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DIFFRACTION STUDIES OF THE ATOMIC STRUCTURE OF LARGE ANGLE [001] TWIST BOUNDARIES

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Abstract - The results of the application of diffraction techniques to study the atomic structure of grain boundaries are reviewed. The determination of the projected structure of a large angle [001] twist boundary is described. The influence of f.c.c. metal type and bonding type on boundary structure is examined. Generalizations are made concerning the structure of large angle [001] twist boundaries based on the results of the diffraction studies.

I. Introduction

Diffraction techniques have been used extensively to determine the atomic structure of three dimensionally periodic structures. In recent years it has also been possible to use these techniques to obtain information on the atomic structure of internal interfaces, such as grain boundaries /1/. The difficulty in applying diffraction to grain boundaries comes from the lack of periodicity along the direction normal to the interface, since the boundary structure is only two dimensionally periodic (in the plane of the interface). Two diffraction approaches have been devised for studying grain boundaries which will be described below.

Before discussing these approaches, it is important to examine the reciprocal lattice associated with the grain boundary. All of the diffraction observations were made on manufactured bicrystals (see reference 2 for details). A typical bicrystal with a small angle [001] twist boundary at its midplane is shown schematically in Fig. 1(a), and the reciprocal lattice of this boundary is shown in Fig. 1(b), where the H and K axes lie parallel to the boundary, and the L-axis is normal to the boundary plane. The periodic strain field associated with the grain boundary gives rise to extra reflections, which are in the form of reciprocal lattice rods (relrods) since the boundary is not periodic along the z-direction /3,4/. Reflection intensities in the L=0 plane are related to the structure of the boundary projected onto the interface plane while the profiles of the relrods are related to the structure along the direction normal to the interface. The two approaches mentioned above involve (1) measurements made on the reflections in the L=0 plane, which can be used to obtain the boundary
structure projected onto the interface, and (2) measurements on the intensity profiles along the relrods, which can be used to obtain information on the behavior of the structure along the direction normal to the interface.

Fig. 1 - (a) Bicrystal containing a small angle [001] twist boundary with misorientation \( \theta \). (b) Schematic three-dimensional reciprocal lattice for the grain boundary in (a).

This paper will discuss the application of diffraction techniques to study (1) the projected structure of large angle [001] twist boundaries, (2) the influence of f.c.c. metal type on boundary structure and, (3) the influence of bonding type (ionic, metallic, covalent) on boundary structure.

II. The Projected Structure of the \( \Sigma=5 \) (\( \theta=36.87^\circ \)) [001] Twist Boundary in Gold/5/.

The study discussed in this section is concerned with determining the boundary structure projected onto the interface plane since there are a number of experimental observations in the \( L=0 \) plane (see Fig. 1(b)), which only contain information on the \( x,y \) coordinates of the atoms. The first time diffraction techniques were used to determine the projected structure of a grain boundary, it was advantageous to choose a boundary with a small number of atoms in the unit cell. The boundary that was studied was the \( \Sigma=5 \) (\( \theta=36.87^\circ \)) [001] twist boundary in Au. In this case the number of atoms in each (001) plane in the unit cell is 5 and since the projected position of each atom is determined by its \( x,y \) coordinates, the number of coordinates to be determined per plane is 10. If the number of planes associated with the boundary (containing atoms with large displacements from perfect crystal positions) is 4 (2 above and 2 below the boundary), the maximum number of coordinates that must be determined is 40. For the actual boundary under consideration, however, the number of variables is much smaller. Fig. 2(a,b) shows top and side views, respectively, of the unit cell of the \( \Sigma=5 \) twist boundary, with 2 atomic planes above and below the boundary plane. The structure shown is in the coincidence site configuration; that is, at the corners of the unit cell the two crystals are in the correct stacking for a f.c.c. structure. Following Bristowe and Crocker /6/, it is seen that this unit cell has the symmetry elements shown in Fig. 2(c). The experimentally determined structure factor rules showed that the symmetry of the boundary studied was that given in Fig. 2(c). This symmetry determines the minimum number of atoms whose positions must be located in order to completely characterize the unit cell contents.

Examination of Fig. 2(a) shows that for each (001) plane in the unit cell one atom is fixed at either (0,0) or (1/2,1/2) by the translation state of the boundary. The remaining 4 atoms in each plane are symmetry related by the 4-fold axis. Determining the \( x,y \) coordinates of one of these atoms in each plane, fixes the positions of the other three atoms. It is also seen that the atoms in the upper and lower crystals are related by the two-fold screw axes lying in the interface plane. Therefore, if it is assumed that the grain boundary is 4 atomic layers thick, it is necessary to determine the \( x,y \) coordinates of only 2 atoms (marked A,B in Fig. 2(a)) in order to determine the atomic structure projected onto the boundary plane.
The assumption that significant atomic relaxations for a $\gamma=5$ boundary are limited to a region which is only 4 atomic layers thick ($\sim 0.8$ nm for Au) is based on experimental considerations. The width of the strained region for a $\gamma=377$ ($\phi=23.8^\circ$) twist boundary in gold was experimentally determined, from the intensity profiles of various relrods, to be $\sim 0.8$ nm /4/. The intensity profiles for relrods for the $\gamma=5$ ($\phi=36.9^\circ$) boundary were qualitatively observed to be broader suggesting that this boundary is thinner than the $\phi = 23.8^\circ$ boundary. Thus the assumption that significant relaxations are restricted to a four-layer region in the vicinity of the interface plane is quite reasonable.

The determination of the projected $\gamma=5$ boundary structure proceeds by the standard reliability factor approach that has been used for crystal structure determinations /7/. In this method the $x$ and $y$ coordinates for the two independent atoms labelled A and B in Fig. 2(a) are scanned in small increments over an area covering the range of atomic displacements which generate all possible grain boundary configurations. For each configuration the magnitude of the structure factors are calculated and compared to experimentally observed structure factors using the definition of the reliability factor, $R$, given below,

$$R = \sqrt{\frac{\sum W_j (|F_o^b| - |F_c^a|)^2}{\sum W_j |F_o^b|^2}}$$

where $F_o^b$ = the experimentally observed structure factor of the jth reflection.

$F_c^a$ = the calculated structure factor of the jth reflection.

$W_j$ = weighting factor ($0 \leq W_j \leq 1$).
The set of $x_A, y_A, x_B, y_B$ coordinates which leads to the smallest value for $R$, provides the best fit to the diffraction observations. Thus the determination of the $\Sigma=5$ structure becomes a search for minimum values for the function $R(x_A, y_A, x_B, y_B)$. Such a search yields the $\Sigma=5$ structure shown in Fig. 3.

![Fig. 3 - Atomic displacements for the projected $\Sigma=5$ CSL unit cell. This structure had the smallest $R$ (\sim 0.15).](image)

Examination of Fig. 3 reveals several interesting points about the structure. Note that the displacement associated with atom A (first plane from the boundary) is much larger than the displacement associated with atom B (second plane from boundary). This rapid decrease in magnitude for the atomic relaxations in planes away from the boundary is as expected for a large angle boundary. In order to understand the origin of the relaxations, consider the forces acting on atom A. The atoms in the lower crystal act to hold atom A in its unrelaxed position in order to preserve f.c.c. stacking. The atoms in the upper crystal act to displace atom A, with the nearest atoms having the largest effect. In the unrelaxed configuration, atoms A and $A_1$ are 23% closer than the nearest neighbor distance in a perfect f.c.c. crystal. Thus the observation that in this structure these atoms move apart is physically quite reasonable. Examination of the boundary structure shows that it exhibits symmetry related displacements which can be interpreted as local rotations about '0' elements. For [001] twist boundaries, the '0' elements consist of lines perpendicular to the boundary, some of which pass through coincidence sites /8/. The degree of rotation is large (\sim 20°). Since the magnitude of the rotation is \sim \pi/2, small regions of median f.c.c. structure are produced.

It is interesting to compare the atomic displacements found in the present study, with predictions from computer modeling for the same boundary. A number of central pairwise potentials were employed, all of which were empirical and some of which had been matched to data relevant to gold. The projected atomic displacements for the $\Sigma=5$ boundary calculated for the different potentials are shown in Fig. 4 for the atoms labeled C (first plane) and D (second plane) in Fig. 3. The displacements determined by the diffraction analysis are also presented. It was shown that the values of the reliability factor for the computer generated structures are much higher than that for the diffraction structure. It is clearly seen that the structure determined from the diffraction analysis has an atomic displacement in the first plane away from the boundary which is at least twice as large as those predicted from computer modeling. It is interesting to see that the direction of the atomic displacement in the first plane is approximately the same for all structures. As expected, in all cases the magnitude of the displacements of the atoms in the second plane is smaller than in the first plane.
III. The Influence of F.C.C. Metal Type on Grain Boundary Structure

In a recent computer modeling study /9/ it was predicted that the atomic structure of a θ=22.6° (θ=13) [001] twist boundary should be different for different f.c.c. metals. In order to check this prediction, the structure of the θ=13 (θ=22.6°) [001] twist boundary contained in Au, Ag, Cu and Pt bicrystals was studied using X-ray techniques. Specifically, X-ray diffraction patterns showing the same regions of reciprocal space were obtained and compared for the four metals. The intensities of the reflections in these patterns are proportional to the square of the structure factors of these reflections. It is expected that if the boundary structures are significantly different, then the relative intensities of the grain boundary reflections observed from the different metals will also be different.

The specimens of Au, Ag and Cu were produced by UHV deposition of thin single crystals onto pre-oriented cleaved NaCl single crystal substrates followed by hot isostatic pressing in UHV to form the bicrystals containing the [001] twist boundary. The Pt single crystals were produced by electron beam deposition onto cleaved NaCl in an ion pumped vacuum system operating at 10⁻⁶ Torr. The Pt single crystals were pressure sintered in air at 600°C to form a bicrystal. It is expected that the Pt bicrystals will not be as clean as those of Au, Ag and Cu.

Examples of the experimental observations are presented in the form of sets of X-ray diffraction patterns taken in the vicinity of the f.c.c. reflections, with approximately the same diffraction geometry for all metals. Fig. 5 shows patterns taken in the vicinity of the 200 f.c.c. reflections, with grain boundary reflection 6,6,0 on the Ewald sphere. (For the coordinate system used for indexing see ref. 9.) The indices of the grain boundary reflections are indicated on the patterns using only the H,K notation, except for reflection 6,6,0 where L is exactly zero. For the other reflections, L has small deviations from zero. Several grain boundary reflections are clearly visible. These can be compared for the four metals and it is seen that the relative intensities of the reflections are quite similar. For example, listing the observed reflections in decreasing order of intensity yields the sequence 6,6; 4,4; 2,6; 3,5 for all four metals.
Fig. 5 - X-ray diffraction patterns from the 200 region of reciprocal space with the 6,6,0 reflection on the Ewald sphere. $\Sigma=13$ ($\theta=22.6^\circ$) [001] twist boundary.

Fig. 6 - X-ray diffraction patterns from the 220 region of reciprocal space. $\Sigma=13$ ($\theta=22.6^\circ$) [001] twist boundary.

Fig. 6 shows patterns taken in the vicinity of the 220 f.c.c. reflections for Au, Ag and Pt, with grain boundary reflections 11,1,0 and 11,1,0 on the Ewald sphere, while for Cu, reflections 11,1 and 10,4 have an equal L deviation, [0.06], from the Ewald sphere. It is seen that the reflections 10,0; 10,4; 11,1 are in a decreasing order of intensity for Au, Ag and Cu, while for Pt reflection 10,0 is quite strong and reflections 11,1 and 10,4 are approximately equal in intensity.
Additional observations in different regions of reciprocal space also demonstrated that the relative intensities of the grain boundary reflections are in the same sequence for Au, Ag and Cu, while Pt showed different behavior. An extensive analysis of these observations showed that the \( \Sigma=13 \) [001] twist boundary has the same symmetry and similar structure in Au, Ag and Cu, and that the symmetry and structure is different for the \( \Sigma=13 \) boundary in Pt. The symmetry of the \( \Sigma=13 \) boundary structure in Au, Ag and Cu is as shown in Fig. 2(c), which is that of the space group \( P42_{1}^{\text{I}}/2 \). The space group of the Pt boundary structure is \( P42_{1}^{\text{I}}/2 \).

The possibility of impurity segregation at the boundaries used in the study by Budai, Donald and Sass /11/ was the motivation for the present work. The results of Budai et al. on Au and Ag were completely reproduced in the present study, which confirms their conclusion that the \( \Sigma=13 \) [001] twist boundary structure is similar in Au and Ag. This agreement between the results from clean and possibly impure boundaries, leads to the suggestion that a small variation in boundary composition may not influence the boundary structure in the particular case under investigation.

The conclusion of the present work disagrees with the computer modeling predictions of Bristowe and Sass that the boundary structure should be different in Au and Ag \( \Sigma=13 \) [001] twist boundaries. In a more recent study, Wolf /12/, using pseudopotentials, has predicted that the \( \Sigma=13 \) boundary structure should be the same in Au, Ag and Cu, in agreement with the experimental results reported here. The calculated structure factors for the boundary structures predicted by Wolf do not, however, agree with the observed structure factors. In particular, Wolf's structures predict that reflection \( 11,1 \) has higher intensity than reflection \( 10,4 \), which is the opposite of the experimental observations for Au, Ag and Cu in Fig. 6. Wolf has suggested that the reason the computer modeling predictions do not agree with the experimental observations is because the computer calculations must be performed at constant density, while it is known that there is a local expansion at the \( \Sigma=13 \) boundary in Au /13/.

In section II it was noted that the important atomic displacements in the \( \Sigma=5 \) boundary involved rotations about 0-elements to achieve local regions of f.c.c. structure. In an attempt to produce a boundary structure that agreed with the experimental observations, a similar type of displacement field was used for the \( \Sigma=13 \) boundary. Such an approach has been described by Brokman and Balluffi /14/. When this was done, it was found that the observed intensity sequence of grain boundary reflections could be reproduced by the use of large local rotations about 0-elements, as noted for the \( \Sigma=5 \) boundary. In fact, it was rotations giving local regions of median f.c.c. structure that resulted in the correct order of the intensities of reflections 10,4 and 11,1. In a previous combined computer modeling-X-ray diffraction study by Bristowe and Sass, it was also shown that the best match to the X-ray observations was given by large rotations about 0-elements. (See Fig. 4(c) of ref. 9.)

Based on the results from the \( \Sigma=5 \) and \( \Sigma=13 \) boundary studies taken together, it is tempting to speculate that the important atomic displacements in [001] twist boundaries in f.c.c. metals involve large rotations about 0-elements to produce small regions of median f.c.c. structure. More extensive studies are required to check the validity of this suggestion.

IV. The Influence of Bonding Type on Grain Boundary Structure

The previous studies were concerned primarily with the structure of the grain boundary projected onto the interface plane. In this section a diffraction approach is described which can be used to study the structure of grain boundaries along the direction normal to the interface. This technique is sensitive to deviations in plane spacing, composition and atomic density from that in the perfect crystal. A diffraction analysis is performed in order to relate realistic model structures of the boundary to diffraction effects. The diffraction technique is then used to study the influence of bonding type (ionic, metallic,
covalent) on boundary structure. This was done by using electron diffraction to study the structure along the direction normal to the interface of [001] twist boundaries with the same misorientation in NiO (ionic bonding), Au (metallic bonding) and Ge (covalent bonding).

Lamarre and Sass /13/ obtained diffraction information from an edge-on [001] twist boundary in a Au bicrystal. They interpreted their results in terms of local changes in plane spacing normal to the boundary. For simplicity, Lamarre and Sass represented the grain boundary as a uniform thin crystal with a plane spacing different from that in the neighboring perfect crystals. This model is clearly too simple, and was considered to be the first step towards a more realistic representation of the grain boundary. In this paper the previous work is extended by using a more realistic model of the boundary displacement field and carrying out a diffraction analysis based on this model. As an introduction the thin crystal model of a grain boundary used by Lamarre and Sass is reviewed.

In the thin crystal model the [001] twist boundary at the midplane of a bicrystal is envisaged as a thin crystal, 2N planes thick with a (002) plane spacing, $d_b$, that is different from the spacing, $d_0$, in the perfect crystal surrounding the boundary region (Fig. 7(a)). It is considered more likely that $d_b$ is greater than $d_0$, although this assumption does not affect the results of the analysis. It is suggested that a local expansion normal to the interface will give rise to extra scattering effects in the [001] direction in reciprocal space at a distance $1/d_b$ from the origin, as shown in Fig. 7(b). It is also suggested that the grain boundary reflection will be elongated by an amount proportional to $1/W$, where $W$ is the thickness of the grain boundary region. The limitations of this approach are that: (1) it is physically unrealistic for the strain field surrounding the interface to contain a sharp step, and it is more likely to decrease smoothly to zero with increasing distance from the interface, and (2) diffraction from the thin crystal region cannot be treated independently from the perfect crystal diffraction.

The diffraction analysis in the present paper is based on the kinematical theory of scattering, which is more correctly applied to the interpretation of X-ray diffraction results than electron diffraction results where dynamical effects may be important. The analysis will be used only to relate peak positions and widths to boundary structure, and therefore this approach is considered valid for the interpretation of the electron diffraction observations.

The advantage of the thin crystal model is that it provides a simple way to visualize the diffraction effects due to changes in plane spacing at a grain boundary and the diffraction problem can be solved analytically /15/; the disadvantage is that it is too simple an approximation to the structure of the grain boundary and therefore cannot be used to predict accurately the diffraction
effects from a grain boundary. It seems reasonable to expect that the strain field normal to an [001] twist boundary will decrease in magnitude with increasing distance from the boundary plane. In this paper an exponentially decaying strain field is used.

For the exponential model the fractional positions of the diffracting planes along the z-direction normal to the interface are given by

\[ z(1) = \frac{(1 + \delta)}{4} \]
\[ z(j) = z(j-1) + (1 + \delta e^{-(j-1)/N})/2 \quad \text{for } j \geq 1 \]
\[ z(-j) = -z(j) \]

This strain field is characterized by a maximum strain, \( \delta \), between the two planes either side of the interface, and a number of planes, \( N \), within which the strain on each side of the boundary falls to \( \delta/e \). Summing the displacement terms in equations (1) we find that the fractional rigid body displacement \( R \) is given by:

\[ R = \frac{\delta e^{1/N} + 1}{(e^{1/N} - 1) / 2} = \frac{\delta \coth(1/2N)}{2} \]

which tends to \( N \delta \) as \( N \) increases.

An example of a computer generated intensity profile calculated for an exponentially decaying strain field with \( \delta = 0.15 \), \( N = 1.45 \), and \( R = 0.45 \) \( d_0 \), is plotted along the L-direction in Fig. 8 as a broken line. The intensity profile for the thin crystal boundary is shown as a solid line in Fig. 8 for \( \delta = 0.15 \) and \( R = 0.45 \) \( d_0 \), and so the two profiles can be compared on the basis of equal maximum expansion and rigid body displacement, but a different form of strain field decay. The 002 reflection is asymmetric in both profiles. However, for L values less than \( \approx 1.8 \) the intensity is greater for the thin crystal model than the exponential model. For L values between \( \approx 1.8 \) and 2 the reverse is true. This behavior is even more obvious in the case of the 004 reflection. This can be explained at least qualitatively by the nature of the strain field. In the exponential model there are many interplanar spacings which differ only very slightly from \( d_0 \) and only one interplanar spacing which has suffered the maximum strain. Thus the intensity for the exponential model is relatively large for the part of the profile that corresponds to small strains (i.e., close to 002). In the thin crystal model three interplanar spacings are strained by \( \delta \) and all the rest are unstrained, producing more extra intensity in the higher strain part of the profile (i.e., far from 002).

**Fig. 8 - Intensity profiles:**

solid line for thin crystal model, \( \delta = 0.15 \), \( N = 2 \);
broken line for exponential model, \( \delta = 0.15 \), \( N = 1.45 \).
The analysis up to this point has concentrated on the influence of changes in plane spacing along the direction normal to the interface on diffraction effects from the boundary. However, the diffraction technique described in this section is sensitive not only to changes in plane spacing at the boundary, but also to any deviation in structure away from that of the perfect crystals neighboring the boundary. Therefore, it is necessary to examine the influence of segregation, point defects, rumpling or reconstruction of the atom planes, and a tilt component in the boundary. An extensive treatment of diffraction from boundaries, which includes these effects, will be published elsewhere /15/.

In order to study the diffraction effects from the boundary described above using electron diffraction, it is necessary to examine edge-on [001] twist boundaries. The procedures to produce these specimens will be only briefly summarized here. Specimens containing a [001] twist boundary in Au in the edge-on orientation were produced by epitaxial growth on a NaCl bicrystal substrate containing an edge-on [001] twist boundary; the substrate was obtained by hot pressing together two cleaved NaCl single crystals /13/. Bicrystals containing a [001] twist boundary in NiO were produced by hot pressing together two cleaved NiO single crystals at the desired misorientation /16/. A slab containing the edge-on boundary was then cut from this bicrystal with a diamond saw and ion thinned to produce a specimen suitable for electron microscopy. Bicrystals containing a [001] twist boundary in Ge were grown from the melt using two preoriented seed crystals. The electron microscopy specimen was obtained in the same manner as for NiO.

The experiment to observe the diffraction effects described using Fig. 7 involves the detection of weak grain boundary scattering which is in the vicinity of matrix reflections of the type O0L. To make the required observations using electron diffraction it is necessary to tilt the Ewald sphere by small increments, in order to explore the region of reciprocal space in the vicinity of the matrix reflections. Diffraction patterns were taken using a Siemens 102 electron microscope operated at 125 kV, with a well-defocused second condenser lens and exposure times of 30 to 900 seconds. The orientation of the Ewald sphere was changed in small steps (0.1° - 0.25°) by varying the direction of the incident electron beam using the dark-field beam deflection coils.

Fig. 9(a-c) shows three diffraction patterns taken from a (e=22°)[001] twist boundary in NiO. These patterns are part of a long series recorded with different incident beam directions as described above, and a streak displaced away from O02 towards O00 is clearly visible. Similar experiments were performed on the same type of twist boundary in Au and Ge, and a characteristic diffraction pattern for each material is shown in Fig. 10, together with Fig. 9(b) from NiO for comparison.

The streaks in the diffraction patterns in Fig. 10(a-c) show significant differences for the three materials. The NiO streak extends from L=1.3 to L=2.4. The end of the Au streak near O00 is at L=1.7. The other end is obscured within the strong O02 matrix reflection but its maximum extent is to L=2.15. The Ge streak is very short which poses considerable problems in recording its complete length due to the saturation of the film by the diffuse scattering around the O04 matrix reflection. However, the streak visible in Fig. 10(c) extends from L=1.96 to 2.06 which is a very slight asymmetry in the opposite direction to that observed for NiO and Au. A qualitative comparison among the experimentally observed streaks shows that they go from longest to shortest and most to least asymmetric in the order NiO, Au, Ge.

Based on the diffraction analysis presented above using an exponentially decaying strain field, diffraction profiles for various values of \( \delta \) and \( N \) were calculated in an attempt to match the experimental observations in Fig. 10. It was assumed that the streaks were due solely to a change in plane spacing in the boundary region. For the NiO streaks a good match was obtained for \( \delta = 0.4 \pm 0.2 \) and a boundary width of \( 2d_0 + d_0 \). For the Au streaks a match was found for \( \delta \) between 0.1 and 0.2 and a boundary width of \( 3d_0 \pm d_0 \). In the case of Ge the small
Fig. 9 - Electron diffraction patterns from a long series taken from a 22° [001] twist boundary in NiO. The beam orientation changes in steps of 0.5° between patterns. The arrows indicate streaks in the vicinity of the matrix reflections.

Fig. 10 - Electron diffraction patterns showing the characteristic grain boundary diffraction streaks from 22° [001] twist boundaries in

(a) NiO,
(b) Au,
(c) Ge.

asymmetry in the streak was not considered to be definitive evidence of a contraction at the boundary, since calculations showed that small asymmetries of this type could be caused by either reconstruction or segregation of point defects to the boundary. The shortness of the streak indicated a relatively large boundary width of the order of $5d_0 \pm 2d_0$. 
If these observations are considered to be representative of the effect of bonding on boundary structure, then they can be used to make predictions about the behavior of the structure of the grain boundaries. Thus, along the direction normal to a [001] twist boundary it is expected that for material with: (1) ionic bonding there will be a large expansion, (2) metallic bonding there will be a small expansion, and (3) covalent bonding there will be little if any change in plane spacing. The boundary widths also appear to change with material type, from a relatively narrow boundary in the case of an ionic material to a wider boundary for a covalent material.

The problems associated with this technique come under three main headings: (1) recording the full extent of the streak and its intensity profile; (2) assessing the effects of the dynamical nature of electron diffraction on the kinematically calculated diffraction profiles; and (3) determining the contribution of the additional structural effects listed above to the observed diffraction patterns. Progress has been made on the solution of all three problems. However, at this stage it is only possible to report qualitative results. In order to check the predictions from the diffraction study, for example, the large value of $\delta$ for the NiO boundary, it will be necessary to use other experimental techniques, such as high resolution electron microscopy.

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References