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Site symmetry approach applied to the supercell model of $MgAl_2O_4$ spinel with oxygen interstitials: *Ab initio* calculations

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ABSTRACT

In this study we simulate structural, electronic and phonon properties of $MgAl_2O_4$ spinel containing a single neutral oxygen interstitial (O_i) *per* crystalline *L*4 and *L*8 supercells, *e.g.*, its dumbbell formed with one of the nearest regular oxygen atoms of the lattice (O_i-O_{reg}). Due to the splitting of the Wyckoff positions in supercell models of a perfect crystal, five possible O_i positions with different site symmetry have been identified and studied (C_1, C_s, C_{3v} D_{2d} and T_d). First principles hybrid HSE06 DFT functional calculations on perfect and defective spinel structures have been accompanied by geometry optimization. The calculated properties of spinel crystal (lattice constants, bulk modulus, band gap as well as frequencies of infrared- and Raman-active vibrational modes) are in a good qualitative agreement with the corresponding experimental data. The formation energy of O_i is found to be minimal for the interstitial site of the lowest symmetry (C_1). The results obtained are important, in particular, for understanding the radiation and chemical stability as well as other key properties of $MgAl_2O_4$ spinel-type oxide crystals.

1. Introduction

Ternary spinel-type AB_2O_4 oxides known and studied for a rather long time [1–3] belong to the class of advanced compounds with various electrical, magnetic and optical properties. Spinel-structured magnesium aluminate ($MgAl_2O_4$), both single-crystalline and ceramic, characterized by cubic close-packed spatial crystalline morphology, possesses high transparency from visible to infrared wavelength range, enhanced strength and increased melting temperature, excellent chemical and radiation resistance as well as low electrical losses [4–6]. Combination of these properties makes magnesium aluminate suitable for a number of technological applications, although all of them require to consider influence of $MgAl_2O_4$ structural defects on the corresponding processes: (*i*) involvement in construction of fusion and fission reactors (inert matrices for nuclear fuels [7], windows for fusion reactors transparent in the radio-frequency range [8], *etc.*) where spinel demonstrates remarkable resistance to formation of structural damage caused by neutrons and light ions, *e.g.*, amorphous microareas inside $MgAl_2O_4$ lattice, which essentially weaken further penetration of irradiation; (*ii*) defective spinel crystals, colored or colorless, depending on what kind of point defects prevails in them (neutral or charged vacancies, native interstitials and anti-sites, impurity substitutes, pairwise defects, *etc.*), used in different electronic and optical devices [9–11] (as to irradiation in the range of visible spectrum, just presence of *F* centers is mainly responsible for it); (*iii*) supporting material for catalytic reactions possessing long-term durability [12,13] (it was found that oxygen vacancies at surface layers of a support play prominent role in dispersion of catalytic metal nanoclusters, their migration and stabilization); (*iv*) thin films of Mg-spinel used in humidity-measuring devices [14].

Essential theoretical efforts have been undertaken aiming to properly describe equilibrium geometry and electronic structure as well as chemical and physical (*e.g.*, elastic) properties of $MgAl_2O_4$ bulk in absence of any types of structural defects [15–19]. Mainly first principles calculations (within either plane-wave methods [15–17] or Gaussian-type orbital formalism [18]) as well as force-field simulations [19] were performed for this purpose.

Much more attention was paid so far to theoretical clarification of single defects' and their aggregates' influence on the structural, electronic and optical properties of $MgAl_2O_4$ and related ternary compounds [20–26]. According to systematic studies of defective $MgAl_2O_4$, presence of native defects can promote important changes in those properties [20]. The formation energies of various isolated defects in the most stable charge states were calculated for: (*i*), vacancies of magnesium (V_{Mg}), aluminum (V_{Al}) and oxygen (V_O); (*ii*) oxygen interstitial (O_i), (*iii*) magnesium and aluminum anti-sites (Mg_{Al} and Al_{Mg}),

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(*iv*) complex defects ($V_O + O_i$, $V_O + Al_{Mg}$, $V_O + Mg_{Al}$, $Mg_{Al} + Al_{Mg}$, *etc.*). It was concluded that anion vacancies can adequately compensate the observed deficit of positive charge. In order to study the influence of anti-site cation defects on the populations of other intrinsic defects [21], those were associated with Schottky and Frenkel reactions. Radiation-induced damages in magnesium aluminate were studied in Ref. [22]: in order to determine both the threshold displacement energies and the damage inflicted to the lattice, a series of molecular dynamical simulations on collision cascades in spinel were performed. The following point defects were chosen as favorable for those simulations: cation anti-site defects possessing small formation energy and high stability (the main source of electrical conductivity in spinel compounds); both O and Mg split interstitials and vacancies; on the other hand, isolated Al interstitials were found to be energetically unfavorable. Density Functional Theory (DFT) plane wave simulations of thermodynamic properties have been performed to study substitutes of isolated cations and oxygen vacancies in Mg-spinel [23]. The calculated formation enthalpy of magnesium cation substituted by Ca, Cu, and Zn ions indicated that transition metal dopants are energetically stable in $MgAl_2O_4$ bulk at low oxygen chemical potential. Point and small cluster defects in $MgAl_2O_4$ bulk spinel were simulated using both first principles (DFT) and empirical potential (modified Buckingham) approaches [24]. It was found that the latter overestimates the formation energies, but correctly assesses the relative favorability of various defect structures. Large-scale *ab initio* defect calculations performed on a large number of spinel oxides revealed the major trends of controlling their doping ability [25]. However, in spite of undertaken efforts, a number of properties of both perfect and defective spinel-type $MgAl_2O_4$ bulk are not yet completely clear.

Traditional approach to the aforementioned supercell models of the defective crystals usually begins with arrangement of a point defect (*e.g.*, O_i interstitial) at a position possessing the highest site symmetry. However, in our recent simulations of neutral oxygen atom interstitial in various supercells of binary α-Al_2O_3 oxide crystal the calculated formation energy of O_i was found to be minimal for the interstitial site of the lowest symmetry (C_1) [26]. The latter was found to be unstable with respect to the low-barrier transformation into split interstitial (dumbbell between it and one of its nearest regular oxygens O_i-O_{reg}) with an energy gain of 2.5 eV. Obviously, oxygen interstitial transport in corundum can be controlled by the dumbbell bond breaking and reforming. According to earlier simulations, neutral O_i atoms analogously tend to form split interstitials with O_{reg} in binary MgO oxide as well [27,28], morphology of which differs from that of α-Al_2O_3 by not only due to more simple face-centered cubic structure but also higher ionicity. The most stable O_i configuration in MgO was found to be dumbbell with an energy gain of 1.45 eV.

The purpose of our current study is to apply site symmetry formalism for better understanding of neutral O_i interstitial behavior in different supercell configurations of $MgAl_2O_4$ bulk (including possibility of its inter-lattice migration). The contents of the current paper is organized as the following: in Section 2, we adapt the formalism of site symmetry approach for O_i interstitials in Mg-spinel crystal; in Section 3, we describe computational scheme of *ab initio* hybrid DFT-LCAO calculations using HSE06 functional on perfect and defective $MgAl_2O_4$ spinel structures as well as their electronic and phonon properties; analysis of obtained results is given in Section 4, while the most important conclusions are formulated in Section 5.

2. Site symmetry approach to oxygen interstitials in spinel structure

The symmetry of $MgAl_2O_4$ spinel structure is described by non-symmorphic space group 227 $Fd\bar{3}m$ with face-centered cubic (*fcc*) lattice, the primitive unit cell of which (Fig. 1a) includes two formula units (14 atoms). For origin choice in description of this space group [29], atoms in spinel structure are distributed over Wyckoff positions in the following way. Mg and Al atoms occupy Wyckoff positions 8*a* (1/8 1/8 1/8) and 16*d* (1/2 1/2 1/2), corresponding to site symmetry groups *S*24 (space groups $\bar{4}3m$ *vs.* Schoenflies' point group T_d) as well as *S*12 ($\bar{3}m$ *vs.* D_{3d}), respectively. O atoms occupy Wyckoff positions 32*e* ($x\,x\,x$) with one free parameter x and site symmetry groups *S*6 (3*m* *vs.* C_{3v}). The multiplicities of Wyckoff positions are given here and in what follows for conventional (cubic) unit cell which consists of four primitive unit cells, *i.e.*, 8 formula units of $MgAl_2O_4$ spinel crystal (Fig. 1). In this study we use the designation *SP* for the site symmetry point group, consisting of *P* point symmetry operations.

For the oxygen interstitial in spinel structure, any of the following vacant Wyckoff positions could be used as an initial position in geometry optimization calculations: (a) two positions being parameter free – 8*b* (3/8 3/8 3/8) and 16*c* (0 0 0) with site symmetries *S*24 ($\bar{4}3m$ *vs.* T_d) and *S*12 ($\bar{3}m$ *vs.* D_{3d}), respectively; (b) one parameter-dependent positions 48*f* (x 1/8 1/8) and 96 *h* ($0\ y\ -y$) with site symmetries *S*4 (2*mm* *vs.* C_{2v}) and *S*2 (2 *vs.* C_2), respectively; c) two parameter-dependent positions 96 *g* ($x\,x\,z$) with site symmetry *S*2 (*m* *vs.* C_s) and general three parameter-dependent position ($x\,y\,z$) with site symmetry *S*1 (1 *vs.* C_1). Due to the undefined values of all the parameters contained in vacant Wyckoff positions, we place the interstitial oxygen in parameter-free positions 8*b* or 16*c* and model the defective crystal within Supercell model (SCM) [30].

Defining $\boldsymbol{a}_i(\Gamma_1)$ (i = 1, 2, 3) as the basic translation vectors of the initial direct Bravais lattice of type Γ_1 while $\boldsymbol{A}_j(\Gamma_2)$ (j = 1, 2, 3) as the basic translation vectors of the new Bravais lattice of type Γ_2 with the same point symmetry but composed of supercells, we can express the latter as:

$$\boldsymbol{A_j}(\Gamma_2) = \sum_i l_{ji}(\Gamma_2\Gamma_1)\boldsymbol{a_i}(\Gamma_1), \quad |\det l| = L \tag{1}$$

where $l_{ji}(\Gamma_2\,\Gamma_1)$ are integer elements of the matrix $l(\Gamma_2\,\Gamma_1)$ defining the transition from the lattice of Γ_1 type to the lattice of Γ_2 type. L is the number of primitive unit cells (Fig. 1a) in the supercell. We consider here two supercell transformation matrices:

$$\begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}, L = 4 \tag{2}$$

and

$$\begin{bmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{bmatrix}, L = 8 \tag{3}$$

Matrix (2) transforms the initial face-centered cubic lattice to a simple cubic lattice *i.e.*, the corresponding supercell is already mentioned as conventional cell for face-centered cubic lattice. This supercell consists of 8 $MgAl_2O_4$ formula units (Fig. 1b), *i.e.*, 56 atoms.

The transformation (3) with a diagonal matrix maintains the lattice type increasing the primitive unit cell translation vectors twice. The corresponding supercell consists of 16 $MgAl_2O_4$ formula units, *i.e.*, 112 atoms. Both supercell transformations (2) and (3) maintain the cubic point symmetry of the lattice. The interstitial atom in the approach traditional for SCM is placed at the vacant Wyckoff position with the highest possible site symmetry. In our case it is the vacant Wyckoff position 8*b* with the site symmetry *S*24 (T_d). In our opinion, this approach was used in the first principles supercell calculations [26] but, unfortunately, the details of the interstitial oxygen position choice are not given in that publication.

In the SCM models an interstitial oxygen is periodically repeated. Point defects are placed at positions with the site symmetry *SP*. The perfect spinel crystal possesses the symmetry of space group $G = Fd\bar{3}m = T_aF$, where T_a is the translation subgroup (formed by face-centered cubic lattice basic translations), $F = G/T_a = O_h$.

Supercell model of the defective crystal is described by a space group $G_d = T_AF_d$, where G_d, T_A and F_d are subgroups of G, T_a and F,