Prediction of ground-state structures and order-disorder phase transitions in II-III spinel oxides: A combined cluster-expansion method and first-principles study

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Ground-state structures of six II-III spinel oxides are predicted by combining the cluster expansion method and first principles calculations. The ground states of $MgGa_2O_4$ and $MgIn_2O_4$ are found to be inverse spinels with a tetragonal lattice, whereas those of $MgAl_2O_4$, $ZnAl_2O_4$, $ZnGa_2O_4$, and $ZnIn_2O_4$ are normal spinels with a cubic lattice. Order-disorder transition behaviors are examined using Monte Carlo simulations. The order-disorder transition to exchange octahedral and tetrahedral cations takes place as commonly accepted. In inverse spinels, a new kind of transition to exchange II and III cations in octahedral sites can be recognized, which has not been reported experimentally. Their transition temperatures are evaluated.

I. INTRODUCTION

Spinel oxides have been of great interest for many scientists not only due to their electronic and magnetic properties but also from mineralogical viewpoints. The spinel oxides have a general formula AB_2O_4. Cations A occupy one-eighth of fourfold-coordinated tetrahedral sites in a face-centered-cubic close-packed oxygen sublattice and cations B occupy half of sixfold-coordinated octahedral sites in normal structure. Barth *et al.* found that some spinels have inverse configurations, which are represented by a formula of $B[AB]O_4$.[1] Intermediate configurations $(A_{1-x}B_x)[AB_{2-x}]O_4$ also exist, where round and square brackets denote the tetrahedral and octahedral sites, respectively. The degree of inversion x ranges from 0 (normal spinel) to 1 (inverse spinel). As temperature increases, spinels, in particular $MgAl_2O_4$, were reported to show disordering to exchange tetrahedral and octahedral sites using various experimental techniques.[2–10] Many studies have been performed to categorize spinels into normal and inverse structures. Site preference of specific cations has been examined as well. Experimentally, the ground states of many spinels, especially the inverse spinels, have not yet been clarified because thermal equilibrium conditions are difficult to attain at low temperatures due to very low diffusion rates. For example, reported structure of $MgGa_2O_4$ scatters in a wide range of x values, i.e., 0.67,[11] 0.75,[12] 0.81,[13] 0.84–0.90,[14] and 1.[1] Additionally, it is often assumed that the symmetry of $MgGa_2O_4$ is the same as that of the normal spinels, i.e., cubic, but actual symmetry can be different considering a large degree of inversion. From a theoretical approach using an empirical model of electrostatic energy, II-III spinels with a larger internal parameter were estimated to have lower Madelung energy.[15] Larger cations were thought to prefer the tetrahedral site. The site preference depending on the number of d electrons in transition metal spinels were also discussed within the ligand field theory.[16,17] These classical calculations have indicated that the structure of the spinels is determined by the balance of many contributions such as the Madelung energy, the Born repulsive energy, ordering energy of cations, site preference energy, and polarization energy. The complexity renders quantitative determination of structural properties difficult.

Recent progress in first principles techniques makes it possible to predict material properties even in complicated systems quantitatively and systematically. For instance, structural properties of 18 compounds of II-III and IV-II spinels with normal and inverse structures were investigated[18] with the special quasirandom structure (SQS) models.[19] However, information obtained by a simple first principles calculation is limited to zero temperature for fixed alloy structures. Ground state structures are difficult to achieve in general due to the limitation in the size and number of models considered. An elaborate approach is necessary to elucidate them. We used the cluster expansion method,[20–22] which is often applied for phase diagram calculations.[23–25] Effective Ising Hamiltonian, which is dependent on lattice configuration, can be made from first principles total energies. Once the Hamiltonian is constructed, the ground state can be determined by searching the minimum energy in lattice configurations. Combining statistical mechanics methods such as Monte Carlo simulations or mean field approximations with the cluster expansion, the order-disorder phase transition can also be evaluated. In our previous study of $MgAl_2O_4$,[26] the ground state and order-disorder transition behavior were quantitatively reproduced using this combined approach. In the present paper, we report a systematic study on ground states and phase transition behavior of six II-III spinel oxides, $MgAl_2O_4$, $MgGa_2O_4$, $MgIn_2O_4$, $ZnAl_2O_4$, $ZnGa_2O_4$, and hypothetical $ZnIn_2O_4$.

II. METHODOLOGY

Within the cluster expansion formalism, configurational states are characterized by pseudospin configuration valuables σ_i for respective lattice sites i. Any function of the discrete configuration variables σ can be expanded in polynomials called cluster functions φ_α. The cluster function φ_α is simply defined as the product of configuration valuables σ_i which form a cluster α,

$$\varphi_\alpha = \prod_{i \in \alpha} \sigma_i, \qquad (1)$$

in addition to the empty cluster function $\varphi_0 = 1$. The configurational energy E can be expanded in cluster functions, and

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by averaging them, one can obtain the equation of

$$E = \sum_{\alpha} v_{\alpha} \langle \varphi_{\alpha} \rangle, \qquad (2)$$

where the coefficients v_{α} are called effective cluster interaction (ECI) with clusters α. The volume V can be also expanded as

$$V = \sum_{\alpha} V_{\alpha} \langle \varphi_{\alpha} \rangle, \qquad (3)$$

where V_{α} are coefficients of the cluster functions φ_{α}. In the present study, the oxygen atoms were not included explicitly in the cluster expansion, and we defined the up and down spins as the divalent and trivalent cations, respectively. The ECI can be determined by least-square fitting of Eq. (2) or Eq. (3) to the total energies or volumes of ordered structures obtained by the first-principles technique.

For the calculation of the total energies, we used the projector augmented-wave (PAW) method[27,28] within the local density approximation (LDA)[29,30] as implemented in the Vienna *ab initio* simulation package (VASP).[31–33] We calculated the total energies of 138 ordered structures selected randomly for each compound of the spinels. The Ga-*d* and In-4*d* states were treated as the part of valence. *k* points were sampled on the basis of the Monkhorst-Pack scheme[34] with $2 \times 2 \times 2$ grids. The plane-wave cutoff energy was set at 500 eV. Atomic positions and lattice constants were relaxed until the residual forces became less than 0.005 eV/Å.

In the cluster expansion, the cross-validation score (CV)[35,25] can be a criterion of the judgment whether a selected set of ECI reproduces the physical properties well. Focused on a cluster expansion for configurational energy, the CV is expressed as the root mean square of differences between those calculated from first principles and the energies predicted from the cluster expansion,

$$(\text{CV})^2 = \frac{1}{N} \sum_{m=1}^{N} (\hat{E}_{\text{CE}}^{(m)} - E_{\text{FP}}^{(m)})^2, \qquad (4)$$

where $E_{\text{FP}}^{(m)}$ indicates the energy of an order structure m calculated from first principles, and $\hat{E}_{\text{CE}}^{(m)}$ is the energy of the structure m predicted from the cluster expansion without using first-principles calculated energy of the structure m. A set of clusters should be selected so that the CV is minimized. In this work, we employed a genetic algorithm (GA),[36,37] where the information of candidate cluster expansion is lined up as genetic information. This makes it possible to optimize a set of correlated clusters to provide the minimum value of the CV rapidly and precisely. In this study, the mutation rate and the population size were set at 0.05 and 25, respectively. We selected 24 clusters from 94 clusters up to quadruplet that are possible within the unit cell. The CV reached less than 1.5 meV/cation for all the compounds of spinels. Once the best ECI are known, one can calculate finite temperature thermodynamic properties using statistical mechanics methods.

Finite temperature thermodynamic properties were evaluated using canonical Monte Carlo (MC) simulations with the Metropolis algorithm.[38] Supercells for the MC simulations
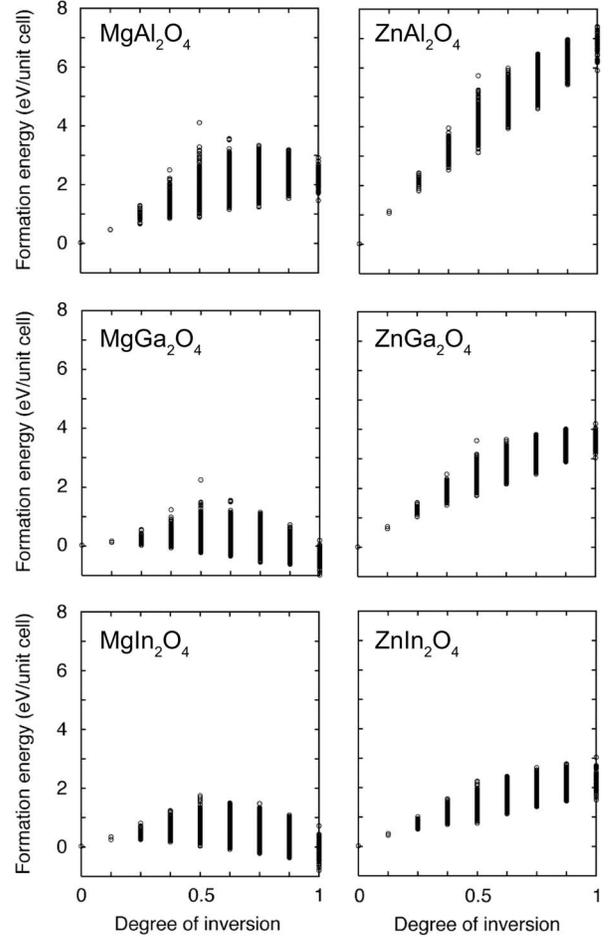

FIG. 1. Predicted formation energies using the ECI for all possible configurations within the 56 atom-unit cell in the six spinels.

were constructed by $10 \times 10 \times 10$ expansion of the unit cell, which contain 24 000 cations. We performed the simulation on 8000 MC steps per cation up to 2000 K to calculate thermodynamic averages after equilibration.

III. RESULTS AND DISCUSSION

A. Ground states

Once the ECI are obtained, the ground state of each compound of the spinels can be predicted in a straightforward manner. The ground state corresponds to the structure having the minimum formation energy. In A(II)B(III)$_2$O$_4$ spinel, the formation energy measured from the energy of the normal structure is expressed as

$$\Delta E = E_{(\text{A}_{1-x}\text{B}_x)[\text{A}_x\text{B}_{2-x}]\text{O}_4} - E_{\text{AB}_2\text{O}_4}, \qquad (5)$$

where $E_{(\text{A}_{1-x}\text{B}_x)[\text{A}_x\text{B}_{2-x}]\text{O}_4}$ is the energy of a cation-exchanged spinel and $E_{\text{AB}_2\text{O}_4}$ is the energy of the normal structure. Figure 1 shows the formation energies for all possible configurations within the unit cell of 56 atoms using the effective Hamiltonian constructed by the ECI in the six spinels. The ground states of the spinels obtained from the formation energies are summarized in Table I. MgAl$_2$O$_4$, ZnAl$_2$O$_4$,

TABLE I. Predicted ground states and lattice constants of the six spinels along with experimental data. The experimental structures and lattice constants are reproduced from Ref. 39.

Formula	Ground state		Lattice constant (Å)		
	Calc.	Expt.	a (Calc.)	c (Calc.)	a (Expt.)
$MgAl_2O_4$	Normal ($Fd3m$)	Normal	8.034		8.083
$MgGa_2O_4$	Inverse ($P4_322$)	Intermediate[a]	8.212	8.200	8.280
$MgIn_2O_4$	Inverse ($P4_322$)	Inverse	8.794	8.803	8.810
$ZnAl_2O_4$	Normal ($Fd3m$)	Normal	8.018		8.086
$ZnGa_2O_4$	Normal ($Fd3m$)	Normal	8.261		8.330
$ZnIn_2O_4$	Normal ($Fd3m$)		8.837		

[a]Reported structure scatters in a wide range of the degree of inversion as shown in Sec. I (Refs. 1 and 11–14).

$ZnGa_2O_4$, and $ZnIn_2O_4$ are predicted to be the normal spinels, while for $MgGa_2O_4$ and $MgIn_2O_4$, inverse configurations are obtained in consistency with experimental reports and the previous calculation.[18] We confirmed that the same ground states appeared in the simulated annealing as will be described later. Calculated lattice constants of the spinels are also shown in Table I. For the inverse spinels, detailed atomic configurations have not been determined by experiments. In the present study, the inverse structures at the ground states of $MgGa_2O_4$ and $MgIn_2O_4$ are found to be the same, which are shown in Fig. 2 along with the normal structure. All tetrahedral sites are occupied by Ga or In cations, and every tetrahedron which consists of nearest-neighbor octahedral sites has two Mg cations. The anisotropic distribution of divalent and trivalent cations at the octahedral sites lowers the symmetry from cubic to tetragonal.

B. Order-disorder transition behavior

Phase transition behavior can also be examined using the known ECI. Figure 3 shows calculated temperature dependence of the degree of inversion for the six spinels. The degrees of inversion in the normal and inverse spinels at the ground state, obtained by simulated annealing to 0 K, correspond to zero and one, respectively. The same ground-state structures as those predicted by the ground-state searches within the unit cell were found. As temperature increases, the
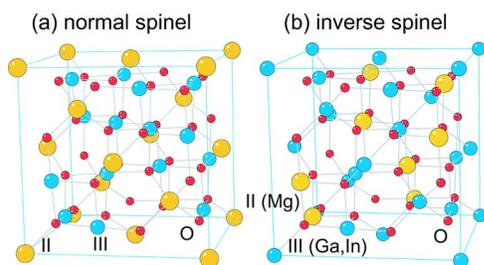
degree of inversion increases and will converge to 2/3 at the high temperature limit. Experimental data for the degree of inversion is available only for $MgAl_2O_4$,[2–10] which agrees well to the present calculation also as shown in our previous paper.[26] For the Zn spinels with the normal structure, the degree of inversion increases in the order of $ZnAl_2O_4$, $ZnGa_2O_4$, and $ZnGa_2O_4$. In the case of the Mg spinels, $MgAl_2O_4$ with the normal structure shows a degree of inversion as large as $ZnIn_2O_4$. $MgGa_2O_4$ and $MgIn_2O_4$ with the inverse structure show nearly the same degree of inversion. This tendency suggests the preference of the tetrahedral site is Zn>In>Ga>Mg>Al, which is not compatible with a proposed trend that the larger ions prefer the tetrahedral sites in II-III spinels;[15] the radii of fourfold-coordinated ions are In(0.76 Å)>Zn(0.74 Å)>Mg(0.71 Å)>Ga(0.61 Å) >Al(0.53 Å).[40]

In these spinels, the order-disorder transitions to exchange the tetrahedral and octahedral sites can be recognized. The transition temperature was defined as a maximum of the specific heat. The specific heat at a constant volume C_v at a temperature T can be calculated from the variance of the energy obtained from the known ECI and Eq. (2). It is expressed as

$$C_v = (1/k_B T^2)(\langle E^2 \rangle - \langle E \rangle^2), \qquad (6)$$

where k_B denotes the Boltzmann constant. The angel brackets indicate the average taken over MC trial steps. The left
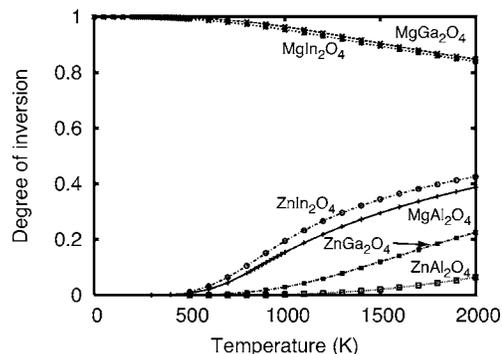

FIG. 2. (Color online) Crystal structures of (a) the normal spinel and (b) the inverse spinel predicted for the ground state of $MgGa_2O_4$ and $MgIn_2O_4$ are also shown. The symmetry of inverse configuration is tetragonal ($P4_322$), where all tetrahedral sites are occupied by trivalent cations, and every tetrahedron which consists of nearest-neighbor octahedral sites has two divalent cations.

FIG. 3. Calculated temperature dependence of the degree of inversion x in six spinels.

TABLE II. Estimated transition temperatures T_c to exchange tetrahedral and octahedral sites and to exchange octahedral and octahedral sites.

Formula	T_c (tetra-octa) (K)	T_c (octa-octa) (K)
$MgAl_2O_4$	860	
$MgGa_2O_4$	1300	270
$MgIn_2O_4$	1100	310
$ZnAl_2O_4$	>2000	
$ZnGa_2O_4$	1600	
$ZnIn_2O_4$	700	

FIG. 5. Calculated temperature dependence of the Warren-Cowley SRO parameter for the second nearest octahedron-octahedron pair in the inverse spinels.

column of Table II shows the resultant transition temperature for the six spinels. The transition does not happen up to 2000 K in the case of $ZnAl_2O_4$ spinel, while the others, including both normal and inverse spinels, show order-disorder transitions.

In similar fashion with the cluster expansion for the formation energy, once the ECI for the volume are obtained, the volume at a certain degree of inversion can be calculated from the average cluster function over MC steps. The CV for the volume reached less than 0.02 Å^3/unit cell for all the compounds of spinels. Figure 4 shows the dependence of the
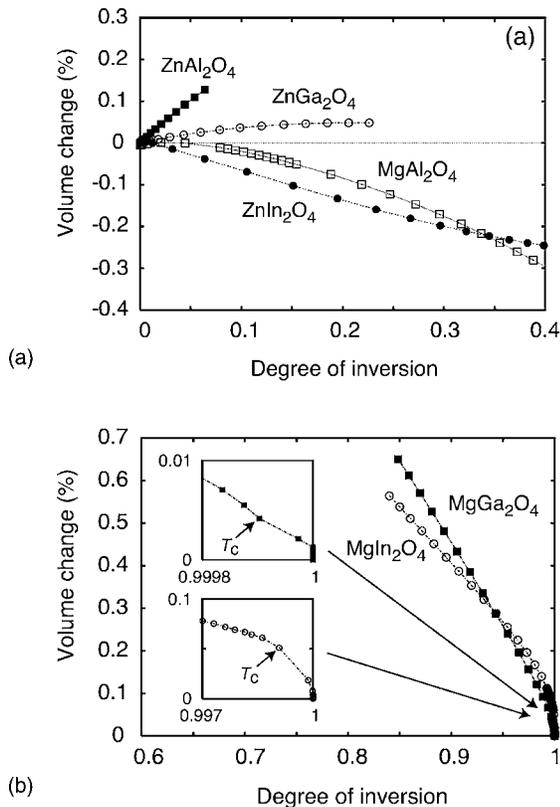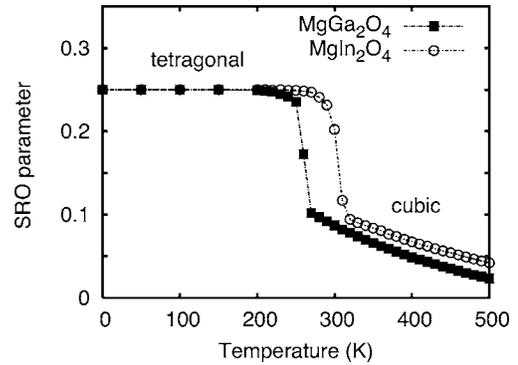

FIG. 4. The dependence of volume on the degree of inversion in (a) normal and (b) inverse spinels. The degrees of inversion at 0 K in the normal and inverse spinels correspond to zero and one, respectively.

volume on the degree of inversion for the six spinels. In the normal spinels of $ZnAl_2O_4$ and $ZnGa_2O_4$, the volume increases as the degree of inversion increases. In the normal spinels of $MgAl_2O_4$ and $ZnIn_2O_4$ and the inverse spinels of $MgGa_2O_4$ and $MgIn_2O_4$, the volume decreases as the degree of inversion increases. Experimental data for the dependence of volume on the degree of inversion is available only for $MgAl_2O_4$,[4] which agrees well to the present calculation.

Another interesting phase transition unknown experimentally is found at lower temperature in the inverse spinels of $MgGa_2O_4$ and $MgIn_2O_4$, which is the order-disorder transition to exchange II and III cations in the octahedral sites. The transition is attributed to the fact that a half of octahedral sites are occupied by II cations and the other half of octahedral sites are occupied by III cations at the ground state. The two kinds of cations at the octahedral sites exchange above the transition temperature. Figure 5 shows temperature dependence of the Warren-Cowley short-range order (SRO) parameter[41] for the second nearest octahedral-octahedral pair in the inverse spinels, determined by MC simulations at a finer interval of 10 K in temperature range of 200–500 K. The transition involves the change of the symmetry from tetragonal to cubic. As can be seen in the insets of Fig. 4(b), the tetragonal to cubic transition is associated with a finite volume gap. The right-hand column of Table II lists the transition temperatures. The transition occurs at 260 K and 310 K in $MgGa_2O_4$ and $MgIn_2O_4$, respectively, which are much lower than the transition temperature to exchange the tetrahedral and octahedral sites. Therefore, the phase transition to exchange the tetrahedral and octahedral sites should occur as the transition to exchange the tetrahedral and disordered octahedral sites.

IV. CONCLUSIONS

We determined the ground states of the six II-III spinel. $MgGa_2O_4$ and $MgIn_2O_4$ have inverse configurations, of which symmetry is found to be tetragonal. We also investigated phase transition behavior in the six spinels up to 2000 K. The order-disorder transition to exchange tetrahe-

dral and octahedral sites was seen in both the normal and inverse spinels. In the inverse spinels, we found that the phase transition occurs with two steps sequentially. They are (1) the cation disordering to exchange octahedral sites in conjunction to the change in symmetry from tetragonal to cubic starting from the ground state, and (2) the transition to exchange the tetrahedral and the disordered octahedral sites.

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