Nonscalability and nontransferability in the electronic properties of the Y-Al-O system

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Based on *ab initio* calculations of electronic structure and properties of five crystals: α-Al_2O_3, $Y_3Al_5O_{12}$, $YAlO_3$, $Y_4Al_2O_9$, Y_2O_3, with different Al to Y ratios and local coordinations, it is concluded that the electronic properties of the Y-Al-O system cannot be simply scaled according to cation ratio, and any of the fundamental properties cannot be transferred from one crystal to another. This finding has an implication on the segregation of Y at the internal boundaries in alumina and the precipitate phases contained therein. It is speculated that possible Y-Al interaction may explain the ''Y effect'' in the Y-containing aluminum oxide. The electronic structure and bonding of $Y_3Al_5O_{12}$, $YAlO_3$, and $Y_4Al_2O_9$ crystals are discussed in considerable detail in relation to their complex structures. [S0163-1829(99)04720-7]

I. INTRODUCTION

Alumina (α-Al_2O_3) and yttria (Y_2O_3) are the two most important ceramic materials. Between these two stable end crystals, there are three congruently melted compounds with different Al to Y ratios: $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), and $Y_4Al_2O_9$ (YAM). They comprise the Y-Al-O system and all have complex structures with distinct and well-defined local atomic coordinations. While the electronic structure and properties of Al_2O_3 have been quite well studied,[1] work on Y_2O_3 is limited[2–4] and that of YAP and YAM are nonexistent. Only very recently, the electronic structure of the YAG crystal was studied for the first time.[5] Both YAG and YAP are important laser optical materials.[6] Single-crystal YAG is usually stabilized by Nd doping. It has been known that Y has a very low solubility in bulk alumina, but a small addition of Y leads to an increase in adhesion of Al-containing oxides.[7,8] As a doping element, Y segregates to the internal grain boundaries (GB's) in α-Al_2O_3, inhibits GB diffusion and increases creep resistance.[9–13] This is the so-called ''Y effect.'' The atomic scale structure of Y at the internal GB is unknown and YAG is frequently precipitated at the GB and interfaces in α-Al_2O_3. Single-crystal YAG also possesses excellent creep resistance and is vital for high temperature structural applications.[14] Indeed, the microscopic understanding of the Y effect is one of the most outstanding problem in materials science and technology.

To understand the structure and properties relationship in the Y-Al-O system and to provide a possible explanation for the Y effect, we have carried out detailed electronic structure calculations and made comparative studies among the five crystals. The electronic structure of alumina[15] and yttria[4] have been reported earlier and that of YAG very recently.[5] Those of YAP and YAM are reported for the first time. We used the first-principles, density-functional-theory-based orthogonalized linear combinations of atomic orbitals (OLCAO's) method[16] in the local density approximation (LDA). The OLCAO-LDA method is very effective for complex multicomponent crystals such as YAG and YAM. The use of atomic basis greatly facilitates the calculation of bond order or overlap population from the wave functions using the Mulliken population scheme.[17] Details about the method have been described elsewhere.[15,16] All calculations were self-consistent, with a full basis set, and well converged in k space integration and lattice summations.

II. STRUCTURES OF CRYSTALS IN THE Y-Al-O SYSTEM

The structural information of the Y-Al-O system are summarized in Table I. Comparatively speaking, α-Al_2O_3 with a rhombohedral corundum structure is the simplest. All Al and O sites are equivalent and cations are octahedrally (o) coordinated. The isoelectronic Y_2O_3 has a bixbyte structure instead, and there are two different o-coordinated Y sites. The most complicated one is YAG with a garnet structure containing 80 (160) atoms in the primitive (cubic) cell.[18] There are two different Al sites, the o-coordinated Al_{oct} and the tetrahedrally (t) coordinated Al_{tet}, while Y is eightfold coordinated. The crystal structure of YAG has been discussed in fair detail.[5]

YAP has a perovskite structure of the $GdFeO_3$ type.[19] The orthorhombic cell contains four formula units with two nonequivalent O sites. The coordinates of the ions in the YAP unit cell are distorted from the positions of an ideal perovskite, and a monoclinic pseudocell representation is equally valid.[19] Both Y and Al are o coordinated and contained in the distorted octahedra formed by the O atoms. There are three different Al-O bonds (1.862, 1.867, and 1.957 Å) and six different Y-O bonds (2.213, 2.471, 2.213, 2.339, 2.338, and 2.656 Å).

The monoclinic YAM crystal is the most peculiar and the least studied. The crystal structure has been accurately determined by x-ray and neutron diffraction on both single-crystal and powder samples.[20] There are nine O, four Y, and two Al sites. Two of the Y ions (Y1, Y3) are sevenfold coordinated and the other two (Y2 and Y4) are sixfold coordinated while both Al1 and Al2 are t coordinated. Of the nine independent O sites, four are bonded to three metal ions and five bond to four metal ions. O1, O2, O4, and O6 have three Y atoms and one Al atom as nearest neighbors (NN's). O3 and O7 each have two Y and one Al as NN's while O8 and O9 each have three Y as NN's. O5 distinguishes itself as the only O atom having two Al atoms as NN's in addition to the other two Y NN's. This plethora of local environments result in a differ-

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TABLE I. Structural information on the crystalline Y-Al-O system.

Crystals	α-Al_2O_3	$Y_3Al_5O_{12}$	$YAlO_3$	$Y_4Al_2O_9$	Y_2O_3
Space group	$R3c$, C_{3v}^6	Ia_3d, O_h^{10}	Pbnm, D_{2h}^{16}	$P2_1/c$, C_{2h}^5	Ia_3, T_h^7
F.U./cell	2	8	4	4	8
Lattice constants (Å):					
(a)	5.128	12.000	5.179	7.375	10.604
(b)			5.329	10.507	
(c)			7.370	11.113	
	$\alpha=55.333°$			$\beta=108.58°$	
No. atoms/cell:	10	80	20	60	40
Density (gm/c.c.)	3.983	4.552	5.352	4.525	5.032
Al:Y ratio	1:0	5:3	1:1	1:2	0:1
No of different sites:					
Y	-	1	1	4	2
Al	1	2	1	2	-
O	1	1	2	9	1
Cation coordination:					
Y	-	8	6	7, 6	6
Al	6	6, 4	6	4, 4	-
Average bond lengths (Å):					
Y-O	-	2.367	2.461	2.334	2.282
Al-O	1.913	1.849	1.895	1.741	-

ent local density of states (LDOS's) for YAM that will be discussed later. The Al-O (Y-O) bond lengths (BL's) in YAM range from 1.667 to 1.821 Å (2.158 to 2.565 Å). The average BL's are listed in Table I. Of the four crystals with Y-O bonds, Y_2O_3 has an average BL of 2.288 Å, smaller than the average BL's in YAG (2.368 Å), YAP (2.340 Å), and YAM (2.334 Å). Likewise, of the four crystals containing Al-O bonds, YAM has the shortest average BL's of 1.741 Å and α-Al_2O_3 has the longest (1.913 Å). Such a tantalizing variety of crystalline bonding structures within the Y-Al-O system form a very interesting case of study.

III. COMPARATIVE STUDY OF THE ELECTRONIC STRUCTURE OF THE Y-Al-O SYSTEM

The electronic structures and properties of the five crystals in the Y-Al-O series are presented and discussed. The results for YAP and YAM will be elaborated in more detail. Our focus will be on the comparative study of the five crystals with an emphasis on their relationship to the local bonding structure. Figure 1 shows the density of states (DOS's) for the valence band (VB) and the conduction band (CB) of the series. There are significant differences in the DOS spectra as will be described below. Other calculated properties are: (1) the band gap E_g and band widths (BW's); (2) the pressure dependence of E_g; (3) the bulk modulus B and the pressure coefficient B'; (4) the effective valence for cation and anion; (5) the electronic portion of the static dielectric constant $\varepsilon_1(0)$. These results are summarized in Table II. The electronic structure calculations were carried out using experimental structures of Table I and then repeated at different crystal volumes V with internal parameters fixed to obtain the pressure dependence of the gap. The B and B' were obtained from fitting the total energy data to the Birch-Murnaghan equation of state.[21] The effective charges were obtained by using a real-space charge analysis scheme.[4,15]

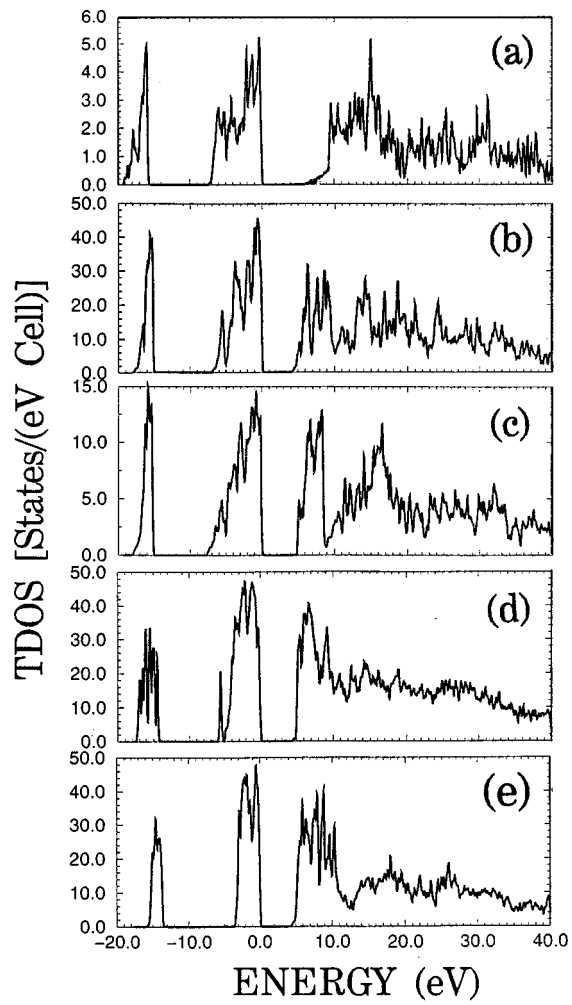

FIG. 1. Total DOS of (a) α-Al_2O_3, (b) $Y_3Al_5O_{12}$, (c) $YAlO_3$, (d) $Y_4Al_2O_9$, (e) Y_2O_3.

TABLE II. Calculated properties of the Y-Al-O system. E_g and BW in eV. B in Gpa and dEg/dP in eV/Gpa. D (id) for direct (indirect) gap.

Crystals	α-Al_2O_3	$Y_3Al_5O_{12}$	$YAlO_3$	$Y_4Al_2O_9$	Y_2O_3
E_g	6.31 (d)	4.71 (d)	4.99 (id)	4.72 (d)	4.54 (d)
dE_g/dP	0.0518	0.0025	0.0119	0.0224	0.0124
B	242	221	234	157	183
B'	3.24	4.00	3.75	5.09	6.92
Cation valence:					
Al	2.75	2.72	2.72	2.72	-
Y	-	2.50	2.51	2.54	2.50
O valence:	−1.83	−1.76	−1.74	−1.73	−1.66
Average bond order:	0.094	0.096	0.083	0.097	0.098
O-2p BW	7.37	6.78	7.58	5.46	3.41
O-2s BW	3.26	2.21	2.58	2.57	1.16
Gap in VB	8.53	8.67	7.94	9.29	11.09
$\varepsilon_1(0)$	3.01	4.62	4.40	5.42	3.20

Due to the different ionic sites and BL's in these crystals, the calculated effective valences are the averaged ones and only approximate. The average bond strengths between cations (Y or Al) and O as characterized by their bond orders (to be discussed later) were obtained from the wave functions of separate minimal basis calculations. The $\varepsilon_1(0)$ were extracted from the complex dielectric functions calculated separately.[22] Figure 1 and Table II provide many interesting observations on the electronic properties of the Y-Al-O system. α-Al_2O_3 has the largest and YAG the smallest E_g.[23] α-Al_2O_3 has a bulk modulus B larger than YAG. The B for YAM and Y_2O_3 are substantially smaller than the other three crystals. α-Al_2O_3 is the most ionic and Y_2O_3 the least ionic. The O-2p and O-2s BW in α-Al_2O_3 are more than double that in Y_2O_3, indicating a fundamental difference in Al-O and Y-O bonding. In Fig. 1(d), a sharp peak at −5.5 eV in the VB of YAM originates from O_5 which has two Al as NN. The calculated $\varepsilon_1(0)$ of YAG, YAP, and YAM are larger than the two end crystals, signaling a possible mixed-ion effect.

Table III displays the relative ranking of the calculated properties of Table II. With the exception of the overall ion-

TABLE III. Relative ranking (in increasing order) of calculated properties in the Y-Al-O system.

Crystals	α-Al_2O_3	$Y_3Al_5O_{12}$	$YAlO_3$	$Y_4Al_2O_9$	Y_2O_3
E_g	5	2	4	3	1
dE_g/dP	5	1	2	4	3
B	5	4	3	1	2
B'	1	3	2	4	5
Ionicity	1	2	3	4	5
Bond order	2	3	1	4	5
O-2p BW	4	3	5	2	1
O-2s BW	5	2	4	3	1
VB gap	2	3	1	4	5
$\varepsilon_1(0)$	1	4	3	5	2

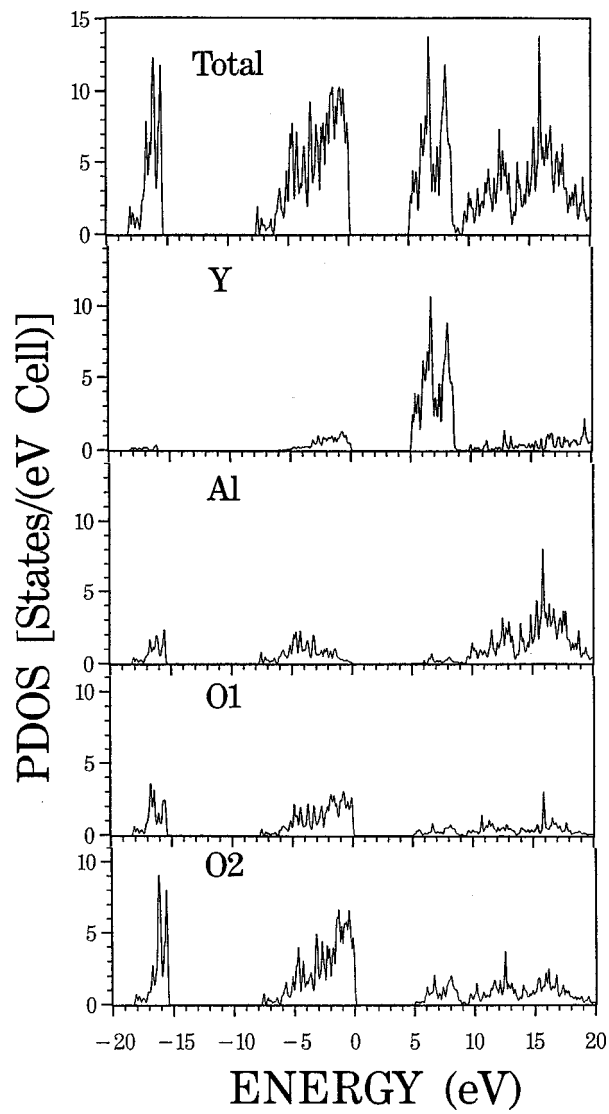

FIG. 2. Atom-resolved LDOS of YAP.

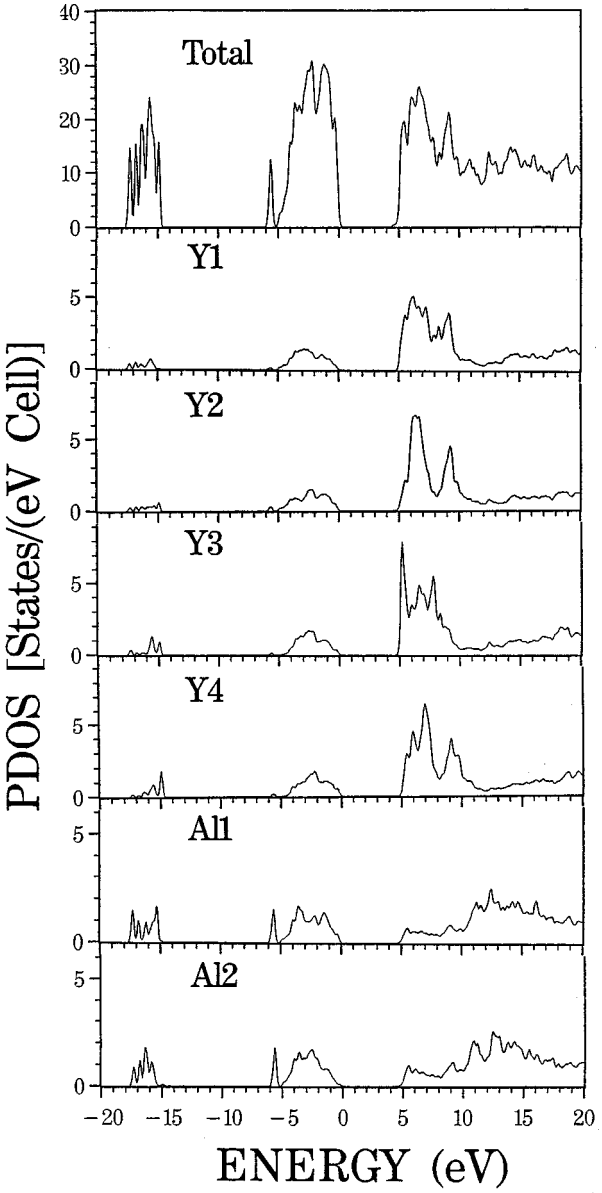

FIG. 3. Atom-resolved LDOS of YAM, Y, and Al sites.

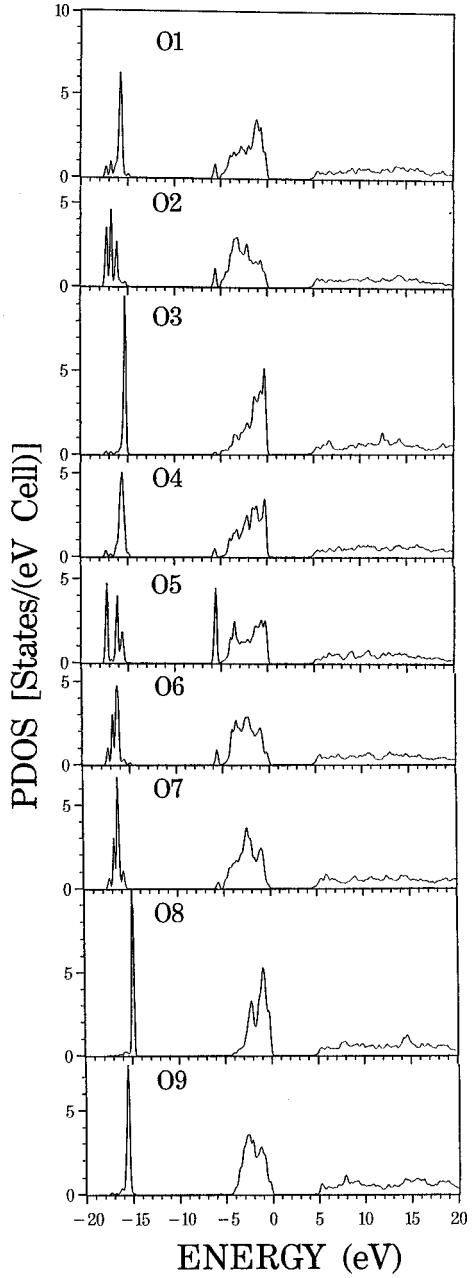

FIG. 4. Atom-resolved LDOS of YAM, nine O sites.

icity, there is no clear trend of scaling of properties with the Al:Y ratio or with any other crystal parameters. The properties of five crystals are distinctive and each is governed by their own structure and local coordination. The properties of YAG, YAP, and YAM cannot be scaled or extrapolated between the two end crystals, or transferred from one to another. To illustrate this point more vividly, we show in Figs. 2–4 the atom-resolved LDOS of YAP and YAM to supplement the total DOS of Fig. 1. The LDOS of α-Al_2O_3, Y_2O_3, and YAG have been presented elsewhere.[4,5,16] In the YAP crystal, both Y and Al are *o* coordinated, so the comparison of their LDOS establishes the relative positions and spectral weights of their electronic states both in the VB and in the CB. The multiple structures in the O-2*s* and O-2*p* segments of the VB reflect the many different BL's in the crystal discussed above. The LDOS in the YAM crystal is the most tantalizing. Without going into too detailed a description, we surmise that the LDOS reflect the local bonding environment of each atom described in Sec. II. For the metal atoms, the LDOS of Y2 and Y4 resembles each other since they are both sixfold coordinated. Similarly, the LDOS of Y1 and Y3 are close because both are sevenfold coordinated. We also note that the LDOS of Al1 and Al2 in YAM which are both *t* coordinated differ from that in YAP where it is *o* coordinated. The variety of LDOS for the nine O sites in YAM (Fig. 4) is really fascinating but can be understood by a carefully analysis of their local coordinations and different BL's. The most outstanding one is O5 which is the only O bonds to two Al atoms. Since the bonding energy of Al-O is lower than that of Y-O, this results in a sharp peak at −5.5 eV. Also, both O8 and O9 have only three Y atoms as NN and therefore they do not have any structures around −5.5 eV. Figures 3 and 4 also show that the LDOS of both Y and Al have some amplitudes in the O-2*s* region from −15.0 to −17.8 eV. This indicates possible a interaction between Al and Y through a collective bonding with the O atoms.

Figures 5 and 6 show the orbital decomposed LDOS of Al

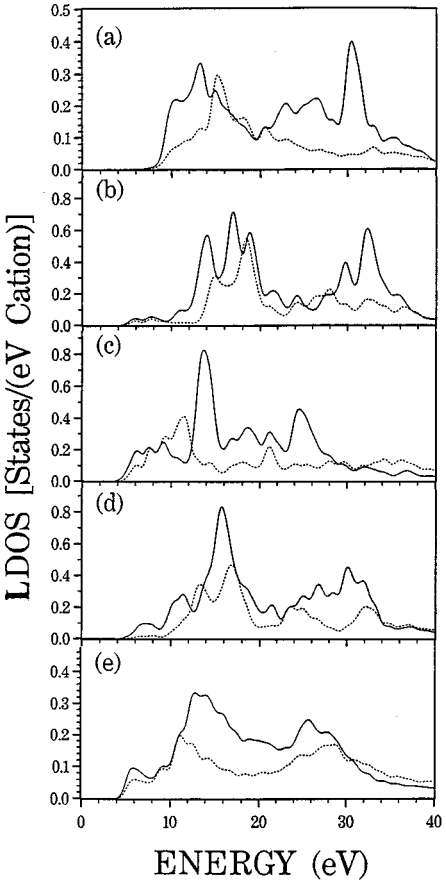

FIG. 5. Atom and orbital-resolved LDOS of Al in the conduction band. Solid line: $(s+d)$ component, dashed line: p component. (a) α-Al_2O_3; (b) $Y_3Al_5O_{12}$, octahedral site; (c) $Y_3Al_5O_{12}$, tetrahedral site; (d) $YAlO_3$; (e) $Y_4Al_2O_9$ (average of two sites).

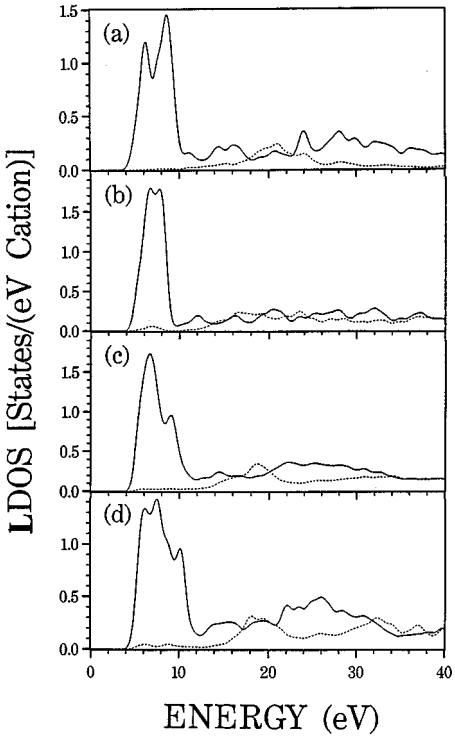

FIG. 6. Atom and orbital-resolved LDOS of Y in the conduction band. Solid line: $(s+d)$ component, dashed line: p component: (a) $Y_3Al_5O_{12}$; (b) $YAlO_3$; (c) $Y_4Al_2O_9$ (average of 4 sites); (d) Y_2O_3 (average of two sites).

and Y of the five crystals in the CB region. The CB LDOS are important because in the dipole approximation to the inelastic electron scattering, they are often used to interpret electron-loss near-edge structure (ELNES) and x-ray absorption near-edge structure (XANES) spectra. In recent years, ELNES obtained from analytic transmission electron microscope have been used as ''fingerprints'' to characterize the local bonding structure in unknown materials and structures.[24] Recent ELNES measurements on the Y-Al-O system show very different O-K, Y-K, and Al-$L_{2,3}$ edges.[25] Figure 5 shows the broadened LDOS of Al in the CB region for the four Al-containing crystals. The even parity components $(s+d)$ (solid line) should mimic the experimental $L_{2,3}$ edge, and the odd parity (p) component (dashed line), the K edge. For the YAG crystal, the LDOS for Al_{oct} and Al_{tet} are shown separately [Figs. 5(b) and 5(c)]. For YAM, the LDOS is the average of the two Al sites. Similarly, the LDOS for Y in the Y-containing crystals are shown in Fig. 6. For YAM and Y_2O_3, the LDOS are the averages over different Y sites. Several conclusions can be drawn. First, the LDOS of Y and Al are very different. The peak from Y-4d is more localized and closer to the CB edge. The Al-3d LDOS has more structures and are at higher energies. Second, The LDOS for the same cation in different crystals are very different. This is especially true for Al. In YAG, LDOS for Al_{oct} and Al_{tet} differ substantially both in structure and amplitude. Al_{tet} has a higher pre-edge structure (at 6–12 eV) but less number of prominent peaks. The pre-edge structure in Al_{tet} is due to interaction between Al_{tet} and the Y ion (to be discussed later) which is also present in YAM [Fig. 5(e)]. In α-Al_2O_3, there is no such pre-edge structure since there is no Y. Third, Al in α-Al_2O_3 and YAP are all o coordinated and, in YAM all t coordinated. In YAG, both coordinations are present. Yet, the LDOS of Al with similar coordination also show marked differences in peak positions and amplitudes. This clearly demonstrates that coordination alone cannot adequately characterize the LDOS of the ion. Their local environment beyond the first NN shell and variations in BL must be taken into account. In the case of Y LDOS, different local environments result in different widths of the Y-4d peak and its splitting. The splitting is more complicated than the simple crystal field splitting, and is most pronounced in YAG with eightfold coordinated Y and the longest Y-O bond.

The bond order (also called the overlap population) $\rho_{\alpha,\beta}$ is a convenient way to quantify the strength of bonding between a pair of atoms α and β. The bond orders of the all Al-O and Y-O bonds in the five crystals were obtained from separate minimal basis calculations, and are plotted in Fig. 7 against their BL's. Several interesting points emerge: First, the bond order of Al-O is generally larger than that of Y-O, consistent with the notion that Al-O is a stronger bond than the Y-O bond. Second, the bond order roughly scales with the BL with larger values for the shorter bond. But there are obvious deviations from this linear relationship which depend on the details of individual local atomic environment. Third, the YAM crystal has the most variety of Al-O bonds and Y-O bonds. It has a higher Al-O bond order than in other crystals but it also has very low Y-O bond orders for those

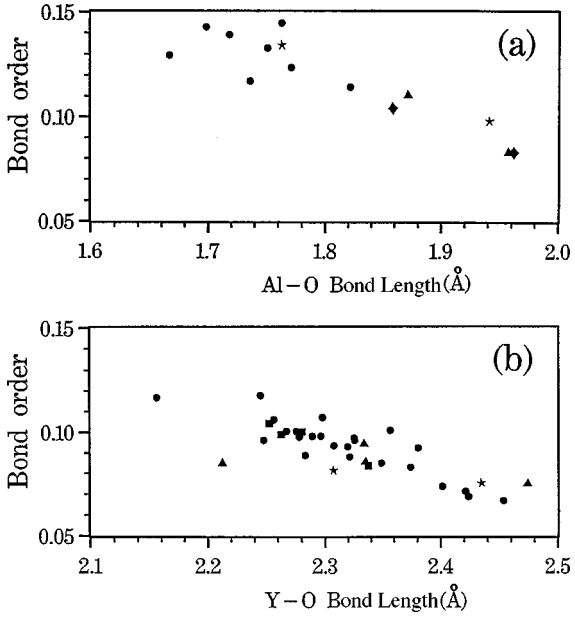

FIG. 7. Bond order of (a) Al-O bonds and (b) Y-O bonds. Different symbols for different crystals: ♦ (α-Al_2O_3), ★ ($Y_3Al_5O_{12}$), ▲ ($YAlO_3$), ● ($Y_4Al_2O_9$), ■ (Y_2O_3).

bonds with larger BL's. The average cation-anion bond order in the five crystals α-Al_2O_3, $Y_3Al_5O_{12}$, $YAlO_3$, $Y_4Al_2O_9$, and Y_2O_3 are 0.094, 0.096, 0.083, 0.097, and 0.098, respectively. Y_2O_3 has the largest average bond order mainly because it has the shortest Y-O bond. α-Al_2O_3 has the smaller average bond order than YAG and YAM because it has a longer Al-O bond. With the exception of YAP, the average bond orders of the other four crystals are quite close. It is tempting to relate the average bond order in a crystal to its mechanical properties. However, in real materials, defects, impurities and microstructures control the macroscopic scale mechanical properties which are not addressed tin the present study.

Figure 8 shows the calculated valence charge density in YAG on a [001] plane containing Al_{oct}, Al_{tet}, and Y ions. The O ions are in planes slightly above or below. A less than spherical distribution of charges on all ions are obvious and the difference at Al_{oct} and Al_{tet} sites is noticeable. The charge distribution around the larger Y ion is remarkable.[4] Within the Y ionic sphere of charge, there is a ring (radius 0.3 Å) of near zero charge due to the coincidence of the third node of

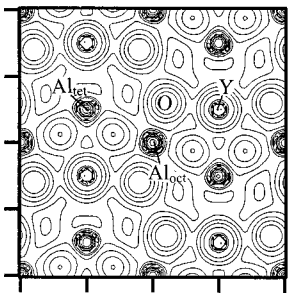

FIG. 8. (a) Valence charge distribution in YAG in a [001] plane containing Al_{oct}, Al_{tet}, and Y ions. The O ions are off plane. The contour lines are in units of 0.001, 0.002, 0.004, 0.008, 0.016, 0.032, 0.064, 0.128, 0.256 electron/(a.u.^{3}).

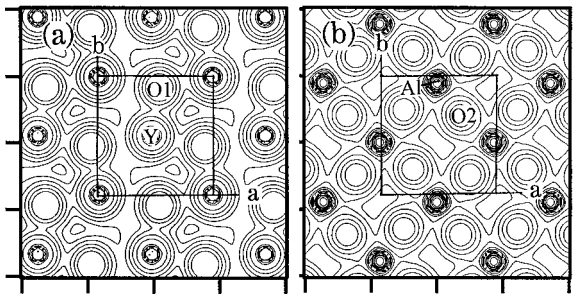

FIG. 9. Valence charge distribution in YAP in two planes perpendicular to the c axis and containing (a) Y-O1 bonds; (b) Al-O2 bonds atoms. The thin lines outline the unit cell boundary. Contour line units are the same as Fig. 8.

Y-5s and the first node of Y-4d wave functions.[4] The majority of the Y charges (5s and 4d) reside outside the ring which aid to the covalent character in the Y-O bonding. The Y-4d electron plays a significant role in the inter-atomic bonding. It is sufficiently extended, at a lower orbital energy and is very different from the Al-3p electron. This accounts for the differences in the LDOS of Al and Y. For the same reason, a Y impurity in bulk α-Al_2O_3 has its defect levels lowered into the gap, providing a natural explanation for the so-called donor effect of Y in sapphire.[26] Figure 8(a) also gives evidence for Y-Al_{tet} interaction because of a slight charge build up between the two ions. This interaction leads to the pre-edge structure in the LDOS of Al_{tet}. The Al_{oct} is well shielded by the O ions and there is little Y-Al_{oct} interaction.

The valence charge distribution in YAP and YAM in a few selected crystal planes are shown in Figs. 9 and 10, respectively. Unlike in YAG, there is no low index planes which contain the Al, Y, and O atoms. We select two planes in YAP perpendicular to the **c** axis and each containing the Y-O1 and Al-O2 bonds, and three planes in YAM perpendicular to the **b** axis, each containing the Y, Al, and O atoms. It can be seen from these diagrams that the charge distribution surrounding an Al in YAP (YAM) resembles that of Al_{oct} (Al_{tet}) in YAG in Fig. 8 because of the similarities in the local coordination.

IV. DISCUSSION AND CONCLUSIONS

The results presented in the previous section show the nonscalability and nontransferability of the electronic prop-

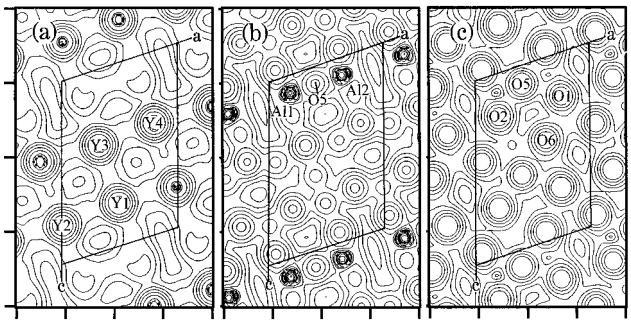

FIG. 10. Valence charge distribution in YAM in three planes perpendicular to the b axis and containing (a) Y atoms, (b) Al atoms, and (c) O atoms. The thin lines outline the unit cell boundary. Contour line units are the same as Fig. 8.

erties in the Y-Al-O system due to a combination of factors including different local environments, different orbital configurations of Y and Al, possible interactions between Al and Y, and a less ionic character of the Y-O bond. At a general grain boundary in α-Al_2O_3 where Y ions segregate, the local bonding structure will most likely be similar to those found in YAG, YAP, or YAM. Therefore, one possible explanation for the Y effect would be the bonding between Y and Al_{tet} which inhibits movement of the Al ions resulting in the reduction of the creeping rate. Recently, Cho *et al.* had argued that the reduction in the creeping rate in α-Al_2O_3 could be due to a ''site-blocking'' effect for the GB diffusion.[13] Our calculation implies that the segregation of the Y ions to the GB in α-Al_2O_3 is not just facilitated by the lower density at the GB and the larger size of the ion, but also by the possibility of forming stable Y-O and Y-Al bonds in reducing the overall strain energy. A complete understanding of the Y-effect may require proper modeling of the GB structures in conjunction with analytic and high resolution TEM studies, with and without Y ions. The present calculation for the crystalline Y-Al-O system is the necessary first step towards such understanding.

ACKNOWLEDGMENTS

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