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CONF-961202--71

Presented at Fall Meeting of the Materials Research Society,
Boston, Massachusetts, December 2-6, 1996; to be published in
Atomic Resolution Microscopy of Surfaces and Interfaces,
ed. by D. J. Smith and R. Hamers, Materials Research Society,
Pittsburgh, PA, 1997

**DETERMINATION OF THE 3-DIMENSIONAL ATOMIC STRUCTURE AT
INTERNAL INTERFACES BY ELECTRON ENERGY LOSS
SPECTROSCOPY**

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January 1997

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DETERMINATION OF THE 3-DIMENSIONAL ATOMIC STRUCTURE AT INTERNAL INTERFACES BY ELECTRON ENERGY LOSS SPECTROSCOPY

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ABSTRACT

The fine structure of a core-loss edge contains detailed information on the local atomic environment. It can be used as an extremely sensitive probe of the fluctuations in structure and bonding that can occur at internal interfaces. Interpretation of such fluctuations requires only a knowledge of the location of the electron probe when the spectrum is acquired and a means of interpreting the spectrum. The location of the probe can be controlled with atomic precision in the STEM by the use of the Z-contrast image, while the real space cluster methodology of multiple scattering analysis is ideally suited to the task of interpretation. This approach is used here to derive 3-dimensional models for tilt grain boundaries in TiO_2 and SrTiO_3 .

INTRODUCTION

Materials properties associated with interfaces are dominated by atomic scale fluctuations in composition, structure and bonding. Although electron energy loss spectroscopy (EELS) provides a powerful tool to probe these features [1], low signal, lens aberrations, image coherence and specimen drift often preclude the use of spectrum imaging and energy filtered imaging for these high-resolution problems. However, by utilizing Z-contrast imaging in conjunction with EELS in the scanning transmission electron microscope (STEM) [2,3], these limitations are largely overcome and EELS appears capable of providing fundamental 3-D characterization of interface structure with atomic resolution and sensitivity [4,5].

The main premise in utilizing these combined techniques is that the properties of defects and interfaces must be associated with structural differences relative to the bulk. If those structural differences can be located, then it is only necessary to perform spectroscopy in their vicinity to uncover the structure-property relationship. For crystalline materials in zone-axis orientations, the Z-contrast image provides this atomic resolution structural map [6]. This direct image can be used to position the electron probe with atomic precision and, unlike high-resolution imaging in a conventional TEM, does not interfere with spectroscopy. For core-losses (above 100eV), the spectrum has the same atomic resolution and incoherent features as the Z-contrast image, thus allowing direct correlation of the spectrum with an individual structural feature [7].

MULTIPLE SCATTERING ANALYSIS OF THE ENERGY LOSS SPECTRUM

There are several methods which may be employed to interpret the energy loss spectrum. The simplest approach is to assign the various features to molecular orbitals formed by the interaction of an atom with its nearest neighbors [8]. Molecular orbital theory uses group theory to produce molecular orbitals from a linear combination of atomic orbitals. However, group theory relies heavily on the symmetry of a molecule and therefore does not cope well with low symmetry structures such as those found at grain boundaries. This approach also becomes very clumsy to apply to anything but the smallest cluster of atoms and so potentially significant contributions to the electronic structure from second and third neighbor atoms are difficult to include. The use of the symmetry projected density of states as derived from band structure calculations [9] is at the other end of the analysis scale. Although such calculations potentially

provide the most accurate representation of the band structure, they also rely heavily on the symmetry of a system. While techniques which allow band structure calculations to be applied to disordered structures have been developed, they require the use of very large unit cells containing many atoms with periodic boundary conditions. As a result of these considerations the computation time for such calculations is prohibitive.

An alternative method of spectrum interpretation is through multiple scattering calculations. This methodology was originally developed for near-edge structure interpretation in X-ray absorption spectroscopy (XANES) [10]. Application to electron microscopy is possible since the theory of ELNES and XANES are exactly analogous; the absorption processes are identical - only the radiation used to excite the atoms is different. Multiple scattering calculations model the density of states by considering the scattering of the excited photoelectron from neighboring atoms. The different paths which may be taken by a photoelectron alter the matrix elements for a particular transition due to the constructive or destructive interference which occurs between the outgoing and returning photoelectron wave (figure 1).

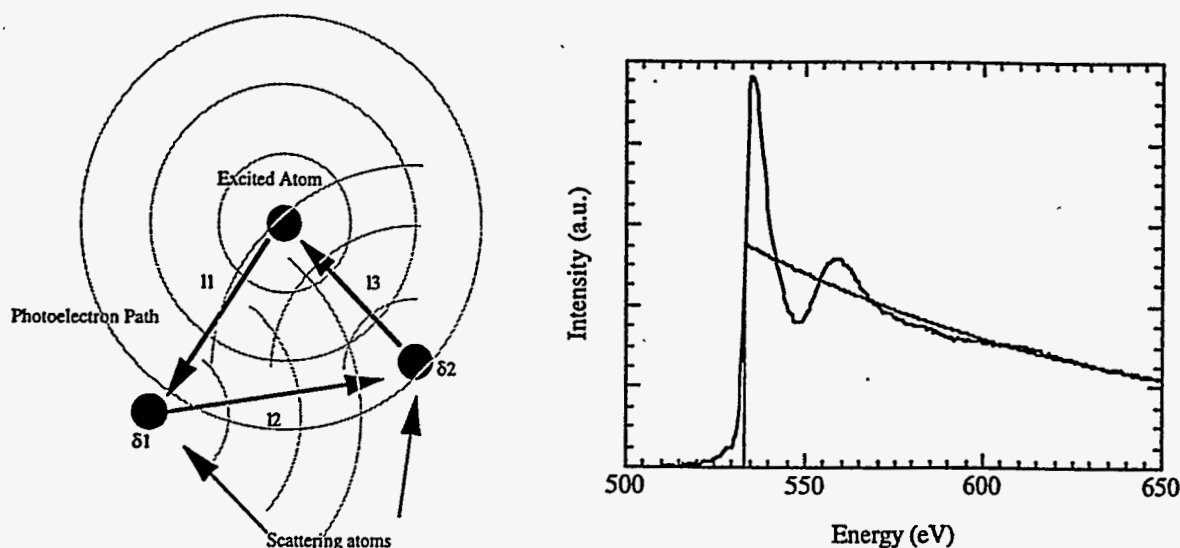


Figure 1: (a) Schematic of the scattering of the photoelectron wave from surrounding atoms. (b) the interference effects lead to a modulation of the K-edge intensity.

In effect, the resultant spectrum may be described as a simple absorption edge of hydrogenic form, due to an isolated atom, with intensity modulations due to the structure of the solid (figure 1). i.e. the absorption $\alpha(E)$ is given by

$$\alpha(E) = \alpha_0(E) \left[1 + \sum_{n=2} X_n(E) \right]$$

where $\alpha_0(E)$ is the atomic absorption and $X_n(E)$ is the multiple scattering signal of order n ($n > 1$) which contains all the structural information [11]. Since this description of the density of states is based on a real space cluster of atoms, several unique opportunities are presented. The lack of symmetry no longer seriously affects the calculation and the effects of dopant atoms on ELNES may be simply investigated by substituting atom types within the cluster and recalculating the scattering. Additionally, by limiting the order of the terms included in the summation and the allowed scattering paths, the structural origins of particular features in the spectrum may be determined. Multiple scattering therefore allows spectral changes to be directly interpreted in terms of structural changes, and is ideal for the study of interfaces.

The multiple scattering calculations shown here were performed using commercial FEFF6 codes [12]. These codes use the overlapping-atom prescription of Mattheiss [13] to model the atomic potential within the muffin tin approximation. From the resulting potential, scattering phase shifts and matrix elements are calculated. Core hole effects are included using the $(Z+1)^*$ approximation [14] where * denotes the excited atom. The curves shown are calibrated by alignment of the first spectral feature with experiment and broadening of 1eV is added to allow direct comparison with experimental spectra. For the purposes of the calculation, the atomic clusters are divided into shells of atoms where a single shell is composed of atoms which lie between two radii about the excited site. The order of scattering is controlled simply by placing an upper limit on the number of scattering events which are allowed.

(210) SYMMETRIC [001] TILT BOUNDARY IN TiO_2

Figure 2 shows a Z-contrast image of the $\Sigma 5$ (210) tilt grain boundary in TiO_2 (rutile). The bulk sample was prepared by the laser float zone method in an Argon/2% Oxygen atmosphere (the resulting crystal was dull white) and then polished and ion-milled to electron transparency.

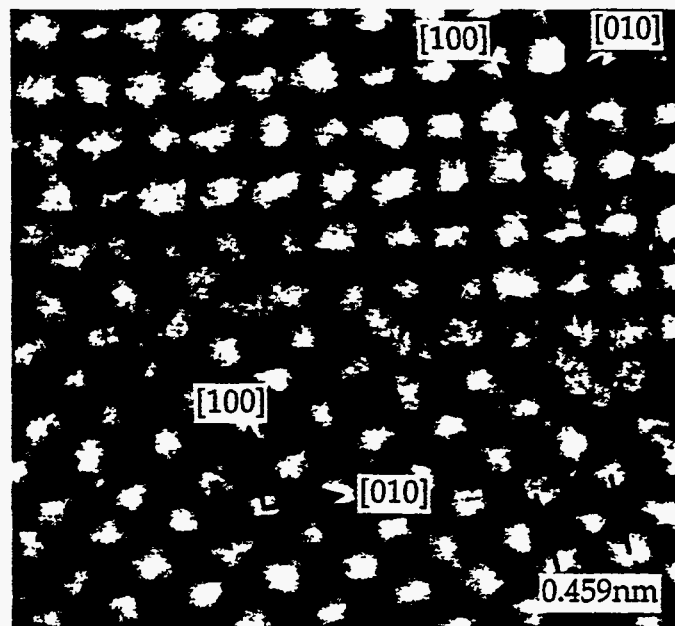


Figure 2. Z-contrast image of a $\Sigma 5$ (210) tilt boundary in TiO_2 .

The direct image provided by the Z-contrast technique makes it straightforward to propose a structure for the interface. However, interface models based only on this Z-contrast image must account for the fact that the rutile crystal contains two Ti sub-lattices which are related to each other by a translation of $1/2[111]$ and a rotation of 90° . If the Ti at position $(0,0,0)$ is labeled A and the Ti at position $(1/2,1/2,1/2)$ labeled B, there are three possible structures for the interface plane consistent with the Z-contrast image; AA, BB and AB (Figure 3). As the information present in the image is simply a 2-D projection of each Ti sub-lattice it is impossible to distinguish between the models from the image alone.

Electron energy loss spectroscopy from the interface region allows this ambiguity in the interface structure to be resolved. Figure 4 shows experimental Oxygen K-edge spectra and titanium L-edge spectra from the bulk and the interface. The comparison of the two spectra in

each case shows very little change. It is therefore clear that the bonding at the interface is very similar to the bulk. This appears to be consistent with the AB interface shown in figure 3.

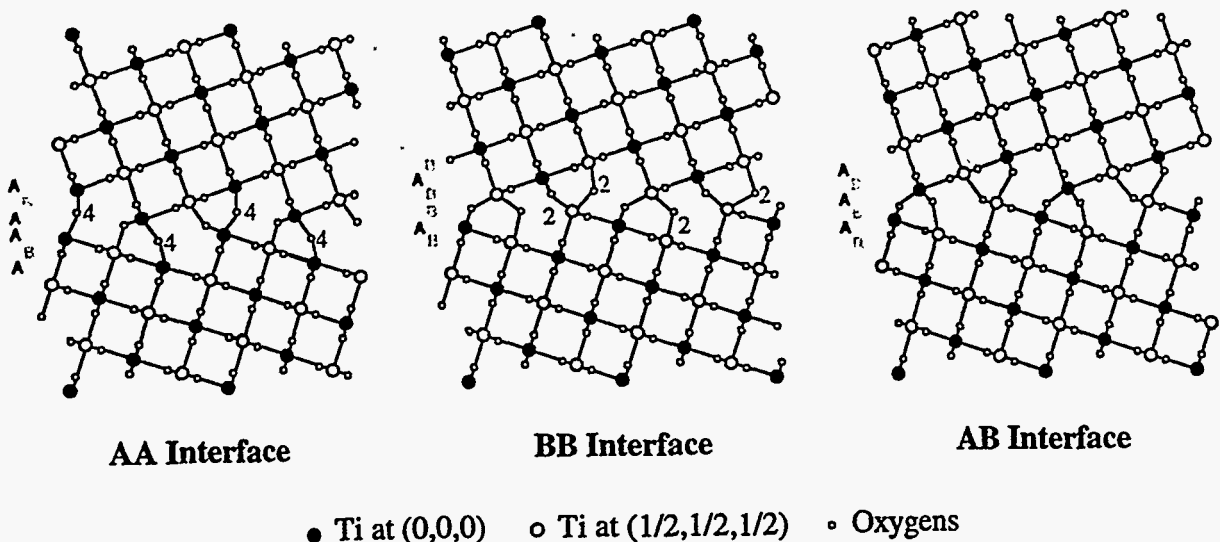


Figure 3: The three possible interface structures for the (210) boundary in TiO_2 consistent with the experimental image. Note the AA and BB structures contain oxygen sites with different coordination from the bulk (i.e. 2-fold and 4-fold as opposed to the bulk 3-fold coordination).

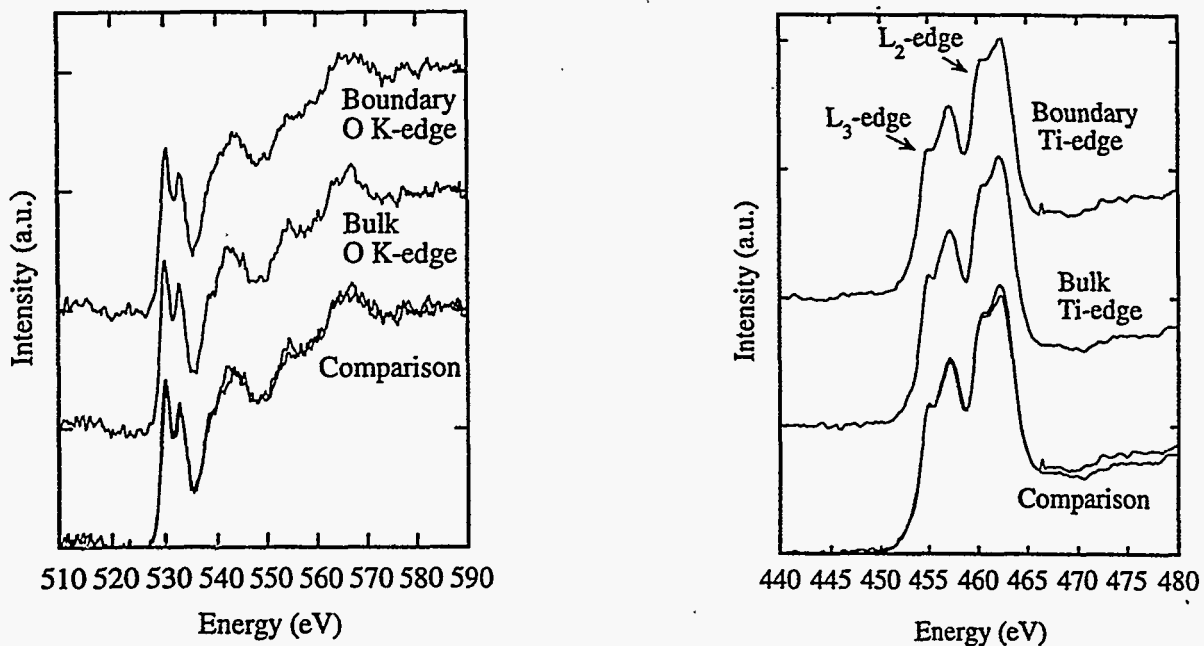


Figure 4. (a) Oxygen K-edge (b) Ti L₂₃-edge from the bulk crystal and the boundary plane.

The assignment of the AB interface as consistent with both the image and the spectrum can be confirmed by multiple scattering analysis [4]. In figure 5, the expected energy loss spectrum for 2-fold, 3-fold and 4-fold coordinated oxygen is compared to the experimental spectrum from the interface. It can be seen that the expected spectrum from 2- and 4-fold coordinated oxygen is considerably different from the 3-fold spectrum and the experiment. The 3-fold coordinated

spectrum shows good agreement with the experiment except for the splitting of the first peak. This peak is due to transitions to states involving the Ti 3d levels and the splitting of these states occurs as a result of the effects of the anisotropic crystal field at the atomic sites (i.e. crystal field splitting). Since the multiple scattering calculations are performed within the muffin tin approximation, spherical symmetry is imposed and the calculations cannot reproduce the splitting.

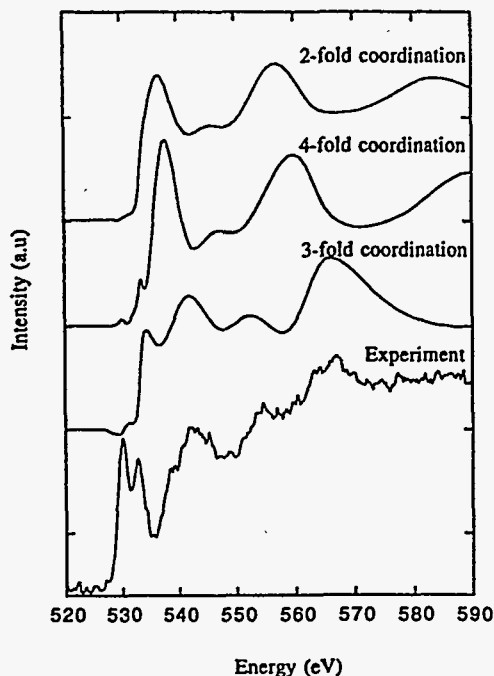


Figure 5: A comparison of the expected spectrum for 2-, 3- and 4-fold coordinated oxygen (calculated from multiple scattering theory) with the experimental grain boundary oxygen spectrum.

45° ASYMMETRIC [001] TILT BOUNDARY IN SrTiO₃

Figure 6 shows the Z-contrast image and schematic structure of a 45° asymmetric [001] tilt grain boundary in SrTiO₃. Positions where the atomic columns appear too close together are highlighted in the schematic. These atomic positions are known to be real features in the image and have been postulated to be partially occupied, thus avoiding the problems of like ion repulsion [15]. This partial occupancy hypothesis can be tested by multiple scattering analysis [5]. The oxygen K-edge spectra and titanium L-edge spectra obtained from the bulk and boundary are shown in figure 7. The titanium spectrum from the interface shows no change from the bulk spectrum. From this it can be determined that the valence and coordination of the titanium atoms at the boundary remains unchanged. The changes in the oxygen edge are slight, but visible on all the main peaks in the spectrum.

The multiple scattering simulation of the experimental bulk oxygen spectrum is found to reproduce the five main peaks and their relative intensities for an 8 shell cluster containing 99 atoms (figure 8). The fact that the intensities of some of the peaks require such a large cluster to be fully reproduced indicates that they are sensitive to long range order (particularly peak a). It is therefore not surprising that the presence of the grain boundary would destroy this long range order and have an effect on the spectrum. However, using the multiple scattering formulation, it is possible to go a step further in the analysis of the spectrum and begin to address the presence of lattice vacancies in the boundary core. Such vacancies will have a markedly different effect on the fine-structure than distortions of the lattice. Distortions will generally broaden peaks by destroying the symmetry. Vacancies on the other hand will completely remove scattering paths that can lead to an enhancement or reduction in the intensity of a particular feature (depending on whether the scattering event would lead to destructive or constructive interference). Figure 8 shows the effect on the bulk spectrum of the removal of

titanium, strontium and oxygen atoms from the cluster. It is apparent from these simulations that vacancies of different species have noticeably different effects on the spectrum

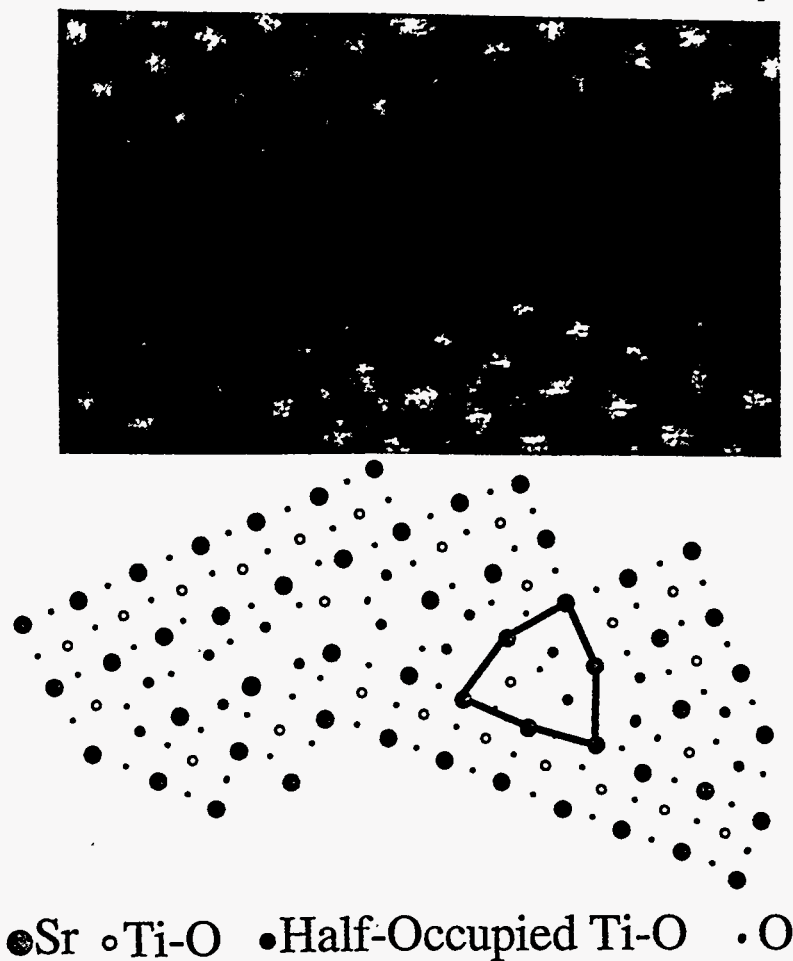


Figure 6: (a) Z-contrast image and (b) schematic of a faceted 45° [001] tilt boundary in SrTiO_3

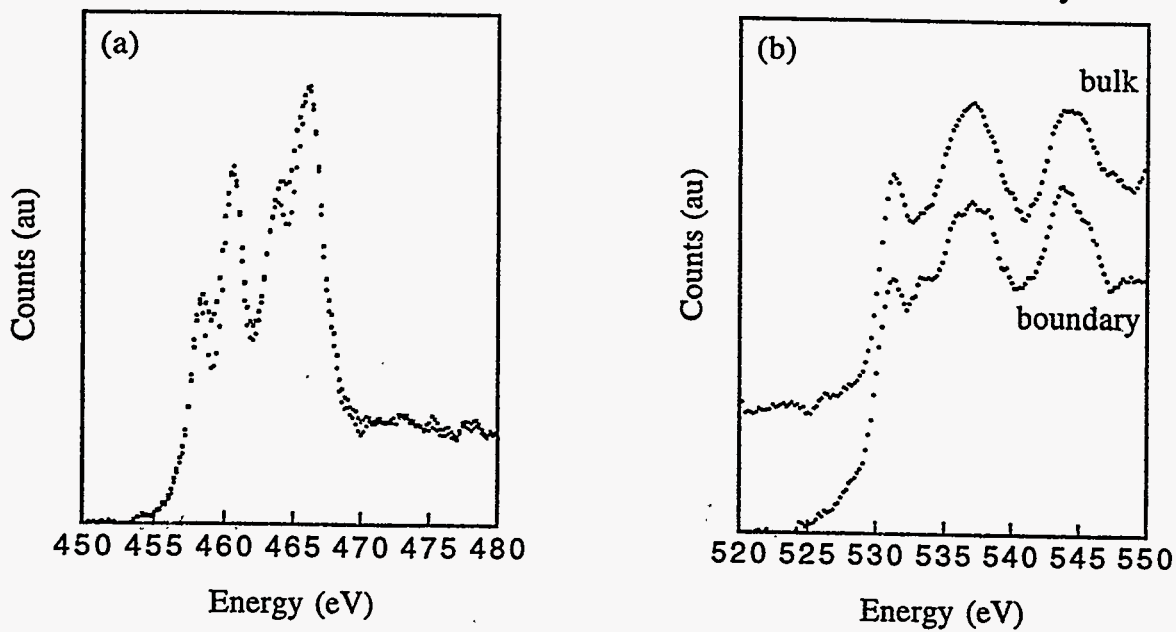


Figure 7. (a) Ti L_{23} -edge (b) Oxygen K-edge from the bulk crystal and the boundary plane.

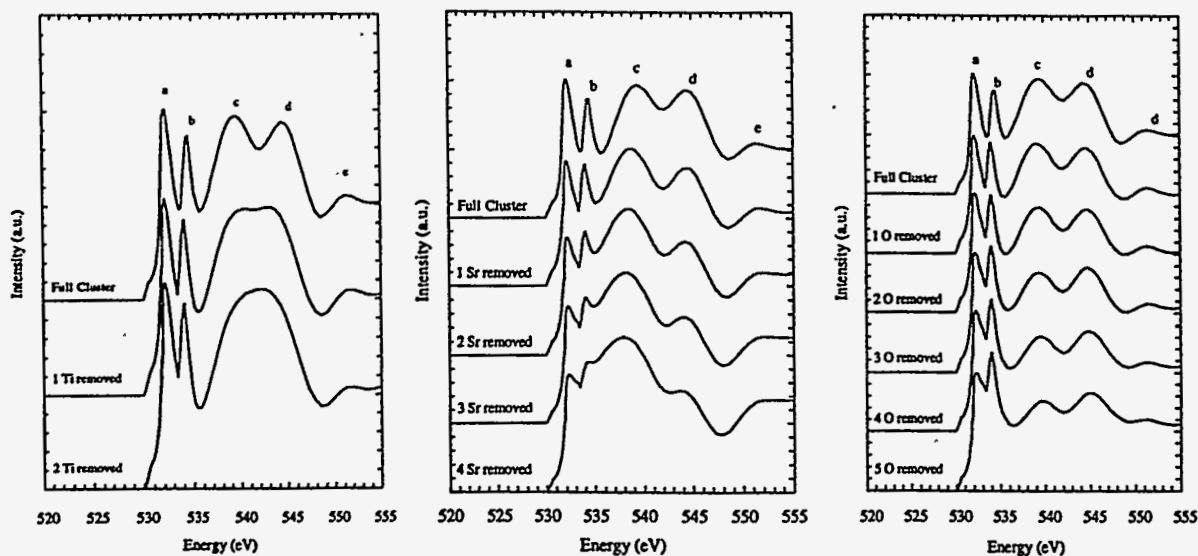


Figure 8: Comparison of the simulated bulk spectrum with a cluster containing (a) titanium vacancies (b) strontium vacancies and (c) oxygen vacancies.

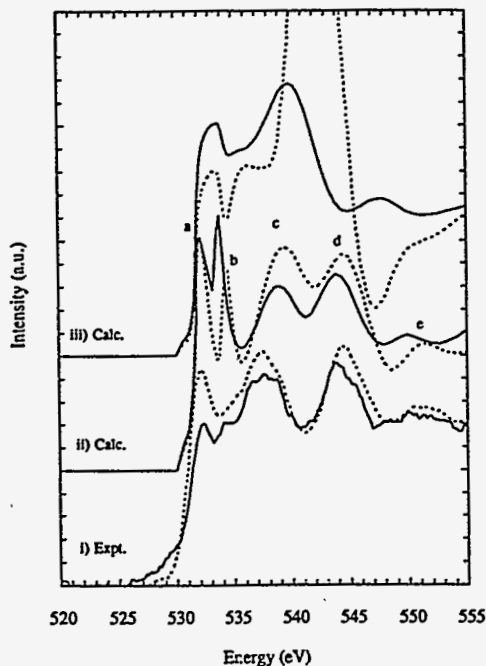


Figure 9: Comparison of i) the experimental bulk and interface spectra with ii) the spectra simulated from a bulk cluster and a cluster containing 4 oxygen vacancies. For comparison, the simulated spectrum from the grain boundary in figure 6 is also shown, assuming the atom columns that appear too close together are fully occupied (iii).

Having determined the effect of vacancies on the oxygen K-edge spectrum, we are now in a position to interpret the changes seen in the experimental spectrum from the grain boundary. Figure 9 compares the changes seen experimentally with the changes in the oxygen K-edge spectra obtained from two clusters. The first cluster contains the bulk structure of SrTiO_3 , while the second cluster contains 4 oxygen vacancies. This number of vacancies reproduces the changes in the 5 peak positions and intensities seen experimentally by moving from the bulk to the boundary. At first glance it is not obvious why the experimental spectra are reproduced by

the incorporation of oxygen vacancies when the image infers partial occupancy of the titanium sites. However, we know from the titanium L-edge spectrum that even with partial occupancy the titanium atoms must maintain the bulk valence and coordination. The only way for this to occur at the boundary is for the partially occupied titanium columns to be accompanied by oxygen vacancies. For comparison, the simulated spectrum for the structural unit highlighted in figure 6 is also shown in figure 8, but in this case the titanium columns are taken to be fully occupied. This spectrum is dramatically different from the experiment and is a strong indication for partial occupancy.

CONCLUSIONS

Electron energy loss spectroscopy is a powerful tool for the analysis of interfaces. The increased sensitivity of the spectrum to light elements means that it supplies complementary information to that present in the image, whether it be a Z-contrast image or a conventional high-resolution TEM image. Analysis of the spectra obtained from the interface can take characterization to a new level, by distinguishing different 3-dimensional atomic structures with the same projection, and indicating the presence of vacancies associated with given defect structures. Such characterization will undoubtedly aid in the unraveling of structure-property relationships at interfaces. The next step in the process is to use these techniques in a predictive manner for structure refinement or to propose new routes for materials processing.

ACKNOWLEDGMENTS

Aspects of the TiO₂ study were performed in collaboration with P. D. Nellist, I. Majid, Y. Liu and J. B. Vander Sande. The authors are grateful to J. T. Luck for technical assistance. This research is funded by NSF under grant No. DMR-9503877 and by the US DOE under contract no. DE-ACOS-96OR22464 with Lockheed Martin Energy Research Corporation.

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