

Theoretical Formation Energy of Oxygen-Vacancies in Oxides

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Formation energies of neutral and charged oxygen vacancies in MgO, ZnO, Al₂O₃, In₂O₃ and SnO₂ have been calculated by a first principles plane-wave pseudopotential method. Two kinds of polymorphs, *i.e.*, an ordinary phase and a high-pressure or an hypothetical negative pressure phase, have been chosen in order to see the effects of crystal structure. Supercells composed of 54 to 96 atoms were employed, and structural relaxation around the vacancy within second nearest neighbor distances was taken into account. Defect levels were obtained from the difference in total energies of the neutral and charged supercells that contain a vacancy. Ionization energies of the vacancy were calculated as the difference in the bottom of the conduction band and the defect levels. They are found to be proportional to band-gaps with a factor of approximately 0.5, which are prohibitively large for the *n*-type conduction.

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1. Introduction

Various kinds of metal oxides are used in modern technology. They are structural components, transparent conductors, solid state ionics, and catalysis, just to mention a few examples. Oxygen vacancies play major roles in diffusion-related phenomena as well as electrical and many other properties commonly in these oxides. Experimental information to elucidate directly the defect properties such as formation energy and migration energy of vacancies is very limited in spite of the importance. This is mainly due to the lack of high purity samples of good qualities that are necessary for detailed experiments. Because of the difficulty of the experimental works, calculations of the defect properties under various kinds of theoretical frameworks have been made. Early works using empirical and semi-empirical methods were very instructive and they provided good insight into the defect problems. However, these calculations cannot be predictive. In the worst cases, they may lead to wrong conclusion. In recent years, first principles calculations using supercells of reasonable sizes are gradually practicable. They can be used as important tools to solve the defect problems. In the present study, following a systematic investigation of neutral anion vacancies in selected oxides and nitrides,¹⁾ we report a systematic study of formation energies of oxygen vacancies in 10 kinds of oxides. Not only neutral vacancies but also charged vacancies are studied, since charged oxygen vacancies have been believed to occur in many oxides of simple metals.

2. Computational Procedures

The calculations in this work were performed within the generalized gradient approximation (GGA)²⁾ to density functional theory (DFT), using a plane-wave basis pseudopotential (PW-PP) method.³⁾ In order to reduce the size of the plane-wave basis-set, ultrasoft pseudopotentials⁴⁾ were

adopted. Theoretical heat of formation and lattice parameters of perfect crystals were calculated using primitive cells. They can be found in our previous report.¹⁾ Calculations of vacancies were made using the supercells in which the lattice parameters were fixed at the theoretical values for the perfect crystals. The number of atoms in the supercell was different depending on their crystal structures. It ranges from 54 to 96 atoms. Numerical integration over the Brillouin zone was carried out at the Γ point for the supercell calculations. The choice of the Γ point has been deliberately made in order to model the defect formation energy in the dilute limit.¹⁾ Plane-wave cutoff energies were chosen to be 380 eV, which were confirmed to achieve the convergence of the formation energies within 0.07 eV for the cutoff energies up to 700 eV. Spin polarization was not considered except for the case of O₂ since it is unlikely to affect the present results significantly. The atomic positions of the first and the second nearest neighbors of the defects were relaxed. The optimization procedure was truncated when the residual forces for the relaxed atoms were smaller than 2.5×10^{-9} eV/m.

The formation energies of oxygen vacancies were obtained as the difference in total energies of two supercells using the following equation.

$$E_{\text{VO}}^{\text{F}}(q) = E_{\text{T}}(\text{M}_a\text{O}_{b-1}, q) - E_{\text{T}}(\text{M}_a\text{O}_b, q) + \mu_{\text{O}} + qE_{\text{F}}, \quad (1)$$

The formation energy of a vacancy in a compound depends on the atomic chemical potentials of constituents and the electronic chemical potential, *i.e.*, the Fermi energy, E_{F} . The formation energy in eq. (1) corresponds to the vacancy in a charge state, q . E_{T} is the total energy of the supercell with the charge state q . a and b are the number of M and O atoms included in the supercell of the perfect crystal. μ_{O} is the atomic chemical potential of O. For charged vacancies, the total charge of supercells was neutralized using jellium background. Energy shifts associated with the jellium neutralization were estimated by the total energy difference be-

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tween the neutral (normal) and positively charged supercells of the perfect crystal; for the latter case, electrons were removed from the valence band maximum and the jellium neutralization was included. Correcting this energy shift should correspond to setting the valence band maximum to be the reference of the Fermi energy. Thus, the total energies of the supercells with positively charged vacancies were evaluated with this reference.

3. Results and Discussion

Figure 1 shows schematically the formation energy of an oxygen vacancy in M_aO_b as a function of the Fermi energy at two extreme cases. At the oxidation limit (or O-rich limit), μ_O is given by $E_T[O_2]/2$. At the reduction limit (or M-rich limit), μ_O is given by $(E_T[M_aO_b] - a \times E_T[M(\text{solid})])/b$. According to eq. (1), the formation energies at two cases differ by the difference in μ_O . It corresponds to the formation energy of M_aO_b per O atom, i.e., $\Delta H[M_aO_b]/b$ where $\Delta H[M_aO_b]$ is given by $E_T[M_aO_b] - (a \times E_T[M(\text{solid})] + b/2 \times E_T[O_2(\text{solid})])$. Although experimental data are generally defined with $O_2(\text{gas})$ as the standard not with the $O_2(\text{solid})$, we used $O_2(\text{solid})$ with the space group of $C2/m$ as the standard. The difference in E_T between the gas and the solid was found to be only 0.04 eV/atom. The energies that are marked by a square, a triangle and a circle in Fig. 1 are those obtained by calculations using eq. (1) and $E_F = 0$. Lines with a slope of q in eq. (1) are shown in the graph. E_F is measured from the top of the valence band. The charge state showing lowest formation energy at a given Fermi energy is highlighted as thick lines. In Fig. 1 the slope of the thick line changes from 2 to 1 at the intersection of lines with $q = +1$ and $q = +2$. The energy of intersection will be

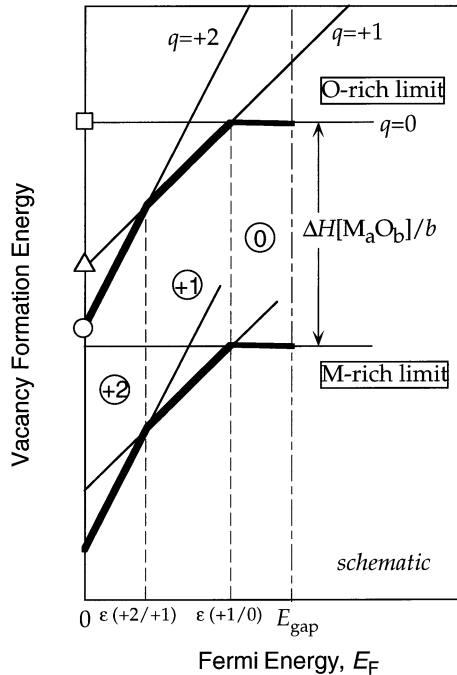


Fig. 1 Schematics of the formation energy of oxygen vacancies in oxides as a function of the Fermi energy. Thick lines correspond to the lowest formation energy at a given E_F . A number in a circle shows the charge that is most favorable at the given E_F .

denoted by $\varepsilon(+2/+1)$. The $q = +2$ state is more stable when $E_F < \varepsilon(+2/+1)$, and the $q = +1$ is favorable when $E_F > \varepsilon(+2/+1)$. There is another point of intersection at higher Fermi energy that corresponds to $\varepsilon(+1/0)$. The favorable charge state is shown in Fig. 1 with a number in a circle.

In five among ten oxides, we found that the point of intersection for $q = +1$ and $+2$ shows greater Fermi energy than the point of intersection for $q = +2$ and 0, as shown in Fig. 2 for rock-salt MgO. The $q = +1$ state is not expected to occur in this case. Charge state changes from $q = +2$ to 0 at $\varepsilon(+2/0)$. On the other hand, the direct transition from $q = +2$ to 0 is not expected to occur for the rest of the crystals. The idea is schematically drawn in Fig. 3. Note that the vertical axis of Fig. 3 is not the one-electron energy but the total energy.

Theoretical formation energies of oxygen vacancies obtained in the present study for five oxides with two different crystal structures for each compound are listed in Table 1 together with the values of ε , $\Delta H[M_aO_b]$ and the band

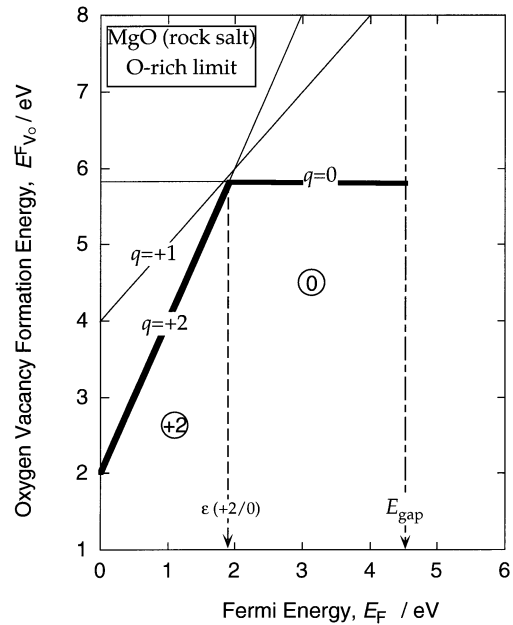


Fig. 2 The formation energy of oxygen vacancy at the oxidation limit in MgO with rock-salt structure as a function of the Fermi energy.

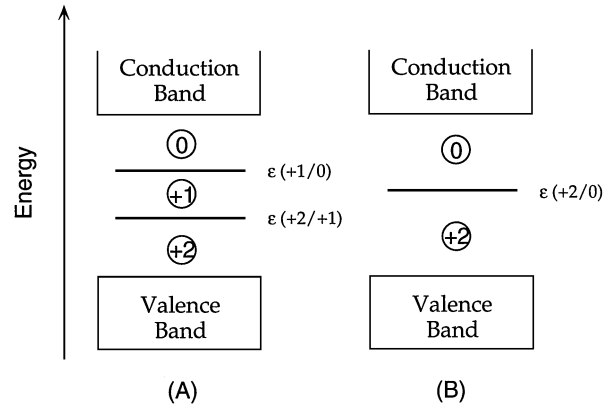


Fig. 3 Schematics of the defect levels. Vertical axis corresponds not to the one-electron energy but to the total energy. (A) corresponds to the case when $\varepsilon(+2/+1) < \varepsilon(+2/0)$, and (B) shows the case with $\varepsilon(+2/0) < \varepsilon(+2/+1)$.

Table 1 Theoretical heat of formation and formation energy of oxygen vacancies with $q = 0$ (neutral) and $q = 2$ (doubly ionized). Band-gap and defect levels are shown together.

Compound	Stable condition*	Structure	Heat of formation of compound (eV)	Formation energy of oxygen vacancy** (eV)		Band gap in perfect crystal (eV)	Defect level (eV)		
				$q = 0$	$q = +2$		$\varepsilon(+2/0)$ (eV)	$\varepsilon(+2/+1)$ (eV)	$\varepsilon(+1/0)$ (eV)
MgO	hypo. NP	wurzite	-5.36	5.78	2.04	3.54	1.87	1.90	1.85
	normal	rock salt	-5.51	5.83	1.99	4.51	1.92	1.98	1.85
ZnO	normal	wurzite	-3.06	3.13	2.15	0.96	0.49	0.88	0.11
	HP	rock salt	-2.75	1.88	0.80	1.06	0.54	0.53	0.56
Al ₂ O ₃	hypo. NP	bixbyite	-16.15	7.14	0.18	6.09	3.48	3.80	3.16
	normal	corundum	-16.35	7.08	1.32	6.90	2.88	3.07	2.69
In ₂ O ₃	normal	bixbyite	-7.81	1.53	0.29	1.05	0.62	0.56	0.67
	HP	corundum	-7.67	1.63	0.23	1.00	0.70	0.68	0.72
SnO ₂	normal	rutile	-6.04	3.49	2.41	1.26	0.54	0.50	0.58
	HP	fluorite	-5.05	-0.45	-0.41	0.29	-0.02	-0.05	0.01

*HP: high pressure phase, hypo. NP: hypothetical negative pressure phase.

**Values at $E_F = 0$ and the O-rich limit.

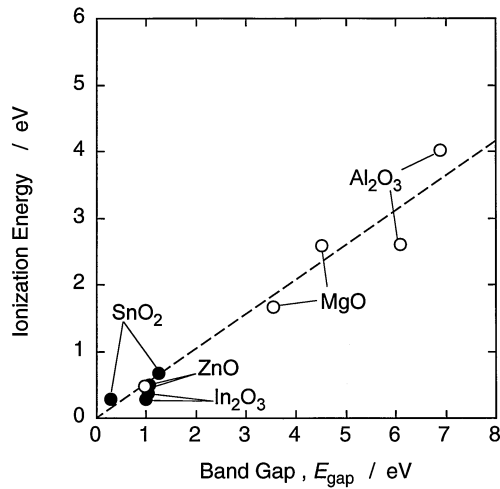


Fig. 4 The ionization of the oxygen vacancy as a function of the band gap for perfect crystal.

gap, E_{gap} . A high-pressure (HP) phase or an hypothetical negative pressure phase (hypo-NP) was chosen in order to compare the results with those of the ordinary phase. E_{gap} was calculated from the difference of the one-electron energies. Using total energies, it can also be calculated as $\{E_T^{(1)} - E_T^{(0)}\} - \{E_T^{(0)} - E_T^{(-1)}\}$, where $E_T^{(N)}$ indicates the total energy of the perfect lattice cell with additional N electrons. E_{gap} by two methods agree well within the difference of 0.1 eV. ε in *Italic numbers* in Table 1 corresponds to unfavorable transitions. The formation energy of a neutral oxygen vacancy at $E_F = 0$ is greater than that of a doubly ionized oxygen vacancy except for the case of fluorite-SnO₂. Consequently $\varepsilon(+2/0)$ shows positive values. In other words, the defect level is located within the band-gap as shown in Fig. 3.

The ionization energy of the vacancy can be defined as the difference of $\varepsilon(+2/0)$ or $\varepsilon(+1/0)$ and E_{gap} . Figure 4 shows the ionization energy as a function of E_{gap} . The ionization energy of the oxygen vacancy is almost proportional to the E_{gap}

with a factor of approximately 0.5. The trend is quite natural from the viewpoint of a simplified ionic model in which the bottom of the conduction band is composed of cation orbitals. Since the oxygen vacancy level is also composed of cation orbitals in the ionic model, the good correlation between E_{gap} and the ionization energy can be anticipated. In the previous paper, we have reported a rough correlation between the formation energy of a neutral oxygen vacancy and E_{gap} .¹⁾ The mechanism behind the relationship was explained using the simplified ionic model similar to the above discussion. However, the formation energies of a neutral oxygen vacancy of oxides of p -block elements in the Periodic table, such as ZnO, In₂O₃ and SnO₂ were found to be strongly dependent on the crystal structure as represented by the coordination number of cations. On the other hand in Fig. 4, the ionization energy does not show such dependence on the crystal structure. In other words, the ionization energy is less sensitive to the crystal structure than the formation energy of a neutral oxygen vacancy.

Oxides of p -block elements are often used as host-materials for transparent n -type conductors. Some experimental works concluded that the n -type conductivity in these compounds originates from the oxygen vacancies.⁵⁾ According to the present work, however, the absolute value of the ionization energy is the order of a few 100 meV that is prohibitively large for the n -type conduction. This implies that the presence of oxygen vacancies alone cannot contribute to the n -type conductivity in any of these compounds. The conclusion has already been obtained on wurzite-ZnO in our previous report.^{6,7)} Similar to that case, other kinds of defects, such as cation interstitials, defect complexes or unknown residual impurities could be the origin of donors in these compounds when they are undoped.

The use of GGA to treat the exchange and correlation terms on the DFT calculations is known to underestimate the E_{gap} . The error in the E_{gap} should affect the formation energy of vacancies as well as the defect levels. A method to correct

the formation energies of defects to overcome the underestimation has been suggested.⁸⁾ According to the prescription, the conduction band is rigidly shifted upward to match the experimental band gap. Donor-type defect states, which are expected to have characters similar to states in the conduction band, are assumed to increase by the energy of the conduction band shift multiplied by the occupation number of the defect states. The ionization energy of the oxygen vacancy is therefore unchanged even when we adopt the correction.

4. Conclusion

Formation energy of neutral and charged oxygen vacancies in five kinds of oxides with two crystal structures for each has been systematically evaluated using first principles plane-wave pseudopotential method. Supercells composed of 54 to 96 atoms were used. Five among 10 crystals showed $\varepsilon(+2/0)$ smaller than $\varepsilon(+2/+1)$. On the other hand, the direct transition from $q = +2$ to 0 was found unfavorable for the rest of the crystals. Defect levels appeared within the band-gap except for the case of fluorite-SnO₂. The ionization energy of the oxygen vacancy was found to be well scaled by the band-gap of the perfect crystal. Difference in crystal structures did not change the relationship. All crystals examined in the present study exhibited ionization energies that were

prohibitively large for the n -type conduction. It is concluded that the presence of the oxygen vacancies alone cannot contribute to the n -type conductivity in any of these compounds.

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