Electronic Structure of a Near Σ11 a-axis Tilt Grain Boundary in α-Al₂O₃

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The electronic structure and interatomic bonding of a near Σ11 a-axis tilt grain boundary in α-Al₂O₃ are determined using first-principles calculations based on a model structure constructed by Kenway. This Σ11 boundary, which has a low grain boundary energy, has been the focus of various previous studies, including high-resolution transmission microscopy (HRTEM) and pair potential based structural studies. The relaxed structure model, which contains 72 Al atoms and 108 O atoms, is periodic in two dimensions and reproduces the grain boundary structure obtained by HRTEM. To accurately identify the changes arising in the boundary, parallel calculations on the bulk supercell models containing the same number of Al and O atoms with and without surfaces were also carried out. This grain boundary does not have deep levels in the band gap, and its defect states appear mainly near the O-2p derived valence band maximum and the Al-3s derived conduction band minimum. The calculated partial densities of states for Al in the conduction band region are in good agreement with recent measurements on the near-edge energy loss spectrum and the valence electron energy loss spectrum. By means of Mulliken population analysis, the effective charges, the bond order, and the partial density of states of the grain boundary atoms are identified and elucidated. In the region of the grain boundary, there is increased charge transfer from Al to O, arising mainly from the lower coordination number of the grain boundary atoms and therefore the reduction in the covalent bond formation. In addition, it is found that as the Al-O bond lengths decrease, the Al-O charge transfer increases. For this Σ11 boundary, the structural features most associated with grain boundary electronic structure changes are undercoordination and shortened bond lengths.

1. Introduction

The atomic and electronic structure and chemical composition of grain boundaries (GB) and other interfaces in ceramics in many ways dictate the processing, and the mechanical, electrical and optical properties of polycrystalline ceramic materials. Therefore, a detailed understanding of the physical properties of the grain boundaries in ceramics such as α-Al₂O₃ has long been a goal of ceramics research. This focus on grain boundaries has encompassed studies of mass transport and grain boundary diffusion, sintering, creep, conductivity and grain boundary segregation, and grain boundary structure and energy studies. Various groups have used electron microscopy to study the atomic structure and composition of grain boundaries, typically in commercial-grade α-Al₂O₃. At the same time, there have been pair potential based calculations and electron studies of surfaces and stacking faults in alumina, but less activity in grain boundaries, due to their complexity. The electronic structure of crystalline α-Al₂O₃ has been the focus of theoretical and experimental studies in the last few years, yet to date study of the grain boundary electronic structure of α-Al₂O₃ has been stifled, due to the structural complexity of grain boundaries.

It is only recently that the necessary experimental and theoretical advances have converged to permit detailed atomic level study of a well-characterized, clean grain boundary in alumina. This is based on Morris et al.'s clean-room processing and laser float zone growth of near Σ11 (2Σ11) grain boundaries of known purity and orientation. Studied with Höche et al.'s high-resolution transmission electron microscopy and image simulation and modeled using Kenway's static lattice calculations. This combined effort has led to an understanding of the grain boundary structural units. Essential to the present work is a detailed atomic structure model, consisting of full 3-D atomic coordinates, for this near Σ11 boundary in α-Al₂O₃. Based on Kenway's near Σ11 grain boundary atomic structure model, we can calculate the grain boundary electronic structure using the standard methods applied to perfect crystals. The grain boundary is modeled by a supercell containing a large number of atoms. The electronic structure calculation of the supercell grain boundary model is then not much different from that of a crystal with a very complex structure. In addition to the atomic structure of the near Σ11 boundary, recently there have been scanning transmission electron microscopy studies, using electron energy loss spectroscopy (EELS) of the near-edge structures and the valence electron energy loss of the interband transitions of the near Σ11 boundary, supplying information which can be compared to the results calculated in the present work.

In this paper, we report the results of such a calculation on the near Σ11 (2Σ11) GB in α-Al₂O₃, based on the Kenway model. Because of the low symmetry of crystalline α-Al₂O₃, the modeling and calculation of the GB in α-Al₂O₃ is much more difficult than, say, in MgO or Si. We will first describe the Kenway model. Next, the strategy and the method of calculation for 2Σ11 GB are outlined. The results of our calculation are presented and analyzed in comparison with the available EELS data. We further discuss our results and their implications in terms of trends in interatomic bonding in low energy GB's.

II. The Kenway Model

Kenway has constructed a 2Σ11 GB model for α-Al₂O₃ using a static lattice calculation based on the minimization of total energy described by atomistic model potentials. The model is a bicrystalline tilt boundary with Σ11 angle of 35.2°, and has a low GB energy of 1.7 J m⁻², or 0.11 eV/Å. The model contains 72 Al atoms and 108 O atoms and has no interstitials or vacancies. It is periodic in two dimensions (along 0.0, -4.7688, 0.0) and (0.0, -2.3844, 13.6278) directions) and has...
“free surfaces” in the direction perpendicular to the GB. The “free surfaces” are the result of the difficulty in the modeling process of having a simple transitional vector perpendicular to the GB to recover the same structure as the GB itself. The 180-atom model actually corresponds to the inner region of the GB model where the atoms are allowed to relax until the forces acting on them vanish. There is a much larger extended region in the modeling process where the atoms are held fixed but contribute to the total potential for the force calculation. Since the model is elongated in the direction perpendicular to the GB, the area of the “free surface” is rather small, and its effect on the electronic structure calculation of the GB is expected to be minimal. The beauty of the Kenway model is that it mimics closely the structure of the Σ11 GB obtained by HRTEM.16 This is illustrated in Fig. 1. Figure 1(a) shows the HRTEM picture for the Σ11 GB where the dotted lines depict the repeating unit of the group of GB atoms. Figure 1(b) shows the array of O atoms close to the top layer in the Kenway model. The agreement is excellent.

A detailed analysis of the Kenway model shows that there are 25 O atoms and 14 Al atoms that can be defined as the GB atoms. These are shown in Fig. 2 as lightly shaded atoms. The GB atoms are rather loosely defined as those within 3 Å from the GB line. There are 13 O and 11 Al atoms which are surface atoms far away from the GB. The rest of the atoms can be described as bulklike atoms. It should be emphasized that the bonding of those bulklike atoms is slightly distorted from the perfect crystal situation as a result of the relaxation process in modeling the GB. In the perfect corundum structure, each O atom is bonded to four Al atoms, and each Al atom is bonded to six O atoms in a distorted octahedron. There are two types of Al–O bonds with bond lengths (BL) 1.86 and 1.97 Å, respectively. The average O–O and Al–Al separations are 2.72 and 2.76 Å, respectively. We have analyzed the structural arrangement of the GB atoms in order to correlate with the calculated electronic structure. We define somewhat arbitrarily that a pair of Al and O atoms are bonded if their distance of separation is less than 2.16 Å. Our finding can be summarized as follows: (1) Of the 14 GB Al atoms, six are fully bonded with coordination number 6, five have coordination number 5, and three have coordination number 4. (2) Of the 25 GB O atoms, 14 are fully bonded with coordination number 4, and 11 are underbonded with coordination number 3. (3) The maximum and the minimum Al–O BL in the GB region are 2.16 and 1.75 Å, respectively. (4) As is evident in Fig. 2, the bond orientations in the GB regions are greatly distorted, and the deviations of the bond angles from the crystalline values are expected to be large. (5) In the bulklike region, all the atoms are fully coordinated, and the maximum and the minimum Al–O BL are 2.05 and 1.85 Å, respectively.
III. Computational Procedures

The electronic structure and the optical properties of $\alpha$-Al$_2$O$_3$ crystal have been studied by Ching and Xu$^{11}$ using the self-consistent orthogonalized linear combination of atomic orbital method (OLCAO) in the local density approximation.$^{10}$ One advantage of the OLCAO method is that the self-consistent field (SCF) potential for the crystal is expressed as a superposition of atom-centered effective $O$ and $Al$ potentials. We use these self-consistent bulk potentials for the GB calculation. While it is desirable to have a self-consistent calculation on the GB model itself, such as in the case of simple metals$^{12,23}$ and semiconductors,$^{24}$ the computational effort involved will be quite prohibitive at this time. The use of SCF bulk potential is the best compromise. Since these atom-centered potentials are reasonably transferable, and since in the OLCAO method the basis function itself is also atom-centered, the effect of the GB is accurately reflected in the geometry of the model itself. This is quite different from the empirical tight binding model,$^{25}$ in which the interaction parameters are generally fixed and their variation with the local atomic structure cannot be accurately predicted. In the first-principles OLCAO method, the interactions up to any number of nearest neighbors are calculated within the given set of linear and basis function. Another advantage of the OLCAO method is its atomic and orbital description of the electron states, which greatly facilitates the interpretation of the calculated result. In the present calculation, we start with a minimal basis, which includes the $Al$-3$s$, $Al$-3$p$ orbitals and O-2$s$, O-2$p$ orbitals for all the atoms in the model. It has been demonstrated in many cases that a minimal basis OLCAO calculation$^{10}$ can give accurate electronic structure for the valence bands (VB) and the lower conduction bands (CB). The use of a minimal basis also allows us to apply the Mulliken scheme$^{25}$ to calculate the effective charges on each atom, and the bond order between any pair of atoms. For a more accurate description of the CB, we later extend our basis to include the $Al$-3$d$, $Al$-4$s$, and $Al$-4$p$ orbitals in the calculation.

In order to have a comparative study of the $\Sigma 11$ GB as described by the Kenway model and the perfect bulk crystal, we carry out a parallel supercell calculation on $\alpha$-Al$_2$O$_3$ containing the same number of $Al$ and $O$ atoms as the Kenway model. The bulk supercell model is constructed by tripling the area of the basal plane and doubling the $c$-axis in the hexagonal unit cell description of the corundum structure. The hexagonal cell itself is three times larger than the primitive trigonal cell which contains four $Al$ and six $O$ atoms. This is illustrated in Fig. 3. In order to estimate the effect of the "free surface" in the GB model, calculation on bulk supercell model is repeated with the free surface in the $c$ direction terminating on the $Al$ atoms. This is accomplished by making the repeating distance 10 times the $c$ parameter of the bulk supercell model. In all calculations, the secular equations to be solved are only $720 \times 720$ for a minimal basis calculation and $1368 \times 1368$ when an extended $Al$ basis is used. Because the supercell is fairly large, the corresponding Brillouin zone (BZ) is quite small, and extensive BZ $k$-point sampling is unnecessary. We used four $k$-points in the GB model and six $k$-points in the bulk supercell calculations. These are the corner $k$-points of the reduced BZ where the matrix equations are all real.

In the OLCAO method, it is trivial to calculate the effective charge $Q^n_\alpha$ on each atom and each orbital $\rho_{\alpha\beta}$ as

$$\rho_{\alpha\beta} = \sum_{n,occ} C_{\alpha n}^n C_{\beta n}^n S_{\alpha\beta}$$

$$Q^n_\alpha = \sum_{\beta} \rho_{\alpha\beta}$$

where $C_{\alpha n}^n$ is the eigenvector coefficient for the state $n$ with atomic specification $\alpha$ and orbital specification $i$, while $S_{\alpha\beta}$ is the overlap matrix of the Bloch function. The effective ionic valence is then obtained by subtracting $Q^n_\alpha$ from the formal valence electron number. Also, the bond order which qualitatively describes the strength of the bond between a pair of atoms and $\beta$ can be defined as

$$q_{\alpha\beta} = \sum_{n,occ} \sum_{ij} C_{\alpha n}^n C_{\beta n}^n S_{\alpha\beta}$$

From $\rho_{\alpha\beta}$, the localization index (LI) of each electronic state $n$ can be evaluated as

$$LI_n = \sum_{\alpha,\beta} \left| \sum_{ij} C_{\alpha n}^n C_{\beta n}^n S_{\alpha\beta} \right|^2$$

![Fig. 3.](image)

(a) Bulk supercell $\alpha$-Al$_2$O$_3$ model and (b) basal plane of (a).

![Fig. 4.](image)

Calculated total DOS of (a) bulk $\alpha$-Al$_2$O$_3$ supercell model, (b) bulk $\alpha$-Al$_2$O$_3$ supercell model with surface, (c) near $\Sigma 11$ grain boundary model.
Fig. 5. Calculated localization index of the states for (a) bulk $\alpha$-Al$_2$O$_3$, supercell model, (b) bulk $\alpha$-Al$_2$O$_3$, supercell model with surface, (c) near $\Sigma$11 grain boundary model.

For each state, LI is a measure of the spread of the electron charge among all the sites of the model. LI ranges from 1 for a completely localized state to $1/N$ for a completely delocalized state, where $N$ is the dimension of the secular equation. We expect the GB structure of $\alpha$-Al$_2$O$_3$ to introduce localized states because of the bond length and bond angle distortions in the GB region. The identification of these states and their orbital origin is of considerable importance and interest.

IV. Results

Figures 4(a–c) show the calculated total density of states (DOS) of the bulk supercell model, the supercell model with surface, and the GB model respectively. For a more accurate comparison, the leading edges of the VB of the three spectra are aligned. For the bulk model, the broadened DOS is close to that for the crystalline calculations in the rhombohedral structure. There is a slight difference because, in the GB calculation, the basis function does not include O-3s and O-3p orbitals. In addition, the DOS calculation in the crystalline case used a much larger number of k-points for high resolution. Figure 4(b) shows that the Al-terminated surface has only a minor effect for the states near the top of the VB and the bottom of the CB. The DOS for the GB model, which contains free surfaces in one direction, is shown in Fig. 4(c) and is only slightly different from that of the bulk model Fig. 4(a). The main differences are:

1. There are a significant number of states extending into the gap region from both the VB and the CB edges and at the leading edges of the O-2s band. (2) There are deep levels introduced into the fundamental band gap. This is consistent with Kenway$^{15}$ that $\Sigma$11 is a low-energy GB. (3) In the upper VB region, the sharpness of the structures is somewhat reduced. However, the peak or the shoulder positions remain at about the same locations, indicating no fundamental change in the bonding interaction. (4) The small peak at $-17.7$ eV in the O-2s band becomes a shoulder with an increase in the band width. (5) There are also changes in the shape of the CB DOS profile. Figure 5 shows the calculated LI for the three models as in Fig. 4. For the bulk model, all the states are relatively extended with very small LI as expected for perfect crystal with translational symmetry. For the surface model, localized states originating from the surface atoms appear near the band edges. For the GB model, a large number of localized states appear at the top of the O-2s band, the top of the upper VB, and the entire lower part of the CB. It is understood that some of these localized states belong to the surface atoms far away from the GB. Figure 5 clearly shows that the localized states in the GB model are the same ones which induce the greatest change in the DOS spectra shown in Fig. 4. To verify that a specific localized state indeed originates from the GB atoms or the surface atoms, we analyze the atomic components that contribute to the LI for one of the top states, A, near the VB edge and another state, B, near the CB edge. The result is shown in Fig. 6. State A localizes mainly on the GB O atoms, and state B localizes on the GB Al atoms, but also on some surface atoms. The fact that a localized state near the CB edge can localize on both the GB atoms and surface atoms is quite puzzling. One possible explanation is that since the distance from the surface to the GB line in the Kenway model is quite short, about 10 Å, two types of localized states may somehow interact.

Fig. 6. Atomic components of two of the localized states: (a) at the VB edge, (b) at the CB edge.
correlation and anticorrelation is also true for the average BL of
the GB atoms. In Figs. 9 and 10, we display the atom-resolved
partial DOS (PDOS) for the GB AI and O atoms, respectively.
These GB atoms are divided into different groups according to
their NN coordination number. For comparison, the PDOS for
O and AI atoms from the bulk supercell model are also shown
at the top panel. It can be seen that for the VB, the difference
in the PDOS between the GB and bulk atom is not very significant
even for the undercoordinated atom. In the CB region, the most
significant difference is near the CB edge for AI atoms in the
GB with low coordination number of 4. It is understood that
the changes in the PDOS of the GB atoms are affected by the actual
local bonding configurations in addition to the NN coordination
numbers.

Bruley has recently reported spatially resolved electron
energy loss near-edge structure (ELNES) of the \( \Sigma \)11 GB in
\( \alpha\text{Al}_2\text{O}_3 \).\(^{18}\) It was found that the GB has introduced additional
fine structure on the \( L_{2,3} \) edge. By using a real space "difference"
spectra method (for the photodiode counts), information
about the altered bonding of the AI atoms in the GB region can
be inferred. Müllens et al. have analyzed the spatially
resolved valence band EEL data from a dedicated scanning
transmission electron microscope.\(^{19}\) They have concluded that
the interband transitions in the 14 to 22 eV range for the GB
region have been reduced in comparison with the bulk region.
By means of a quantitative critical point analysis of the
interband transition strength, they concluded that the ionicity in
the GB is increased, or, equivalently, there is a reduction in the
covalent bond formation. However, they found the reduction of
the band gap in the GB region to be only of the order of 0.1 eV.
In order to interpret the experimental data, we display the
orbital-resolved AI PDOS calculated for the GB model in the

![Figure 7](image_url)

**Fig. 7.** A close-up view of the atoms in the Kenway model in the grain boundary region. The numbers on the atoms and on the bond are the calculated effective ionic valence and the bond order, respectively. From the perfect crystal supercell calculation, the effective ionic valence of O is -0.62 and of AI is +0.93.
Fig. 8. Correlation of the effective ionic valence of the grain boundary atoms with the nearest-neighbor coordination number and with the average bond length. The arrows indicate the effective ionic valence for the bulk case.

Fig. 9. Atom-resolved PDOS of Al atoms: (a) bulk, (b) GB Al atoms with NN = 4, (c) GB Al atoms with NN = 5, (d) GB Al atoms with NN = 6.

Fig. 10. Atom-resolved PDOS of O atoms: (a) bulk, (b) GB O atoms with NN = 3, (c) GB O atoms with NN = 4.
and their validity has not been fully established yet. Theoretical calculations, especially those with no adjustable parameters involved, on realistic GB models are extremely valuable in obtaining a deeper insight about the fundamental role of the GB in determining the macroscopic material properties. The present study is the first step toward a systematic study of the grain boundaries in ceramics and ceramic composites.

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References


