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**ATOMIC-SCALE STRUCTURE AND CHEMISTRY OF INTERFACES BY
Z-CONTRAST IMAGING AND ELECTRON ENERGY LOSS SPECTROSCOPY
IN THE STEM**

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**ATOMIC SCALE STRUCTURE AND CHEMISTRY OF INTERFACES BY Z-CONTRAST
IMAGING AND ELECTRON ENERGY LOSS SPECTROSCOPY IN THE STEM**

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ABSTRACT

The macroscopic properties of many materials are controlled by the structure and chemistry at grain boundaries. A basic understanding of the structure-property relationship requires a technique which probes both composition and chemical bonding on an atomic scale. The high-resolution Z-contrast imaging technique in the scanning transmission electron microscope (STEM) forms an incoherent image in which changes in atomic structure and composition can be interpreted intuitively. This direct image allows the electron probe to be positioned over individual atomic columns for parallel detection electron energy loss spectroscopy (EELS) at a spatial resolution approaching 0.22nm. In this paper we have combined the structural information available in the Z-contrast images with the bonding information obtained from the fine structure within the EELS edges to determine the grain boundary structure in a SrTiO₃ bicrystal.

INTRODUCTION

The development of the incoherent Z-contrast imaging technique (1) using a dedicated STEM now enables the acquisition of directly interpretable images of materials interfaces at atomic resolution. The spatial resolution of the image is governed by the microscope probe size and by holding the probe stationary for microanalysis, the spatial resolution of the analytical signal can now be identical (2). The detector arrangement in the STEM has the added advantage of allowing the Z-contrast image to be collected simultaneously with the analytical signal (3). In this paper we utilize such advantages to propose, using experimental information alone, the atomic structure of a grain boundary in a SrTiO₃ bicrystal. Such an approach has not hitherto been possible using other experimental techniques.

In the VG HB501 UX dedicated STEM, the image is formed by scanning a 2.2Å probe across the specimen. The integrated output from various imaging detectors is displayed on a TV screen scanning at the same rate. The Z-contrast signal is collected from a high angle annular detector where, by collecting the component of the electron signal scattered through large angles (typically 75 to 150 mrad) the resultant image is dominated by thermal diffuse scattering. In this high angle regime lateral coherence between individual columns is destroyed, enabling an image showing incoherent characteristics to be produced with a spatial resolution limited by the size of the scanning probe (4). Provided the incident electron probe is smaller than the lattice spacing (for a sample oriented to a major zone axis) the resultant image will be a map of the columnar scattering intensity. Furthermore, the relative intensity of scattering from each column reflects the changes in the composition on an atomic scale. For thicker samples, where beam spreading might be expected to degrade the resolution, theoretical calculations (4) have shown that the spatial resolution is preserved by channeling of the electrons down the atomic columns, provided the sample is oriented on a major zone axis. Experiments have confirmed the electron channeling effect in thicker samples (~500Å) where the image merely reduces in contrast as the incident beam becomes depleted by the increasing number of scattering events.

The key aspect of this technique is that intensity distributions in high-resolution Z-contrast images provide a direct image of the atomic column sites which is sensitive to both structure and composition on an atomic scale (5). High resolution CTEM images are more difficult to interpret in such terms since reversals in image contrast as a function of focus and specimen thickness can occur. As the Z-contrast signal is collected from an annular detector, the inelastic signal, which is scattered through significantly lower angles can be collected simultaneously to form an energy loss spectrum. Consequently, the high-resolution Z-contrast image can be used to position the electron probe on specific atomic sites to collect EELS data.

Due to the formation of the small probe used for the Z-contrast imaging, the beam current is reduced by a factor of 50 over that which is normally available for EELS in the STEM. Such a reduction in the EELS signal, coupled with the requirement of short acquisition times to reduce specimen drift effects when collecting from individual atomic columns, requires a large increase in the sensitivity of the detection system. This has been carried out using a charge coupled device (CCD) parallel detection system based on a design by McMullan et al (6). The range of signal detection afforded by the CCD system means that as well as elemental quantification, information on the local bonding can also be obtained from the electron energy loss near edge structure (ELNES) within each edge (7).

In order to achieve atomic resolution EELS microanalysis, the range over which the fast electron can cause a particular excitation or energy loss must be less than the inter-atomic spacing. This interaction can be described classically by an impact parameter (8). Previous work has shown that for energy losses greater than $\sim 300\text{eV}$ and a collection angle of 30mrad (typical in the work presented here) the impact parameter is sufficiently small that the spatial resolution of the EELS signal is dominated by the incident probe size of 2.2\AA (7). It should be noted that this classical approach is probably an overestimate of the impact parameter since screening of the atomic electrons will further reduce the effective impact parameter (9).

A GRAIN BOUNDARY STUDY IN A SrTiO_3 BICRYSTAL.

SrTiO_3 is an important electroceramic material whose electrical properties are controlled by the atomic, chemical and electronic structure at the grain boundary. Figure 1(a) shows a Z-contrast image from a 25° tilt boundary in a SrTiO_3 bicrystal. The image was acquired from a cross-sectional specimen oriented in the $\langle 100 \rangle$ direction and the common boundary plane is (920). The brighter regions in the image correspond to the strong scattering power of the heavier Sr columns (which have a spacing of 3.9\AA in the $\langle 100 \rangle$ direction) whilst the lighter Ti columns are just discernible above the background. By applying image analysis techniques, it is possible to reduce the image noise. Figure 1(b) shows a maximum entropy reconstruction (10) from the raw image of figure 1(a) in which it is much easier to see the position of the Ti atoms between the Sr atoms. Although the position of the Sr and Ti columns can be clearly located, it is not possible to determine the O structure at the grain boundary from the Z-contrast image alone. However, by using the Z-contrast image to accurately position the probe at the grain boundary for EELS acquisition, the fine structure within the EELS edges can then be used to investigate the O and Ti bonding at the boundary.

Figure 2 shows a series of Ti spectra acquired at 4\AA intervals across a SrTiO_3 grain boundary. In the cubic perovskite structure of SrTiO_3 this step size is approximately equivalent to the unit cell dimensions of 3.9\AA . The spectra were acquired in line scan mode to reduce the radiation damage in the sample. Note the changes in fine structure across the series, in particular the decrease in intensity of the first peak at the grain boundary. From molecular orbital calculations the fine structure within the EELS edges can be assigned as transitions from the core level to antibonding states as indicated for a Ti-O octahedron in figure 3. The first peak in both the Ti and O edges arises from transitions to a π^* antibonding level and the second peak from transitions to a σ^* antibonding level (11). The higher energy region of the conduction band involves many overlapping transitions and it is not possible to assign a peak in the EELS edge

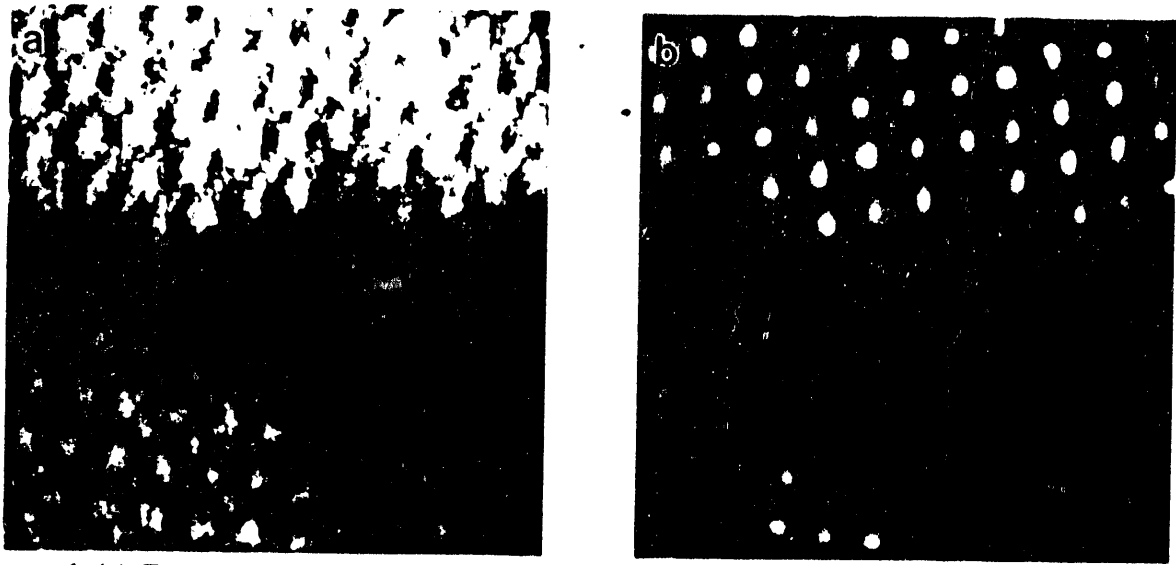


Figure 1 (a) Z-contrast image of a 25° grain boundary in a SrTiO₃ bicrystal. (b) Maximum entropy reconstruction from the raw Z-contrast image in (a).

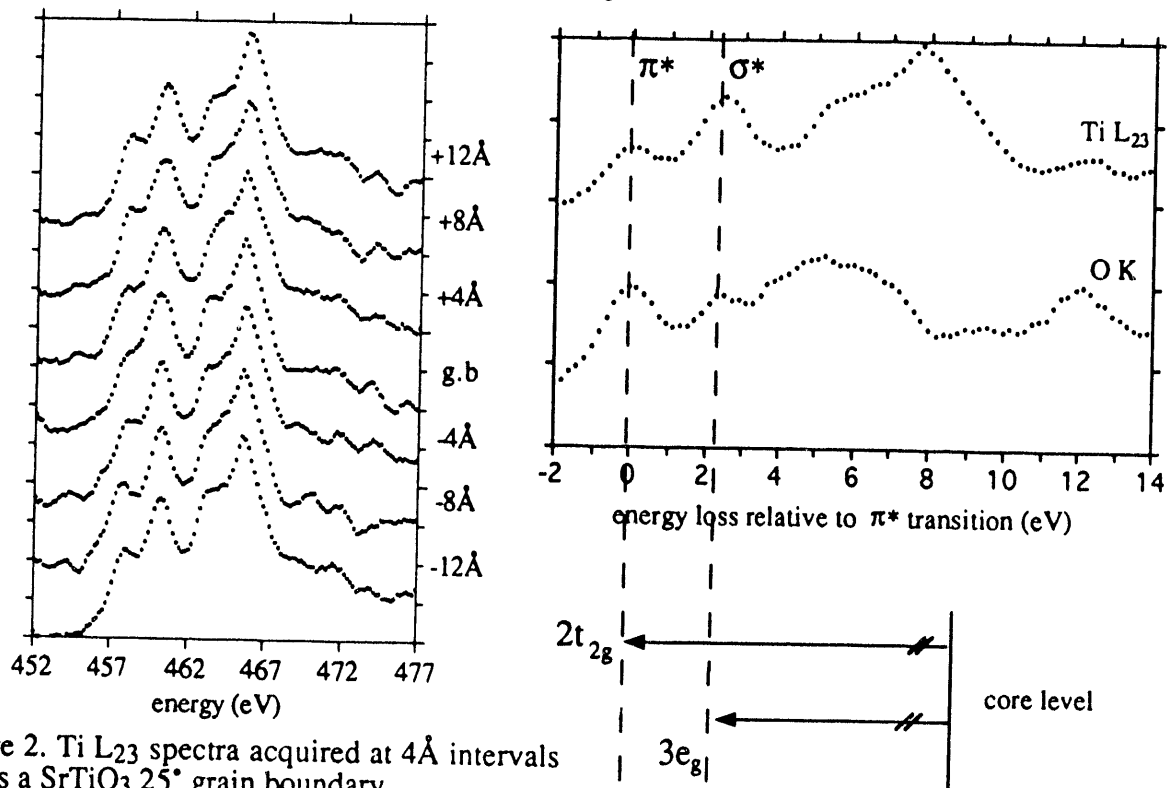


Figure 2. Ti L₂₃ spectra acquired at 4Å intervals across a SrTiO₃ 25° grain boundary.

Figure 3. Molecular orbital assignments for the fine structure in the Ti and O edges.

to an individual transition. The changes in the Ti edges observed in figure 2, therefore, correspond to a decrease in intensity of transitions to the π^* antibonding level.

The fine structure in the Ti edge can also be used to give information on the local atomic environment of Ti (reference 12 and the references therein). The intensity of the sharp peaks, known as white lines, found at the onsets of the Ti L₂ and Ti L₃ absorption edges reflects the filling of the d-states in transition metals (13,14). After normalising the white line intensity relative to the trailing background, any changes in this normalised intensity will reflect changes in the d-state occupancy caused by a change in the local atomic environment of the Ti atoms. In the bulk SrTiO₃, the Ti atoms are octahedrally coordinated to O and have a valency of 4+.

Figure 4(a) shows the normalised white line intensity across the grain boundary measured from the Ti spectra of figure 2. Within the experimental limits the normalised white line intensity remains constant across the grain boundary indicating that the local atomic environment is similar at the grain boundary. Previous studies of chemical shifts in the EELS edge energy have observed energy shifts of between 1 and 3eV with a change of valency in transition metals such as Mn, Ti and Fe (15,16). From the series of spectra in figure 2 there is no observed chemical shift in edge energy suggesting that the Ti valency remains the same throughout the sample. Further evidence of constant valency across the grain boundary comes from the L_2/L_3 ratio shown in figure 4(b). Although there is experimental evidence of changes in L_2/L_3 ratio with changes in valency (16,17) the relationship between d-band occupancy and L_2/L_3 ratio is not linear and it is difficult to assign a value for the valency from these ratios alone. However, one might expect any changes in this L_2/L_3 ratio at the grain boundary to indicate a change in valency. Within the experimental limits, figure 4(b) shows no such change in L_2/L_3 ratio in the grain boundary spectra. All the evidence suggests that Ti remains octahedrally coordinated to O and that the valency of the Ti atoms is 4+ throughout the sample.

The changes in fine structure of the Ti edge at the grain boundary observed in figure 2 were quantified by fitting gaussian profiles to the π^* peak and the results are shown in figure 4(c). There is a ~15% decrease in the intensity of the π^* transitions at the grain boundary relative to those in the bulk material. The decrease in intensity of the π^* transition is not sharp and extends over ~8Å which is consistent with the extent of the grain boundary region observed in the Z-contrast image of figure 1. This suggests that the Ti-O bonds, which gives rise to the π^* transitions, are affected by the grain boundary. Therefore, although the Ti atoms remain octahedrally coordinated to O at the grain boundary the Ti-O bonds themselves have become distorted across the boundary.

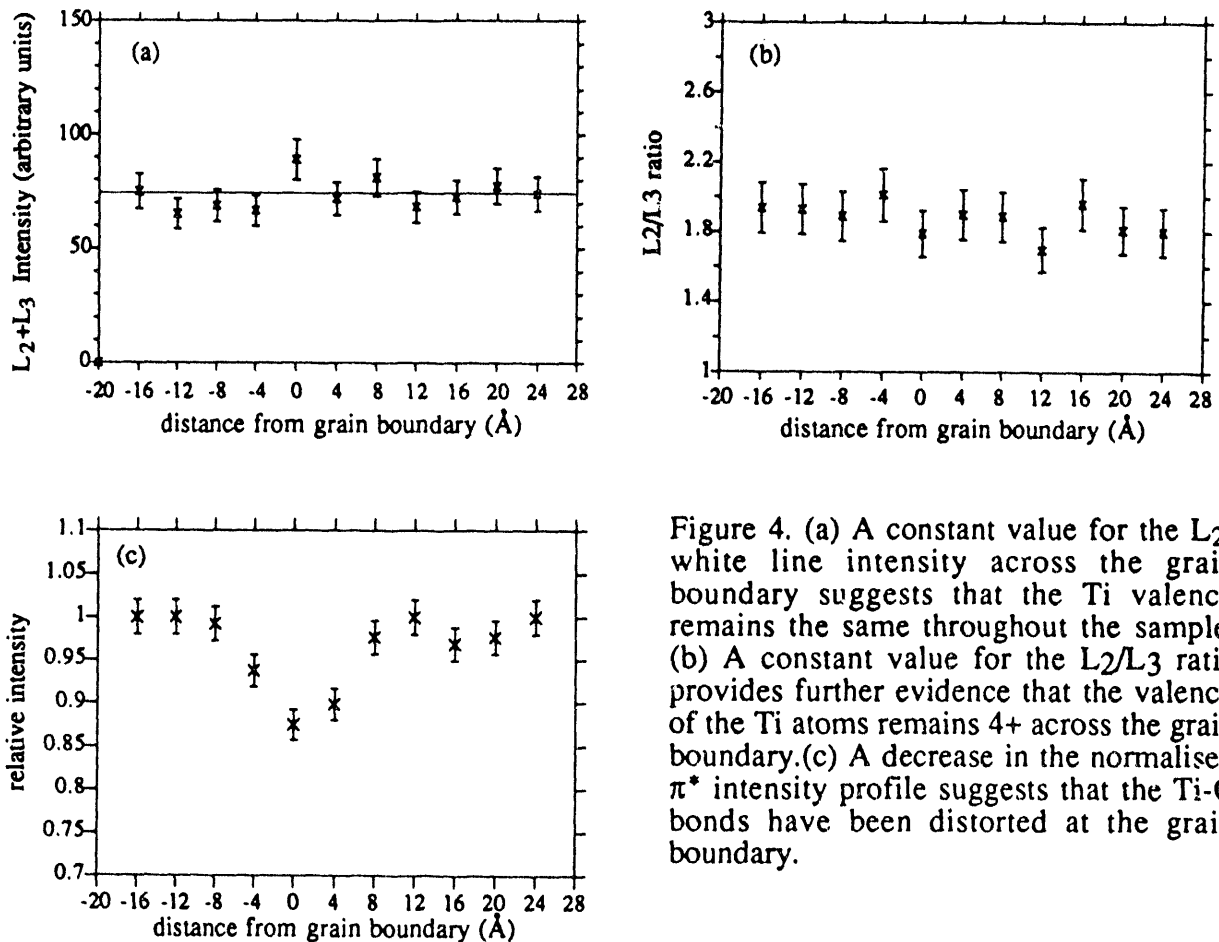


Figure 4. (a) A constant value for the L_{23} white line intensity across the grain boundary suggests that the Ti valency remains the same throughout the sample. (b) A constant value for the L_2/L_3 ratio provides further evidence that the valency of the Ti atoms remains 4+ across the grain boundary. (c) A decrease in the normalised π^* intensity profile suggests that the Ti-O bonds have been distorted at the grain boundary.

A similar series of O spectra were acquired across a second grain boundary region at 4Å intervals. For simplification, the results are shown in figure 5 as a comparison of spectra in the bulk and at the grain boundary. From the figure, it is clear that there is an increase in the intensity of the σ^* peak relative to the π^* peak in the grain boundary spectrum. This increase in σ^* transitions may be explained qualitatively by considering the oxygen coordination in SrTiO₃ (18). In the linear O-Ti coordination of SrTiO₃, shown schematically in figure 6, only the p_x orbitals contribute to the σ bonding. In comparison, in the threefold O-Ti coordination of TiO₂ (rutile), also shown in figure 6, both the p_x and p_z orbitals contribute to the σ bonding thus increasing the σ contribution to the bonding. A corresponding increase in the σ^* peak is observed experimentally in the O edge of TiO₂ compared to the O edge of SrTiO₃. In an analogous manner, the increase in the σ^* peak of the grain boundary spectrum in figure 5 suggests that the linear coordination of the O-Ti bonds in SrTiO₃ is distorted at the grain boundary producing a larger number of σ^* transitions.

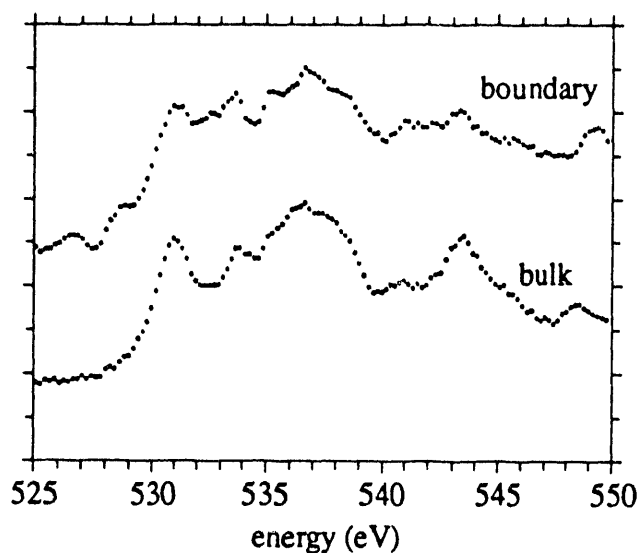


Figure 5. A comparison of O K-edge spectra acquired at the grain boundary and in the bulk of a SrTiO₃ bicrystal.

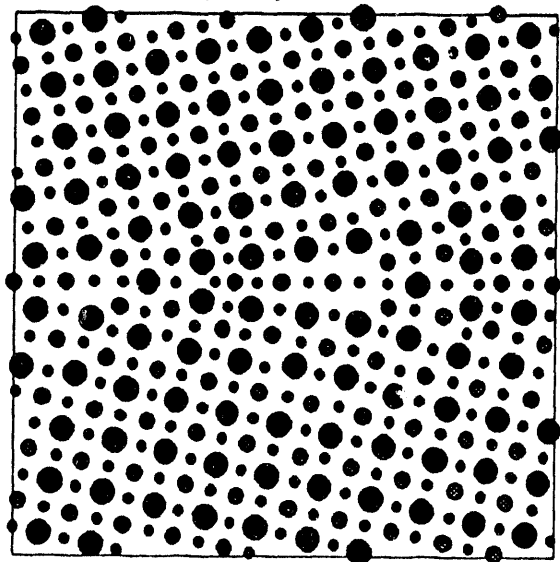


Figure 7. Grain boundary structure for a SrTiO₃ bicrystal based on the structural information obtained from the Z-contrast image and the bonding information available in the fine structure of the Ti and O EELS edges. The larger black circles represent Sr, the medium gray circles Ti and the smaller black circles O.

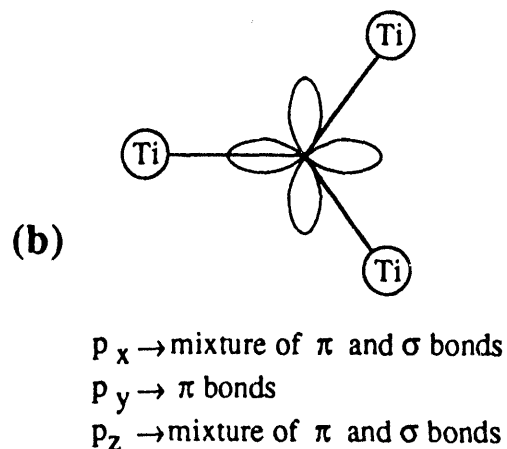
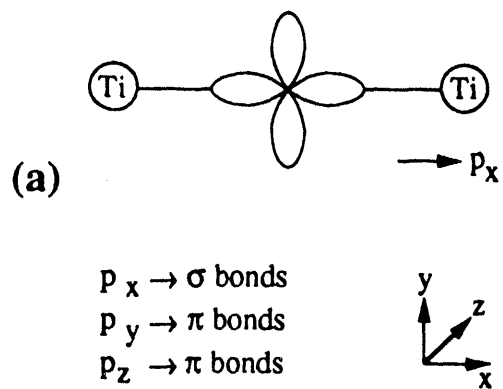


Figure 6. Consideration of molecular orbital contributions to the π and σ bonds in (a) the linear coordination of SrTiO₃ and (b) the threefold coordination of TiO₂ (rutile).

Using a combination of the structural information obtained from the Z-contrast image and the bonding information obtained from the EELS it is possible to determine the likely structure at the grain boundary, purely from experimental data. The boundary structure calculated for this 25° tilt boundary is shown in figure 7. The disruption of the Ti-O linear coordination at the grain boundary can be clearly seen in this boundary reconstruction. The width of the grain boundary region in the reconstruction is ~8Å which is consistent with the Ti and O EELS data and also reflects the extent of strain contrast seen in the Z-contrast image of figure 1.

CONCLUSIONS

Using the dual technique of Z-contrast imaging and parallel-detection EELS we have probed the grain boundary structure in a SrTiO₃ bicrystal on an atomic scale. From these experimental results alone we have been able to determine the grain boundary structure without the need for image simulations. Although the disruption of the linear coordination of the Ti-O bonds at the grain boundary in SrTiO₃ is perhaps not surprising the fact that this result can be directly observed on an atomic scale presents new and exciting possibilities for the study of grain boundaries.

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REFERENCES

- (1) S.J. Pennycook and D.E. Jesson, *Phys.Rev.Lett*, **64**, 938, (1990)
- (2) N.D.Browning et al, *Nature*, **366**, 143 (1993)
- (3) A.V. Crewe, J. Wall and J. Langmore, *Science*, **168**, 1338, (1970)
- (4) S.J. Pennycook and D.E. Jesson, *Ultramicroscopy*, **37**, 14, (1991)
- (5) S.J. Pennycook, *Annu. Rev. Mater. Sci.*, **22**, 171, (1992)
- (6) D.McMullan et al, *Institute of Physics Conference Series* **98**, **55**, (1990)
- (7) N.D.Browning and S.J.Pennycook, *Microbeam Analysis*, **2**, 81, (1993)
- (8) S.J.Pennycook, *Contemp.Phys*, **23**, 371 (1982)
- (9) P.E.Batson, *Ultramicroscopy*, **47**, 133 (1992)
- (10) S.F.Gull and J.Skilling, *IEEE Proc*, **131F**, 646 (1984)
- (11) L.A.Grunes et al, *Phys.Rev.B*, **25**, 7157 (1982)
- (12) R.Brydson, H.Sauer and W.Engel in Transmission Electron Energy Loss Spectrometry in Materials Science, edited by M.Disko, C.Ahn and B.Fultz (The Minerals, Metals and Materials Society, 1992) pp 131.
- (13) M.DeCrescenzi et al, *Phys.Rev.B*, **39**, 5520 (1989)
- (14) D.H.Pearson, C.C.Ahn and B.Fultz, *Phys.Rev.B*, **47**, 8471 (1993)
- (15) J.H.Paterson and O.L.Krivanek, *Ultramicroscopy*, **32**, 319 (1990)
- (16) M.T.Otten et al, *Ultramicroscopy*, **18**, 285, (1985)
- (17) X.W.Lin et al, *Phys.Rev.B*, **47**, 3477 (1993)
- (18) R.Brydson et al, *J.Phys:Condens.Matter*, **4**, 3429 (1992)

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