

Resonant defect states and strong lattice relaxation of oxygen vacancies in WO₃

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We find, from first principles calculations, that an oxygen (anion) vacancy in WO₃ not only generates a donorlike state near the fundamental band gap, derived from the top valence bands, but also gives rise to an additional pair of defect states: a hyper-deep resonant state in the valence band and a high-lying resonant state in the conduction band, derived from *s*-like bonding and antibonding bands, respectively. These states show distinctively different properties from their counterparts in other conventional semiconductors. With a change in the charge state of the vacancy, a strong lattice relaxation is found for the W ions nearest to the vacancy, accompanied by large changes in the energies of all the defect states.

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Since the discovery of its electrochromism by Deb in 1969,¹ tungsten oxide (WO₃) has emerged as one of the most interesting and promising electrochromic materials. However, despite three decades of intense studies,^{2,3} the physical mechanism for the coloration still remains controversial.^{1,4-6} Agreeably, the coloration is due to extrinsic light absorption with energy below the intrinsic band gap of WO₃ ($E_g \sim 3$ eV), but the origin of the transition is not at all clear. Deb's vacancy model¹ suggests that the oxygen vacancy (V_O) is involved in the optical transition; while all the other models suggest that the optical transition occurs via the charge transfer between non-equivalent W sites in one way or the other.⁴⁻⁶ Also, another not well explained but important property of WO₃ is the enhancement of the conductivity with the increase of O deficiency.^{2,3} There have been numerous theoretical studies on the electronic structure of WO₃: non-self-consistent and/or semiempirical calculations,⁷⁻¹⁰ and self-consistent first-principles calculations.¹¹⁻¹⁵ However, the properties of V_O have been studied theoretically only in amorphous WO₃,¹⁶ and a related system, KNbO₃.^{17,18} Here, we perform a theoretical investigation on the structural and electronic properties of V_O in cubic WO₃. Although in reality WO₃ often appears in different structures with lower symmetry than cubic, we believe that this simple structure is a logical starting point for gaining an understanding of the coloration phenomenon. On one hand, this study results in valuable insights on the role of V_O in the electrochromism of WO₃; on the other hand, WO₃: V_O serves as a model system for revealing some intriguing aspects of the vacancy which may be of general interests and importance for V_O in oxides.

Since the pioneering work of Coulson and Kearsley,¹⁹ a vacancy is commonly known to generate localized states near the fundamental band gap.¹⁹⁻²⁶ While most studies on vacancies have focused on the defect states near the band gap, it has been found that the vacancy in Si and GaAs can also generate a deep resonant defect state inside the valence

band,^{25,27} due to the dehybridization of the broken bonds of the nearest neighbor atoms. The situation is expected to be quite different for highly ionic crystals in which the coupling of an anion with the nearest neighbor cations is usually weak for the deep valence band due to the large mismatch in the orbital energies. Through a first-principles calculation, we obtain a comprehensive picture for the formation of defect states associated with the anion vacancy in a highly ionic crystal like WO₃. We find that (1) contrary to the covalent or mostly covalent semiconductor case, here the *vacancy configuration* needs to involve atoms in the next shell of the same type atoms as the missing anion. (2) Beside generating a doublet donorlike state (to be called E_3) near the band gap, V_O gives rise to a pair of singlet defect states: a hyperdeep one (to be called E_1) associated with the *s*-like bonding valence band (VB) and a high-lying one (to be called E_2) mainly derived from the *s*-like antibonding conduction band (CB). The antibonding E_2 state is located several eV above the first CB minimum (CBM), compared to that in a typical covalent, III-V or II-VI, semiconductor where such a state is below the CBM. (3) With a change in the charge state of the vacancy, the lattice relaxation for the nearest cations exhibits a large swing from one side of the ideal position to the other, which has not been reported before for similar systems.

A self-consistent first-principles pseudopotential method, in the framework of density functional theory within the local density approximation (LDA), is used in this study.²⁸ The $5d$, $6s$, and $6p$ orbitals of W and $2s$ and $2p$ orbitals of O are included as valence states for generating the corresponding pseudopotentials. Spin-orbit interaction is neglected in our calculation. The energy cutoff for the plane wave basis was 70 Ry. In cubic WO₃, the primitive unit cell Ω_0 contains four atoms: three O atoms at $(0,0,0)$, $(a/2,0,a/2)$, and $(0,a/2,a/2)$ and one W atom at $(0,0,a/2)$, where a is the lattice constant. The defect structure is simulated by a supercell of size $n_1 \times n_2 \times n_3$ times of Ω_0 for which the O atom at

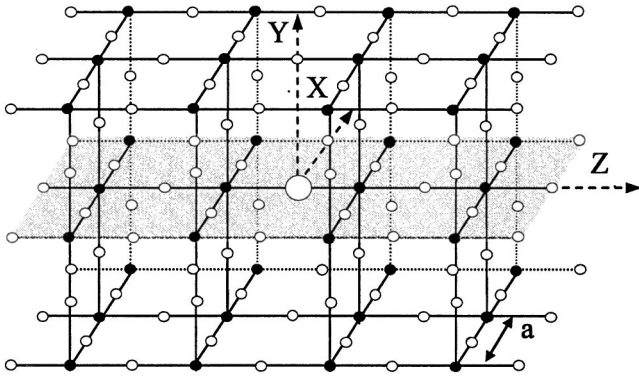


FIG. 1. A schematic show of the $2 \times 2 \times 4$ supercell with the V_O (the large open circle) at the origin. Small solid and open circles represent the W and O atoms, respectively.

the origin is removed. The defect structure has a local symmetry of C_{4v} ,¹⁷ with the symmetry axis along [001]. Three supercell sizes, with 32, 48, and 64 atomic sites, respectively, have been used to mimic the interaction of the vacancies, by choosing $n_1=n_2=2$ and $n_3=2, 3,$ and 4 . Figure 1 shows schematically the structure of the $(n_1, n_2, n_3)=(2, 2, 4)$ supercell. All atomic configurations are obtained by minimizing the total energy. The calculated bulk properties, $a=3.84 \text{ \AA}$ and $E_g=0.43 \text{ eV}$, agree well with previous self-consistent calculations: $a=3.73\text{--}3.84 \text{ \AA}$ and $E_g=0.3\text{--}0.6 \text{ eV}$,^{11–15} and the experimental value of $a=3.71\text{--}3.78 \text{ \AA}$.^{12,29} The band gap, however, is much smaller than the experimental value of 2.62 eV (obtained for the monoclinic phase)³⁰ due to the well known LDA error. The dispersion curves and the bandwidths are also found to be in general agreement with those of previous calculations, as shown in Fig. 2.^{11–15}

With the removal of one O atom, the number of valence electrons remained in the system is $2(N_0-3)$, where N_0 is the number of occupied valence states for the ideal structure. We find that for all the three supercell defect structures, there are only N_0-4 states (including the localized E_1 defect state) remaining in the VB, which is consistent with the fact that

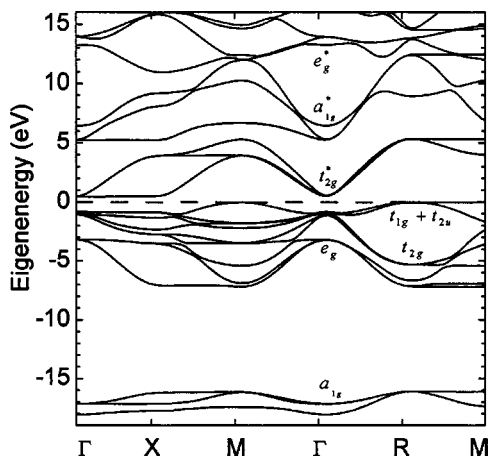


FIG. 2. Band structure of a cubic WO_3 . The energy reference is at the top of the valence band (indicated by the dashed line), and the Γ conduction band minimum is at 0.43 eV .

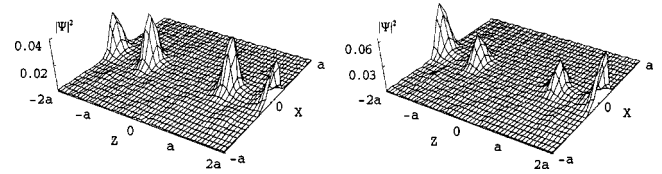


FIG. 3. Charge distribution, in the x - z plane (see Fig. 1), of the hyperdeep bonding defect state E_1 for the 63-atom supercell before (left) and after (right) the high-lying antibonding state E_2 is occupied (i.e., in the V_O^{++} and V_O^0 state, respectively). Note that the vacancy is at the origin $(0,0,0)$.

four oxygen orbitals have been removed. More specifically, one state is removed from the lowest VB which is known as the “ a_{1g} ” band (in the language of chemical bond description, see Fig. 2) mainly originating from the O $2s$ orbitals.² The other three states are removed from the highest VB which is known as the “ $t_{1g}+t_{2u}$ ” band derived from the O $2p$ orbitals.² Note that now the valence band has one state short to accommodate all the valence electrons. We will show that the electronic structure critically depends on which excited state should the two “extra” electrons occupy.

The first intriguing result is the finding of a *hyperdeep* defect state E_1 (with a_1 symmetry) near the a_{1g} band which is $\sim 15\text{--}17 \text{ eV}$ below the top of the VB. The wave function of this defect state is found localized neither on the vacancy site nor on the nearest W sites, but on the nearby O sites along the [001] direction from the missing O atom. This state is characterized as a defect state primarily for the following two reasons: (1) the k projection of its wave function has a nearly uniform distribution over the k points in the Brillouin zone (BZ), while other bulklike states tend to have projections only at a few specific symmetrically related k points; and (2) the wave function has very little distribution at other O sites not along the [001] axis, despite their being closer to the vacancy. Figure 3 shows the charge distribution (the square of the wave function) of this defect state for the largest supercell.

Beside the E_1 state, we have observed three additional states, one singlet (E_2 , also with a_1 symmetry) and one doublet (E_3 , with E symmetry), both lying above the CBM. The primary contributors to the CB states are the W $5d$ orbitals:^{2,15} the first CB is commonly considered as an antibonding band due to the hybridization of W $5d_{xy}, 5d_{yz},$ and $5d_{xz}$ with the O $2p$ (known as the “ t_{2g}^* ” band), and the second CB is viewed as an antibonding band due to the hybridization of W $5d(x^2-y^2)$ and $5d(z^2)$ with the O $2s$ (known as the “ a_{1g}^* ” band). The E_2 and E_3 levels are found located in between the t_{2g}^* and a_{1g}^* band. The wave function of E_2 is strongly localized at the vacancy site, or to be exact, between the vacancy and the nearest W’s, whereas E_3 is weakly localized at the closest O’s along the [100] and [010] direction [i.e., $(a,0,0)$, and $(0,a,0)$]. Figure 4 shows the charge distributions typical for these defect levels for the largest supercell.

We next discuss the origins of these defect states. Roughly speaking, the high-lying a_{1g}^* CB is an antibonding band of the deep a_{1g} VB. The band-projection analysis indi-

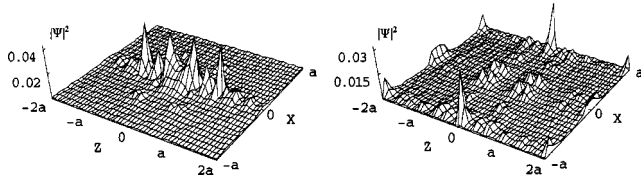


FIG. 4. Charge distribution, in the x - z plane, of the high-lying antibonding defect state (E_2 , left) and the donorlike defect state (E_3 , right) for the 63-atom supercell, with the vacancy at the charge state V_O^0 .

states that E_1 is primarily constructed from the states of the a_{1g} band, E_2 has the largest contribution from the high-lying a_{1g}^* band, but also with some components from the a_{1g} band. Thus E_1 can be viewed as a *bonding* state, and E_2 an *anti-bonding* state of the *vacancy configuration*. The formation of this *bonding* state can be understood as follows. The removal of the O at the origin effectively creates a repulsive potential for the electron at the core of the vacancy,²² which drives the “extra” electron of the nearest W away from the vacancy site along the lowest energy direction [001]. An actual examination of the potential profile indeed qualitatively confirms this intuition. These states are analogous to bonding and anti-bonding states generated by two off-center potential wells. Also, to some extent, the appearance of the E_1 state here is similar to the case of an isoelectronic impurity, which was also found to have a hyperdeep *bonding* and a high-lying *anti-bonding* localized state.³¹ For E_3 , the band-projection analysis reveals that it is mainly derived from the two highest VB’s ($t_{1g} + t_{2u}$ and t_{2g}). Considering their difference in origins, one can expect that a hypothetical correction to the LDA error would shift the E_2 state up with the whole CB by a value roughly given by the difference between experimental and LDA band gaps, but the E_3 state would be influenced to a very small extent only. Thus, in reality the E_3 state is expected to behave as a donor state. There are certain distinct differences between (E_2, E_3) in WO_3 and their counterparts (a_1, t_2) in a typical III-V or II-VI semiconductor, in terms of their relative position and origins. In the latter, they are believed to originate from the VB, and a_1 is typically lower than t_2 , because the s -like VB is typically lower than the p -like VB.^{27,32} In contrast, in WO_3 , the E_2 state has an antibonding nature associated with the high-lying antibonding s -like CB, and is energetically above the VB derived E_3 state. On one hand, such a reversal in the order of defect levels could result in a partially filled E_3 state, and, thus, offer a plausible explanation for the unusual dependence of the conductivity on O deficiency. On the other hand, the optical transitions involving the E_3 state could be related to the below band gap absorption believed to be responsible for the coloration effect in WO_3 . Further exploration of these issues will be left for a future study.

The second intriguing finding emerges from the issue regarding how to allocate the two “extra” electrons. One option is to allow them to occupy an extended state, say, the bottom of the CB, and the corresponding vacancy is considered to be a positive bivalent state (V_O^{++}), following the convention. This option is similar to the commonly adopted

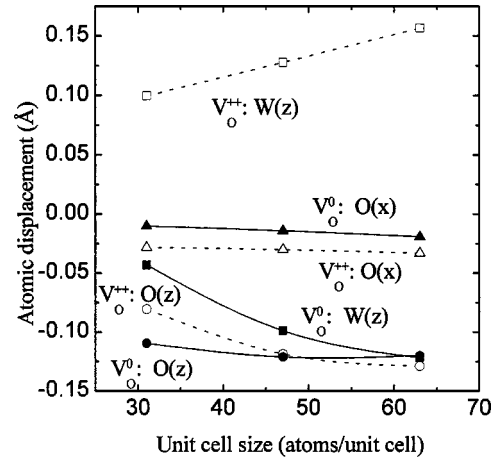


FIG. 5. The dependences of atomic relaxation on the supercell size and the vacancy charge state, along the z and x direction for the O and W ion nearest to the vacancy, at $(a/2, 0, a/2)$ and $(0, 0, a/2)$, respectively.

procedure of using a uniform background for calculating a charged defect, but more relevant to the optical transition. Another option is to have them occupy one of the defect states, say, the E_2 state. This option is similar to the common practice of occupying an a_1 defect state for calculating a neutral defect, i.e., V_O^0 , though such an a_1 state is normally located near the fundamental band gap. We will focus on the two most commonly studied vacancy states: V_O^{++} and V_O^0 , and leave the results for other possibilities (e.g., occupying the E_3 state) in a future paper. Switching the occupation between these two options results in not only a large swing of the nearest W atoms from one side of the ideal position to the other, as shown in Fig. 5, but also brings about huge changes in the energies of the defect states (as large as 1–2 eV), as shown in Fig. 6. The effects on the defect state wave functions can also be seen in Fig. 3 for the E_1 state. Note that the relaxation magnitudes for V_O^0 are similar to those found in the previous study in $KNbO_3$,^{17,18} but that there the relaxations for the positively charged state were found to have

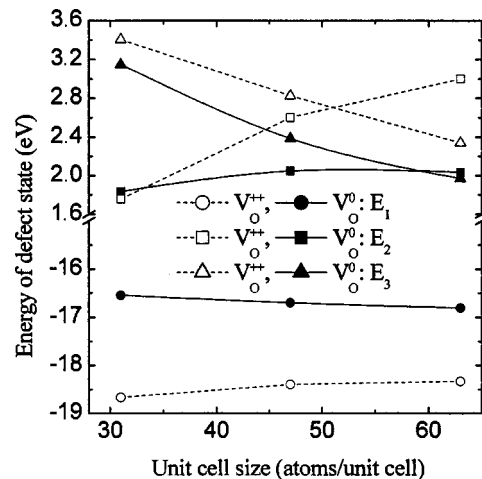


FIG. 6. Dependences of the energy levels on the supercell size and the vacancy charge state for three defect states.

very little difference from the neutral state. However, the phenomenon of the swing in relaxation has been generally observed in III-V and II-VI semiconductors.³³

Note that the notations V_O^{++} and V_O^0 introduced above only offer a very crude description for the *change* in the number of electrons, reduced by 2 for the V_O^{++} and no change for the V_O^0 , at the V_O site with respect to the perfect crystal. In fact, at the V_O site, there is actually no charge distribution for the V_O^{++} state (because the vacancy itself is neutral) but there is for the V_O^0 state (because two electrons occupy the E_2 state), when inspecting the total charge distribution of the system. Microscopically, as shown in Fig. 5, for V_O^{++} , the nearest two W ions move outward from their ideal positions, due to the loss of the Coulomb attraction from the O ion that used to be at the origin; while the eight nearest O ions move toward the vacancy, due to the loss of the balancing repulsion from the O ion. For V_O^0 , the nearest W ions move instead inward, due to the attraction of the two added electrons at the “ V_O site;” and those nearest O ions move back slightly, due to the restored repulsion. As the charge state changes from V_O^{++} to V_O^0 , the E_1 level moves from below the a_{1g} band to above it, and concurrently the energy of the E_2 state lowers significantly, as shown in Fig. 6. The changes in the energy levels can be understood in terms of

the drop of the electrostatic energy at the vacancy site and the rise of the electrostatic energy at the O sites along the [001] direction. The relative movement of E_1 and E_2 further corroborates their bonding-antibonding relation. With the change in the E_2 state occupation, the other defect state E_3 also experiences major changes both in its energy (see Fig. 6) and wave functions. However, the effects on the bulklike states are found to be minimal.

In summary, via self-consistent calculations, we provide a comprehensive understanding for the formation of vacancy defect states in strongly ionic crystals like WO_3 , which is very different from that for covalent semiconductors. We have found that the oxygen vacancy in WO_3 can generate three types of defect states: a hyperdeep one associated with the s -like bonding band, a high-lying one associated with the s -like antibonding band, and a donor state associated with the valence bands near the fundamental band gap. Such a finding is expected to be quite generally applicable to other related oxides.

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