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Anomalous mechanical strengths and shear deformation paths of 
\( \text{Al}_2\text{O}_3 \) polymorphs with high ionicity

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Abstract

Alumina formed by selective oxidization provides an effective way to protect aluminide alloys against corrosion for sustainable applications. Despite a broad interest and investigations on \( \text{Al}_2\text{O}_3 \) polymorphs such as \( \alpha\text{-Al}_2\text{O}_3 \) and \( \theta\text{-Al}_2\text{O}_3 \), their intrinsically mechanical strengths and atomic deformation mechanism have not yet been fully understood. Here using density functional theory, we show that the calculated shear moduli and mechanical strengths of \( \theta\text{-Al}_2\text{O}_3 \) are substantially lower than those of \( \alpha\text{-Al}_2\text{O}_3 \), explaining why \( \theta\text{-Al}_2\text{O}_3 \) is much weaker than \( \alpha\text{-Al}_2\text{O}_3 \). An analysis of shear deformation paths and electronic structure indicates that the longest Al-O ionic bonds are responsible for the lattice instability of both polymorphs during shear, showing however a different anisotropic feature. This study sheds a novel view on the failure of thermally grown \( \alpha\text{-Al}_2\text{O}_3 \) and \( \theta\text{-Al}_2\text{O}_3 \), and it should help to improve the performance of thermal barrier coatings.

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I. INTRODUCTION

Alumina polymorphs are important ceramic materials with many desirable properties such as high hardness, chemical inertness, thermal shock resistance and wear resistance, which brought them many technological applications such as protective coatings, abrasives, insulators, and catalysts [1-4]. The most stable form of alumina is $\alpha$-$\text{Al}_2\text{O}_3$ which is termed as a quasi-harmonic crystal with negligible intrinsic anharmonic effects [5]. Beside of the $\alpha$-$\text{Al}_2\text{O}_3$, alumina may adopt a series of metastable transition polymorphs such as $\gamma$, $\eta$, $\theta$, $\gamma'$, and $\delta$ structures with different fcc packing of oxygen, and $\alpha$, $\kappa$, $\kappa'$, and $\iota$ structures based on hcp packing lattice [6,7]. Some other structures include $\theta'$, $\theta''$, $\lambda$, $U$ and $\chi$ are also reported in publications [6,7]. When $\text{Al}_2\text{O}_3$ adopts the fcc packing lattice, a phase transformation of alumina may appear in the following four sequences [7]:

i) $\gamma$-$\text{AlO(OH)}$ (Boehmite) $\xrightarrow{100^\circ-500^\circ\text{C}} \gamma$ $\xrightarrow{700^\circ-800^\circ\text{C}} \delta$ $\xrightarrow{900^\circ-1000^\circ\text{C}} \theta$ $\xrightarrow{1000^\circ-1100^\circ\text{C}} \alpha$-$\text{Al}_2\text{O}_3$

ii) $\alpha$-$\text{Al(OH)}_3$ (Bayerite) $\xrightarrow{200^\circ-300^\circ\text{C}} \eta$ $\xrightarrow{600^\circ-800^\circ\text{C}} \theta$ $\xrightarrow{1000^\circ-1100^\circ\text{C}} \alpha$-$\text{Al}_2\text{O}_3$

iii) Amorphous (Anodic film) $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$

iv) Melt $\rightarrow \gamma \rightarrow \delta, \theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$

With these alumina polymorphs and hydroxides as input, Peintinger et al. [6] systematically investigated their relative stability by means of the hybrid density functional theory, and then obtained the following energetic order: gibbsite $<$ bayerite $<$ boehmite $<$ akdalaite $<$ $\alpha$-$\text{Al}_2\text{O}_3$ $<$ $\kappa$-$\text{Al}_2\text{O}_3$ $<$ $\theta$-$\text{Al}_2\text{O}_3$ $<$ $\delta$-$\text{Al}_2\text{O}_3$ $<$ $\gamma$-$\text{Al}_2\text{O}_3$ $<$ $\eta$-$\text{Al}_2\text{O}_3$ $<$ $\iota$-$\text{Al}_2\text{O}_3$. Lee et al. [8] compared the band gap of some alumina and provided an order of $\alpha > \kappa > \theta > \gamma$, which is agreement with the most recent results by
Among these alumina polymorphs, the $\alpha$-$\text{Al}_2\text{O}_3$ and $\kappa$-$\text{Al}_2\text{O}_3$ are used as wear protective coatings on tools due to their superior mechanical properties, whereas the metastable $\gamma$-$\text{Al}_2\text{O}_3$ and $\theta$-$\text{Al}_2\text{O}_3$ are used as catalytic supports because of their lower surface energy [10]. It is generally known that the $\alpha$- and $\theta$-$\text{Al}_2\text{O}_3$ play an important role on the performance of the early oxidation of Ni-Al alloys in thermal barrier coatings (TBCs), whereas the others are generally regarded as defectively metastable ones [11-13]. However, the stress concentration due to the fast phase transformation of $\theta$- to $\alpha$-$\text{Al}_2\text{O}_3$ is an essential factor that leads to the alumina scale cracking and spallation at $\text{Al}_2\text{O}_3$/alloy interface in the TBCs [14,15]. To better understand the effect of metastable $\theta$-$\text{Al}_2\text{O}_3$ on the performance of TBCs, much effort has been accordingly made to evaluate the properties of $\theta$-$\text{Al}_2\text{O}_3$ in experiments and theoretical calculations. However, only limited equilibrium data, such as structural stability, electronic structure and elastic constants have been reported so far. Therefore in the present study, we shall take the former two polymorphs as our focused ones. In the previous theoretical studies, the band gaps of $\alpha$-$\text{Al}_2\text{O}_3$ are calculated to be about 6.72 eV [8], 6.1 eV [16] and 6.24 eV [17], which underestimate the experimental value of 8.8 eV [16,18]. The indirect band gaps of 5.04 eV [8] and 4.98 eV [17] are also reported for $\theta$-$\text{Al}_2\text{O}_3$, which are about 1.3-1.7eV smaller than that of $\alpha$-$\text{Al}_2\text{O}_3$. Although the calculated site- and orbital-resolved partial electronic density of states (EDOS) show profound dependence on local coordination of Al and O atoms, the derived effective charge and bond order show similarity for both $\theta$-$\text{Al}_2\text{O}_3$ and $\alpha$-$\text{Al}_2\text{O}_3$.
These results evoke a fundamental question whether both polymorphs could possess a comparable mechanical property.

For this purpose, a comparatively mechanical test of $\alpha$-$\text{Al}_2\text{O}_3$ and $\theta$-$\text{Al}_2\text{O}_3$ was performed by Shang et al. [19] several years ago. They obtained a positive value of $C_{14}$ for $\alpha$-$\text{Al}_2\text{O}_3$ by means of \textit{ab initio} DFT calculations, in good agreement with the previous experiments and theoretical studies by Gladden et al. [20] and Hovis et al. [21]. With this validation, the derived bulk moduli and shear moduli of $\alpha$-$\text{Al}_2\text{O}_3$ are shown to be much higher than those of $\theta$-$\text{Al}_2\text{O}_3$, providing a guidance for the understanding of the failure origin of TBCs. In Shang’s latter work [22], the calculated temperature-dependent elastic constants enable a more realistic stress analysis at elevated temperatures in thermally grown oxides containing $\alpha$- and $\theta$-$\text{Al}_2\text{O}_3$, which provide a deeper understanding of the failure of TBCs in gas-turbine engines.

Although numerous investigations have been performed on the structure and elastic properties of $\text{Al}_2\text{O}_3$ polymorphs, relatively little work has been devoted to the calculations of ideal strength and deformation paths which are critical for an in-depth understanding of the failure of turbine parts operating under extreme conditions. In general, a higher elastic modulus does not guarantee a higher strength since the former one describes only the reversible response of a crystal to a small strain, whereas the ideal strength gives an upper limit of stress that an ideal crystal can sustain at large strain [23,24]. In the present paper, we shall take $\alpha$-$\text{Al}_2\text{O}_3$ and $\theta$-$\text{Al}_2\text{O}_3$ polymorphs as an illustrative one to show that although both are experimentally
accessible and have similar effective charge and iconicity [17], their mechanical strengths and shear deformation paths are substantially different.

Recent advancement of computational techniques has made it a routine method to calculate the ideal strengths in a reasonable precise by means of first principles methods and provided a way to analyze the deformation paths and electronic instabilities under various loadings [23,25,26]. It is generally recognized that the ideal strength is a fundamental indicator of material strength [27], which is defined as the minimum stress required to plastically deform an ideal crystal and the stress required for the formation of stacking faults [28]. A close connection between Peierls-Nabarro (PN) stress of dislocations and ideal shear strength has also made it possible to evaluate the mechanical strength of a real material via a comprehensive analysis of two intrinsic mechanical parameters: shear moduli and shear strength [25,29]. In addition, the ideal shear strength has attracted much more attention with the progress of nanotechnology, which provides a way to quantitatively measure the near ideal strength which can be obtained from modern first principles calculations [27,30].

II. COMPUTATIONAL METHODS

The ab initio density functional theory (DFT) calculations [31,32] were performed using the Vienna ab initio simulation package (VASP) code with the Perdew-Burke-Ernzerhof (PBE) [33] version of Generalized Gradient Approximation (GGA) for exchange-correlation functional. For the electronic density of states (EDOS) calculations, we chose the screened hybrid functional of Heyd, Scuseria, and
Ernzerhof (HSE06) [34], where correlation is described in GGA (PBE) and the exchange is a mixture of 25% exact (HF) exchange and 75% PBE exchange. The integration in the Brillouin zone was done on special \( k \) points of \( 9 \times 9 \times 9 \) grids for the phases under consideration, energy cutoff of 600 eV, which was sufficient to keep total energy convergence at \( 10^3 \) meV/atom or less. Atomic positions are relaxed using the conjugate gradient method until the forces on all the atoms were converged to less than \( 10^3 \) eV/Å.

As a further check of the validity of the applied PAW-PBE potentials, we determine the elastic constants and moduli by applying a set of small deformations \( \delta \) between -0.02 and +0.02, and calculate the second order coefficients in a polynomial fit of the total energy as a function of the distortion \( \delta \). Atomic relaxations were allowed when straining the cell. The applied strain configurations and the corresponding strain-energy density variations \( \Delta E/V_0 \) for hcp \( \alpha \)-Al\(_2\)O\(_3\) structure are given as follows: \( \varepsilon=(\delta,0,0,0,0,0) \) with \( \Delta E/V_0=(C_{11}+C_{12})\delta^2 \), \( \varepsilon=(0,0,0,0,0,\delta) \) with \( \Delta E/V_0=1/4(C_{11}-C_{12})\delta^2 \), \( \varepsilon=(0,\delta,0,0,0,0) \) with \( \Delta E/V_0=1/2C_{33}\delta^2 \), \( \varepsilon=(0,0,0,\delta,0,0) \) with \( \Delta E/V_0=1/2C_{44}\delta^2 \), and \( \varepsilon=(\delta,\delta,0,0,0,0) \) with \( \Delta E/V_0=(C_{11}+C_{12}+2C_{13}+1/2C_{33})\delta^2 \). For \( \theta\)-Al\(_2\)O\(_3\), \( \varepsilon=(\delta,0,0,0,0,0) \) with \( \Delta E/V_0=1/2C_{11}\delta^2 \), \( \varepsilon=(0,\delta,0,0,0,0) \) with \( \Delta E/V_0=1/2C_{22}\delta^2 \), \( \varepsilon=(0,0,\delta,0,0,0) \) with \( \Delta E/V_0=1/2C_{33}\delta^2 \), \( \varepsilon=(0,0,0,\delta,0,0) \) with \( \Delta E/V_0=1/2C_{44}\delta^2 \), \( \varepsilon=(\delta,\delta,0,0,0,0) \) with \( \Delta E/V_0=(1/2C_{11}+C_{12}+1/2C_{22})\delta^2 \), \( \varepsilon=(0,\delta,0,0,0,0) \) with \( \Delta E/V_0=1/2C_{55}\delta^2 \), \( \varepsilon=(0,0,\delta,0,0,0) \) with \( \Delta E/V_0=1/2C_{66}\delta^2 \), \( \varepsilon=(\delta,\delta,0,0,0,0) \) with \( \Delta E/V_0=(1/2C_{11}+C_{12}+1/2C_{33})\delta^2 \).

The \textit{ab initio} DFT calculations of stress-strain dependences conducted here are
technically similar to our previous studies [35-39] to which we refer for further details. The atomic basis vectors of a given unit cell were firstly projected onto the Cartesian coordinate system with one cell axis vector being parallel to the strain direction for the tension loading. In case of shear deformation, one cell axis vector was perpendicular to the slip plane and another one was parallel to the slip direction in that plane. Afterwards, the crystal has been incrementally deformed by transforming the unstrained cell basis vector matrices to the strained ones using the deformation matrices. In order to keep the crystal under a stress state of uniaxial tension or shear, the strained cell has been relaxed for both the cell basis vectors and for the atom position inside the unit cell by keeping the applied strain component fixed and relaxing the other five strain components until their conjugate stress components i.e., Hellmann-Feynman stresses reached negligible values.

III. RESULTS AND DISCUSSION

The $\alpha$-$\text{Al}_2\text{O}_3$ with a space group of $R-3c$ has the most symmetric ordering of Al atoms, which leads a higher density compared to other polymorphs. The relaxed topological bond structure of $\alpha$-$\text{Al}_2\text{O}_3$ is shown in Fig. 1(a), the Al cations and the O anions are located at 12c (0, 0, z) and 18e (x, 0, 0.25) Wyckoff positions, respectively. The obtained values of the x- and z-coordinate are 0.306 and 0.352, which are in good agreement with the previous results (x=0.306 and z=0.347) [40]. The $\alpha$-$\text{Al}_2\text{O}_3$ can also be represented in a hexagonal lattice with six layers of close-packed O atoms filled by Al atoms at the octahedral holes sites. Each Al atom is bonded to six O atoms with
two nonequivalent bond distances, and each O atom has four neighbor Al atoms [see Fig. 1(b)]. Figure 1(c) shows the crystal structure and local coordination of anions of $\theta$-Al$_2$O$_3$ that belong to monoclinic system with a space group of $C2/m$, with all the ions located at $4i$ (x, 0, z) Wyckoff positions. Our calculated coordinates of O are: (0.160 0 0.109), (0.495 0 0.257), (0.826 0 0.433), and those of Al: (0.090 0 0.796) (0.342 0 0.683), being in agreement with the previous values of O: (0.163 0 0.123), (0.489 0 0.261), (0.830 0 0.439) and those of Al: (0.101 0 0.794) (0.352 0 0.687) [41]. The Al atoms occupy four octahedral and four tetrahedral interstitials of O sublattice [42] [see Fig. 1(d) and (e)]. The calculated lattice parameters of $\alpha$-Al$_2$O$_3$ are $a=4.806\text{Å}$, $c/a=2.7285$ and those of $\theta$-Al$_2$O$_3$ are $a=11.922\text{Å}$, $b=2.940\text{Å}$, $c=5.668\text{Å}$, $\beta=104.0^\circ$. They are in agreement with the available theoretical and experimental values ($a=4.8195\text{Å}^a$, $5.180\text{Å}^b$, $c/a=2.7284^a$ for $\alpha$-Al$_2$O$_3$ and $a=11.923\text{Å}^b$, $11.8530^c$; $b=2.941\text{Å}^b$, $2.904^c$; $c=5.671\text{Å}^b$, $5.622^c$, $\beta=103.90^a$, $103.8^ac$ for $\theta$-Al$_2$O$_3$) ($^a$Ref. [43], $^b$Ref. [19], $^c$Ref. [44]). There is only one type of O coordination in $\alpha$-Al$_2$O$_3$, but $\theta$-Al$_2$O$_3$ has three different types of O coordinations which produce a more complicated bond anisotropy. Figure 1(c) shows that O$_1$ is bonded to one Al$_{tet}$ and three Al$_{oct}$ cations, where Al$_{oct}$ (Al$_{tet}$) stands for the Al in octahedral (tetrahedral) coordination. One further see in that figure that O$_2$ is bonded to two Al$_{tet}$ and one Al$_{oct}$ cations, and O$_3$ is bonded to one Al$_{tet}$ and two Al$_{oct}$ cations [17]. The Al-O bond lengths of 1.9901 (1.969$^d$) Å and 1.8730 (1.857$^d$) Å ($^d$Ref. [17] ) for $\alpha$-Al$_2$O$_3$ [see Fig. 1(b)] show some difference from those of $\theta$-Al$_2$O$_3$ in which seven in equivalent Al-O bond lengths are 1.7701, 1.7702, 1.8134, 1.8881, 1.8883, 1.9566, 2.0208 Å [see Fig.
1(d) and (e)], in agreement with the previous values of 1.710, 1.745, 1.896, 1.904, 1.936, 2.025 Å (Ref. [17]) respectively. The difference of local coordination between $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$, especially the bond anisotropy and the longest Al-O bonds are responsible for the different mechanical properties and the deformation paths during shear, as it will be shown.

Based on the reaction $4\text{Al} + 3\text{O}_2 = 2\text{Al}_2\text{O}_3$, the calculated energy difference per formula unit between $\alpha$- and $\theta$-Al$_2$O$_3$ is 0.047 eV, which is consistent with previous reports where the following values were reported $\Delta E(\theta-\alpha)=0.03$ eV/formula unit in Ref. [42] and 0.04 eV/formula unit in Ref. [45] thus confirming that $\alpha$-Al$_2$O$_3$ is thermodynamically more stable than $\theta$-Al$_2$O$_3$.

The elastic constants were determined by applying an appropriate set of distortions within elastic limits [46,47]. Table 1 shows the calculated and measured values of the elastic constants $C_{ij}$ for $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$, respectively. The elastic constants satisfy the Born stability criteria [43,48,49], thus confirming that both hexagonal $\alpha$-Al$_2$O$_3$ and monoclinic $\theta$-Al$_2$O$_3$ are mechanically stable. Voigt average bulk modulus of $B_V$ of $\alpha$-Al$_2$O$_3$ (235.6 GPa) is much larger than that of $\theta$-Al$_2$O$_3$ (187.4 GPa), i.e. the former alumina is more incompressible than the latter one. Additionally, it is found that the anisotropy ratio between $C_{11}$ and $C_{33}$ is nearly unity for $\alpha$-Al$_2$O$_3$, while it is about 1.5 for $\theta$-Al$_2$O$_3$, suggesting a higher elastic anisotropy for the latter one. A well-established consideration of whether a crystalline solid is intrinsically ductile or brittle [50-52] can be approximately characterized by the ratio of the shear modulus to the bulk modulus, $G/B$, by considering $B$ as the resistance to fracture and
the resistance to plastic deformation [52-54]. The critical $G/B$ ratio which separates ductile and brittle materials is around 0.57, i.e., if $G/B < 0.57$ the material behaves in a ductile manner, otherwise the material is brittle. The relatively high ratio of $G/B \approx 0.63$ for $\alpha$-$\text{Al}_2\text{O}_3$ reveals that it is intrinsically brittle, in agreement with the experiments. The somewhat lower value of 0.58 for $\theta$-$\text{Al}_2\text{O}_3$ is closer to the boundary brittle/ductile.

We next investigate the ideal strengths of both $\text{Al}_2\text{O}_3$ polymorphs. For $\alpha$-$\text{Al}_2\text{O}_3$, the {	extit{ab initio}} DFT calculations were performed with unit cell along $<0001>$, $<\overline{1}2\overline{1}0>$ and $<10\overline{1}0>$ directions for tension and on $(0001)<\overline{1}2\overline{1}0>$, $(0001)<10\overline{1}0>$ and $(10\overline{1}0)<\overline{1}2\overline{1}0>$ slip systems for shear. The crystallographic directions of $<010>$ and $<001>$ of monoclinic $\theta$-$\text{Al}_2\text{O}_3$ are chosen to be parallel to the $y$ and $z$ axes in Cartesian coordinate system respectively. Figure 2(a) shows the calculated stress-strain curves for $\alpha$-$\text{Al}_2\text{O}_3$. The ideal tensile strength of $\alpha$-$\text{Al}_2\text{O}_3$ along the $<0001>$ direction of about 58.3GPa is much larger than in the two other directions. The anisotropy ratio of tensile strengths for $\alpha$-$\text{Al}_2\text{O}_3$ of $\sigma_{(0001)} = 58.3$: $\sigma_{(10\overline{1}0)} = 36.5$: $\sigma_{(\overline{1}2\overline{1}0)} = 26.3$ GPa $\approx 2.22:1.39:1$ is slightly larger than those of $\theta$-$\text{Al}_2\text{O}_3$ [see Fig. 2(b)]: $\sigma_{<010>} = 28.9$: $\sigma_{\{001\}_{\text{normal}}} = 14.8$: $\sigma_{<100>} = 13.9$ GPa $\approx 2.08:1.06:1$. It is interestingly noted that the anisotropy of ideal tensile strengths does not follow the aforementioned elastic anisotropy for both $\text{Al}_2\text{O}_3$ polymorphs. The tensile strength of 26.3 GPa along weakest $<\overline{1}2\overline{1}0>$ direction of $\alpha$-$\text{Al}_2\text{O}_3$ is comparable to the maximum value of 28.9 GPa of $\theta$-$\text{Al}_2\text{O}_3$ along the $<010>$ direction. Because plastic deformation occurs in shear, one must compare the calculated anisotropic ideal shear strengths [35, 36, 55,
The lowest shear strengths of 14.4 GPa of α-Al₂O₃ is found in the (0001)<1210> slip system [Fig. 2(a)]. This value is about 67% higher than the lowest shear strength of 4.7 GPa found for θ-Al₂O₃ [Fig. 2(b)], providing a direct theoretical evidence that θ-Al₂O₃ is intrinsically much weaker than α-Al₂O₃.

As a further understanding of the deformation paths of both Al₂O₃ polymorphs in shear, the change of Al-O bond length and valence charge density differences (VCDD) during shear deformation are compared in Fig. 3. The VCDD is defined as the difference between the calculated total valence charge density of the crystal minus the superposition of the valence charge densities of neutral atoms [39]). Negative value (yellow color in Fig. 3) means a depletion of charges as compared to neutral atoms (bond weakening). To emphasize the variation of charge depletion between Al-O bonds, we show only the negative isosurface of VCDD in Fig. 3. Note that the expansion of negative VCDD isosurface between Al-O bonds indicates their weakening during shear deformations. Although both α-Al₂O₃ and θ-Al₂O₃ have similar ionic bonds, their bond deformation paths and electronic instability modes are substantially different as seen from the change of bond topology and deformed VCDD isosurfaces shown in Figure 3. Figure 3(b) and 3(c) show the typical Al-O bond length and VCDD at shear strain of γ=0.1934 (before) and γ=0.3400 (after instability) for α-Al₂O₃, and Fig. 3(e) and 3(f) show them at shear strain of γ=0.0924 (before) and γ=0.1366 (after instability) for θ-Al₂O₃. In case of α-Al₂O₃, the shear instability occurs between Al {0001} and O {0001} planes [Fig. 3(b) and 3(c)] with an increase of Al-O bond length from 2.33 to 3.04 Å, whereas in case of θ-Al₂O₃, the shear
instability appears between Al/O {001} planes with the Al-O bond lengths increasing from 2.23 to 2.73 Å [Fig. 3(e) and 3(f)]. In Figure 3, it can also be seen that the dramatic change of VCDD before and after instability of $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$ (see the yellow isosurface marked by big blue arrows), which shows the process of Al-O bond strength becomes weak to bond cleavage.

To quantify the electronic origin of distinct mechanical strength in both Al$_2$O$_3$, we first use the quantum theory of atoms in molecules proposed by Bader [57,58] to quantitatively analyze the change of charge transfer during shearing. The calculated nonequivalent values of Bader charges are presented as below: For $\alpha$-Al$_2$O$_3$, at equilibrium: $(\text{Al}^{2.4751})_2(\text{O}^{+1.6501})_3$, at $\gamma=0.1934$ (before instability): $(\text{Al}^{2.4732})_2(\text{O}^{+1.6488})_3$, at $\gamma=0.3400$ (after instability): $(\text{Al}^{2.4640})_2(\text{O}^{+1.6427})_3$; For $\theta$-Al$_2$O$_3$, at equilibrium: $(\text{Al}^{2.4442/-2.4637})_2(\text{O}^{+1.6431/+1.6346/+1.6303})_3$, at $\gamma=0.0924$ (before instability): $(\text{Al}^{2.4451/-2.4749})_2(\text{O}^{+1.6481/+1.6359/+1.6360})_3$, at $\gamma=0.1366$ (after instability): $(\text{Al}^{2.4479/-2.4733})_2(\text{O}^{+1.6340/+1.6442/+1.6431})_3$. It is seen that the highly ionicity of $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$ are nearly identical. The minor difference of Bader charges between $\alpha$- and $\theta$-Al$_2$O$_3$ provides an electronic message to be related to the significant differences of their ideal tensile and shear strengths. Further consideration of the distributions of nonequivalent highly ionic Al-O bonds for $\theta$-Al$_2$O$_3$, we may get an explanation on the choice of deformation paths of both structures during the shear loadings (see the change of bond lengths and VCDD isosurface marked in Fig. 3).

In order to develop a deeper understanding of the mechanical properties of $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$, we next to analyze the electronic density of states (EDOS) and
localized charge accumulation between Al-O bonds. Fig. 4(a) and (b) shows the total EDOS which presents three distinct regions: the lower part of the valence bands is dominated by O 2s states and the upper part by O 2p- and Al 3s-, 3p-like states. Both α-Al2O3 [Fig. 4(a)] and θ-Al2O3 [Fig. 4(b)] are insulators with band gaps of about 7.6 and 6.2 eV, respectively. The previously calculated band gaps of α-Al2O3 are 8.6 eV [6], 9.1 eV [59], and 8.5 eV [60], and that of θ-Al2O3 is 6.9 eV [6], by utilizing HSE functional. A higher value of the band gaps of α-Al2O3 was reported in Ref. [59] due to the Hartree-Fock mixing parameter in HSE calculation is 32 %, higher than the standard HSE06 (25 %). Note that the calculated band gap for α-Al2O3 by HSE06 pseudopotentials is much more close to the experimental values (~8.8eV) as compared to the previous studies [16,18]. The upper valence band width (from -7.5 eV to 0 eV) of α-Al2O3, which is dominated by overlapping of O 2p and Al 3p orbitals, shows strong similarity to θ-Al2O3. To get the difference of bond strength between α-Al2O3 and θ-Al2O3, Fig. 4(c) and 4(d) show the contour plot of the VCDD cross section for α-Al2O3 and θ-Al2O3. The circled regions between the longest Al-O bonds in Fig. 4(c) and 4(d) indicate the magnitude of charge depletion. It can be clearly seen that the longer Al-O bonds for θ-Al2O3 corresponds to a higher depletion of valence charge density between them and a significant bond weakening, providing a physical explanation why α-Al2O3 is stronger than θ-Al2O3.

IV. CONCLUSIONS

In conclusion, we have studied the structural, thermodynamic, mechanical,
electronic properties and shear deformation paths of $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$ by means of 
\textit{ab initio} DFT calculations. The resulting equilibrium properties of $\alpha$-Al$_2$O$_3$ and 
$\theta$-Al$_2$O$_3$ are consistent with the experimental and theoretical data. The relatively high 
bulk modulus of $\alpha$-Al$_2$O$_3$ confirms that it is a low-compressible material, whereas the 
relatively low ratio of the shear modulus to bulk modulus shows that it is still 
intrinsically brittle, somewhat more than $\theta$-Al$_2$O$_3$. The shear strengths of $\theta$-Al$_2$O$_3$ is 
much lower than that of $\alpha$-Al$_2$O$_3$ due to the highly ionic Al-O bonds with the longest 
bond length that is more profound for $\theta$-Al$_2$O$_3$. The longest Al-O bond lengths 
determine the deformation paths in both Al$_2$O$_3$ polymorphs.

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References


Table 1. The elastic constants ($C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$, $C_{66}$), bulk moduli ($B_V$), Young moduli ($E$), shear moduli ($G_V$) (GPa), and Poisson ratio ($\nu$) of $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$ compared with previous calculations and available experimental measurements.

<table>
<thead>
<tr>
<th>Property</th>
<th>$\alpha$-Al$_2$O$_3$</th>
<th>$\theta$-Al$_2$O$_3$</th>
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<tr>
<td></td>
<td>This work</td>
<td>GGA</td>
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<tr>
<td>$C_{11}$</td>
<td>455.2</td>
<td>437.2*,$451.5^b$</td>
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<td>$C_{22}$</td>
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<td>$C_{33}$</td>
<td>457.1</td>
<td>443.3*,454.9*</td>
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<tr>
<td>$C_{44}$</td>
<td>132.6</td>
<td>125.5*,131.7*</td>
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<tr>
<td>$C_{55}$</td>
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<tr>
<td>$C_{66}$</td>
<td>151.6</td>
<td>146.4*</td>
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<tr>
<td>$C_{12}$</td>
<td>152.0</td>
<td>144.3*,148.4*</td>
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<tr>
<td>$C_{13}$</td>
<td>112.2</td>
<td>101.5*,107.6*</td>
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<tr>
<td>$B_V$</td>
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<tr>
<td>$G_V$</td>
<td>149.4</td>
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<tr>
<td>$E$</td>
<td>370.0</td>
<td>353.6*</td>
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<tr>
<td>$\nu$</td>
<td>0.238</td>
<td>0.2362*</td>
</tr>
</tbody>
</table>

*a* Ref.[43], *b* Ref. [21], *c* Ref. [44], *d* Ref. [17], *e* Ref. [48]
Figure Captions:

**FIG. 1** (Color online): Lattice topology and polyhedra of the (a) Hexagonal $\alpha$-Al$_2$O$_3$ and (c) Monoclinic $\theta$-Al$_2$O$_3$. In each polyhedron, one Al cation is bonded to six O anions for $\alpha$-Al$_2$O$_3$, four or six O anions for $\theta$-Al$_2$O$_3$ structures respectively. The surrounding bond arrangements and length neighbor to each O atom for (b) $\alpha$-Al$_2$O$_3$ and (d) (e) $\theta$-Al$_2$O$_3$. The large and small spheres represent the Al (cations) and O (anions) respectively. O$_1$, O$_2$, O$_3$ are the O atoms with different local coordinations.

**FIG. 2** (Color online): The stress-strain curves calculated by *ab initio* DFT method for (a) $\alpha$-Al$_2$O$_3$ and (b) $\theta$-Al$_2$O$_3$ under various tension and shear deformations. Three tensile deformations are along crystallographic directions: $<0001>$, $<\bar{1}2\bar{1}0>$ and $<10\bar{1}0>$ for $\alpha$-Al$_2$O$_3$ and $<100>$, $<010>$ and perpendicular to (001) for $\theta$-Al$_2$O$_3$; the shear deformations are along: (0001)$<\bar{1}2\bar{1}0>$, (0001)$<10\bar{1}0>$ and (10$\bar{1}$0)$<\bar{1}2\bar{1}0>$ for $\alpha$-Al$_2$O$_3$ and (100)$<010>$, (001)$<010>$ and (001)$<100>$ for $\theta$-Al$_2$O$_3$.

**FIG. 3** (Color online): The isosurfaces of valence charge density difference (VCDD) of $\alpha$-Al$_2$O$_3$ (a) equilibrium, (b) before and (c) after instability under shear deformation along the weakest (0001)$<\bar{1}2\bar{1}0>$ slip system, and those of $\theta$-Al$_2$O$_3$ (d) equilibrium, (e) before and (f) after instability under shear deformation along the weakest (001)$<010>$ slip system (i.e. $\tau_{yz}$). The isosurfaces maps of the VCDD correspond to -0.014 electrons/Bohr$^3$. Yellow color means negative value. The crystallographic directions of $<010>$ and $<001>$ of monoclinic $\theta$-Al$_2$O$_3$ are parallel to the y and z axes in
Cartesian coordinate system respectively as represented in Fig. 3(d).

**FIG. 4.** (Color online): The calculated electronic density of state (DOS) for (a) $\alpha$-$\text{Al}_2\text{O}_3$ and (b) $\theta$-$\text{Al}_2\text{O}_3$ and the cross-sectional plot of the valence charge density difference (VCDD) for (c) $\alpha$-$\text{Al}_2\text{O}_3$ and (d) $\theta$-$\text{Al}_2\text{O}_3$ to indicate the VCDD between the longest Al-O bonds. The circled region indicates the charge depletion between the longest Al-O bonds for both Al$_2$O$_3$. 

FIG. 1 (Color online): Lattice topology and polyhedra of the (a) Hexagonal $\alpha$-$\text{Al}_2\text{O}_3$ and (c) Monoclinic $\theta$-$\text{Al}_2\text{O}_3$. In each polyhedron, one Al cation is bonded to six O anions for $\alpha$-$\text{Al}_2\text{O}_3$, four or six O anions for $\theta$-$\text{Al}_2\text{O}_3$ structures respectively. The surrounding bond arrangements and length neighbor to each O atom for (b) $\alpha$-$\text{Al}_2\text{O}_3$ and (d) (e) $\theta$-$\text{Al}_2\text{O}_3$. The large and small spheres represent the Al (cations) and O (anions) respectively. $\text{O}_1$, $\text{O}_2$, $\text{O}_3$ are the O atoms with different local coordinations.
FIG. 2 (Color online): The stress-strain curves calculated by \textit{ab initio} DFT method under various tension and shear deformations for (a) $\alpha$-Al$_2$O$_3$ and (c) $\theta$-Al$_2$O$_3$ and the top view structures for (b) $\alpha$-Al$_2$O$_3$ and (d) $\theta$-Al$_2$O$_3$. Three tensile deformations are along crystallographic directions: $<0001>$, $<\bar{1}2\bar{1}0>$ and $<10\bar{1}0>$ for $\alpha$-Al$_2$O$_3$ and $<100>$, $<010>$ and perpendicular to (001) for $\theta$-Al$_2$O$_3$; the shear deformations are along: (0001)$<\bar{1}2\bar{1}0>$, (0001)$<10\bar{1}0>$ and (10$\bar{1}$0)$<\bar{1}2\bar{1}0>$ for $\alpha$-Al$_2$O$_3$ and (100)$<010>$, (001)$<010>$ and (001)$<100>$ for $\theta$-Al$_2$O$_3$. 
FIG. 3 (Color online): The isosurfaces of valence charge density difference (VCDD) of \(\alpha\)-Al\(_2\)O\(_3\) (a) equilibrium, (b) before and (c) after instability under shear deformation along the weakest (0001)[\(\bar{1}2\bar{1}0\)] slip system, and those of \(\theta\)-Al\(_2\)O\(_3\) (d) equilibrium, (e) before and (f) after instability under shear deformation along the weakest (001)[010] slip system (i.e. \(\tau_{yz}\)). The isosurfaces maps of the VCDD correspond to -0.014 electrons/Bohr\(^3\). Yellow color means negative value. The crystallographic directions of <010> and <001> of monoclinic \(\theta\)-Al\(_2\)O\(_3\) are parallel to the y and z axes in Cartesian coordinate system respectively as represented in Fig. 2(d).
**FIG. 4.** (Color online): The calculated electronic density of state (DOS) for (a) $\alpha$-Al$_2$O$_3$ and (b) $\theta$-Al$_2$O$_3$ and the cross-sectional plot of the valence charge density difference (VCDD) for (c) $\alpha$-Al$_2$O$_3$ and (d) $\theta$-Al$_2$O$_3$ to indicate the VCDD between the longest Al-O bonds. The circled region indicates the charge depletion between the longest Al-O bonds for both Al$_2$O$_3$. 