong *c*-axis texture. Similar results are obtained in β -alumina type materials [3]. By changing the type of suspension fluid and/or the settlement time after agitation, the size range of the selected powders can be varied. After settling, the suspension contains more fine particles at the top of the fluid, and coarse particles at the bottom.

The support on which the suspension is deposited can be either a continuous film or a holey carbon-coated film covering a metal grid. In the latter case, adjustment of the size of the holes leads to size selectivity; larger particles will be caught by the support film, but smaller particles will fall through. Large thin particles bridging the holes of the support film are most desirable for high resolution electron microscopy, since these will have no background signal from the support film. However, larger particles are also more prone to charging under the electron beam, so some compromise is necessary. To increase the density of particles on the support, multiple droplets of the suspension can be used. The deposition process can furthermore be enhanced by backing the support grid with filter paper to provide for rapid extraction of the suspension fluid. Conversely, by applying a single droplet of the suspension onto the support film and waiting for the fluid to evaporate in air, the full density of particles within the droplet can be collected.

The most commonly used support films used are the polymeric Triafol® or Formvar® holey films which can be coated with carbon to prevent electrical charging and heating of the film under the electron beam. Unfortunately, reaction of the coated film with the electron beam can also lead to the deposition of an amorphous contamination (carbonaceous) layer on the surface of the crystal being imaged. This same contamination layer might influence the rate of irradiation damage of the sample (e.g. sub-threshold damage [4]), and it certainly increases the background noise in the image, so it should generally be avoided by minimizing any beam exposure of the carbon-coated film near the particle(s) of interest.

An alternative is to replace the holey carbon film with one that does not contain carbon. One technique is to coat the original Triafol® or Formvar® film with Si_3N_4 [5], then bake at sufficiently high temperatures to completely remove all of the polymer, leaving a Si_3N_4 replica of the holey film. Because it can be raised to temperatures up to 500° C, this film can be used in heating experiments [6]. It is also mechanically stable and very clean, two more significant advantages for high resolution imaging.

Cleaving

In this technique, a sintered pellet is carefully ground to a thickness of approximately 100 μm , then fractured in a controlled way to produce fragments ranging in size between 0.5 and 1.0 mm. These fragments are then mounted on grids before viewing in the microscope. As in any other cleaving process, it is best to use a sharp edge (e.g. a razor blade) which in this case is simply pressed into the pre-thinned sample. Because of the brittleness of the 1-2-3 compound, the amount of control exerted over the cleaving process is variable, and catastrophic fracture is often observed. It is therefore frequently necessary to select from among several fragments those that appear thin enough for microscopy. Note that by adjusting the initial grinding step (i.e. single sided or two-sided), it is possible to select samples from different locations within similar pellets.

Two principal methods can be used for mounting the fragments onto electron microscopy grids. In the first, the fragments are glued onto the type of grid having a large, single, oval-shaped slot so that the thinnest edges of the fragments are freely suspended over the slot, as shown in Figure 2. A conducting (e.g. silver) epoxy must be used to prevent charging and heating of the sample. Success in this delicate operation normally requires extra fine tweezers and a stereo microscope capable of 20X magnification. It also helps if the epoxy is viscous enough to retain the fragments in place even before the glue completely "sets". An important advantage of this method is that several fragments can be mounted onto the same grid. An important disadvantage is the epoxy curing time. Because most epoxy resins require hours at low temperatures (50° C) or somewhat shorter times (minutes) at higher temperatures (150° C) in order to cure, the sample is susceptible to considerable degradation before it can be viewed in the microscope.

As an alternative, it is also possible to secure the cleaved fragments within a folding grid. This, too, is a delicate operation, which can be made somewhat easier by first folding the grid halves to a shallow opening angle. It may be necessary to first anneal the folding grids (e.g. 15 minutes at 900°C for Au grids) to remove some of their residual strains and prevent brittle fracture. The fragments can then be pre-positioned before completely closing the grids, readjusted into position after closing, then clamping tightly. The successful mount has thin area appearing between the

two sets of grid bars. Trimming can be used to enlarge openings, although it is best to begin with 100-150 mesh grids and fragments of about 1 mm maximum dimension.

Cleaving can be applied universally to any material or composite with suitable fracture properties, including superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin films on substrates. Figure 3 illustrates the type of specimen that can be obtained; note that the thin film/substrate interface is imaged in cross section. The sample was prepared by successive cleaving until a fragment was obtained with a shallow wedge shape.

Ion Milling

Sample preparation by ion milling is generally carried out in three stages: (1) mechanical pre-thinning, (2) rapid ion milling at steep ($12\text{-}20^\circ$) incidence angles, and (3) final ion milling at shallow ($5\text{-}10^\circ$) incidence angles. The first step can drastically cut down on the time in the ion mill, and help to localize the thinning process by "dimpling". The third step, which continues until the sample is electron transparent, also ensures that the surface of the specimen is free of contamination layers.

Because $\text{YBa}_2\text{Cu}_3\text{O}_7$ decomposes in water, all grinding must be done "dry". A wafer thickness of $10\mu\text{m}$ is close to the upper limit for beginning ion milling, since at this starting thickness, the required time in the ion mill is nearly two days. The pre-thinned wafer is cut into small fragments and fastened to single-hole copper grids using silver epoxy before mounting in the ion mill. Acceptable samples can be obtained with a 4 KeV Ar beam at an incident angle of 12° and liquid nitrogen cooling; final low-angle thinning would be required only to remove the amorphous surface layers produced by ion damage. Above all, the specimen should be left in the ion mill under vacuum until *just before* it is put into the electron microscope.

Comparison of Techniques

Although all of the techniques described above will produce specimens that are *thin* enough for high resolution electron microscopy, some are better than others for producing *representative* specimens of the 1-2-3 compound. A very important factor in the comparison of these techniques is the decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, an example of which is given in Figure 4. This decomposition is due to an intercalation of Cu and O along the CuO planes containing the Cu-O-Cu-O chains, causing a stacking fault. Because of this intercalation, the lattice expands along the c-axis leading to local stresses which stimulate additional intercalation in other nearby layers and finally leads to the collapse of the structure. Since the intercalation can only take place along the CuO planes, it can be classified as a surface phenomenon.

Because electron microscopy specimens are so thin, they are especially susceptible to this decomposition reaction. Nevertheless, there are large differences in the rates of decomposition observed in specimens prepared by the three techniques described above. Three factors seem to be important: direct contact with hydrophobic solvents, the presence of an amorphous layer of decomposed $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on the surface of the crystalline phase, and the oxidation state of the compound. The first two factors may be related because the amorphous layer is expected to contain hydroxides and hydrates. The third factor has not been studied systematically, although most results suggest an increasing rate of decomposition with an increase in δ . As shown in Figure 5, it is possible to obtain very clean fracture surfaces by mechanical grinding. Similar results are achieved by cleaving. However, ion milling always causes some amorphization (Figure 6), which complicates high resolution image interpretation.

Following a direct comparison of the density of defects observed in specimens prepared by various techniques from the same starting material, a relative ranking has emerged. Surface decomposition was an increasing problem in this list: (1) freshly cleaved fragments; (2) ground material dispersed in ethanol; (3) the same material left in air for one day; (4) ion-milled material put directly in the electron microscope; (5) ground material dispersed in ethanol and left in flowing air for one day; (6) ion milled material left in air for one day.

Consequently, the type of information required from a transmission electron

microscopy study limits the choice of sample preparation. Although ion milling provides specimens well-suited to a study of the atomic structure of grain boundaries (large thin areas), this technique also promotes the intercalation reaction that results in decomposition of the 1-2-3 phase, and leaves amorphous surface layers in most cases. High resolution images of ion-milled specimens must therefore be interpreted with great care, preferably in conjunction with a parallel study of cleaved specimens to identify sources of decomposition artefacts.

Artefacts

Ion Milling

There are other artefacts associated with ion milling, some of which, like the presence of an amorphous surface layer, are widely known. Others however are more difficult to recognize. When a sample contains microcracks, ion milling can cause the cracks to fill with the same amorphous material that appears on the surface of intact samples, making it impossible to determine whether an amorphous film (e.g. at a grain boundary) was present before ion milling. This problem is further complicated by the fact that brittle materials, like the 1-2-3 phase, might crack as they are thinned, especially if they are prone to experience transformation stresses such as that accompanying the tetragonal to orthorhombic transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. An example is shown in Figure 7. Residual strain has caused the [100] oriented grain to locally bend in the grain boundary vicinity, clearly revealed by the deviation from linearity of the (001) mirror planes. This deviation is exactly equal to the opening angle of the amorphous interlayer at the grain boundary plane.

Radiation Damage

Another potential source of artefacts in image interpretation is the microscope itself. It is important to realize when electron irradiation damage is a problem, and how to distinguish it from artefacts induced by specimen preparation. Figure 8 compares high resolution images taken in two electron microscopes, a top

entry JEOL JEM 200 CX operating at 200 kV and the Berkeley Atomic Resolution Microscope (ARM) operating at 1000 kV. Whereas a crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ can be studied for several hours or more using the 200 CX, in the ARM, the edge of the crystal is already completely amorphous after less than 1/2 hour under the beam. No significant reduction in damage was found in the ARM operating at 700 kV. Fortunately, the tilting facilities of the ARM are excellent, and a crystal can be tilted into the desired imaging orientation within a few minutes, before detectable damage sets in.

There may be even more dramatic changes on a shorter time scale due to beam heating. Figure 9 illustrates the rearrangement of twin boundaries caused by short exposure to an intense beam that raised the temperature of the specimen above the orthorhombic-to-tetragonal transition temperature. Although this may be an interesting advantage for studying dynamic changes in some systems, the loss of oxygen in the microscope environment limits its application to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Conclusions

Sample preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for high resolution electron microscopy is complicated by the instability of the 1-2-3 phase with respect to oxygen intercalation. Representative samples are best prepared by cleaving, followed by grinding, then ion milling. A detailed comparison appears in Table I. In every case the thinned specimens should be immediately inserted into the microscope, imaged under low dose conditions, and compared with specimens prepared under other conditions to identify artefacts.

Acknowledgements

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References

1. R. Kilaas and R. Gronsky, *Ultramicroscopy* **16**, 193 (1985).
2. M.A. O'Keefe, in 37th Ann Proc. Electron Microscopy Soc., Amer., G.W. Bailey (ed.), Claitor's, Baton Rouge, (1979), p.556.
3. H.W. Zandbergen, D.J. Mylhoff, D.J.W. Ydo and G. VanTendeloo, *Mat. Res. Bull.* **19**, 1443 (1984).
4. L.W. Hobbs, *Ultramicroscopy* **3**, 381 (1979).
5. H.W. Zandbergen, A. Pruyboom and G. VanTendeloo, *Ultramicroscopy* (in press).
6. H.W. Zandbergen, R. Gronsky, and G. Thomas, *phys. stat. sol. (a)* **105**, 000 (1988).

TABLE 1
COMPARISON OF PREPARATION TECHNIQUES

	<u>Grinding</u>	<u>Cleaving</u>	<u>Ion Beam Thinning</u>
chance of overlap by another crystal	very low	high	good
study of surface phenomena	good	very good	poor
sample drift under the electron beam	minimal	variable	variable
labor time / equipment time	5 min./5 min.	0.5 hr. /0.5 hr.	3 hrs/2 days
sample stability after preparation	moderate	good	poor
alteration of sample by preparation	low	none	considerable
suitable for study of grain boundaries	yes	yes	yes
number of grain boundaries per grid	low	low	high
representative of bulk situation	no	no	possibly
surface condition	clean	clean	amorphous layer
determination of original location of crystal in pellet	impossible	easy	easy
<i>in situ</i> high temp studies	difficult ¹	possible	possible
<i>ex situ</i> heating and re-examining in microscope	possible up to 600°	possible ² up to 900°	difficult ³
cost in \$	1	1	100

¹Because of possible bad thermal contact between crystals and heating device.

²with Au folding grids

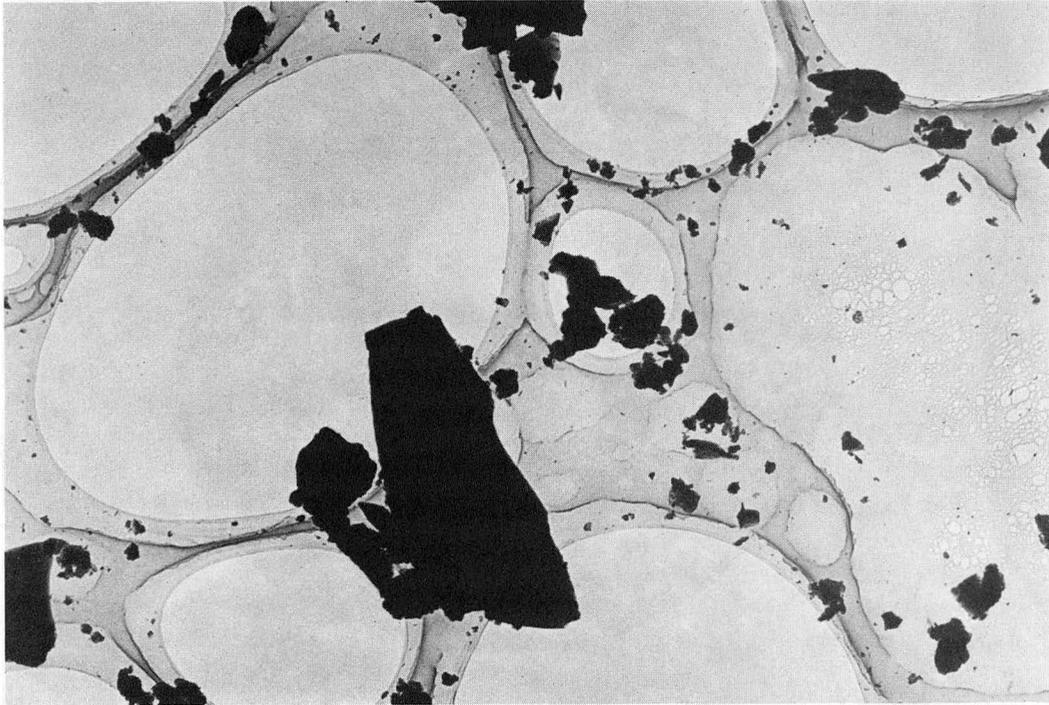
³Although a specimen can be prepared containing only $\text{YBa}_2\text{Cu}_3\text{O}_7$, the amorphous layer constrains heating experiments considerably. Since the specimen is so unstable in air, it is impossible to heat the crystal in the same state as that observed in the electron microscope.

Figure Captions

- Fig. 1 Carbon-coated holey Formvar[®] film covered with a dispersion of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ particles obtained by grinding. (XBB 870-10608)
- Fig. 2 Cleaved wedge-shaped fragments of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ glued to a Cu single slot grid. The thin areas of the wedge-shaped fragments are located in the center of the slot. (XBB 870-10609)
- Fig. 3. Cross-sectional micrograph of a sample prepared by cleaving, showing a 600 nm thick layer of $\text{YBa}_2\text{Cu}_3\text{O}_7$ on [001] oriented SrTiO_3 (dark region to left). Note the planar defects (bright bands) running across the film and that the c axis of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase is parallel to [100] of the substrate everywhere but region A where it rotates 90° . (XBB 870-10593)
- Fig. 4 High resolution image of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ showing the effect of intercalation of Cu and O. Note the bending of the lattice near the free edge. (XBB 870-10599)
- Fig. 5 High resolution image of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, ground and suspended in ethanol. The surface contains no defects nor amorphous material. (XBB 870-10603)
- Fig. 6 High resolution image from an ion-milled specimen of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, showing a thick amorphous layer at the thin edge. (XBB 870-10604)
- Fig. 7 High resolution image of a grain boundary with a thick amorphous layer near the edge, diminishing gradually to zero at the thicker part of the specimen. It is believed that the amorphous layer is an artifact. Because of stresses induced by ion milling the lower grain bent away from the interface, causing an opening into which amorphous material was deposited during ion milling. Bending of (001) planes is observed in the lower grain. (XBB 870-10595)
- Fig. 8 Sequence of high resolution images of same region in a crystal showing

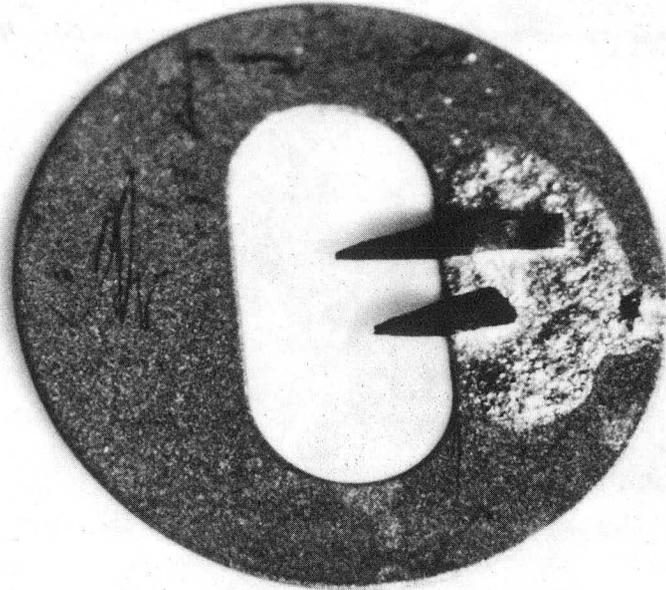
amorphization by the electron beam. (a) JEOL JEM 200 CX, 1/2 hour exposure (b) and (c) Atomic Resolution Microscope operating at 1000 kV, 10 minute and 30 minute exposure, respectively. The sample was left in air for 16 hours between the two microscope sessions. (XBB 870-10607)

Fig. 9 Sequence showing the effect of beam heating on the microstructure of YBa₂Cu₃O₇. One cycle through the orthorhombic-tetragonal-orthorhombic transition has completely rearranged the twin boundaries from initial (a) to final (b) configurations seen here. (XBB 870-10594)



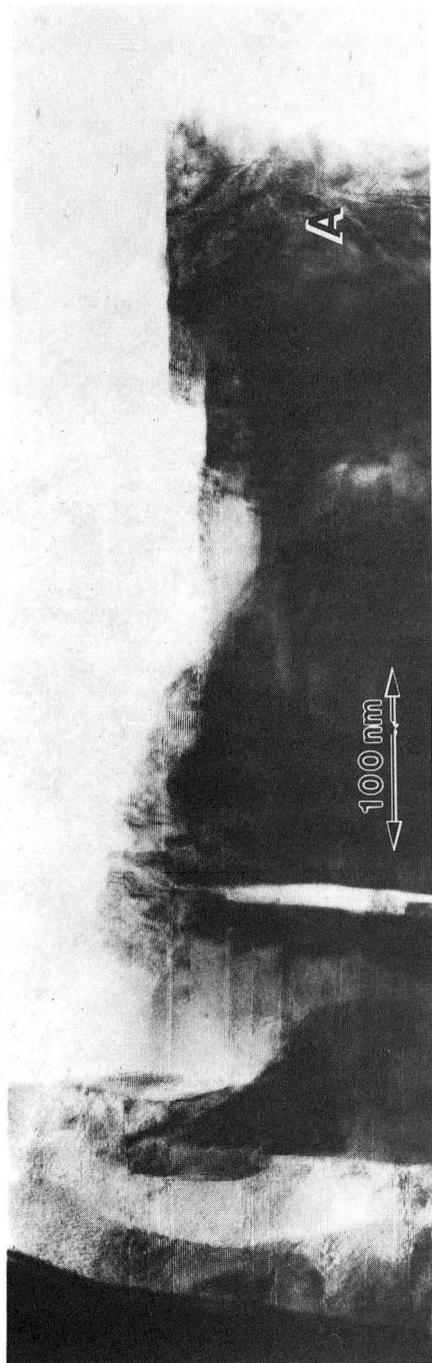
XBB 870-10608

Fig. 1



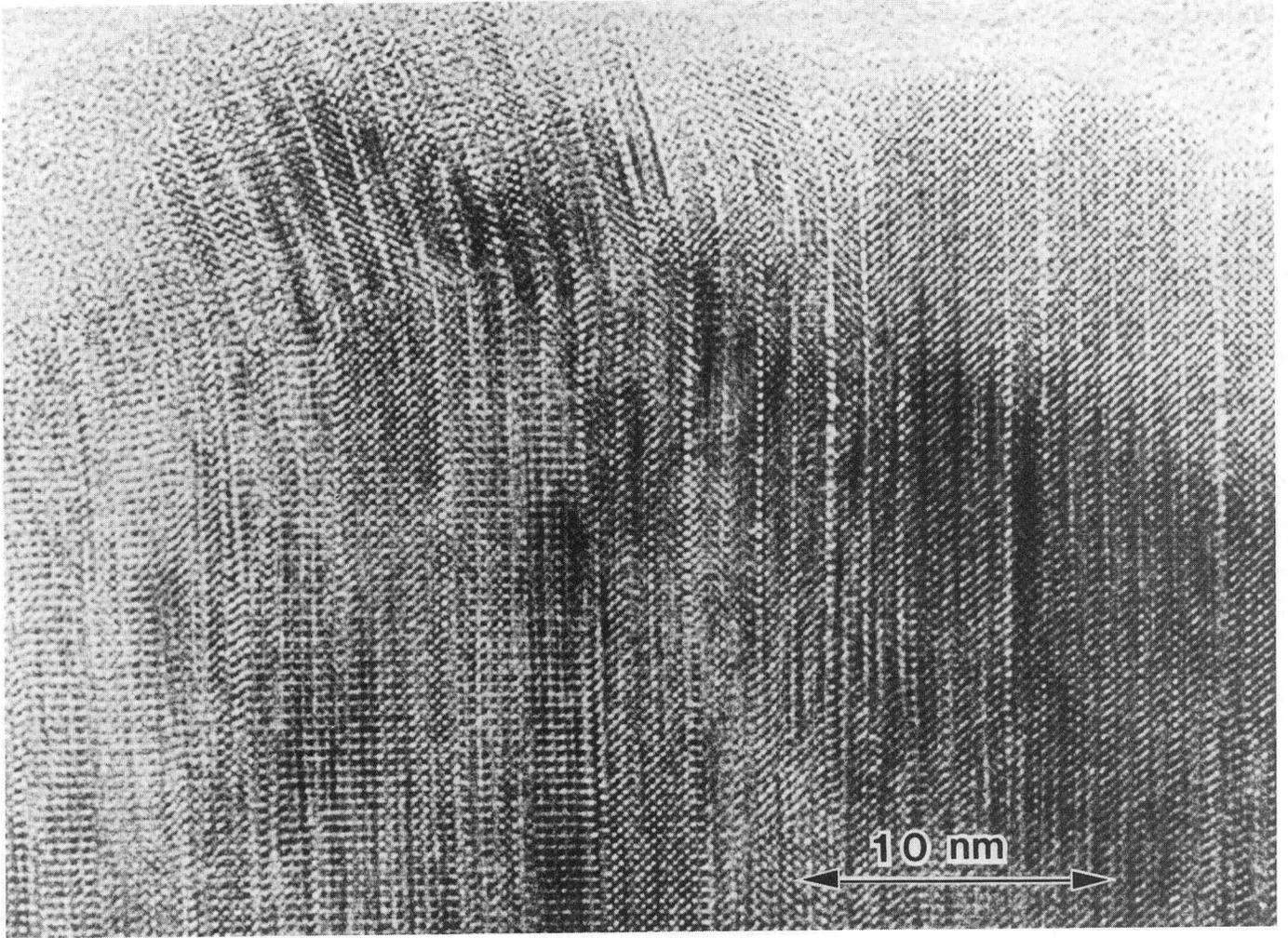
XBB 870-10609

Fig. 2



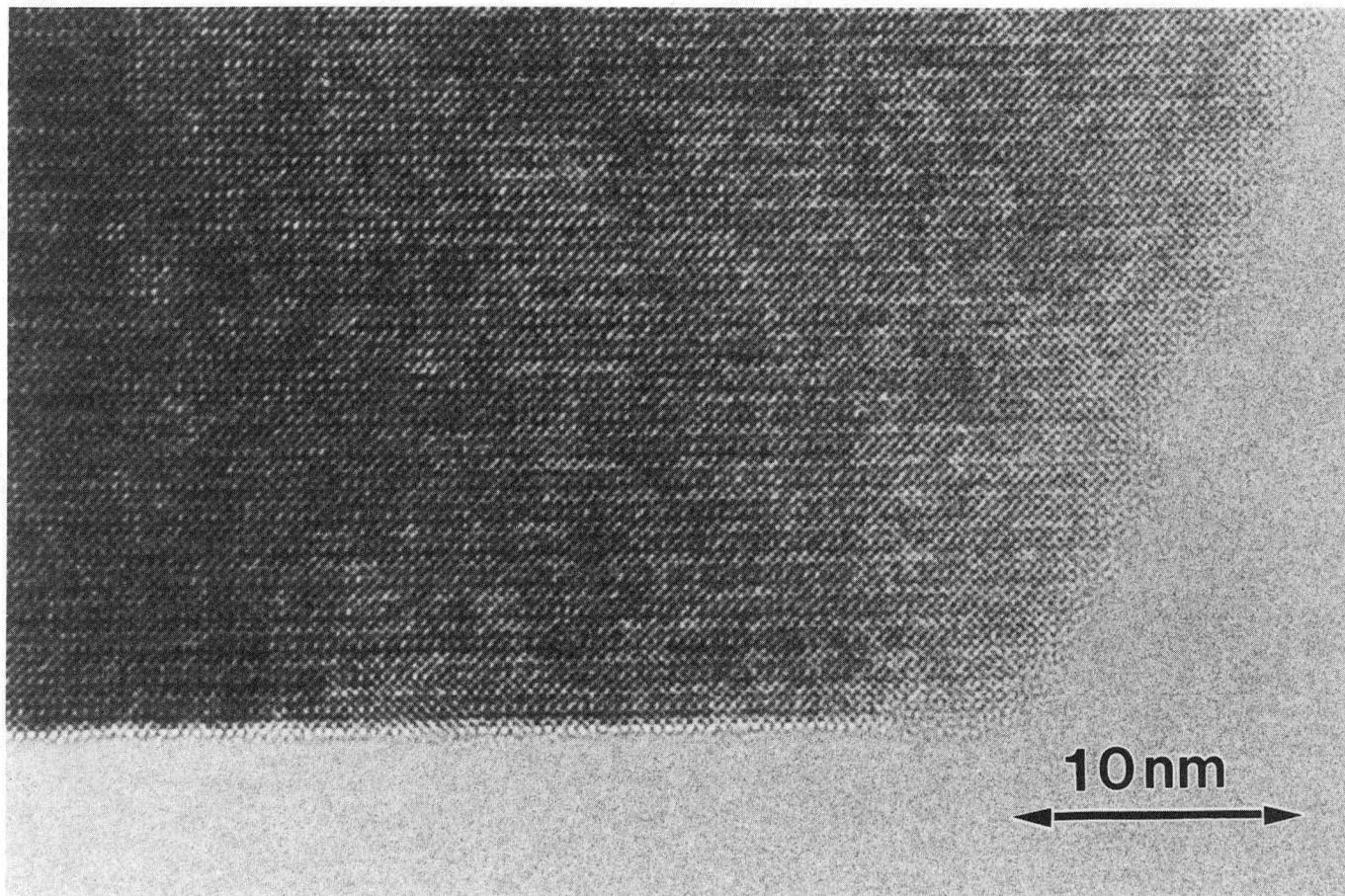
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Fig. 3



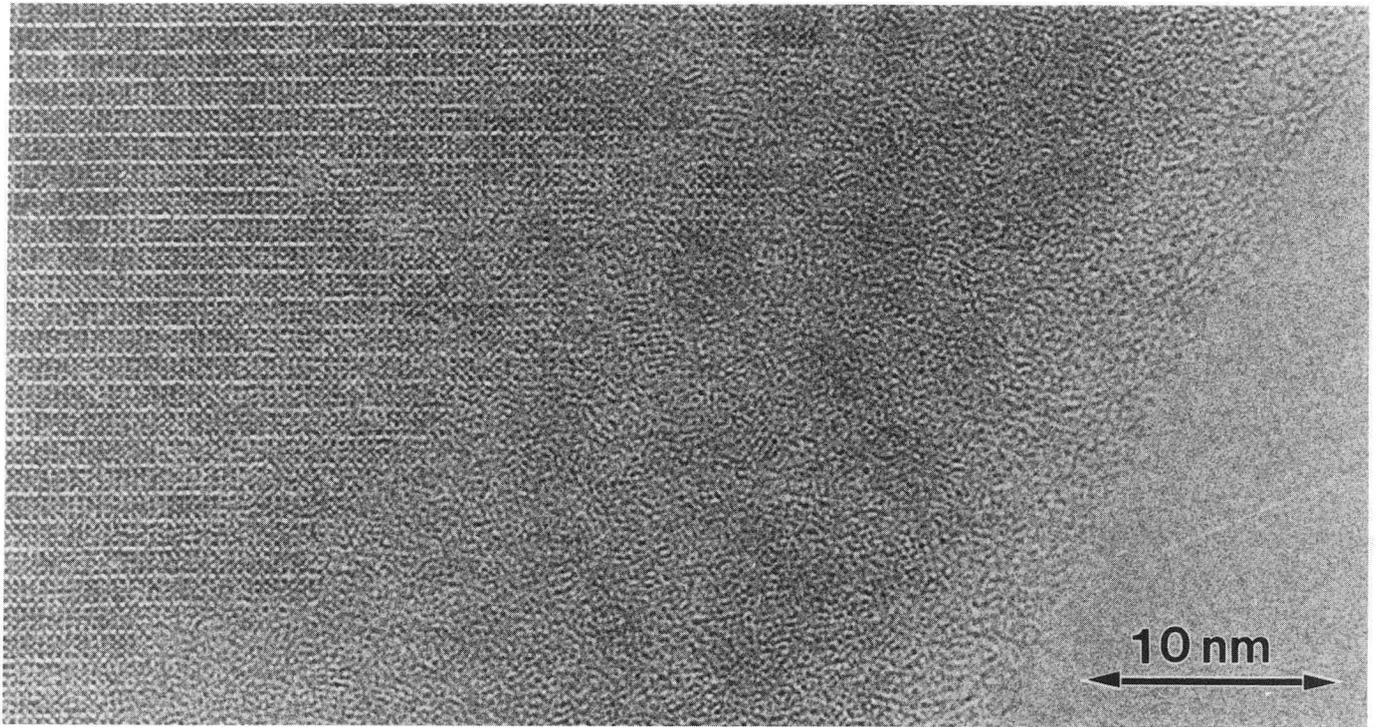
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Fig. 4



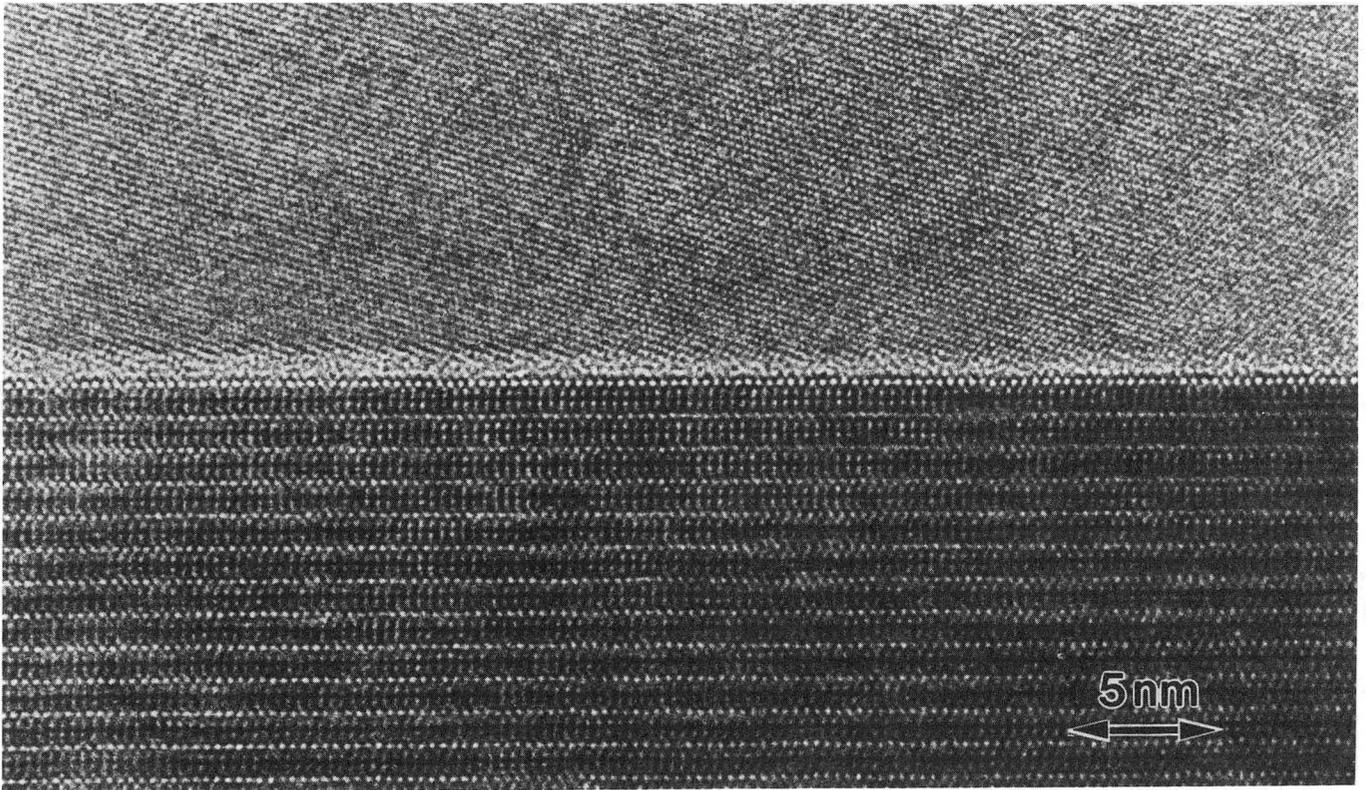
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Fig. 5



XBB 870-10604

Fig. 6



XBB 870-10595

Fig. 7

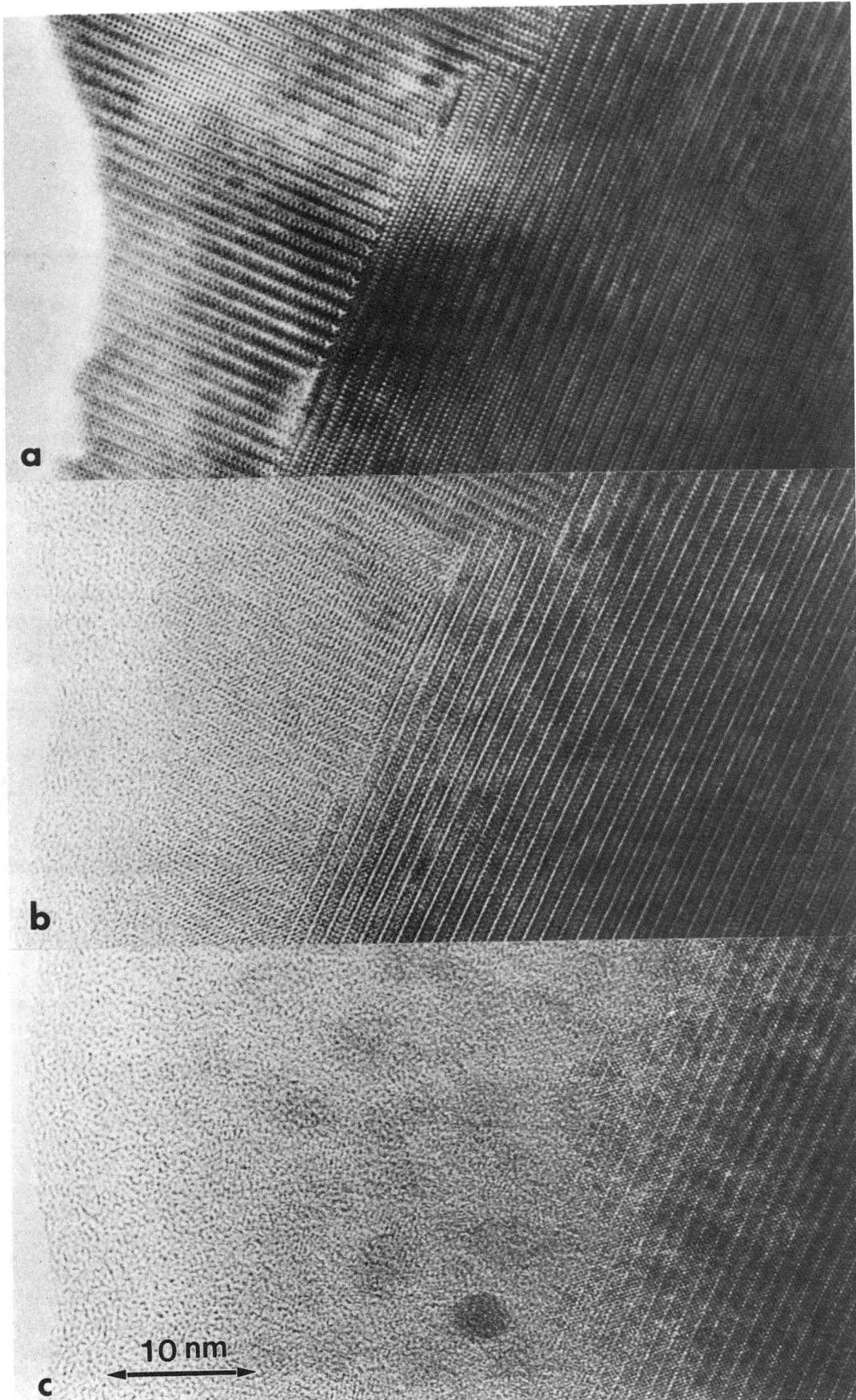
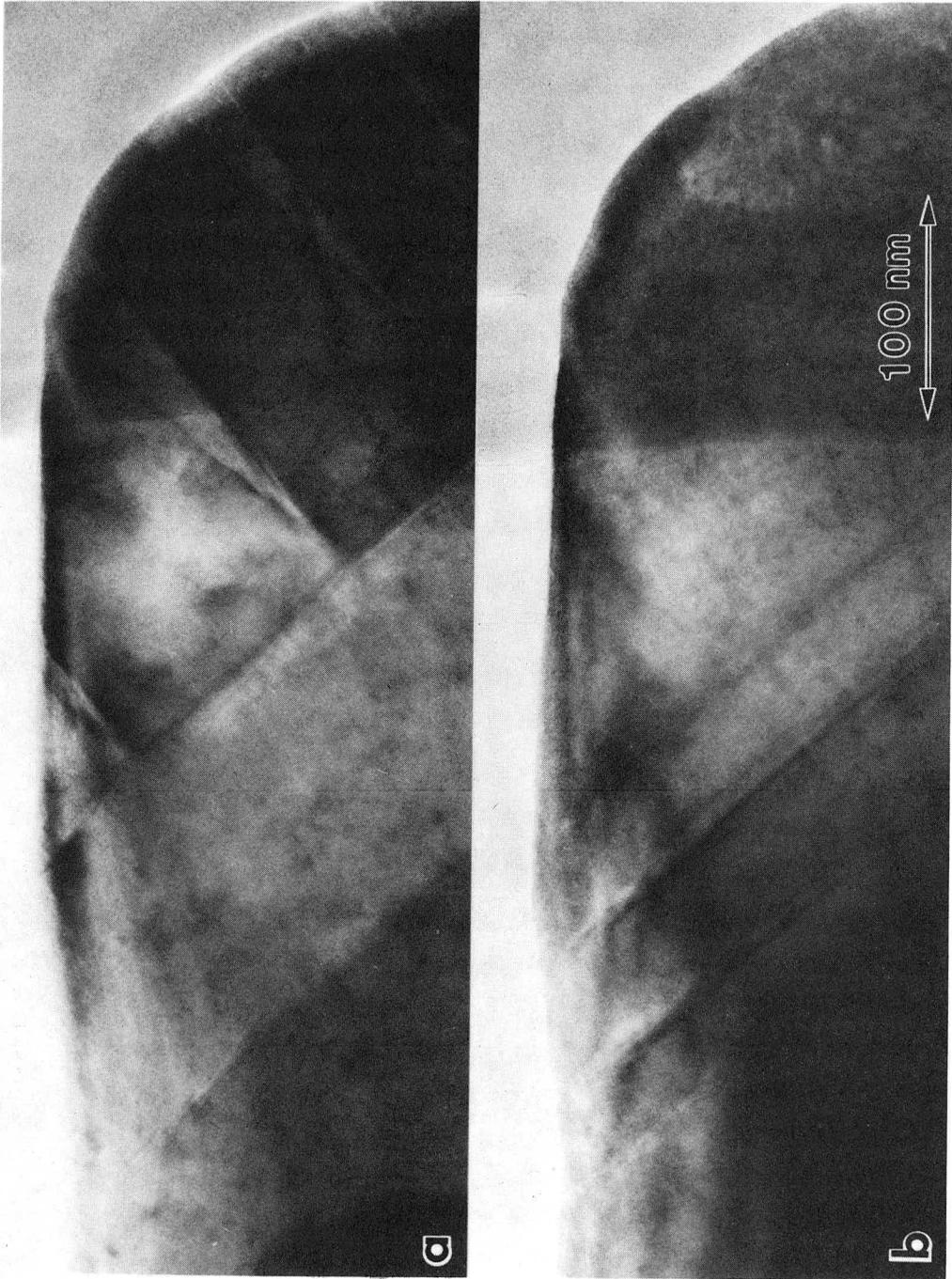


Fig. 8

XBB 870-10607



XBB 870-10594

Fig. 9

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