Exceptionally long-ranged lattice relaxation in oxygen-deficient Ta$_2$O$_5$

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1. Introduction

Metal oxides play a significant role in modern physics, chemistry, and technology [1–17]. The presence of defects can result in nontrivial modifications on the electronic properties of metal oxides. The emergence of high-$T_c$ superconductivity or colossal magneto-resistance is due to the doping of transition metal oxides [18–21]. The presence of defects can result in the leakage current in Ta$_2$O$_5$ [22,23]. Magneto-resistance is due to the doping of transition metal oxides also play a key role in the leakage current in Ta$_2$O$_5$ [13,32], a material of importance to both dielectrics [13,32,33] and catalysis applications [34,35]. The presence of oxygen vacancies improves the functionality of electrode materials [36] and the catalytic behavior of oxides [37,38]. Band gap narrowing effects are reported in TiO$_2$ by the co-doping of extrinsic defects [39]. The structural properties of defects on surfaces can be characterized by experimental tools such as scanning tunneling microscope (STM) [37,38,40–41] or scanning electron microscope (SEM) [42], and defects in bulk by the transmission electron microscope (TEM) [43] or X-ray diffraction (XRD) [44,45]. The electronic structures of defects can be detected from the measurements including electrical transport and optical absorption [46,47], the electron paramagnetic resonance (EPR) [48–51] and the X-ray photoemission spectroscopy (XPS) [52–55]. First-principles calculations can provide insightful details such as charge transfer, vacancy formation energy, and bonding geometry of the defects, which are not easily accessed by the state-of-the-art experimental tools. In the simulation of defects, the supercell approach is widely employed, by which the equation of quantum mechanics is solved within a unit cell subject to the periodic boundary condition [56,57]. The success of supercell approach is due to the fact that the defect-induced lattice distortion is generally short-ranged especially for a neutral defect. This is not always true as shown by hybrid classical-\textit{ab} \textit{initio} calculations for a neutral vacancy in α-quartz [58]: The lattice displacement extends over 13 Å from the vacant site. Such behavior is not yet reported from other calculations being possibly obscured by the limited size of the simulation cell: typically $\sim 10$ Å × $10$ Å × $10$ Å [59–67].

In this work, we focus on Ta$_2$O$_5$, a material which has a large dielectric constant [13,68–75] and a variety of coexisting polymorphs [76]. We investigate the lattice relaxation in a supercell which sufficiently elongates in one unit cell axis ($\sim 41$ Å). We find that the lattice relaxation associated with a charge-neutral vacancy can extend beyond 18 Å from the vacant site. The lattice relaxation has significant effects on the vacancy formation energy as well as the electronic structures. The result is analyzed using the long-ranged Hellmann–Feynman forces and the density response of electrons as well as the potential energy surface which indicates softness of the Ta–O bond lengths.

2. Methods of investigation

Our study is based on density functional theory (DFT) calculations carried out by the Vienna \textit{ab} \textit{initio} simulation package
using a plane wave basis set and the projector-augmented-wave (PAW) potentials \cite{79,80}. For structural relaxation, the exchange–correlation interactions of electrons are described by the PBE functional \cite{81}. The band gap given by DFT-PBE calculation is \( \sim 1.96 \text{ eV} \), which is much smaller than the experimental value \(( \sim 4 \text{ eV})\) \cite{32}. To overcome the problem of band gap underestimation, the PBE0 hybrid functional \cite{82} is employed for the calculation of electronic density of states. The calculated band gap by the PBE0 functional is \( \sim 3.91 \text{ eV} \), comparing well with the experimental value. The energy cutoff for plane waves is 600 eV. The construction of the primitive cell of Ta2O5 is detailed in recent work \cite{83}. For the simulation of an oxygen vacancy, we take a \((2 \times 1 \times 2)\) supercell, whose geometric parameters are: \( a = 12.664 \text{ Å}, b = 40.921 \text{ Å}, c = 7.692 \text{ Å}; \alpha = 90^\circ, \beta = 90^\circ, \gamma = 89.16^\circ \). A \((1 \times 1 \times 1)\) k-mesh is generated using the Monkhorst-Pack scheme \cite{84}. The structural optimization is stopped when the total energy converges to the level of \( 10^{-3} \text{ eV} \).

The O atoms in Ta2O5 can be classified according to their geometric positions \cite{83,85}: O on the basal planes (in-plane site) and O sitting between the basal planes (cap sites). The properties of an oxygen vacancy (Vo) are studied by removing one O atom from the supercell. We have performed calculations on a number of vacancy structures whose geometries and energetic parameters can be found elsewhere \cite{83}. Here, we will focus on two typical vacancy configurations: The cap site vacancy (referred to as Vo I), and the in-plane site vacancy (referred to as Vo II). We study the lattice relaxation induced by their charge-neutral states. The single-vacancy configurations we study here are actually periodically arranged vacancies with a concentration of \( \sim 0.45\% \).

3. Lattice relaxation around the vacancies

Fig. 1 shows the variation of Ta–O bond lengths plotted against the distance \( R \) from the Vo site. For each \( R \), plotted are the maximum, minimum and average of the variation. The lattice relaxation is strikingly long-ranged for the vacancy at the cap site (Vo I) and is shorter for the inplane site (Vo II). For Vo I, the maximum of the absolute deviation \( \delta R_{Ta-O} \) remains 0.025 Å even when \( R \) increases to 20 Å. Interestingly, compared with \( \delta R_{Ta-O} \) near the vacancy sites \((R \leq 3 \text{ Å})\), larger values are found at longer distances \((6 \text{ Å} \leq R \leq 10 \text{ Å})\). For both Vo I and Vo II, though \( \delta R_{Ta-O} \) shows a general trend of decreasing with increasing \( R \), the distribution of \( \delta R_{Ta-O} \) is highly fluctuated, in contrast to the intuitive experience from a continuum model which one would expect that the distortion decays monotonically with \( R \). For distances beyond 10 Å, the lattice relaxation extends mainly along the \( b \)-axis. In this context, a larger simulation cell, such as a \((2 \times 1 \times 3)\) or \((3 \times 1 \times 3)\) supercell may be necessary to evaluate the relaxation effects in both \( a \)-axis and \( c \)-axis. Such simulations are beyond the present affordable computational resources and are left for the future study.

Fig. 2 shows the Hellmann–Feynman (HF) forces \cite{86} acting on the atoms of the unrelaxed defective structures. The distance within which the HF forces are not negligible is \( \sim 19 \text{ Å} \) for Vo I and is \( \sim 9 \text{ Å} \) for Vo II. The forces are long-ranged when compared with other systems such as oxygen-deficient \( \beta\)-PtO2 \cite{87} (see also the Fig. A1 of Appendix A), in which the distortion and the HF forces are negligible for \( R \geq 6 \text{ Å} \). Compared to \( \delta R_{Ta-O} \), the magnitude of HF forces is less fluctuated and has the largest value near the vacancy site, \( R \sim 2.5 \text{ Å} \). One sees the correspondence of the forces and bond length variation from Figs. 1 and 2 although it is not accurately one-to-one, e.g., the global maximum of HF forces does not correspond to the global maximum of \( \delta R_{Ta-O} \). This is understandable when considering the fact that the lattice relaxation is not the behavior of individual atom but the collective motions of all the atoms. Finding a quantitative relation between the bond length variation and the HF forces is an important problem to be solved.

We go on to study the effects of lattice relaxation on the vacancy formation energy and the electron density of states (DOS). For both Vo I and Vo II, three structures are considered: the unrelaxed structure; the partially relaxed structure, in which only the atoms located in a distance of \( R \leq 6 \text{ Å} \) to the Vo site are allowed
to relax; the fully relaxed structure, where all the atoms are relaxed. The calculated vacancy formation energies are summarized in Table 1. The differences in the vacancy formation energy reflect the role of lattice relaxation. Under thermodynamic equilibrium in which the defective systems are subjected to high temperatures [57,88], Vo II would show higher stability than Vo I because of its lower formation energy. In other words, Vo I and the other Vo configurations can be stabilized at low temperatures where the diffusion of vacancies is significantly hindered by the low defect kinetics and high diffusion barrier (the order of vacancy formation energy). The DOS analysis is focused on the electronic states near the valence band maximum (VBM) and the conduction band minimum (CBM). The calculated DOS using PBE0 functional is shown in Fig. 3. For the three differently relaxed structures of Vo I, clear differences are found at: The number of gap states below the Fermi level ($E_F$), the position of the gap states, and the position of $E_F$. In the case of Vo II, the DOS features of the three structures differ slightly around the VBM and CBM, e.g., the peak position of the gap state near CBM (marked in Fig. 3). On the other hand, the position of $E_F$ and the overall DOS of the partially-relaxed and fully-relaxed structure are similar, which is in accordance with the relatively small difference in the vacancy formation energy of both structures of Vo II (Table 1).

Then, what is the origin of the long-ranged HF forces? Similar to molecules or atomic clusters [89], the HF forces on the atoms of a crystal (regarded as a huge molecule) may be expressed as [89,90],

$$\vec{F}_{R_i} = \int n(\vec{r})\nabla V(\vec{r} - \vec{R}_i)d\vec{r} + \vec{F}_{\text{nuc}}$$

$$= -Z_I \int n(\vec{r})\frac{\vec{r} - \vec{R}_I}{|\vec{r} - \vec{R}_I|^3}d\vec{r} + \sum_{j=1}^{N} Z_j Z_I \frac{\vec{R}_I - \vec{R}_j}{|\vec{R}_I - \vec{R}_j|^3}$$

(1)

Table 1
Vacancy formation energy ($E_{vf}$) of differently relaxed structures of Vo I and Vo II.

<table>
<thead>
<tr>
<th></th>
<th>Unrelaxed</th>
<th>Partially relaxed</th>
<th>Fully relaxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vo I</td>
<td>6.159</td>
<td>5.579</td>
<td>4.907</td>
</tr>
<tr>
<td>Vo II</td>
<td>5.317</td>
<td>4.528</td>
<td>4.164</td>
</tr>
</tbody>
</table>

with $n(\vec{r})$ the electron density, $V(\vec{r} - \vec{R}_I) = -Z_I/(\vec{r} - \vec{R}_I)$ the electron–nucleus interaction and $Z_I$, $Z_j$ the effective charge numbers of the nucleus (the ion core in the case of DFT pseudopotential calculations). The number of atoms is $N$. The coordinates of electrons and atoms are $\vec{r}$ and $\vec{R}_I$ ($I = 1, ..., N$), respectively. The term $\vec{F}_{\text{nuc}} = \sum_{j=1}^{N} Z_j Z_I \frac{\vec{R}_I - \vec{R}_j}{|\vec{R}_I - \vec{R}_j|^3}$ is the electrostatic force on the atom $I$ due to the presence of other nuclei/ion cores. For a perfect crystal, the relation $\vec{F}_{R_i} = 0$ holds for each atom. The two unrelaxed defective structures discussed in Fig. 2 correspond to the situation in which the removal of an oxygen atom causes changes in the electron density $n(\vec{r})$ and the term $\vec{F}_{\text{nuc}}$, i.e., $n(\vec{r}) \rightarrow n(\vec{r}) + \delta n(\vec{r})$ and $\vec{F}_{\text{nuc}} \rightarrow \sum_{j=1}^{N} Z_j Z_I \frac{\vec{R}_I - \vec{R}_j}{|\vec{R}_I - \vec{R}_j|^3}$. It is straightforward that the HF forces in the unrelaxed defective structures are as follows:

$$\vec{F}_{R_i} = -Z_I \int \delta n(\vec{r})\frac{\vec{r} - \vec{R}_I}{|\vec{r} - \vec{R}_I|^3}d\vec{r} - Z_I Z_{Vo} \frac{\vec{R}_{Vo} - \vec{R}_I}{|\vec{R}_{Vo} - \vec{R}_I|^3}$$

(2)

Fig. 3. (Color online) The electron DOS of unrelaxed, partially relaxed and fully relaxed structures, calculated using the PBE0 functional. The top of valence band is set at 0, and the position of Fermi level ($E_F$) is marked by an arrow.
The term $\delta n(\mathbf{r})$ consists of two parts: the electron density of the removed O atom in the bulk phase, $n_0(\mathbf{r})$, and the charge density perturbation due to the removal of the O atom, $\Delta n(\mathbf{r})$, i.e., $\delta n(\mathbf{r}) = n_0(\mathbf{r}) + \Delta n(\mathbf{r})$. The term $n_0(\mathbf{r})$ is localized around the Vo site and satisfies the relation $\int n_0(\mathbf{r}) d\mathbf{r} = -Z_{\text{Vo}}$, with the induced forces $-Z_I \int \frac{n_0(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_I|^3} d\mathbf{r}$, which largely cancel the second term in Eq. (2). For the atoms which locate far away from the Vo site, only the charge density perturbation $\Delta n(\mathbf{r})$ plays an important role in inducing the HF forces. Long-ranged density perturbation leads to long-ranged HF forces.

To demonstrate perturbation on charge density upon the creation of oxygen vacancy, we compute the electron density difference between the perfect Ta$_2$O$_5$ and the unrelaxed Vo configuration, for Vo I and Vo II, plus one O atom at the corresponding Vo site. The difference is given by $\Delta n = n[\text{Ta}_2\text{O}_5] - (n[\text{Vo}] + n[\text{O}])$, where $n[\text{Vo}]$ and $n[\text{Ta}_2\text{O}_5]$ are the total electron density of the system with and without an oxygen vacancy, respectively. The term $n[\text{O}]$ is the electron density of an isolated O atom. The results are shown in Fig. 4. The perturbation is large near the Vo site and then decreases with increasing distance. In the long distance, the perturbation in Vo I is small but extends in the whole simulation cell without showing an obvious decay. For both Vo I and Vo II, the range of electron density perturbation is consistent with that of the HF forces. The HF forces in regions far away from the Vo sites are mainly induced by the electron density perturbation.

Another factor that may be responsible for the long-ranged lattice relaxation is the potential energy surface that determines the force constants for the variation of the Ta–O bond lengths. Soft force constants imply flexible bond lengths. We investigate the force constant by varying the lengths of a certain Ta–O bond around the optimized one. In the variation, the positions of the Ta and O atoms which form the Ta–O bond are fixed while the positions of the other atoms are either fixed/unrelaxed or relaxed to show the effects of lattice relaxation on total energy. Fig. 5 shows the associated increase in the total energy for the unrelaxed structures. The bonds that show large variation (Bonds 1–3 in Fig. 1) were chosen for analysis. There are flat regions at which the change in energy is remarkably small. When the other atoms are relaxed, the increase in energy is much smaller, as illustrated in Fig. 6 for Bond 1. For Vo II, we find a new minimum structure at which the bond length is $\sim 1.9$ Å. This implies that the geometry optimization is incomplete and imposes more systematic search for the global minimum. However, searching for the global minimum remains a challenge in computational physics, due to the

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Fig. 5. (Color online) Relative energies as a function of the bond lengths of the three Ta–O bonds marked in Fig. 1. The energies are obtained using static calculation, i.e., all the atoms are fixed for each calculation. The energies of the relaxed configurations are set at 0.

Fig. 6. (Color online) Relative energies of the Vo configurations as a function of the lengths of Bond 1 (Fig. 1), for static and relaxed configurations.
complexity of high-dimensional potential energy surface. The above results illustrate softness of the lattice which may also play a role in the lattice relaxation. In summary, we show that the presence of charge-neutral oxygen vacancies in Ta2O5 is associated with exceptionally long-ranged lattice relaxation, which has notable effects on the vacancy formation energy and the vacancy states of electrons. The results are explained by the long-ranged Hellmann–Feynman forces and the soft force constants for the variation of Ta–O bond lengths. The long-ranged character of forces is mainly caused the long-ranged perturbation of charge density. The smooth potential energy surface of the relaxed structures also indicates that the ground state of Ta2O5 crystal structure is highly degenerate, in accordance with the coexistence of polymorphs and the amorphous nature of experimentally grown Ta2O5 [74,91].

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Appendix A

We show that the lattice relaxation and HF forces in oxygen-deficient β-PtO2 are short-ranged.

References