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Presented at the 1986 IEEE International Symposium on Applications of Ferroelectrics, Lehigh, PA, June 8-11, 1986

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T. Yamamoto, and K. Okazaki

June 1986

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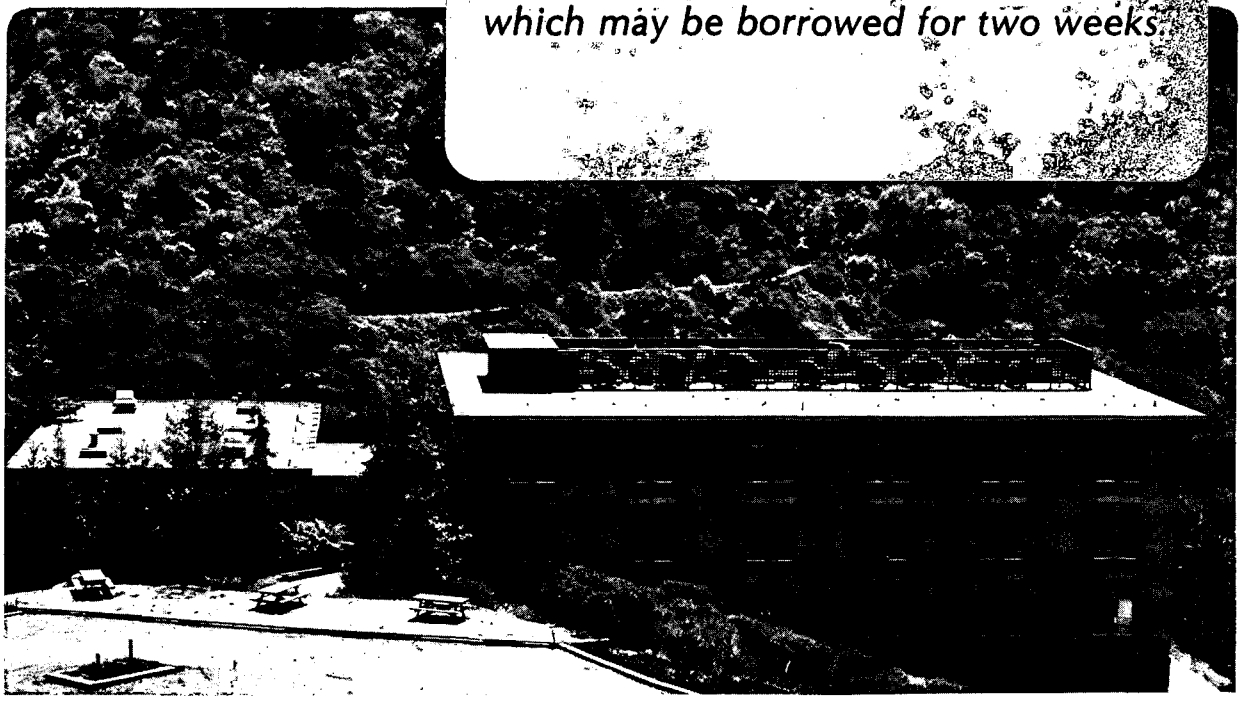

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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ELECTRON MICROSCOPY CHARACTERIZATION OF LEAD ZIRCONATE TITANATE CERAMICS AT THE MORPHOTROPIC PHASE BOUNDARY COMPOSITION

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Abstract

Lead zirconate titanate (PZT) ceramics exhibit excellent dielectric and piezoelectric properties at the morphotropic phase boundary (MPB) composition and it is believed that this is due to the coexistence of tetragonal (T) and rhombohedral (R) phases resulting in easy poling. However only limited microstructural information is available at this boundary composition.

In the present study the structure and chemical composition of PZT ceramics prepared by conventional ceramic processing has been analyzed by electron microscopy. Lattice parameters obtained from X-ray diffraction indicate that the T and R phases are only very slightly distorted from cubic symmetry at the MPB composition. Convergent beam diffraction (CBD) has been used to analyze the structure at the MPB composition using the fact that the symmetry of the CBD pattern is sensitive to the point group of the space lattice. It has been established that both T and R phases are present at the MPB composition. Microanalysis using energy dispersive X-ray spectroscopy has been carried out in conjunction with the structure analysis to establish the chemical composition of the different phases present.

1. Introduction

Lead zirconate titanate ($Pb(Zr,Ti)O_3$,PZT) ceramics are the most extensively used in technological applications among the piezoelectric materials because of their excellent piezoelectric properties at the morphotropic phase boundary (MPB). The subsolidus phase diagram of $PbTiO_3$ - $PbZrO_3$ is shown in Figure 1[1]. The MPB composition have been found

to vary between 45 and 55 mole percent of $PbZrO_3$[2-5]. It has been suggested that the excellent piezoelectric properties at the MPBare due to the coexistence of the tetragonal (T) and rhombohedral (R) phases which results in easy poling[6]. Different studies carried out at the MPB region indicated the co- existence of the T and R phases[2,3,7-11].

Most of the studies on PZT ceramics have been carried out by X-ray diffraction and property measurement techniques to characterize the phases at the MPB. Electron microscopy analysis of this material has been limited to the study of domains and shear plane defects[12-15] and there has been no investigation of the microstructure and morphology. The present study is aimed at characterizing the morphotropic phase boundary of PZT using electron microscopy techniques.

2. Materials and Experimental Procedure

High purity oxide powders of PbO (99.0%), ZrO_2 (99.7%), TiO_2 (99.7%). and Nb_2O_5 (99.78%) were used in the preparation of the PZT ceramics by calcining followed by sintering at 1180° and 1270° C for two hours. Specimens of $PbZr_xTi_{(1-x)}O_3$ with x = 40, 45, 50, 53, 55, 60 and 65% were analzsed in this study. All the samples had an additive of 0.5 mole percent of Nb_2O_5 to improve the electrical properties.

The lattice parameter measurements were carried out using Cu K_α radiation in a Siemens X-ray diffractometer. The microstructures of the polished and etched samples were examined in a scanning electron microscope. Thin foils for transmission electron microscopy were prepared by grinding the specimen down to about 50 μm, followed by Ar+ ion thinning.

The specimens were examined at 100 kV in a Philips 400 analytical electron microscope equipped with energy dispersive X-ray spectrometer and twin lens. Convergent beam diffraction patterns were obtained using a probe size of 40 nm. All the studies were carried out with a cold stage specimen holder at liquid nitrogen boiling temperature to reduce thermal scattering.

3. Results and Discussions

3.1 Scanning Electron Microscopy: The scanning electron micrographs of PZT obtained from tetragonal (T), MPB and rhombohedral (R) phase regions are shown in Figure 2 a,b and c respectively. The large

change in grain size from 3 μm in the T region and at the MPB composition to 12 μm in the R region is due to the different sintering temperatures. Domains are resolved only in the large grains of the rhombohedral phase (Fig.2c).

3.2 X-ray Diffraction Studies: The variation of lattice parameters with composition obtained from the X-ray diffraction studies is plotted in Figure 3. For greater accuracy, only diffraction peaks of higher Bragg angles were used in determining the lattice parameters. These values are in close agreement with the results published in the literature[1,2,16,17].

3.3 Transmission Electron Microscopy Studies: The ferroelectric phases with the tetragonal and rhombohedral crystal stucture near the MPB undergo very small distortions during the transition from the paraelectric cubic crystal structure to the ferroelectric state as can be seen from Figure 3.

In conventional selected area diffraction a parallel beam of electrons is used to obtain the spot pattern where determination of the reciprocal lattice is limited to a precision of about one percent. However, in convergent beam diffraction (CBD) the informations obtained from the intensity variations in diffracted beams due to the range of incident angles with crystal and three dimensional details due to the intersection of the Ewald sphere with more than one lattice plane (Figure 4) provide a wealth of informations. The CBD pattern at a zone axis (zone axis pattern, ZAP), thus obtained using a converged probe contains details at the centre surrounded by concentric rings which are called Zero Order Laue Zone (ZOLZ) details and Higher Order Laue Zone (HOLZ) rings respectively. The symmetry of a ZAP, denoted by diffraction group reflects the point group symmetry of the specimen and relation between the symmetry groups have been derived by Buxton et al.[18].

In the case of PZT, the point groups of the ferroelectric tetragonal and rhombohedral crystal symmetries are 4mm and 3m respectively[1]. The anticipated symmetry of the <100> ZAP patterns for T and R phases are given in Table 1. It can be seen that the CBD pattern obtained from T and R phases at a common zone axis would have mirror planes which are related by a 45 degree rotation and otherwise the CBD pattern would have 4mm symmetry when viewed along the c axis of the tetragonal phase. CBD patterns at other zone axes such as <110> and <111> have symmetry elements common to

both the phases so that they cannot be used to identify the crystal symmetry unambiguously.

The Zero Order Laue Zone (ZOLZ) details of the <100> ZAP obtained from the R phase ($PbZr_{65}Ti_{35}O_3$) are shown in Figure 5. It can be seen that the different diffraction intensities show a higher symmetry than anticipated. Similar details have been obtained from the T Phase ($PbZr_{45}Ti_{55}O_3$) so that the crystal symmetry cannot be distinguished from this alone. The symmetry of the ZAP patterns is obtained by examining the other details such as intensity variation of the HOLZ rings and the intersection of the Kikuchi lines with the HOLZ ring.

Portions of the common zone axis CBD patterns obtained from the T (45 mole percent of $PbZrO_3$) and the R (65 mole percent of $PbZrO_3$) phases are shown in Figure 6. In the case of the CBD pattern from the T phase (Figure 6a) the intensity variation of the HOLZ ring reveals a higher symmetry than a single mirror plane but when the HOLZ ring is examined in conjunction with the intersection of the Kikuchi lines the mirror symmetry of the pattern can be appreciated. The intersection of Kikuchi lines within the (010) Kikuchi band with the HOLZ ring (shown by an arrow) is symmetric only with respect to the mirror along (001). This restricts the additional apparent mirrors present in the pattern.

A part of the CBD pattern obtained from the R phase is shown in Figure 6b. At the outset the HOLZ ring details appear to have higher symmetry than an anticipated mirror along (110). The actual symmetry of the pattern is arrived at by observing the intersection of the Kikuchi line with the HOLZ ring at the points shown by arrow no.1. The triangular intersections of the Kikuchi lines within the (100) are different in size and they are symmetric about the marked (110) mirror plane only. In addition this pattern has an inner ring with weak intensity shown by an arrow no.2. This is due to the transformation of the room temperature R phase to a low temperature phase as seen in the sub-solidus phase diagram (Figure 1). During this transformation the unit cell size doubles with very subtle changes in the lattice, such as rotation of the oxygen octahedra clockwise and anticlockwise along the body diagonal[19]. These effects make the intensity of the ring very weak.

The distortions that give rise to loss of mirror planes in <001> CBD patterns are very small for the

T and R phases at a composition of 45 and 65 mole percent $PbZrO_3$ and even smaller for the MPB at a composition of 53 mole percent of $PbZrO_3$ as shown in the CBD patterns (Figure 7) obtained from the MPB composition. It was thus not possible with this technique to distinguish reliably between T and R phases at this composition. However, the inner ring due to low temperature ordering could be used to identify the rhombohedral phase uniquely. It was found that CBD patterns from some regions showed the presence of the extra ring while patterns from other regions taken under identical experimental conditions did not. This is seen in Figure 7b, where the inner ring is weakly present, (shown by an arrow) whereas it is absent from the pattern shown in Figure 7a. This is clear evidence that two different structures are present.

Bright field images obtained from T and R phases from the MPB specimen are shown in Figure 8 a and b, respectively. The domain structure is similar in both cases and thus cannot be used to identify the phases by inspection.

3.4 Microanalysis: The Energy Dispersive X-ray spectroscopy (EDXS) technique for compositional analysis in the electron microscope is only sensitive to differences in composition of more than 2 mole percent[20]. The spectra obtained from the T and R phases at the boundary are similar and the small differences in the heights of the peaks cannot be attributed to compositional fluctuations alone since the fluctuations from the background is of the same order as that of the estimated differences between the amounts of Ti and Zr. Thus any difference in the amounts of Ti and Zr present in the T and R phases at the MPB composition lies within experimental errors.

4. Conclusions

An electron microscopy study carried out on PZT ceramics prepared by conventional ceramic processing revealed the presence of both the T and R phases at the morphotropic phase boundary. It will be necessary to carry out detailed contrast studies of the domains to try to identify the structure. No differences in amounts of Ti and Zr present in the T and R phases at the MPB could be detected by energy dispersive X-ray analysis. It can be concluded that the width of the two phase region at the MPB composition is less than about 2%.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Figure Captions

Fig.1 Sub solidus phase diagram of $PbTiO_3$-$PbZrO_3$ [1].

Fig.2 Scanning electron micrographs from (a)T region, (b) MPB composition and (c) R region.

Fig.3 Plot of the lattice parameters as a function of the composition.

Fig.4 Schematic of the intersection of the Ewald sphere with reciprocal lattice under convergent beam diffracting condition.

Fig.5 Zero order Laue Zone (ZOLZ) details of <001> ZAP pattern obtained from R phase.

Fig.6 Parts of <001> ZAPs obtained from (a) T phase and (b) R phase showing an inner ring.

Fig.7 Parts of <001> ZAPs obtained from the MPB composition (a) T Phase and (b) R phase. See the text for discussion.

Fig.8 Bright field images of the (a) T and (b) R phases from the MPB composition.

Table 1

Crystal Structure	Point Group	Zone Axis	Whole Pattern Symmetry
Tetragonal	4mm	[100] [010] [001]	A mirror symmetry along [001] 4mm
Rhombohedral	3m	<001>	A mirror symmetry along [110]

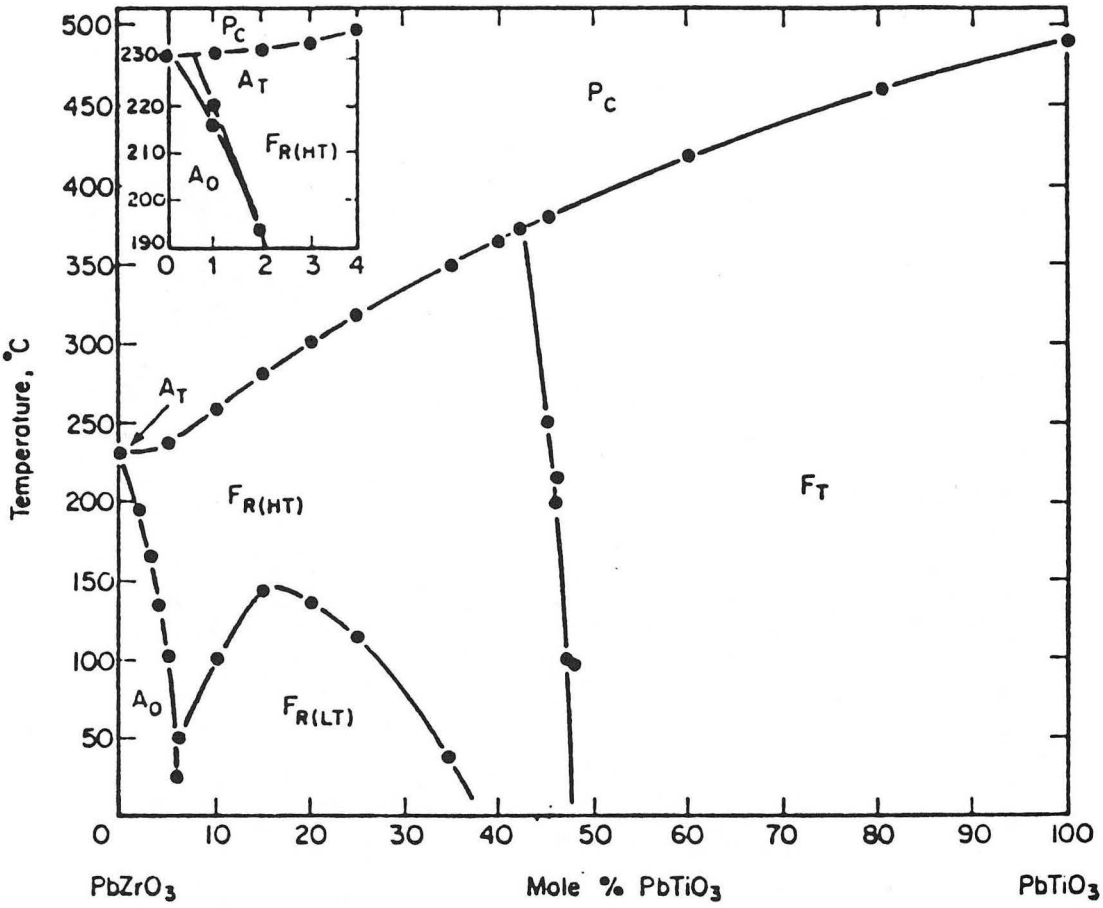

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Fig. 1

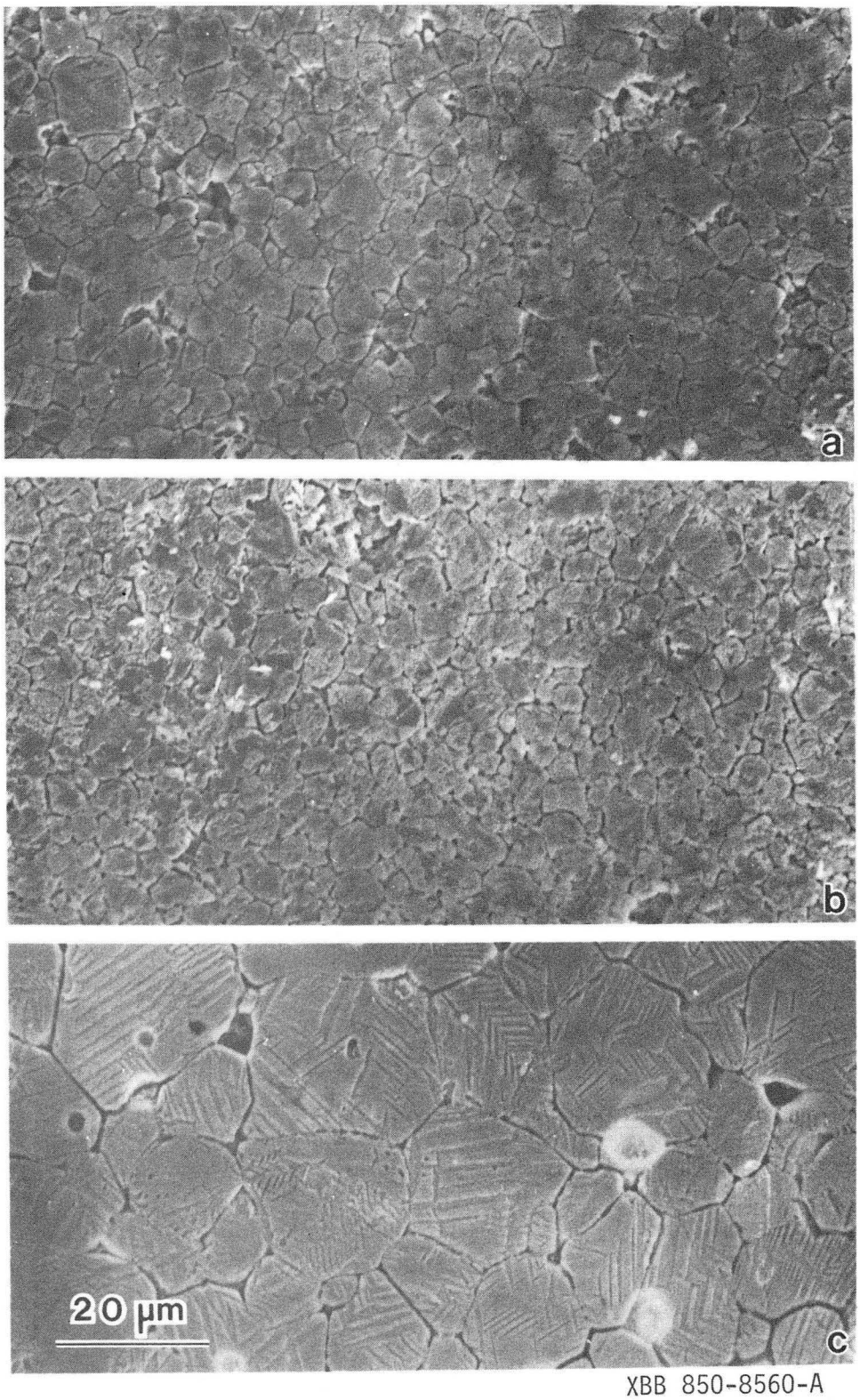

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Fig. 2

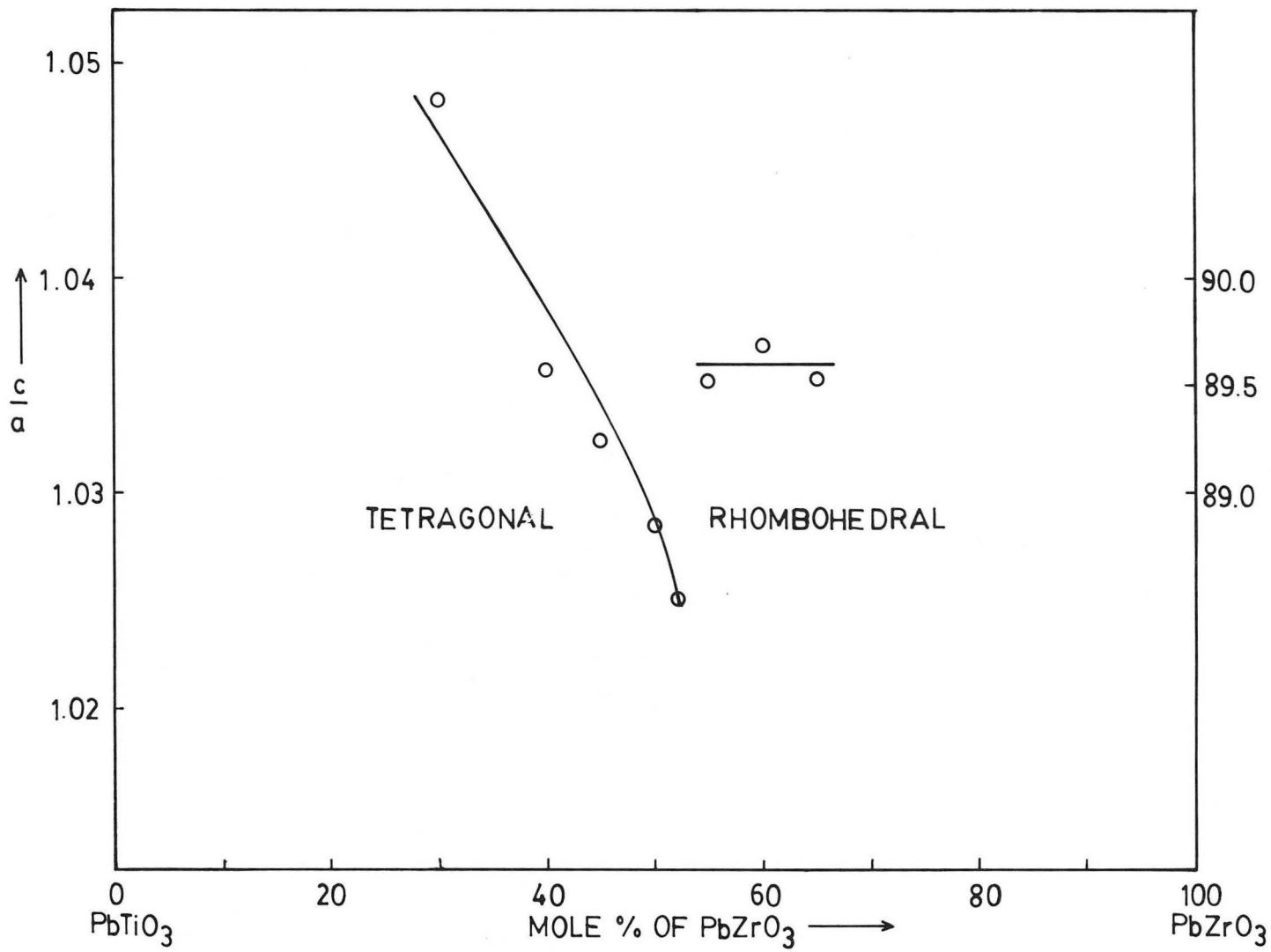

Fig. 3

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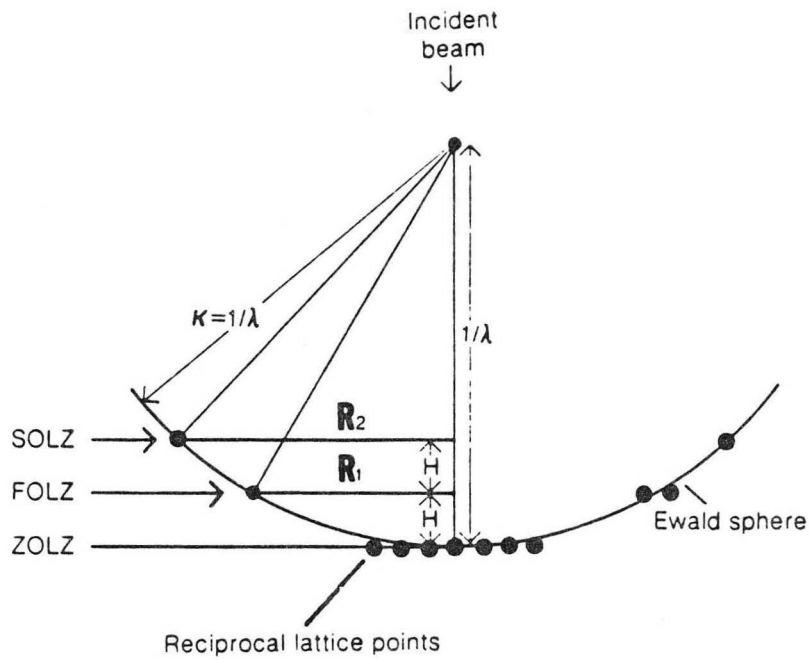

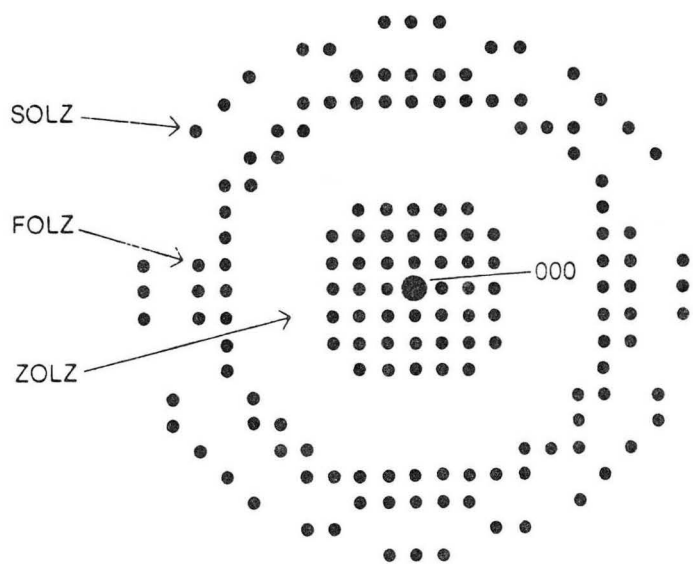

$$H = K - K\sqrt{1 - (R/L)^2}$$

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Fig. 4

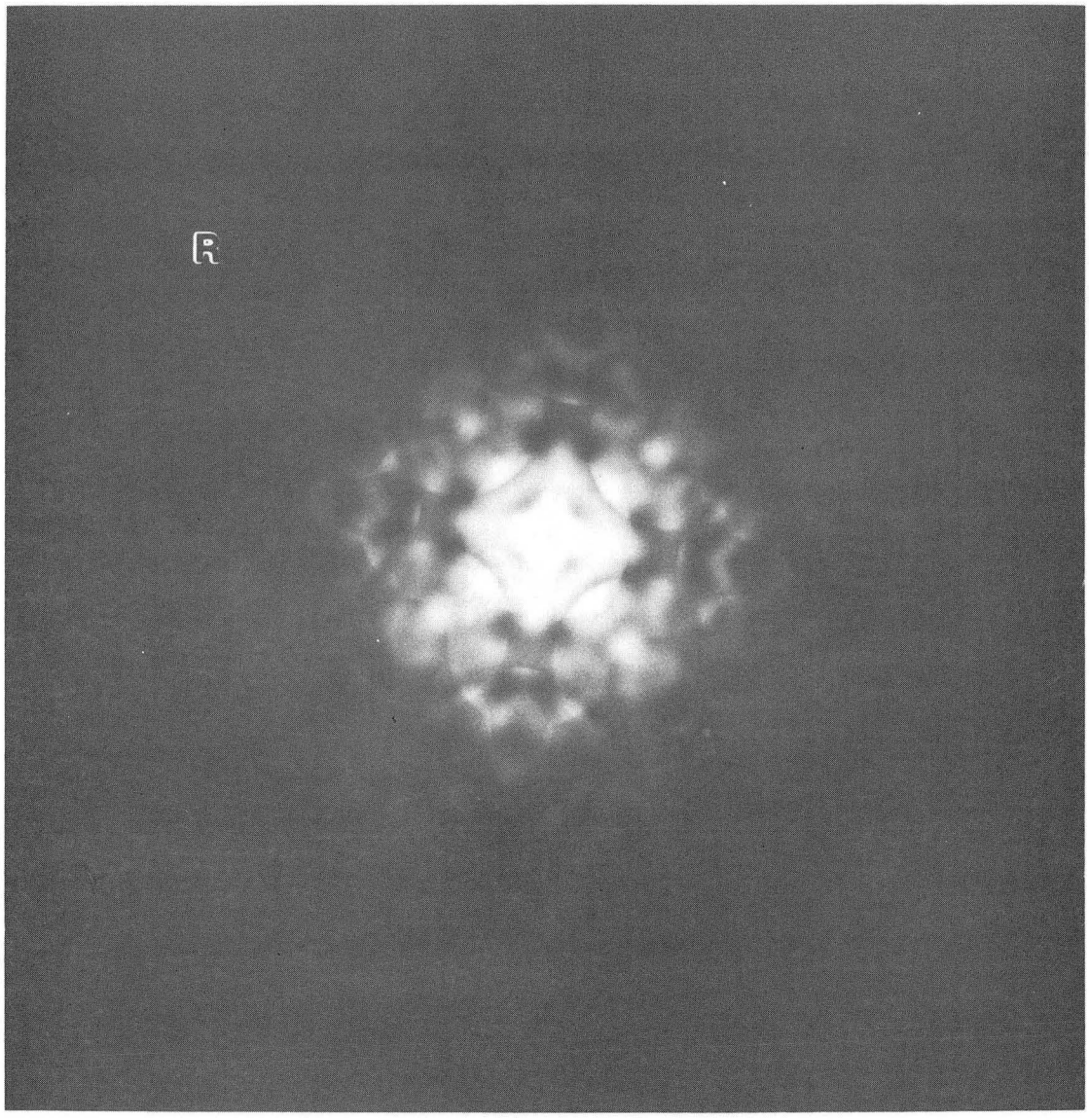

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Fig. 5

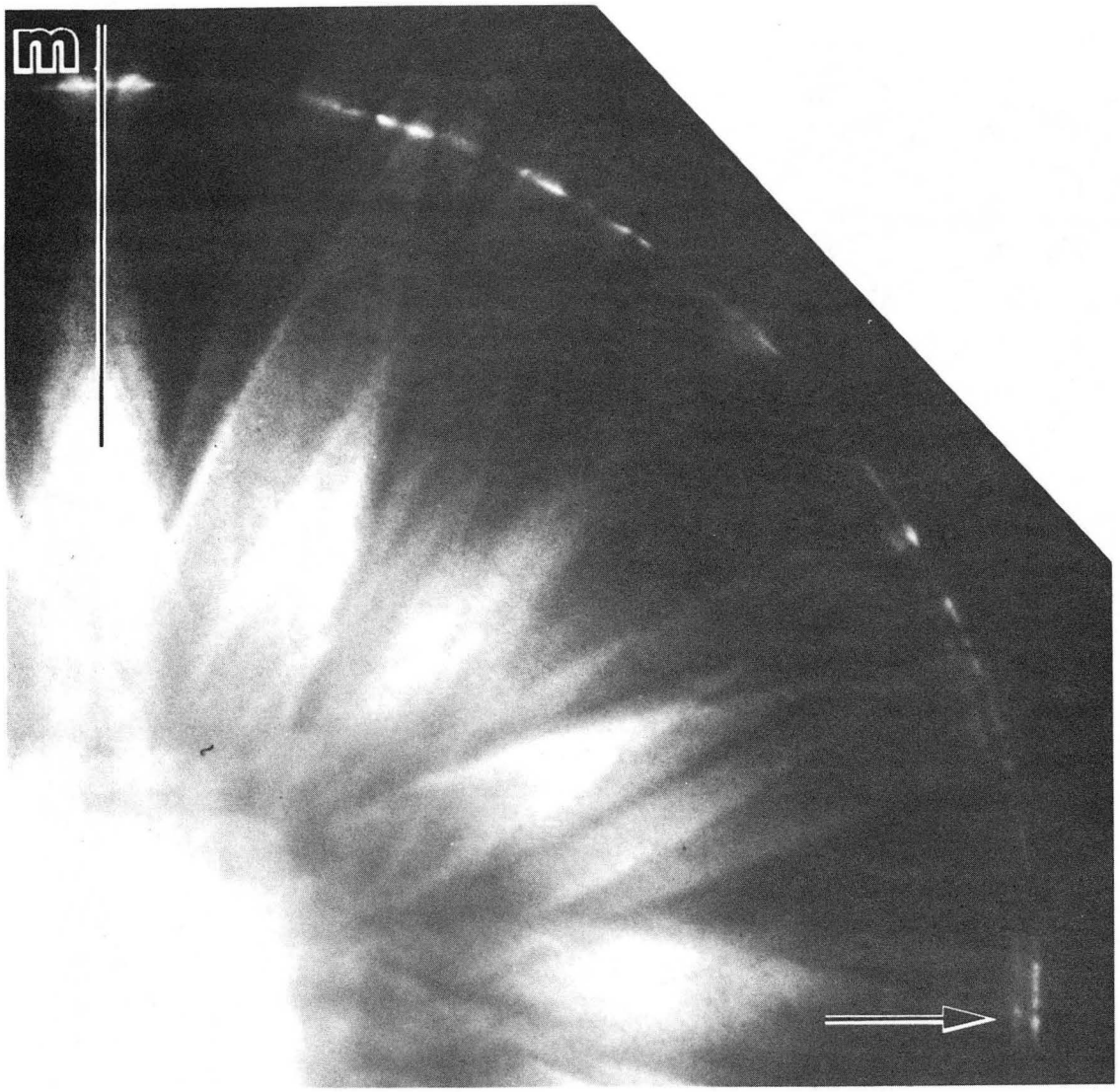

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Fig. 6a

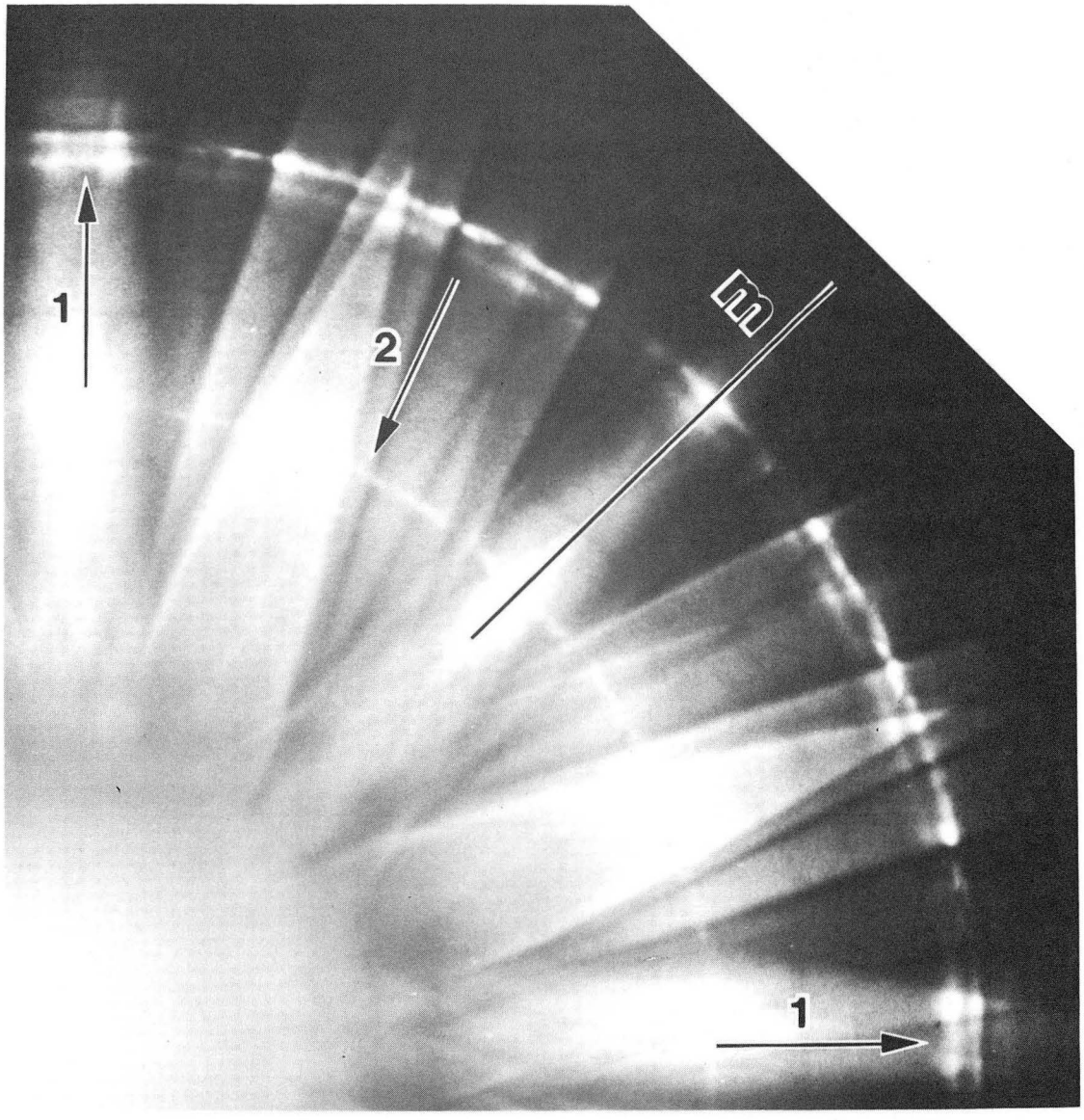

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Fig. 6b

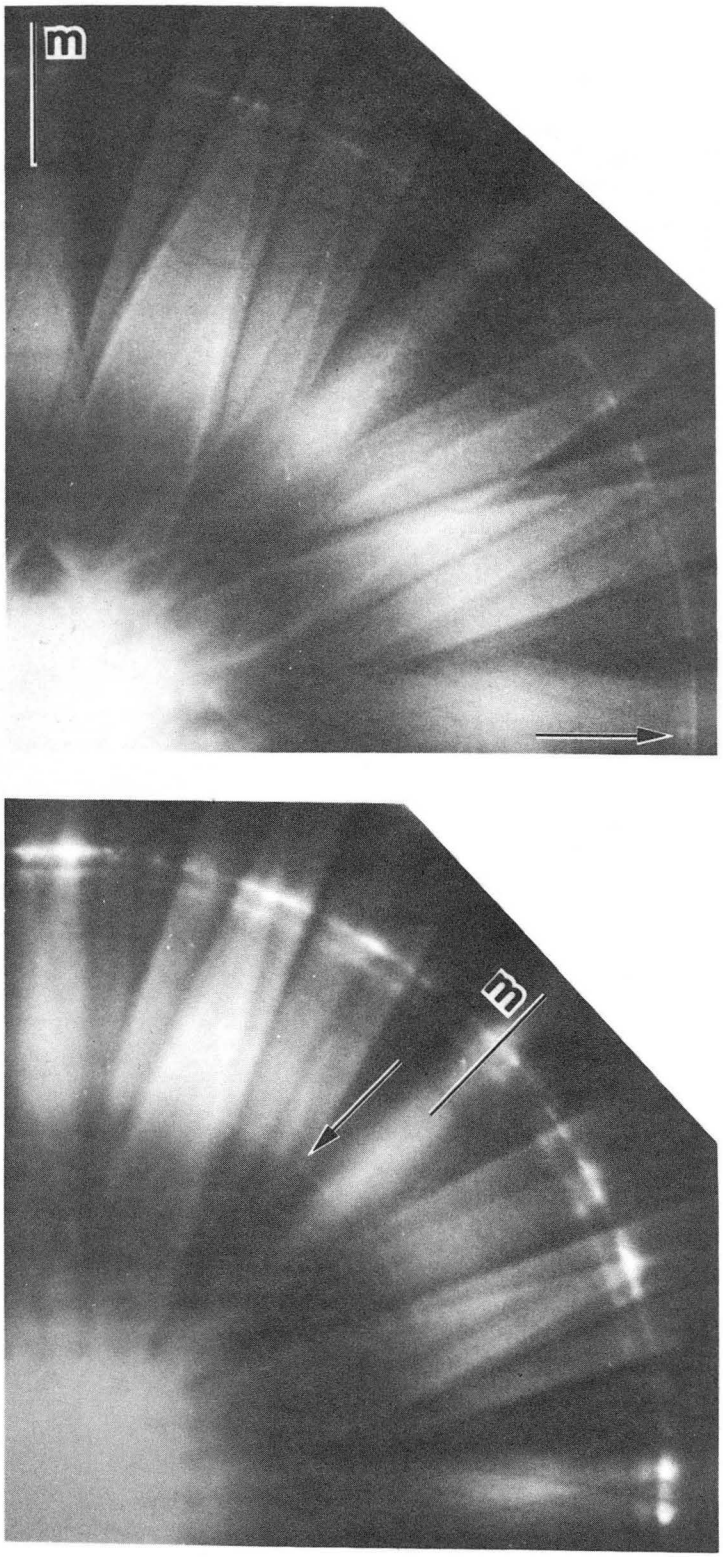

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Fig. 7

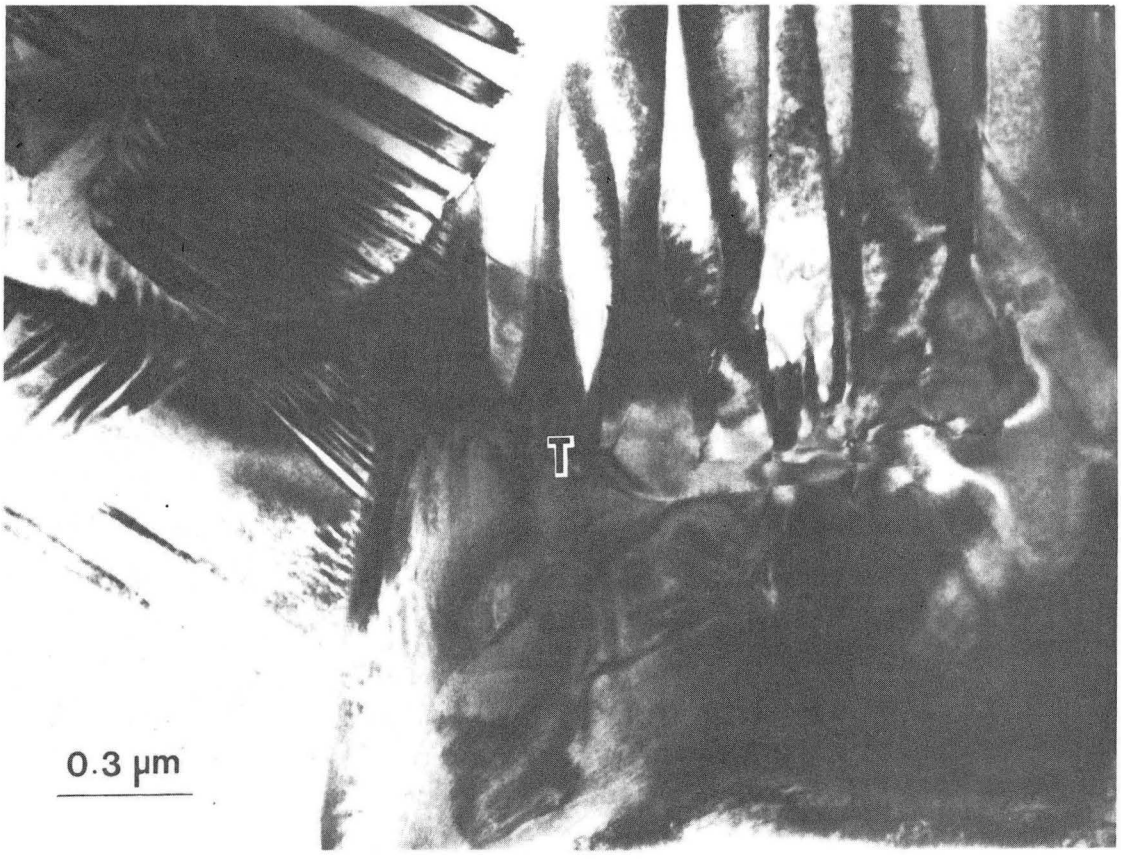

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Fig. 8a

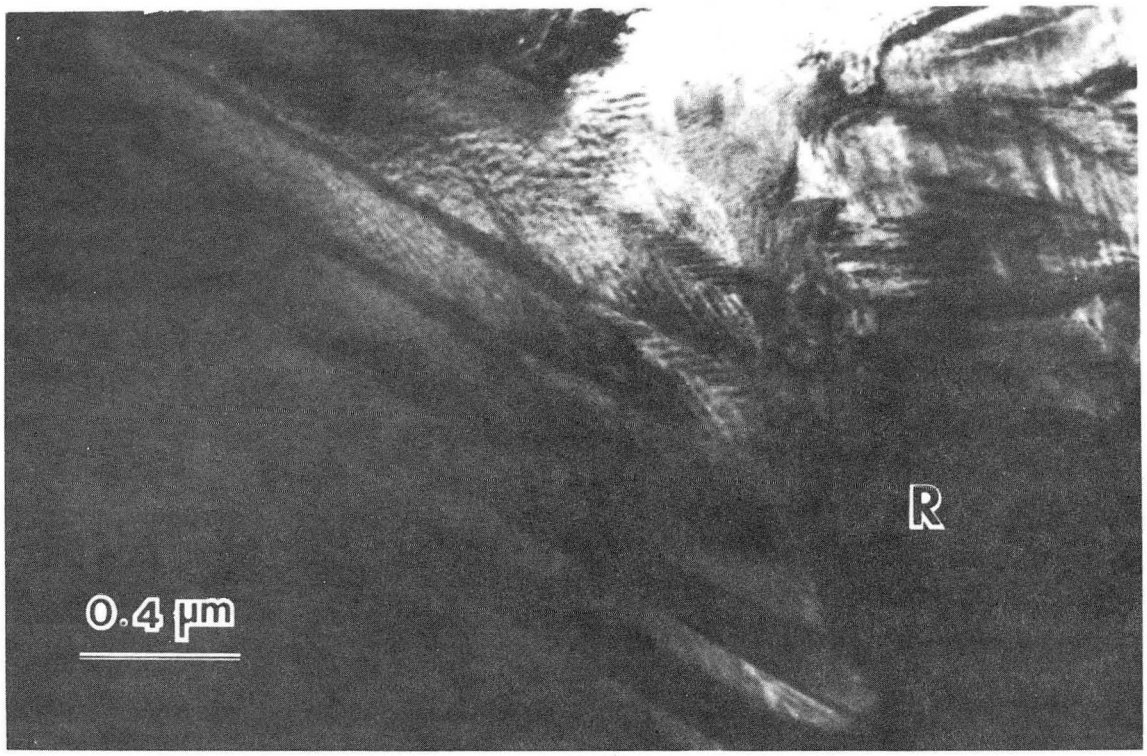

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Fig. 8b

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