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CHARACTERIZATION OF LONG PERIOD POLYTYPOID STRUCTURES IN THE Al_2O_3 - AlN SYSTEM

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ABSTRACT

Long period polytypoid structures observed along the pseudobinary Al_2O_3-AlN composition join at a composition of 95 mol% AlN have been investigated by convergent beam electron diffraction and lattice imaging. Two new long period structures, 32H (Ramsdell notation) and 16H with c-periodicities of 8.3 nm and 4.07 nm respectively, have been independently identified by these two techniques. However, the 32H polytypoid was sometimes found to be intergrown with faulted 27R long period structure of periodicity 7.2 nm. Further, it has been shown that the 32H polytypoid is stabilized by local compositional fluctuations during the sintering process.

INTRODUCTION

The potential utilization of oxinitride ceramics in high temperature applications has stimulated much study of the Si_3N_4-AlN-Al_2O_3-SiO_2 quarternary system [1]. In particular, it has been argued [2] that a systematic study of the phase relations and microstructure of the simpler Al_2O_3-AlN system could provide much needed information for the fabrication of Si-Al-O-N materials and serve as a model for other oxinitride systems. The end members of this pseudobinary Al_2O_3-AlN composition join are independently potential candidates for advanced applications. However, in its pure, single crystal form, Al_2O_3 is an anisotropic material, showing significant directional variation in its properties. An alternate approach is the stabilization of cubic Al_2O_3 by the addition of AlN to form a defect spinel structure. The phase relations [3], crystallography [4] and properties [5] of such cubic aluminium oxinitride spinels have been studied in detail. AlN, on the other hand, combines high thermal conductivity with good mechanical properties, making it a potential candidate for electronic packaging applications. However, until recently it has been rather difficult to process AlN and obtain a fine high density material.

In the Al_2O_3-AlN system, the cation is fixed and the oxygen and nitrogen are varied either advertantly or inadvertantly due to the unavoidable presence of oxygen impurity in the starting AlN powder. This is different from conventional crystal chemistry involving anion-cation relationships where cation substitutions or occupations are considered in a fixed anion framework. However, application of Pauling's [6] balance rule suggests that the addition of nitrogen anions to α-Al_2O_3 causes a local charge imbalance which can be eliminated by changing the coordination of Aluminium from six to four anions. Similarly, the addition of oxygen to AlN would also cause a local charge imbalance which can then be eliminated by changing the coordination of Aluminium from four to six anions. Therefore, small additions of nitrogen or oxygen to either end member seems to result in a variety of modulated structures based on the wurtzite or spinel structures. The structure and formation of these modulated structures called compositional polytypes or polytypoids and the characterization of two new polytypoids is discussed in this paper.

The AlN-Polytype Structure

The polytypism exhibited by these compounds is rather unusual, for unlike the polytypism of materials such as ZnS and SiC, where the unit cell dimensions are fixed by

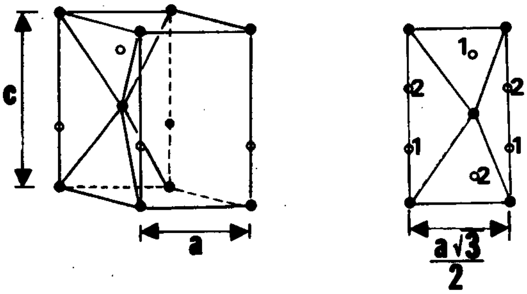

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Figure 1: (a) The 2H-wurtzite AlN structure. The unit cell dimensions are a=3.11 Å and c=4.98A. Open circles represent anions and the closed circles represent the cations. (b) The two different tetrahedral sites are shown as 1 and 2 in this [100] projection.

the periodicity of displacement faulting [7], the polytypism in these compounds is determined by the insertion of a chemically distinct layer into another chemically distinct structure. These polytype structures are based on the 2H-AlN structure (Fig. 1), with unit cell dimensions of a = 3.11A° and c = 4.98A°. In the ideal wurtzite structure, the cations (Al) form a hexagonal close-packed arrangement and the anions (N) occupy half the available tetrahedral (either the upward (1) or downward (2) pointing in Fig. 1) sites, giving rise to an overall composition of AlN and a metal to non-metal ratio (M/x) of 1. As the ratio M/x decreases (by the addition of Al_2O_3, say) more and more of the adjacent tetrahedral sites are occupied until the limit (M/x=1/2) is reached when all the tetrahedral sites are occupied. However, in the hexagonal wurtzite structure, adjacent tetrahedra share a common base and their complete occupation would lead to impossibly short distances between non-metal atoms. This can be avoided by changing the local cation arrangement from hexagonal to cubic. In such a cubic stacked region the downward and upward pointing tetrahedra do not share a common base and hence both can be occupied simultaneously by an anion giving rise to a local layer of composition Mx_2 (Fig. 2). The spacing of these Mx_2 layers is determined by the overall composition [1, 8] and constrained by charge balance. As a result only certain discrete polytype spacings due to the creation of periodic stacking faults can exist. This stacking fault spacing is found to be inversely proportional to the deviation of the ratio M/x from 1. Until now, the closest stacking fault spacing observed is every fourth layer and the highest every 13th layer. In the Ramsdell [9] notation these are referred to as the 8H and 39R structures. The nR polytypes consist of three rhombohedrally-related blocks of n/3 layers each, while the nH polytypes consist of two n/2 layer blocks related by a c-glide plane. Furthermore, for the nR polytypes M/x = n/n+3 and for nH polytypes M/x = n/n+2. It is generally assumed that for 9/10 < M/x < 1 the extra anions can be accommodated by a distorted wurtzite structure ($2H^{\delta}$) formed by an elongation along the c-axis of the conventional 2H structure.

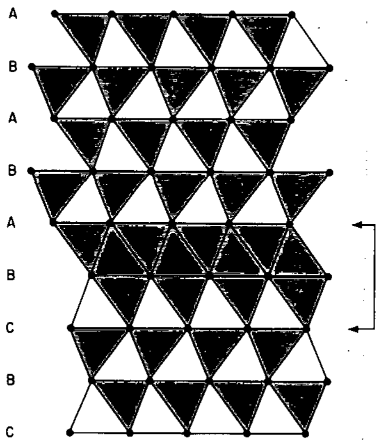

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Figure 2: Representation of the formation of a stacking fault due to an ABC cubic stacking in the basic 2H-wurtzite structure. In this [100] projection, the tetrahedral sites occupied by the anions are shaded.

EXPERIMENTAL PROCEDURE

The Al_2O_3-AlN polytypes were fabricated by a reaction sintering process. The starting powders of α-Al_2O_3 (1.1 µm at 50%) and AlN (14 µm at 50%) were ballmilled using an ethanol fluid medium for 24 hours, isostatically pressed at 25,000 psi and pre-reacted at 1200°C for 24 hours in gas-tight flowing nitrogen before final sintering. Samples of a nominal starting composition of 95 mol% AlN and an actual composition of 85 mol% AlN were prepared. Final reaction and sintering were carried out at temperatures ranging from 1950°C to 2100°C for one hour in an inductively-heated graphite furnace with flowing nitrogen. The samples were contained in a boron-nitride crucible with a sight hole for pyrometric measurements.

Specimens for electron-microscopy observations were prepared by cutting thin slices with a diamond saw, grinding and polishing to form 40 µm thick slices and finally ion-miling to perforation using Argon ions accelerated through a potential of 5kv. The samples were then coated with a thin layer of evaporated carbon to avoid surface charging. The specimens were examined on a JEOL 200 CX transmission electron microscope operated at 200 kV by conventional selected area diffraction, convergent beam electron diffraction and phase contrast imaging techniques. Optical microdiffraction was carried from small regions of the photographic negative using a He-Ne laser.

RESULTS AND ANALYSIS

A low magnification reflected light photomicrograph of the sample is shown in Figure 3. The highly interlocking fibrous character of the microsctructure strongly suggests that the material would exhibit very high toughness - higher than regular oxide or nitride based materials.

Selected area diffraction patterns taken from different samples (Fig. 4) were used as a preliminary means of identification of the polytypes. For a parallel beam of electrons incident in a direction perpendicular to the c-axis, the spacing of reflections along the (001) row indicates the stacking periodicity and the symmetry of the noncentral row with respect to the central (001) row indicates whether the structure is a hexagonal (nH) or rhombohedral (nR) polytype. In this way three polytypes were identified: the well-known 27R and two, as yet unreported, 16H and 32H structures. From the diffraction pattern, the repeat distances along the c-axis can be calculated to be 72A°, 40.7A° and 82.82A° for the 27R, 16H and 32H polytypes respectively.

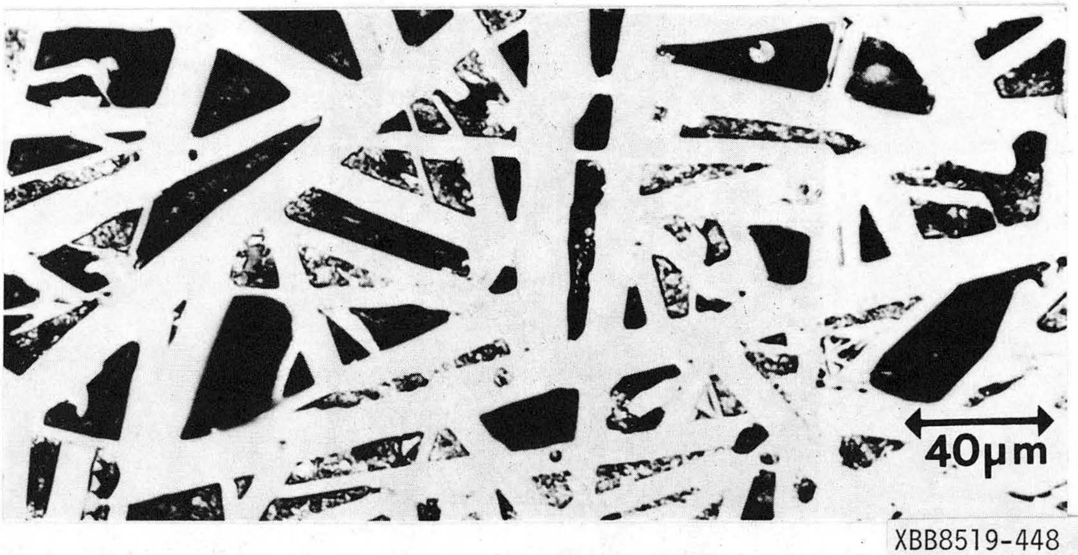

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Figure 3: Reflected light photomicrograph of the sample showing the interesting fibrous microstructure.

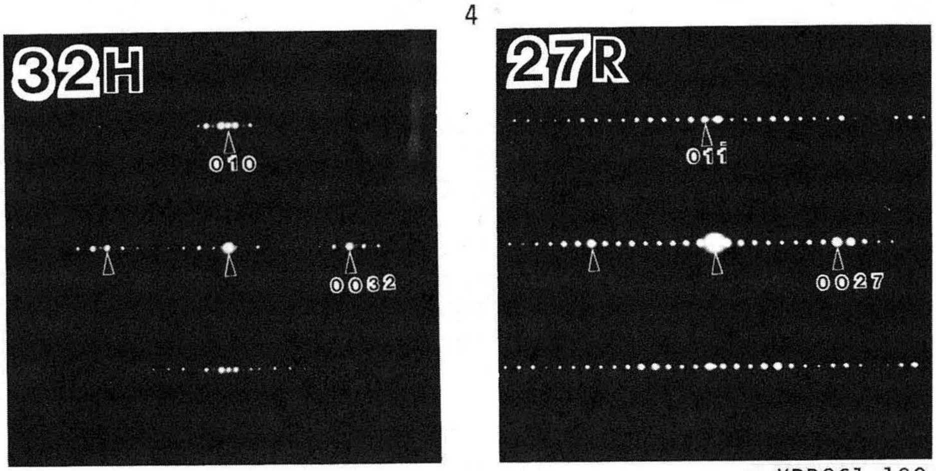

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Figure 4: Representative selected area diffraction patterns of the hexagonal (32H) and rhombohedral (27R) polytypes. Notice the displacement of the non-central row with respect to the central row for the rhombohedral structure in this [100] orientation. The reflections corresponding to the close-packed interplanar planes are marked.

The 32H polytype was also investigated by convergent beam electron diffraction (CBED) which, apart from being sensitive to crystallograpic symmetries provides three-dimensional crystallographic information [10] and unlike conventional SAD, which provides only two-dimensional inter-planar distances and angles. A typical CBED pattern of a 32H polytype oriented such that the c-axis is parallel to the incident beam is shown in Figure 5. The diameter, G of the first order Laue zone (FOLZ) in this pattern can be related to the repeat distance along the c-axis given by the expression

$$G = \sqrt{2KH}$$

where $K=1/\lambda$ and H for a hexagonal structure is given by

$$H = \frac{1}{\left(a^2\,(U^2 + V^2 - UV) + c^2W^2\right)^{1/2}}$$

Here U, V, W are the direction indices in the four-index Miller-Bravais system and a,c are the hexagonal lattice parameters. For the above pattern this gives a periodicity of 41.41A° along the c-axis, which is exactly half of that calculated from the SAD pattern. This is not surprising, for the nH polytypes consist of two blocks of n/2 layers related by a c-glide plane.

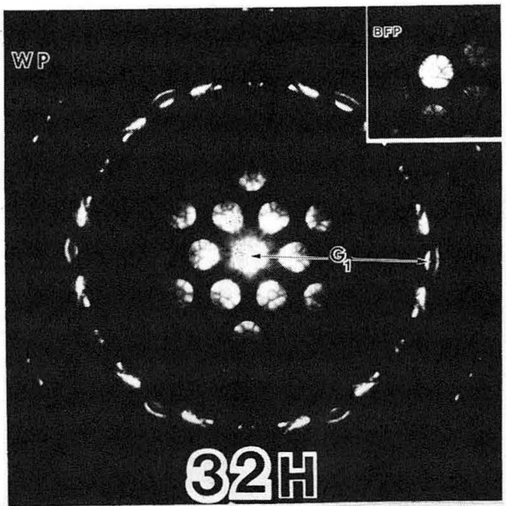

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Figure 5: A convergent beam electron diffraction pattern of the 32H structure in the [001] orientation. The diameter of the FOLZ gives the repeat distance in the c-direction thereby providing three dimensional structure information.

The above electron diffraction patterns and their analysis provide average stacking information. This can be complemented by high resolution phase contrast lattice imaging which not only elucidates the stacking sequences in great detail but also is sensitive to deviations in the ideal stacking sequence at a local level. A series of such images of the three polytypes was taken with the electron beam oriented perpendicular to the c-axis such that the [100] zone axis pattern was obtained. A JEOL 200 cx TEM with a high-resolution pole piece and a first cut-off in the transfer function of 2.5A°, which enables one to resolve individual close-packed lattice layers and obtain details of the atomic stacking sequence, was used.

The repeat blocks of a region of the 32H, 27R and 16H structures with regular periodicities of 42A°, 24A° and 20.35A° and containing blocks of 16, 9 and 8 atomic layers are shown in Figures 6a, b, and c respectively. The change in fringe contrast over every

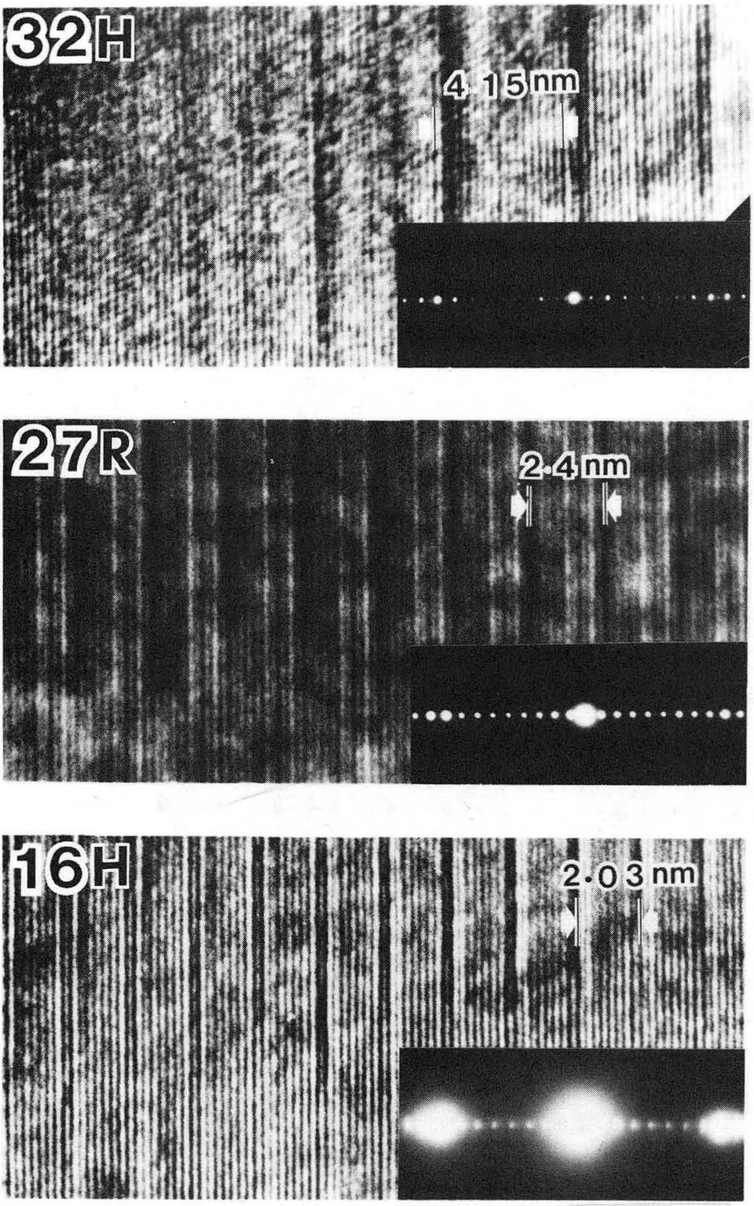

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Figure 6: Lattice images of the 32H (a), 27R (b) and 16H (c) structures formed by the symmetrical 001 reflections. The 001 row electron diffraction patterns corresponding to each image are shown in the inset. Sixteen, nine and eight layer repeat blocks are evident for the 32H, 27R and 16H structures respectively. The complete c-dimension of the unit cell for the hexagonal (a and c) structures consists of two such blocks and for the rhombohedral (b) structure consists of three such blocks.

sixteen, nine and eight layers suggests the presence of stacking or composition change possibly due to the occurance of a Mx_2 layer with cubic stacking at these repeat distances. Idealized projections of the 32H, 27R and 16H unit cells on the (110) planes based on the above results and following the structural guidelines [1] of AlN compositional polytypes are shown in Figure 7.

DISCUSSION

By the combined application of high-resolution lattice imaging and both conventional and convergent beam electron diffraction, the presence of 32H, 27R and 16H polytypes in these samples has been confirmed. Of these, the 32H and 16H polytype structures found in this study have not been reported earlier (Table 1). The anion/cation

TABLE 1

n	M/x	Polytype	c(Å)	Reference
4	4/5	8H	23.04	[1]
5	5/6	15R	41.85	[1]
6	6/7	12H	32.88	[1]
7	7/8	21R	57.12	[1]
8	8/9	16H	40.70	Present work
9	9/10	27R	72.09	[1]
11	11/12	33R	86.46	[8]
12	12/13	24H	Not measured	[8]
13	13/14	39R	101.40	[8]
16	16/17	32H	82.82	Present work
∞	1	2H	4.98	[1]

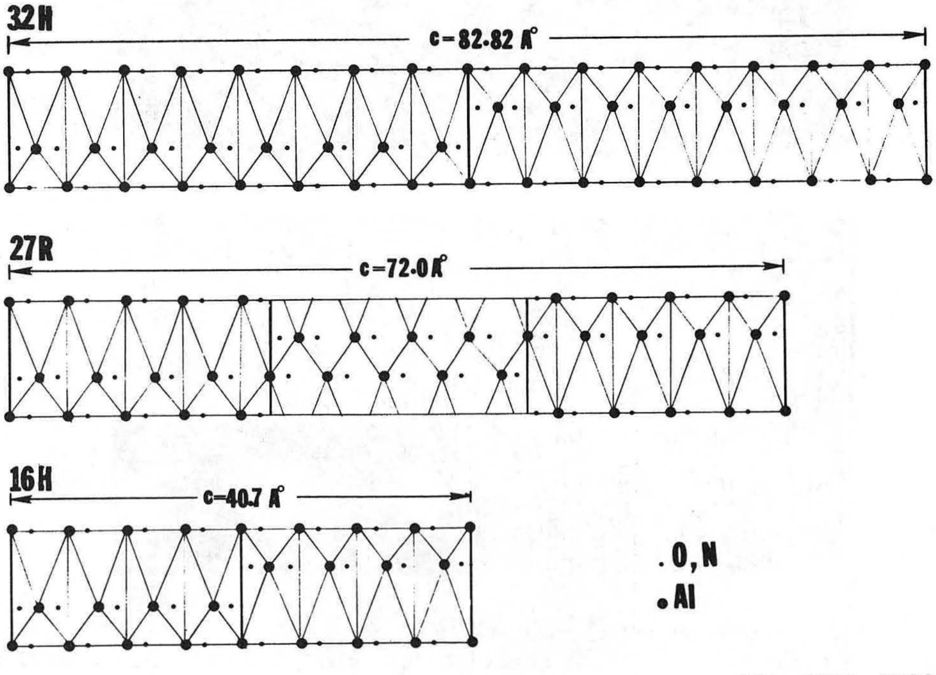

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Figure 7: Projections on the (110) planes of the three polytype structures identified in this study.

ratios have been estimated [1] from the number of layers per symmetry-related block in each of the polytypes and the characteristic polytype spacing, which corresponds to a specific local composition. Our attempts at obtaining an accurate determination of the local composition by energy-dispersive X-ray spectroscopy measurements using an ultra-thin window detector and correlating the anion ratio with lattice fringe spacing [11], were unsuccessful because of the significant absorption of the low energy oxygen and nitrogen x-rays in the specimen.

The 32H polytype calls for special attention, as it corresponds to a metal/non-metal ratio (M/x) of 16/17. It is generally believed [1, 12] that longer polytypes with M/x > 9/10 are unlikely, for they transform to the distorted wurtzite $2H^{\delta}$ structure by a small elongation of the c-axis. However, this polytype has not been found to coexist with the parent 2H structure within any one grain, suggesting that this long period polytype is stable and contrary to earlier observations [8]. Moreover, this structure (32H) is found to coexist with the more frequently observed 27R structure (Fig. 8) indicating that the formation of these polytypes is not due to segregation, as conventionally understood, but is probably a manifestation of the reaction sintering process [13]. As the purest AlN powders that are commercially available do contain about 1.5 mol% Al_2O_3, the formation of stable long period polytypes, such as the 32H structure reported here, are very likely during the processing. On the other hand, the fibrous microstructure of these AlN polytypes indicates good mechanical properties with a considerable deterioration of thermal conductivity. These are being studied at present.

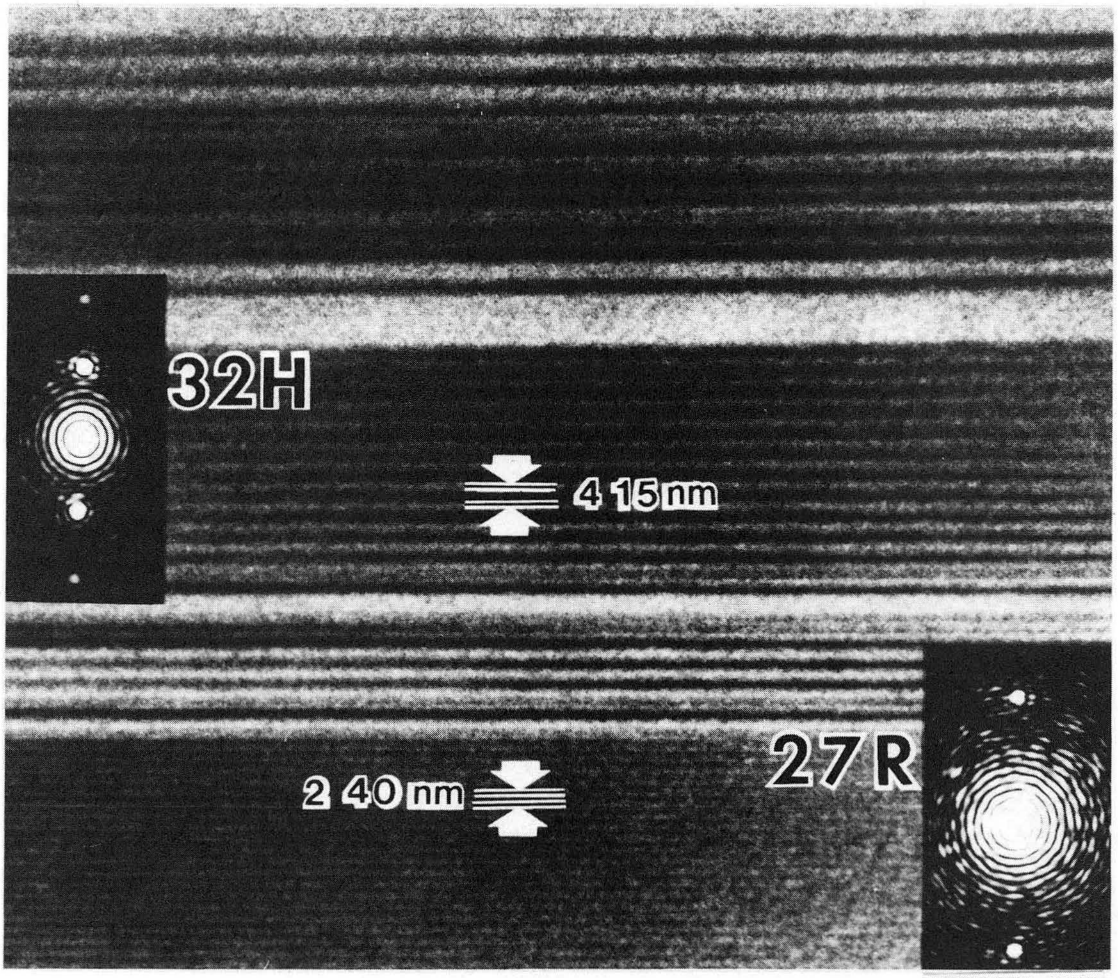

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Figure 8: Low resolution lattice images showing the coexistence of the 32H and 27R polytype-like structures. Accompanying optical diffractograms from local regions of the image have unequivocally identified these two structures as 32H and 27R respectively.

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