Theoretical Studies of Defects in Binary and Ternary Oxides*

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INTRODUCTION

In the past decade, there has been an explosive development of computational techniques utilizing high-speed computers to study the electronic and atomic structural properties of solids. These techniques form an important complement to laboratory experiments for providing a better understanding of spectroscopic properties, as well as the energetics of the solid systems. For ideal metallic and semiconducting crystal lattice with translational symmetry, the conventional energy band structure approaches are capable to provide a good degree of precision in both electronic structure and system energies. On the other hand the molecular-cluster model represents a convenient method of studying those properties that are primarily a function of the local environment of the system, such as vacancy, substitutional and interstitial defects.

In this paper, we will present some preliminary results of electronic structure of substitutional defects and vacancy in binary and ternary cubic zirconium oxides obtained by the embedded molecular-cluster model calculation. The importance of electronic charge redistribution in the solids where the defect is introduced into the perfect lattice will be highlighted and the effect of electron polarization of the surrounding ions of the defect will be discussed.

THEORETICAL APPROACH

A complete discussion of the X_α discrete variational embedded cluster method, based upon the self-consistent local density formalism, has been presented in previous works [1-4]. Only a brief review will be given here. The ground state electronic structure of ideal and defected clusters were obtained using the self-consistent discrete variational method. At the beginning of a self-consistent iteration, charge density for appropriate cations and anions are summed to form crystal densities. Coulomb and exchange potentials are evaluated as would be required for an ordinary band-structure calculation. In the case of vacancy, we introduced a virtual atom with electron wavefunctions but no potential at the vacancy site of the lattice. Cluster wavefunctions and energies are next found by variational solution of the Schrodinger (or Dirac-Slater for the relativistic code) equation, using a basis set constructed from numerical free-atom or ion wavefunctions. The cluster eigenstates are populated

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according to Fermi-Dirac statistics to obtain the charge density. The cluster charge density is decomposed according to a Mulliken population analysis to determine effective ion configurations which are then spherically averaged. The iteration loop is closed by summing ion densities to produce new cluster and crystal densities. This procedure is called the self-consistent-charge approximation to the potential. The embedding potential for ionic host lattice (here the host is everything not explicitly contained in the variational cluster) is obtained by the Ewald summation of long-range Coulomb terms, and direct summation over 200-300 nearby atoms of residual Coulomb potentials and charge densities obtained by self-consistent iterations.

Once the ground state energy levels and charge distributions are obtained, they are analyzed by Mulliken population scheme or volume partitioning to obtain an understanding of the binding mechanisms and as a reference state for comparison with perturbation by introduction of lattice relaxation and ion substitutions. The total energy is calculated in spin-restricted local-density-approximations by summing the various contributions [5]

$$E_t(\rho) = \langle t \rangle + \langle V_{\text{Coul}}^{\text{ne}} \rangle + \frac{1}{2} \langle V_{\text{Coul}}^{\text{ee}} \rangle + \frac{3}{4} \langle V_{\text{xc}} \rangle + V_{\text{Coul}}^{\text{nn}}$$

where t is the kinetic energy, V_{Coul} the Coulomb interaction energy due to both electrons and nuclei and V_{xc} is the exchange and correlation energy, the brackets denote summation over occupied levels making up the density ρ , as well as integration over spatial coordinates. The notation n,e refers to nuclear and electronic components, respectively. The total energies calculated in this fashion are of the order of 10^5 eV, and it is very difficult and expensive to obtain enough accuracy for direct comparison of energy difference. However, it is possible to extract a much more accurate binding energy with respect to some reference system energy over the same volume with the same sampling grid with the atoms in the same position but now assumed to be non-interacting. In this way, cohesive energy values, of the order of a few electron volts, are obtained to better than 0.01 eV.

RESULTS AND DISCUSSION

The effects of anion vacancy, cation substitution, atomic relaxation and cation-vacancy association on the electronic structure, charge transfer and electron polarization of a 31 atom cubic ZrO_2 cluster embedded in a

Table 1. Point group symmetry, gap energy, electronic charges of the cations, anion vacancy of ZrO_2 clusters with cubic fluorite structure.

	$\text{ZrO}_2(\text{A})$	$\text{ZrO}_2(\text{B})$	$\text{ZrO}_2(\text{B,Sc})$	$\text{ZrO}_2(\text{A,C})$	$\text{ZrO}_2(\text{A,V}^*)$	$\text{ZrO}_2(\text{A,V}^*,\text{Sc})$
Point group	Td or O	D_{4h}	D_{4h}	D_{3v} or D_3	Td or O	C_{3v} or D_3
E_g (eV)	6.30	6.67	5.40	5.00	4.57	3.60
E_{V^*} (eV)	--	--	--	--	0.62	0.56
Zr	+3.39	+3.79	+3.70	+3.34	+3.25	+3.26
Sc	--	--	+2.65	+2.63	--	+2.59
O	-1.66	-1.83	-1.81	-1.63	-1.77	-1.81
V^*	--	--	--	--	-0.28	-0.24

Fig. 1. 31 atom cluster of cubic ZrO_2 . Plane 1 is outlined by a dotted line and Plane 2 is marked by the heavy solid line. The numbers indicate the four Zr positions.

crystal lattice contains 64 unit cells of ZrO_2 , have been systematically studied. Because of space limitation, we can only select a few examples to highlight these effects.

Table I lists some of the results obtained from two cubic ZrO_2 cluster configurations with identical lattice parameters. Cluster A is an oxygen-centered cluster with 31 atoms as shown in Fig. 1. Cluster B is a Zr-centered cluster containing 13 atoms. In this cluster, the Zr is surrounded by eight near neighbor oxygens in cubic symmetry and four Zr near neighbors on the (0,0,0) plane in a square array. The gap energy, E_g , is the energy difference between the top of the valence band and the bottom of the conduction band. E_{V^*} is the energy of the vacancy state measured from the top of the valence band. V^* is the electronic charge of the oxygen vacancy. Symbols inside the parenthesis indicate clusters A or B with Sc substitution and/or vacancy. The results show that both the size and configuration of the cluster have an effect on the gap energy and the cation and anion charge. Introduction of vacancy and substitution of Zr by Sc strongly change the gap energy but only weakly affect the total electronic charge of the ions and the vacancy. The spatial distribution of the electron density at the ion and vacancy sites is modified in response to the change in bonding. Electron density redistribution are illustrated in the charge density difference maps of $\text{ZrO}_2(\text{A})$ clusters with and without a vacancy in the center, with a Sc ion substituted for a Zr ion and with two Sc ions substituted for Zr ions. Figures 2a and 2b show the electron density differences in plane 1 and plane 2 between the cluster with a vacancy in the center (vacancy cluster) and the "ideal" cluster. In the calculation all the atomic positions are fixed so that the redistribution of the electron density will not be biased by the atomic relaxation effect. It is quite evident that the change of electron distribution is not isotropic with the introduction of the vacancy in the center of this cubic cluster. The small decrease in the electron density of the surrounding ions is due to the transfer of some valence electrons from the neighboring ions to the vacancy site. Figures 3a and 3b show the charge density difference maps between a cluster of a Sc substituted for one Zr in site 1 and a vacancy in the center and the "vacancy" cluster. The electron density of the ions in the substitutional cluster is shifted away from the ion site in the [111] direction, thus forming butterfly-shaped positive and negative charge density regions in the contour maps. A more complicated electron redistribution is observed when two Sc ions substituted for the Zr ions next to the vacancy (position 1 and 2 in Fig. 1). The charge density difference contour maps show a positive and a negative region aligned in the [010] direction in plane 1 (Fig. 4a) and in the [100] direction in

Fig. 2. Electron density difference map of ZrO_2 with oxygen vacancy; (a) plane 1 and (b) plane 2.

plane 2 (Fig. 4b). This suggests that the electron density has an ellipsoidal shape, again shifted away from the lattice sites, with the long axis pointed in a $[111]$ direction. Results obtained from our calculation of different substituting elements in the same 31 atom cluster show a systematic variation in the atomic polarization. A more detailed report will be published elsewhere.

(a)

(b)

Fig. 3. Electron Density Difference map of one Sc substituted vacancy cluster; (a) plane 1 and (b) plane 2.

(a)

(b)

Fig. 4. Electron density difference map of two Sc substituted vacancy cluster; (a) plane 1 and (b) plane 2.

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