# Theoretical study of structural and electronic properties of $\beta$-Ta$_2$O$_5$ and $\delta$-Ta$_2$O$_5$

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Using density functional theory within the local density approximation (LDA) and generalized gradient approximation (GGA), we discuss the relative stability of the orthorhombic (or the $\beta$) phase and the hexagonal (or the $\delta$) phase of tantalum pentoxide. We find that, both LDA and GGA pseudopotential calculations favor the $\delta$ phase, whereas spin-orbit all-electron calculations favor the $\beta(\delta)$ phase within the LDA (GGA); however, the all-electron energy differences are too small to be significant. The spin-orbit coupling has a significant effect on the band gaps and the band gap is indirect (direct) in the $\delta(\beta)$ phase. The chemical bonding between Ta and oxygen ions is of a mixed type (mainly ionic but partly covalent).

Tantalum pentoxide (Ta$_2$O$_5$) is used as a new capacitor material in high-density dynamic random access memories and considered to be a potential oxide material for gate dielectrics with thicknesses below 4 nm in complementary metal oxide semiconductor devices.[1–3] Below 1630 K, the crystalline bulk phase of Ta$_2$O$_5$ is known to exist[4] and is known as low temperature (or LT)-Ta$_2$O$_5$ or $\beta$-Ta$_2$O$_5$. But, its crystal structure is not uniquely determined[5,6] as processing conditions and impurities have subtle effects on the crystal structure. However, there is a general agreement that $\beta$-Ta$_2$O$_5$ has an orthorhombic structure although a hexagonal phase has long been known.[7] Stephenson and Roth,[4] using the x-ray powder diffraction method, described an orthorhombic unit cell that consists of 22 Ta and 55 O atoms with large number of oxygen vacancies. These vacancies were identified to be the main cause for the large leakage current in the Ta$_2$O$_5$ based devices[8] and later verified with a density functional based calculation by Sawda and Kawakami.[9] Recently, an x-ray diffraction analysis of polycrystalline $\beta$-Ta$_2$O$_5$ powders revealed an orthorhombic structure without any oxygen vacancies.[6] For device applications, a good insulating phase without any oxygen vacancies (and therefore low leakage current) is desired. We present first-principles density functional[10,11] calculations on the $\beta$-Ta$_2$O$_5$ structure without oxygen vacancies within the local density approximation (LDA) and generalized gradient approximation (GGA) in order to understand its structural and the electronic properties. To attempt to determine the ground state, we also perform calculations on the hexagonal phase, $\delta$-Ta$_2$O$_5$. This phase was observed by x-ray diffraction[7] and the only information obtained from this observation was the lattice constants and the unit-cell density. No space group and atomic positions were determined. Fukumoto and Miwa,[12] with the help of the structure factor data of Ref. 7 and three reference hexagonal structures (with space groups $p6/mmm$, $p\bar{6}m2$, and $p6_3/mmc$) used the pseudopotential method within the LDA, and concluded that the crystal structure of $\delta$-Ta$_2$O$_5$ belongs to the space group symmetry $p6/mmm$.

$\beta$-Ta$_2$O$_5$ crystallizes in an orthorhombic structure[6] (space group no 49) with the lattice constants $a=11.748$ bohrs, $b=6.948$ bohrs, and $c=14.728$ bohrs. It has two formula units of Ta$_2$O$_5$ with three Ta-O near neighbor distances of

3.492, 3.674, and 3.809 bohrs (Fig. 1). The hexagonal structure[7,12] (space group no 191) also contains two formula units of Ta$_2$O$_5$ and two Ta-O near neighbor distances of 3.587 and 3.652 bohrs. Its lattice constants are $a=13.697$ bohrs and $c=7.332$ bohrs (Fig. 2).

The optimization of the lattice constants and atomic positions for both the phases are based on a plane wave expansion method[13] employing scalar relativistic ultrasoft pseudopotentials[14] using both LDA (Ref. 15) and GGA (Ref. 16) for exchange and correlation. Thus, all relativistic effects except spin orbit are included in the total energy minimization. The Brillouin Zone (BZ) of the unit cell was sampled with 45 **k** points for the orthorhombic and 70 **k** points for the hexagonal phase in the irreducible wedge of the BZ. The plane wave expansion consists of all wave vectors with $k^2 < 28$ Ry. The total energy convergence was verified with respect to the plane wave basis set size and the number of **k** points to be within 0.01 meV. The total energies and bulk moduli were obtained by zeroing the forces and equilibrating
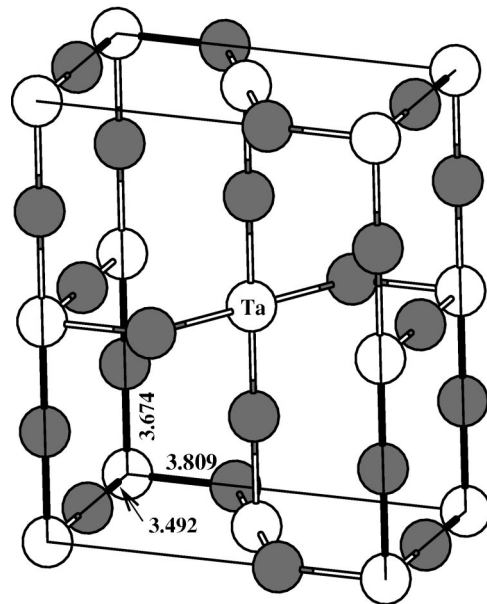


FIG. 1. Schematic diagram of the unit cell of $\beta$-Ta$_2$O$_5$ containing four tantalum ions (open circles) and ten oxygen ions (filled circles). The bond length between a Ta atom and its three nearest neighbor oxygens are shown.
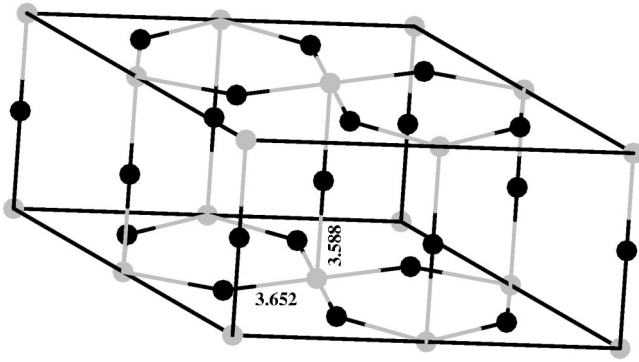
FIG. 2. Schematic diagram of the unit cell of $\delta$-Ta$_2$O$_5$ containing four tantalum ions (gray circles) and ten oxygen ions (black circles). The bond lengths between a Ta atom and its two nearest neighbor oxygens are shown.

the stresses for a set of unit cell volumes. For atomic and lattice relaxations, we used a conjugate gradient method[17] with the criterion that the largest Hellman-Feynman force was less than 1 mRy/bohr and the largest stress difference less then 0.5 mRy/bohr$^3$. The calculated total energy versus volume was fitted with Murnaghan equation of state curve[18] to obtain the bulk modulus and the equilibrium volume, and then the calculation was repeated at the curve minimum. The calculated atomic positions and lattice constants are listed in Table I. Interestingly, both the LDA and GGA lattice constants are smaller than the experimental values for the hexagonal phase. For the orthorhombic structure the LDA lattice constants are all smaller than the experimental while two (one) of the GGA constants are larger (smaller) than experiment, resulting in a GGA unit cell volume only 1.86% larger than experiment. The GGA first and second neighbor distances are in better agreement with experiment than the LDA for both structures. The hexagonal phase is about 0.61 (0.67) eV per unit Ta$_2$O$_5$ less bound than the orthorhombic phase within the LDA (GGA). The bulk moduli are seen (in Table II) to be large and comparable in both phases with the LDA being larger than the GGA. In order to calculate the effect of the spin-orbit coupling (SOC) on the relative ground state

stability and the band gaps, we used a full-potential linear augmented plane wave (FLAPW) method[19] with SOC included on all the atoms in the unit cell using both LDA (Ref. 15) and GGA (Ref. 16) exchange correlation. Sphere radii of 1.74 bohrs in the orthorhombic phase and 1.79 bohrs in the hexagonal phase were used for tantalum and oxygen atoms.[20] The valence wave functions (including the Ta 4$f$) inside the nonoverlapping muffin-tin spheres were expanded into spherical harmonics up to $l=10$ and the potential up to $l=6$. An APW+local orbital[21,22] type basis was used with additional local orbitals for the Ta 5$s$ and 5$p$ semicore states. Convergence of the calculated results with respect to the plane wave expansion parameter $R_{MT}K_{max}$ ($R_{MT}$ is the smallest of the muffin-tin radii used in the calculation and $K_{max}$ is the plane wave cutoff) and **k** point sampling was checked. Forty-five **k** points in the irreducible wedge of the Brillouin zone (IBZ) of the orthorhombic unit cell, 70 **k** points in the IBZ of the hexagonal unit cell, and $R_{MT}K_{max}=8$ (for fixed $R_{MT}$) was found to be sufficient for the accuracy of the calculated total energy (0.01 mRy per unit cell) and the energy gap (0.001 eV).

The current version of WIEN2K calculates forces but not stresses making it difficult to find the combination of lattice constants and atomic coordinates which minimize the total energy. We therefore used the pseudopotential (PP) lattice constants and atomic positions in our all-electron calculations. We calculated the atomic forces and found them to be below 1 mRy/bohr, the threshold used for the relaxation of atomic positions in the PP calculation. Thus, it seems likely our use of PP parameters in the FLAPW calculation, results in stresses satisfying the PP stress criterion. The hexagonal LDA (GGA) ground state energy, calculated without SOC, is 0.231 eV (4.5 meV) per unit Ta$_2$O$_5$ lower (higher) than that of the orthorhombic phase. The SOC makes the hexagonal LDA (GGA) ground state 92 (32) meV per unit Ta$_2$O$_5$ lower (higher) than the orthorhombic phase. The SOC adds approximately 1 eV per unit Ta$_2$O$_5$ to the total energy in each case except the LDA $\delta$ phase where it adds 0.90 eV. Thus, the all-electron energetic stability of the tantalum pentoxide in the GGA is opposite to that in the LDA. It should be noted

TABLE I. The optimized lattice constants (in bohrs) and oxygen positions in $\beta$-Ta$_2$O$_5$ (4$q$ position) and $\delta$-Ta$_2$O$_5$ (6$l$ position). The remaining Ta and oxygen atoms in the unit cell are at high symmetry positions and therefore are not relaxed. The first, second, and third nearest neighbors distances, $d_i$ ($i=1-3$) are also shown (in bohrs).

|  | $a$ | $b$ | $c$ | $x$ | $y$ | $z$ | $d_1$ | $d_2$ | $d_3$ |
|---|---|---|---|---|---|---|---|---|---|
| $\beta$-Ta$_2$O$_5$ |  |  |  |  |  |  |  |  |  |
| LDA | 11.687 | 6.850 | 14.476 | 0.3199 | 0.0006 | 0.5 | 3.425 | 3.619 | 3.731 |
| GGA | 11.931 | 6.984 | 14.696 | 0.3192 | 0.0012 | 0.5 | 3.492 | 3.674 | 3.809 |
| Expt.[a] | 11.748 | 6.948 | 14.728 | 0.3195 | 0.0025 | 0.5 | 3.474 | 3.682 | 3.754 |
| $\delta$-Ta$_2$O$_5$ |  |  |  |  |  |  |  |  |  |
| LDA | 13.251 |  | 7.079 | 0.1880 | 0.3760 | 0.0 | 3.539 | 3.596 |  |
| GGA | 13.455 |  | 7.177 | 0.1890 | 0.3780 | 0.0 | 3.588 | 3.652 |  |
| Expt.[b] | 13.697 |  | 7.332 | 0.1870 | 0.3740 | 0.0 | 3.666 | 3.736 |  |

[a]Reference 6.
[b]Reference 12.

TABLE II. Total energy differences (eV per unit $Ta_2O_5$) $\Delta E$, defined as $E_{tot}(\beta\text{-}Ta_2O_5)$ $-E_{tot}(\delta\text{-}Ta_2O_5)$, bulk modulus $B$ (in GPa), the direct and indirect gaps $E_g^d$ and $E_g^i$ (in eV) with and without spin-orbit coupling. Quantities calculated with the pseudopotential method are shown in parentheses.

| | $\Delta E$ | $B$ | $E_g^d$ | $E_g^i$ |
|---|---|---|---|---|
| $\beta\text{-}Ta_2O_5$ | | | | |
| LDA | $+0.231(+0.675)$ | (294.07) | 0.230(0.185) | |
| LDA+SOC | $+0.092$ | | 0.105 | |
| GGA | $-0.0045(+0.610)$ | (231.47) | 0.230(0.164) | |
| GGA+SOC | $-0.033$ | | 0.090 | |
| $\delta\text{-}Ta_2O_5$ | | | | |
| LDA | | (276.24) | 1.71(1.94) | 1.18(1.31) |
| LDA+SOC | | | 1.35 | 1.05 |
| GGA | | (237.19) | 1.79(1.79) | 1.26(1.18) |
| GGA+SOC | | | 1.49 | 1.07 |

that both LDA and GGA PP calculations find the hexagonal phase lower in energy than the orthorhombic by a non-negligible amount, but the energy differences in the FLAPW calculations are quite small with LDA and GGA having opposite signs (see Table II). Since the experimental equilibrium ground state structure of $Ta_2O_5$ is not known, it is difficult to say which calculated phase is the ground state of the

tantalum pentoxide system. The FLAPW total energy differences are expected to be more accurate than those obtained from pseudopotentials because the $4f$ states were treated as valence electrons in the FLAPW and because of the semicore states which are also treated only in the FLAPW calculations. The $\Delta E$ of the GGA+SOC calculation, which we expect is the most accurate, is too small relative to the errors
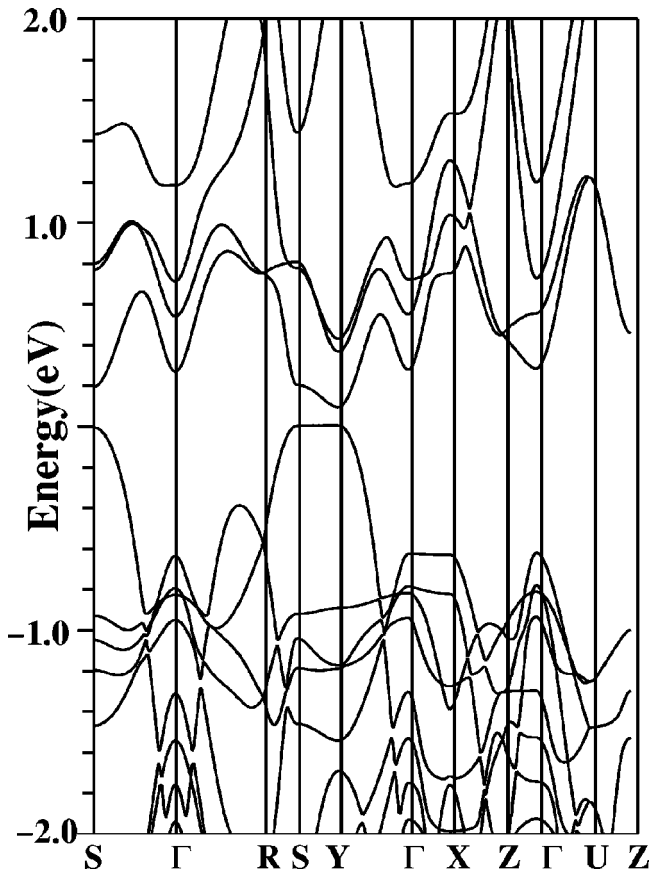


FIG. 3. The GGA energy band structure of $\beta\text{-}Ta_2O_5$ with spin-orbit coupling along a few high symmetry directions in the irreducible Brillouin zone of orthorhombic unit cell. For clarity, only bands around the gap are displayed.
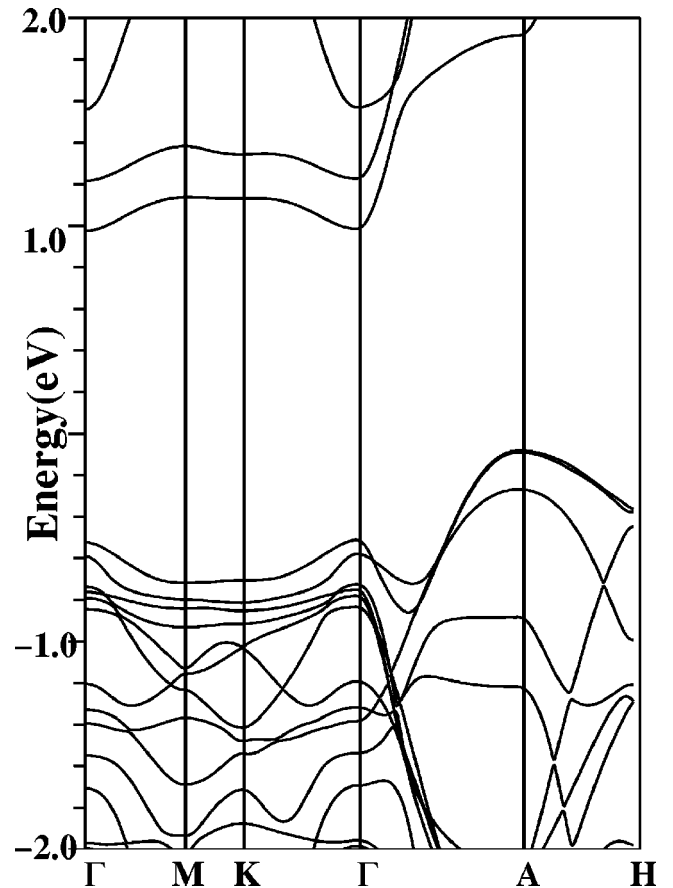
FIG. 4. The GGA energy band structure of $\delta\text{-}Ta_2O_5$ with spin-orbit coupling along a few high symmetry directions in the irreducible Brillouin zone of hexagonal unit cell. For clarity, only bands around the gap are displayed.
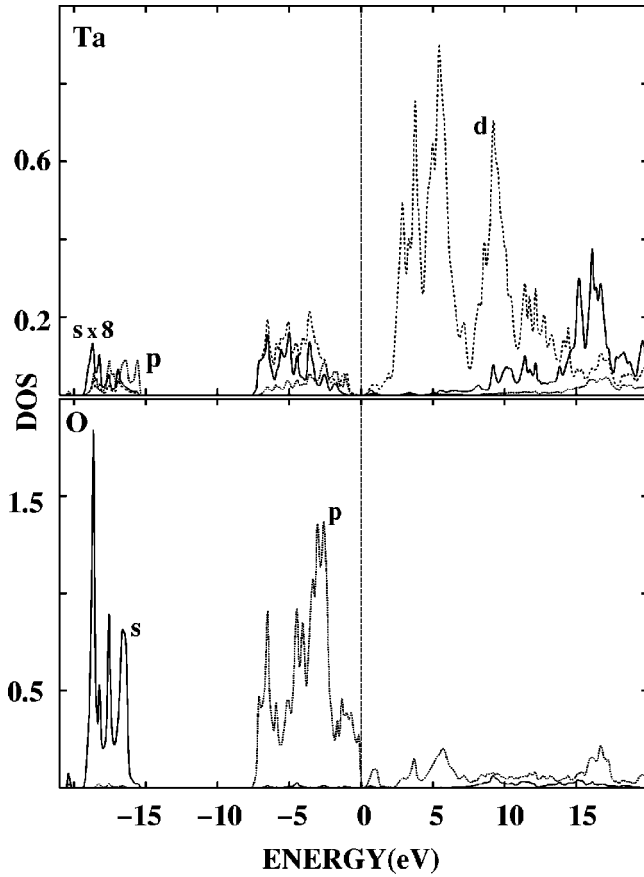
FIG. 5. The GGA $s$ (solid line), $p$ (dotted line), and $d$ (dashed line) projections of the DOS (electrons per cell per eV) for 1.661 bohrs Ta and 1.831 bohrs O spheres in the $\beta$-Ta$_2$O$_5$ structure. The O $d$-DOS is too small to display. The dashed line is at the valence band maximum.



FIG. 6. Same as Fig. 3 but for the $\delta$-Ta$_2$O$_5$ structure. The Ta (O) sphere radii are 1.699 (1.889) bohrs.

introduced by the outer core and density functional approximation to be meaningful. We note that this $\Delta E$, of order 0.04 eV, is the difference of two energies of order $\sim 1.7 \times 10^6$ eV. Thus, our only conclusion can be that our calculation is consistent with the existence of both structures.

The calculated GGA equilibrium volume is closer to the experimental volume both in the orthorhombic and the hexagonal phase so we decided to use the GGA atomic positions and lattice constants for further discussions. The SOC has a significant effect, reducing both the LDA and GGA band gaps. Table II lists the gaps obtained with and without SOC. For comparision, we also list the gaps calculated with the PP. With SOC, we find a significant reduction in direct gaps for both the phases. The GGA+SOC bands around the gaps are displayed in Figs. 3 and 4. For the orthorhombic phase, the gap is direct and at $Y = (2\pi/a)$ (0,0.5,0). With this space group, there are no spin-orbit splittings. However, spin-orbit mixing with the bands directly above it forced the bottom of conduction band to lower energy. The gap is indirect for the hexagonal phase with the valence band maximum at $A = (2\pi/a)$ (0,0,0.5) and the conduction band minimum at $\Gamma = (2\pi/a)$ (0,0,0), and the direct gap is at the later point. The SOC reduction of the energy gap in this case is due to the splitting of the bottom of the conduction band at $\Gamma$. In fact,
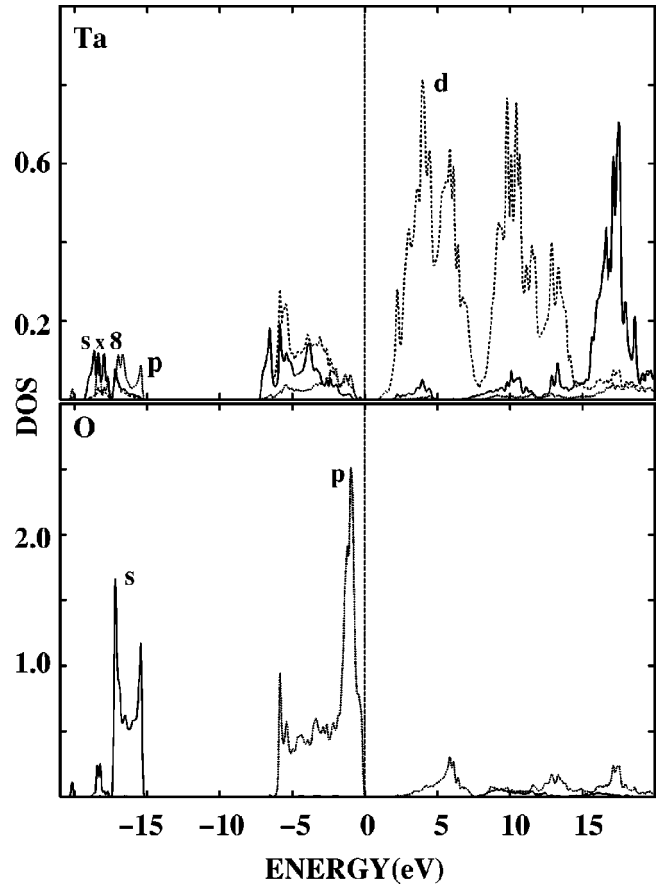
the pair of bands from $\Gamma$ to $M$ to $K$ to $\Gamma$ are only weakly split, and exactly degenerate at $\Gamma$ and $K$ in the absence of SOC. The top of valence band at $A$ consists of a pair of oxygen states whose SO splitting is equal to the line width (in Fig. 4). The next level is unsplit and the lowest two are a SO split level. Sawda and Kawakami[9] used the pseudopotential method within LDA and found a gap of 2.3 eV for the orthorhombic phase with oxygen vacancies. But the calculation used integer occupancies for the oxygen vacancies (i.e., removing one oxygen from the unit cell) in contrast with the experiment which had fractional occupancies of the oxygen vacancies at different oxygen sites. Moreover, the experi-

TABLE III. The integrated valence $s$, $p$ and $d$ charges in 1.661 (1.831) bohrs Ta (O) spheres in the $\beta$-Ta$_2$O$_5$ and 1.699 (1.889) bohrs Ta (O) spheres in the $\delta$-Ta$_2$O$_5$ phase. The total charge contains all valence (including $4f$) electron spherical harmonics.

|  | $s$ | $p$ | $d$ | Total |
|---|---|---|---|---|
| $\beta$-Ta$_2$O$_5$ |  |  |  |  |
| Ta | 0.0700 | 0.3753 | 0.7503 | 15.015 |
| O | 1.6893 | 4.1543 | 0.0124 | 5.891 |
| $\delta$-Ta$_2$O$_5$ |  |  |  |  |
| Ta | 0.0749 | 0.3844 | 0.7947 | 15.102 |
| O | 1.7306 | 4.2311 | 0.0273 | 6.008 |

FIG. 7. A plot of the GGA valence electron charge density from a Ta ion to its two oxygen nearest neighbors for $\beta$-$Ta_2O_5$.
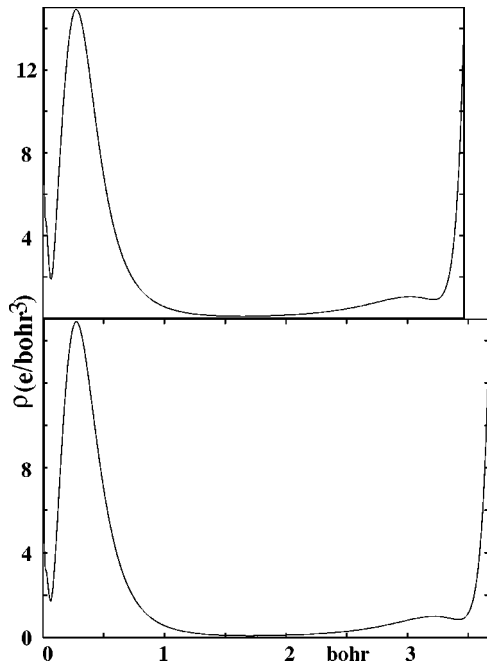


FIG. 8. A plot of the GGA valence electron charge density from a Ta ion to its two oxygen nearest neighbors for $\delta$-$Ta_2O_5$.

mental band gap value of 4.25 eV is obtained for an amorphous thin film phase[23] $TaO_x$ ($x=1.5$). So the exact experimental gap of the bulk orthorhombic phase of $Ta_2O_5$ is not known. We could not find the experimental gap of $\delta$-$Ta_2O_5$ in the literature. Figures 5 and 6 show the $s$-, $p$-, and $d$-projected density of states (PDOS) of Ta and O ions in the $\beta$ and $\delta$ phase, respectively. The projections are shown in a 1.661 (1.831) bohrs Ta (O) sphere in the $\beta$ phase and in a 1.699 (1.889) bohrs Ta (O) sphere in the $\delta$ phase. The reason for such a choice is discussed below. Table III lists the integrated charges. We note that the DOS of the two structures are quite similar. The very tiny feature just below $-20$ eV represents O-$2s$ and Ta-$6p$ hybridized in the Ta-$4f$ bands. A small amount of Ta-$6s$, $6p$, and $5d$ are hybridized with the low lying O-$2s$ bands and somewhat more Ta-$6s$ and considerably more Ta-$5d$ is hybridized into the O-$2p$ bands below the gap. The Ta-$5d$ and $6s$ conduction bands span a range of over 20 eV above the energy gap.

The plots of valence electron charge density from Te to its two nearest neighbors are shown in Fig. 7 for $\beta$-$Ta_2O_5$. We find the minimum charge density, at about 1.661 bohrs from the Ta ion (about 47% of the first nearest neighbor distance 3.492 bohrs), of 97 millielectrons/bohr$^3$ along the nearest neighbor direction, and along the second (third) nearest neighbor directions, the minimum charge density is 85 and 72 millielectrons/bohr$^3$, at a distance of 1.72 (1.73) bohrs, from the Ta ion. The integrated charge within the 1.661 bohrs Ta sphere is 15.015 electrons and within the 1.831 bohrs oxygen sphere is 5.891 electrons. In crystals, ionicity cannot be given a precise value unless the charge density strictly vanishes between the atoms. So there is no unique way of dividing the remaining 8.515 interstitial electrons among the two Ta and five O spheres per formula unit. The simplest assumption is to divide the interstitial electrons equally
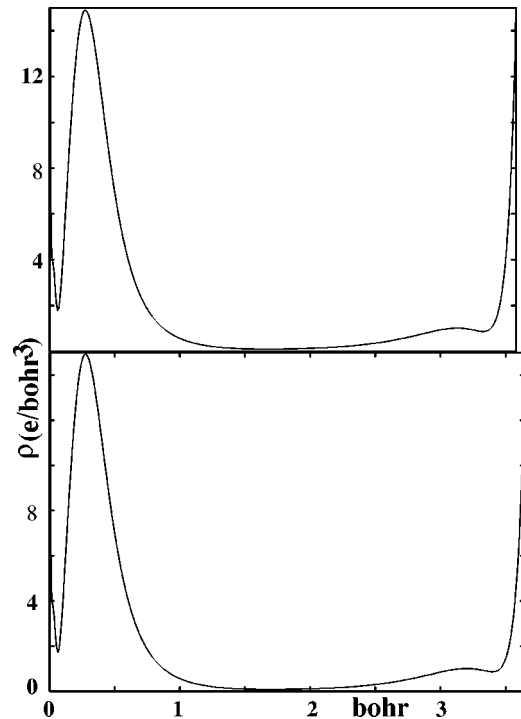
among the spheres. This choice leads to $Ta_2^{2.7686+}O_5^{1.1074-}$. We get, in case of $\delta$-$Ta_2O_5$, the minimum charge density of 91 (85) millielectrons/bohr$^3$, at a distance of 1.699 (1.721) bohrs from the Ta ion, along the first (second) nearest-neighbor direction (see Fig. 8). The 1.699 bohrs Ta sphere contains 15.102 electrons and the 1.889 bohrs oxygen sphere contains 6.008 electrons. This results in 7.756 interstitial electrons and $Ta_2^{2.790+}O_5^{1.116-}$. Any other reasonable definition of ionicity should yield results not too far from these. Although the overlap of the Ta and O charge densities seen in Figs. 5 and 6 is small, the hybridization into the oxygen $p$ bands of 0.75 Ta-$d$ electrons (per Ta sphere) indicates there is a covalent component to the bonding.

In conclusion, we have performed LDA and GGA electronic structure calculations of $\beta$-$Ta_2O_5$ and $\delta$-$Ta_2O_5$ finding lattice constants and ionic displacements in reasonable agreement with experiment and only a small difference in their zero temperature total energies. In addition, the two structures have rather large and similar bulk moduli and very similar ionic and covalent contributions to their binding. The 0.1 eV gap in the orthorhombic phase is direct while the 1 eV gap in the hexagonal phase is indirect. Because density functional energy gaps run the gamut from 100% error in Ge to 100% accuracy in Te, and because the only measured gap in this system was for $TaO_{1.5}$, the accuracy of our calculated gaps is unknown.

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[20] It was suggested to us that a comparision of the total energy of the two structures would be more meaningful if the same muffin-tin radius was used for both structures. We therefore repeated the $\delta$-Ta$_2$O$_5$ calculation for the most significant case (GGA+SOC) with a 1.74 bohrs muffin-tin radius and obtained an increase in total energy of 0.010 eV per Ta$_2$O$_5$ or $\Delta E = -0.043$ eV. The smaller MT radius with its concomitant increase in plane waves would lead one to expect a better converged, i.e., decreased energy. We attribute the increase to the semicore states which are treated in a tight-binding approximation.

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