First-principles study of cation disordering in MgAl$_2$O$_4$ spinel with cluster expansion and Monte Carlo simulation

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The temperature dependence of cationic disorder in MgAl$_2$O$_4$ spinel is investigated using a combination of first-principles total-energy calculations, a cluster expansion, and canonical Monte Carlo simulations. The formation energies of the possible cation-disordered structures within the spinel unit cell are predicted to be all positive, suggesting that the ground state is the normal spinel in consistency with a widely accepted view. The temperature dependence of cationic disorder is well reproduced by considering many effective cluster interactions up to quadruplets. The order-disorder transition temperature is estimated at about 860 K based on the anomaly of specific heat. The cluster expansion of the volume of MgAl$_2$O$_4$ indicates that it decreases as more cations exchange.

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I. INTRODUCTION

II-III spinel oxides have a general formula AB$_2$O$_4$, where A and B cations are divalent and trivalent, respectively. In a normal spinel, the divalent cations occupy one-eighth of four-coordinated tetrahedral sites in a face-centered-cubic close-packed oxygen sublattice and the trivalent cations occupy half of six-coordinated octahedral sites as illustrated in Fig. 1. Some spinels show inverse configurations represented by a formula of B[AB]O$_4$, and intermediate configurations (A$_{1-x}$B$_x$)[A$_x$B$_{2-x}$]O$_4$ also exist, where the parentheses and the square brackets denote the tetrahedral and octahedral sites, respectively. The degree of inversion x ranges from 0 (normal spinel) to 1 (inverse spinel) and must be 2/3 in a completely random configuration.

It has been widely accepted that MgAl$_2$O$_4$ is a normal spinel in the ground state and belongs to the $Fd3m$ space group. At high temperatures, MgAl$_2$O$_4$ was revealed to show disordering between tetrahedral and octahedral sites with many experimental techniques such as neutron[1,2] and x-ray[3,4] diffractometry, high-resolution ^{27}Al nuclear magnetic resonance (NMR),[5–7] electron spin resonance (ESR),[8] and Raman spectroscopy.[9] In addition to the cation distribution, Wood *et al.* suggested that the entropy of MgAl$_2$O$_4$ at high temperatures was lower than the ideal configurational entropy due to short-range ordering.[5] Andreozzi *et al.* observed that both the lattice constant and internal oxygen positional parameter of MgAl$_2$O$_4$ decreased linearly along with the variation of the degree of inversion.[3]

Several computational approaches have also been made to investigate the behavior of cationic disorder. Using empirical interatomic potentials and Monte Carlo simulations, Lavrentiev *et al.* examined lattice constants, bulk moduli, and order parameters of five spinels, MgAl$_2$O$_4$, ZnAl$_2$O$_4$, FeAl$_2$O$_4$, NiAl$_2$O$_4$, and MgFe$_2$O$_4$, over a range of temperature and pressure along with the effects of ionic relaxation and lattice vibrations.[10] Using first-principle calculations based on the

density functional theory (DFT), Wei *et al.* investigated structural properties such as lattice constants, internal oxygen position, band gaps, and tetrahedral and octahedral nearest-neighbor (NN) cation-O bond length, of 18 compounds of II-III and IV-II spinels with normal and inverse structures.[11] The inverse spinels were modeled with the special quasi-random structure (SQS),[12] which was based on the fact that physical properties of an alloy are uniquely determined by its atomic structure, and that the structure can be quantified by atomic correlation functions. The temperature
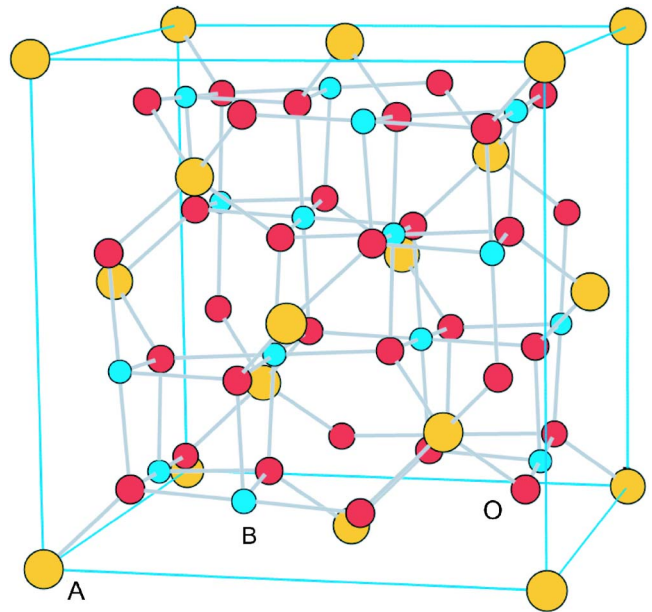

FIG. 1. (Color online) The structure of the normal spinel AB$_2$O$_4$. Cations A and B occupy one-eighth of four-coordinated tetrahedral sites and half of six-coordinated octahedral sites in the oxygen sublattice, respectively. The unit cell consists of 56 atoms containing 24 cations and 32 oxygen ions.

dependence of cationic disorder has also been studied, although only within a few short-range interactions, using statistical mechanics techniques to calculate the finite temperature properties. Warren *et al.* calculated the degree of inversion using a Monte Carlo simulation with a NN pair and a NN triangle interactions parameterized using the energies of 10 ordered structures obtained within local density approximation (LDA).[13,14] Rocha *et al.* studied the effects of high pressure on the cationic disorder using a mean-field approximation, in addition to the behavior under normal pressure.[15] The free energy of disordered spinels was evaluated from a modified effective thermodynamic model combining a regular solution with a quadratic form of the internal energy. In this framework, the internal energy is expressed as the average energy of selected structures since it is parameterized by fitting calculated energies to the quadratic form. The resultant degree of inversion includes an ambiguity associated with the approximation used in the estimation of internal energy as pointed out by themselves. Generally speaking, the prediction of order-disorder transition temperature and phase diagram characteristics needs millielectronvolt accuracy and many-body interactions.[16] Therefore, it is interesting to examine the cationic disorder in $MgAl_2O_4$ with further many-body interactions considered.

In this article, we report first-principle calculations on the cationic disorder in conjunction with a cluster expansion[17–19] and canonical Monte Carlo simulations. The cluster expansion formulates the configurational energy of a multicomponent system and is generally utilized for the calculations of phase diagrams of metal oxides.[20–22] The finite temperature effects were evaluated using canonical Monte Carlo simulations with effective cluster interactions (ECI) obtained from the cluster expansion.

II. METHODOLOGY

Calculating configurational energies for all possible structures allows us to describe the precise energetics of multicomponent systems. However, it is practically impossible except for very simple cases. One of the solutions is a cluster expansion,[17–19] which provides much information on ground states, configurational energy, and short-range order in multicomponent systems. Within this formalism, configurational states are characterized by pseudo-spin configuration variables σ_i for respective lattice sites i. We defined them as +1 (−1) if a magnesium ion (aluminum ion) exists at site i with the sublattice of oxygen fixed. 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 variables 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 by averaging them, one can obtain the equation of

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

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

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

where V_α are coefficients of the cluster functions φ_α. The ECI can be determined by least-square fitting to Eq. (2) or Eq. (3) using the total energies or volumes of ordered structures obtained by first-principles calculations.

An infinite number of clusters are theoretically necessary to reconstruct physical properties using fitted ECI. However, we can calculate a finite number of structural energies and select a finite number of clusters only. Therefore, the truncation of clusters is required to apply first-principles total energies to the cluster expansion practically. Here, a problem is how to select a set of ECI appropriate for a system of our interest. The cross-validation score (CV)[23,24] can be a criterion of the judgment whether a selected set of ECI reproduces the physical properties well. In the case of 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,

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

where $E_{FP}^{(m)}$ indicates the energy of an order structure m calculated from first principles, and $\hat{E}_{CE}^{(m)}$ 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 is selected so that the CV is minimized. In this work, we employed a genetic algorithm,[25,26] 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. Once the best ECI are known, one can calculate finite temperature thermodynamic properties using statistical mechanics methods. The GA found some other sets of clusters that give low CV scores. Some clusters are commonly present in these sets. They are all pairs and some kinds of triplets and quadruplets. All of these ECI with low CV scores were found to give the same formation energies and degree of inversion within the CV scores.

In order to calculate the formation energies of $(Mg_{1-x}Al_x)[Mg_xAl_{2-x}]O_4$ ordered phases necessary for the evaluation of ECI, we utilized the Vienna *Ab Initio* Simulation Package (VASP).[27–29] We defined the formation energy of a cation-exchanged spinel $(Mg_{1-x}Al_x)[Mg_xAl_{2-x}]O_4$ as the difference in total energy between the normal spinel, in which no cations were substituted, and a cation-exchanged spinel:

$$\Delta E = E_{(Mg_{1-x}Al_x)[Mg_xAl_{2-x}]O_4} - E_{MgAl_2O_4}, \qquad (5)$$

where $E_{(Mg_{1-x}Al_x)[Mg_xAl_{2-x}]O_4}$ is the energy of a cation-exchanged spinel and $E_{MgAl_2O_4}$ is the energy of the normal spinel. The interaction between ions and valence electrons was described by the projector augmented-wave (PAW) method.[30,31] The local density approximation (LDA)[32,33] was used as the exchange-correlation function. We performed total-energy calculations for 115 structures which consist of 56 atoms containing 24 cations and 32 oxygen ions and in which cations were substituted with the number of cations kept constant and the sublattice of oxygen fixed. k points were sampled on the basis of the Monkhorst-Pack scheme[34] with $2 \times 2 \times 2$ grids. The plane-wave cut-off energy was set at 500 eV. Atomic positions and lattice constants were relaxed until the residual forces became less than 0.001 eV/Å. The calculated lattice constant for the normal spinel is 8.034 Å, which is 0.6% smaller than an experimental value of 8.083 Å.[35] The anion displacement parameter of the normal spinel was calculated at 0.3885, which is 0.3% greater than an experimental value of 0.3874.[35] The vibrational and electronic degrees of freedom were neglected in this work.

Finite temperature thermodynamic properties were evaluated using canonical Monte Carlo (MC) simulations by the Metropolis algorithm.[36] Supercells for the MC simulations were constructed by $10 \times 10 \times 10$ expansion of the unit cell, which contain 24 000 cations. The simulations were performed on 8000 trial steps per cation for calculating thermodynamic averages of energy and cluster functions after equilibration over 8000 MC steps per cation. The temperature intervals of the MC simulations were set to 100 K from 300 to 2000 K and to 20 K around the critical temperature.

III. RESULTS AND DISCUSSIONS

By minimizing the CV using a genetic algorithm, an appropriate set of clusters for the $(Mg_{1-x}Al_x)[Mg_xAl_{2-x}]O_4$ system was searched. Figure 2 shows the resultant clusters. The 24 clusters were selected from 94 clusters up to quadruplet that are possible within the unit cell. The CV for the formation energy and the volume reached 1 meV/cation and 0.010 Å³/unit cell, respectively. The set of clusters is composed of 5 pairs, 8 triplets, and 9 quadruplets in addition to the empty and the point. Respective ECI for the formation energy and the volume are shown in Table I and Fig. 3. They are recognized that some small clusters such as the point and pairs show relatively large ECI and the values of ECI converge to zero as the number of sites or the distance between the sites in the cluster increases. The point clusters for the tetrahedral and octahedral sites are dependent on each other since we considered the structures in which only cations are substituted and the number of each cation is constant (Mg =8, Al=16). For this reason, we can assess only either of the point clusters for the tetrahedral or octahedral sites. In this study, the point cluster was defined as the tetrahedral sites. Figure 4 shows calculated formation energies using known ECI and Eq. (2) for all possible structures within the configurations of cations in the unit cell. The formation energies are all positive, indicating that the ground state is the normal spinel in consistency with a widely accepted view. This overall energetic trend is seemingly contradictory to the positive value of ECI for the formation energy of the point cluster. However, the point ECI term alone cannot determine the structure.

Similarly, the ECI for the volume of the point cluster is positive in Fig. 3(b), which contributes to the decrease in volume as the number of magnesium cations at the octahedral sites increases, that is, as the degree of inversion x increases. The ECI of the NN tetrahedral-octahedral pair numbered 4 in Fig. 2 is positive and the second largest when considering the total number of the clusters, which contributes to the decrease in volume when different cations occupy the sites that form the NN tetrahedral-octahedral pair. Eventually, the volume of the phases where cations are inverted can be determined in balance with all ECI for the volume.
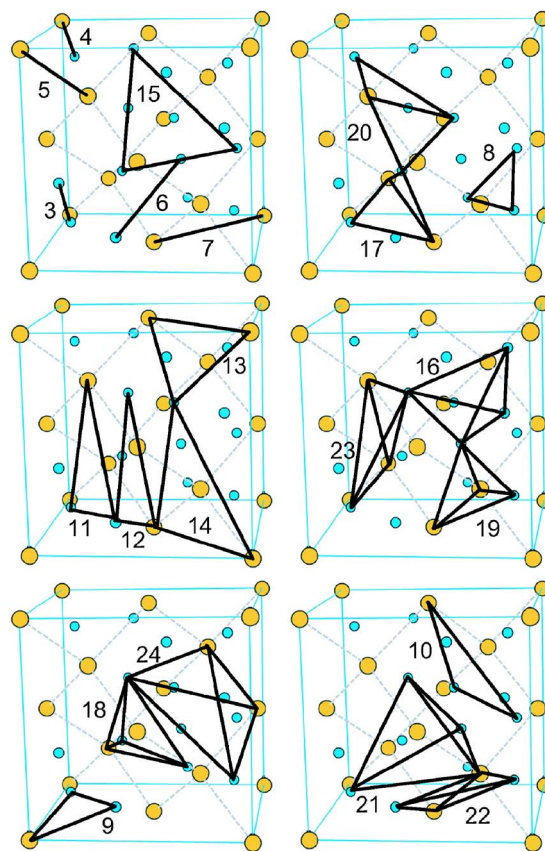

FIG. 2. (Color online) Selected clusters up to quadruplets by minimizing CV with the genetic algorithm. Large and small circles indicate tetrahedral and octahedral sites, respectively. The oxygen sublattice is excluded in this figure for easy visualization. The set of clusters consists of 5 pairs (numbered 3–7), 8 triplets (8–15), and 9 quadruplets (16–24).

TABLE I. Fitted ECI for empty and point clusters. v_α and V_α denote ECI for the energy and for the volume, respectively.

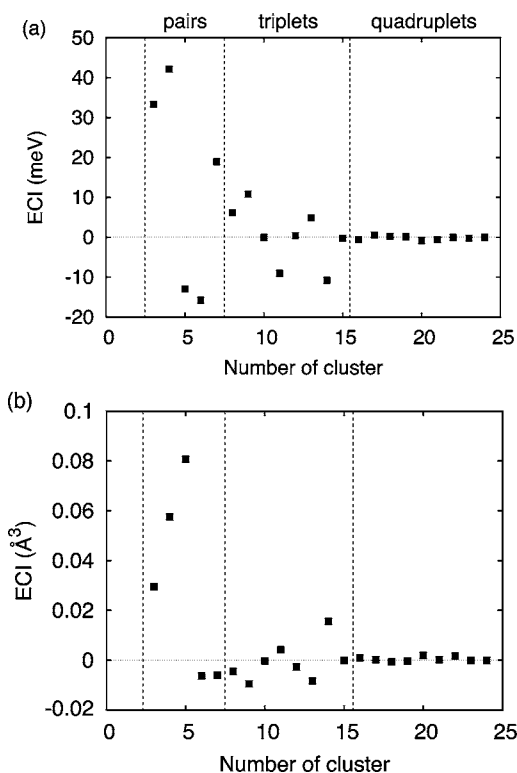| Number	Cluster type	v_α (meV)	V_α (Å³)
1	Empty cluster	227.6	−0.273
2	Point cluster (tetrahedral site)	44.6	0.925

FIG. 3. Fitted ECI for (a) formation energy and (b) volume. The transverse axis corresponds to the cluster numbers shown in Fig. 2.

Figure 5 shows calculated temperature dependence of the degree of inversion from Monte Carlo simulations using known ECI values. Experimental results reported by several groups are also presented along with the results of calculations by Rocha *et al.*[15] and Warren *et al.*[13] Although the experimental values are widely scattered, a tendency can be recognized that the degree of inversion increases with temperature. Below approximately 800 K, some experimental data show nearly no temperature dependence. The saturation may be ascribed to the failure to attain thermal equilibrium condition by experiment. Generally speaking, metal oxides with high melting temperatures are very difficult to attain thermal equilibrium conditions at low temperatures because of very low diffusion rates. The present results show good agreement with the experimental observations, in particular
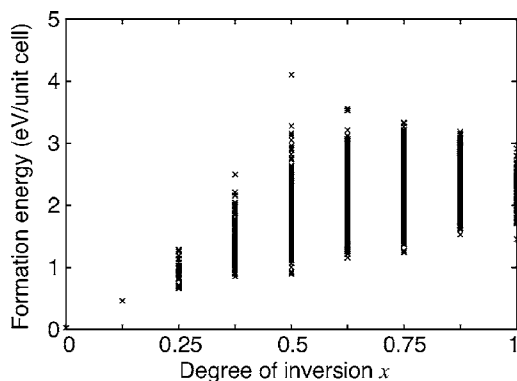

FIG. 4. Predicted formation energies for all possible configurations within the unit cell using ECI.
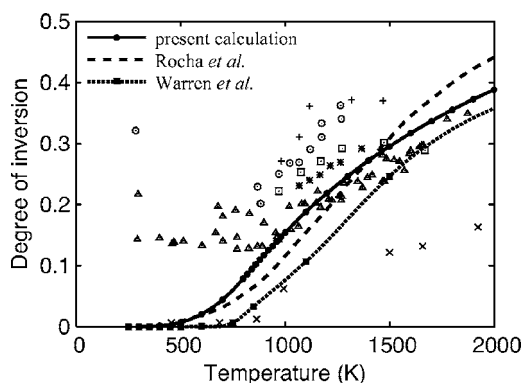

FIG. 5. Calculated temperature dependence of the degree of inversion x in $(Mg_{1-x}Al_x)[Mg_xAl_{2-x}]$, which is shown by the solid curve and the closed circles, compared with the previous calculations using a modified effective thermodynamic model by Rocha *et al.* (Ref. 15) (broken curve) and using a Monte Carlo simulation with a small number of interactions by Warren *et al.* (Ref. 13) (dotted curve and closed square). Also shown are experimental values with neutron diffraction measurements ($\bigcirc$[1]) ($\triangle$[2]), x-ray diffraction measurements ($*$[3]), ($\times$[4]), and NMR ($+$[5]), ($\square$[6]).

the result by Redfern *et al.*[2] The agreement seems to be better than the previous calculations by Rocha *et al.* and Warren *et al.* where smaller numbers of interactions were considered. Using a NN pair and one triplet interactions numbered 4 and 9 in Fig. 2 which Warren *et al.* used, we obtained a CV of 23 meV/cation, which is much larger than our result of 1 meV/cation with 24 clusters. The resultant degree of inversion x at 1000 K is 0.015, which is smaller than a value of 0.154 with 24 clusters by ourselves. This indicates that many interactions are indispensable for predicting the behavior of the order-disorder transition.

The order-disorder transition temperature is 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 known ECI and Eq. (2), and 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 bracket indicates the average taken over the trial steps. Figure 6 shows the specific heat obtained using the formation energies. The transition temperature is estimated to be about 860 K, which is close to experimental values of 750,[37] 870–970,[4] 950,[38] and 930 K.[39] Calculated volumes from Eq. (3) against the degree of inversion are shown in Fig. 7. These values are also very close to the experimental ones measured by x-ray diffraction method.[3] It should be noted that the experimental values were obtained at the room temperature for water-quenched samples after long enough annealing at elevated temperatures. Our theoretical values are for zero temperature. When plotted the volume change as in Fig. 7, the contribution of the difference should be small. As can be seen in Fig. 7, the volume of cation-exchanged spinel decreases as the degree of inversion increases. In other words, the volume has negative dependence on the degree of inversion in consistency with the experimental observation. This can be at-
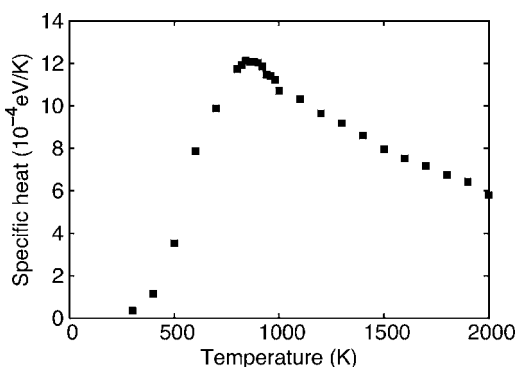
FIG. 6. Calculated specific heat using the formation energies. The transition temperature defined as a maximum value of the specific heat was estimated as about 860 K.
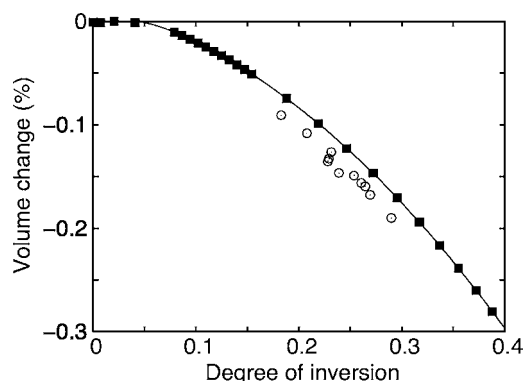

FIG. 7. Volume change from the normal spinel against the degree of inversion. Calculated values are shown by closed squares along with a fitted curve. Experimental values obtained with an x-ray diffraction measurement (Ref. 3) are also shown by open circles.

tributed mainly to the largest and positive ECI of the point cluster as described above.

IV. CONCLUSIONS

We investigated the behavior of cationic disorder in $MgAl_2O_4$ using a combination of first-principles total-energy calculations, a cluster expansion, and canonical Monte Carlo simulations. Effective cluster interactions in the cluster expansion were determined by minimizing the cross validation score (CV) using a genetic algorithm. Among the 94 clusters up to quadruplets that are possible within cation exchange in the spinel unit cell, a set of 24 clusters that provides the minimum CV was determined. The chosen cluster set well reproduced experimentally reported ground state structure, i.e., the normal spinel, and temperature dependence of the cationic disorder. The order-disorder transition temperature

was calculated as a maximum of specific heat. An estimated value of about 860 K is close to experimental values previously reported. Disordering with the increase of temperature gives negative contribution to the volume. The negative dependence of the volume on the degree of inversion was quantitatively reproduced.

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