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Grouping of structures for cluster expansion of multicomponent systems with controlled accuracy

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Control of errors over the whole range of structures is essential when we combine a large set of density-functional theory calculations and the cluster expansion method for predicting the ground-state structures and configurational thermodynamics of multicomponent systems. Minority structures that are far from a random structure are important for such a prediction. In this paper, we propose a procedure based on the cluster analysis of the structure population, which can adequately take into account the errors of minority structures as well as those of random structures. The usefulness of the procedure is demonstrated by applying it to configurational behaviors of MgAl₂O₄ spinel.

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I. INTRODUCTION

The cluster expansion (CE) method¹⁻³ is a powerful tool for predicting the ground-state structures, thermodynamics, and configurational properties of multicomponent systems. In order to make reliable thermodynamics with a high accuracy, a combination of the CE method and density-functional theory (DFT) calculations have mostly been adopted. An optimal CE is generally constructed from the DFT results of many ordered structures that are sampled from the total population of structures. In principle, the CE can be made without losing the accuracy of DFT calculations. To perform calculations at a wide range of structures will be shown.

II. CLUSTER ANALYSIS OF STRUCTURE POPULATION

A. Accuracy of conventional CE for minority structures

The CE method gives an effective representation of the configurational energy. Within the formalism of CE, the configurational energy $E$ of a binary system is expressed using the pseudospin configurational variable $σ_α$ for the respective lattice site $i$ and the effective cluster interactions (ECIs) $V$ as

$$E = V_0 + \sum_i V_i σ_i + \sum_{i,j} V_{ij} σ_i σ_j + \sum_{i,j,k} V_{ijk} σ_i σ_j σ_k + \cdots$$

where $ϕ_α$ is called the correlation function of the cluster $α$, which depends only on the atomic configuration. A principal objective is to estimate unknown ECIs from DFT calculations as precisely as the configurational properties can be predicted within the accuracy of DFT calculations.

The cross validation (CV) score⁴,⁵ has been widely accepted as a quantity for controlling the accuracy of the CE. The leave-one-out CV score is obtained from the squared average over $N_{\text{DFT}}$ input DFT structures as

$$(\text{CV})^2 = \frac{1}{N_{\text{DFT}}} \sum_{n=1}^{N_{\text{DFT}}} (\hat{E}_n - E_n)^2,$$

where $E_n$ denotes the DFT energy of structure $n$, and $\hat{E}_n$ is the energy of structure $n$ predicted by the CE without using the DFT energy of the structure $n$. For the accurate evaluation of the CV score, an optimal set of many DFT structures is necessary.⁶,⁷ In such a case, however, the errors of minority structures are only a minor part of the CV score. When the errors of minority structures are much larger than the average error, as shown in Fig. 2, they tend to be underestimated in the CV score.

Such a situation usually occurs when we truncate CE. The truncation error, which is the major source of total CE error, tends to be larger in minority structures in the general use of pseudospin values of $+1$ and $-1$ since they have larger values of correlation functions than a random structure. To make an accurate CE of such minority structures, an explicit evaluation of the errors of minority structures is essential.
be noted by \( \text{CV-CASP}^{(\xi)} \), which is defined as
\[
(\text{CV} - \text{CV-CASP}^{(\xi)})^2 = \frac{1}{N_{\text{DFT}}^{(\xi)}} \sum_{n=1}^{N_{\text{DFT}}^{(\xi)}} (\hat{E}_n - E_n)^2, \quad (4)
\]
where \( N_{\text{DFT}}^{(\xi)} \) denotes the number of DFT structures belonging to group \( \xi \). To distinguish CV-CASP from the average CV score, the latter will hereafter be called CV-AVE.

### III. Application to Configurational Behavior in Spinel Oxide

#### A. MgAl2O4 Spinel Oxide

We examine the quality of CV-CASP by constructing CEs to determine the configurational properties of cations between fourfold-coordinated tetrahedral and sixfold-coordinated octahedral sites in an fcc oxygen sublattice of MgAl2O4 spinel oxide. The MgAl2O4 spinel is a model system with complex interactions.11 Although the MgAl2O4 spinel is a typical ionic system, its electrostatic energy changes largely along with the change in the internal coordinates of oxygens. This implies that a large number of many-body clusters is required to express the energetics related to the cation configurations in the MgAl2O4 spinel. In such a system, errors associated with cluster truncation are anticipated to be large.

#### B. Computational details

First, CASP is performed in the MgAl2O4 spinel. Since the number of different structures in the total population is countable infinity, we need to prepare the structure population approximately. To construct an approximated structure population, we search for all symmetrically independent structures within the unit cell of the spinel containing 56 atoms in which 24 are cations. The number of such independent structures is 4222. An approximated structure population can also be prepared by other techniques such as a method for obtaining derivative structures.12 CASP is then performed by model-based cluster analysis. Here, we consider the correlation functions of 126 clusters up to quadruplets. The likelihood is maximized using the expectation-maximization (EM) algorithm for each of 100 kinds of Gaussian mixture models. We regard the model with the lowest Bayesian information criterion (BIC)13 among the 100 models as the best one. In the best model, the structure population is divided into four groups, which contain 114, 604, 1071, and 2433 structures, respectively. The ground-state structure, i.e., the normal spinel structure, belongs to group 1 (minority structures).

We then discuss how to find the optimal number of clusters and the optimal set of clusters. Since the accuracy of CE needs to be controlled mainly by four factors, namely, the number of clusters \( m \), the combination of clusters, the number of DFT structures \( N_{\text{DFT}} \), and the combination of DFT structures, we use all 4222 structures as an optimal set of input DFT structures. First, CEs with up to 40 clusters are constructed using a widely used procedure. The pseudospin values of Mg and Al are assigned to be +1 and −1, respectively. The set of clusters that minimizes CV-AVE is searched for from a pool of 126 clusters up to quadruplets using the genetic algorithm (GA).9 for each number of clusters. The ECIs of the selected

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**Figure 1.** (Color online) Schematic illustration of distribution function of structure population in space of correlation functions.

**Figure 2.** (Color online) Schematic illustration of typical distribution function of squared nonrandom errors.
Here, we construct CEs that minimize WCV-AVE with weights proportional to $1/N_{DFT}^{(2)}$. CV-CASP to the weighted fit (WCV-CASP) can also be defined by the same equation as Eq. (4), although the predicted energy is obtained from the weighted fit. The WCV-CASPs for all groups are shown in Fig. 3. Compared with the error with the minimization of CV-AVE, the error for group 1 is reduced. In other words, the minimization of WCV-AVE improves CE particularly for minority structures.

D. Practical procedure for constructing CE based on CASP

Although we have used the approximated structure population as an optimal set of DFT structures so far, a smaller set of DFT structures should be preferred for practical use. In our previous paper, we proposed an iterative procedure for obtaining an optimal set of DFT structures, where CV-AVE minimization and structure selection were repeated. In the procedure, structures that minimize the variance of the predicted energy estimated by linear regression were selected and were called “probe structures.”

The variance-minimization approach to structure selection was adopted. However, since the variance-minimization approach is based on linear regression, assuming that errors are distributed randomly, it is less suitable when a system has a nonrandom error distribution, as illustrated in Fig. 1(b). In such a case, DFT structures should be uniformly sampled in a configurational space. We propose a procedure that combines WCV-AVE minimization and DFT structure selection based on CASP.

The uniform sampling of DFT structures can be achieved by evenly selecting structures from all the groups divided by CASP. Here, CEs are constructed from DFT structures sampled evenly and randomly from all the groups. The number of clusters is fixed at 17. ECI s are estimated by the weighted fit with weights proportional to $1/N_{DFT}^{(2)}$. The set of clusters is optimized as WCV-AVE is minimized. Since DFT structures are picked up evenly from all the groups, all the DFT structures have the unit weight and WCV-AVE corresponds to CV-AVE.

To examine the quality of the CEs constructed by the proposed procedure, CEs are constructed from two kinds of DFT structures prepared by different sampling procedures. One is composed of high-symmetry structures (HSs), which have multiple symmetry operations. The other is composed of randomly selected structures (RAs). The CE error is approximately estimated from the RMS difference between the DFT and CE energies for all the structures in the structure population. Since the accuracy of the CEs made from the CASP and RA samplings is dependent on the selected structures, we perform CE ten times for each $N_{DFT}$ and estimate CE error by averaging the errors of ten CEs. Figure 4(a) shows the dependence of CE error on the number of DFT structures. As can be seen in Fig. 4(a), the CEs with the CASP and RA samplings are better than the CE with the HS sampling. In the CEs with the CASP and RA samplings, the errors are almost the same and converge at $N_{DFT} = 120$.

In order to examine the accuracy for a wide range of structures from a different viewpoint, the dependence of CE error on the DFT energy at $N_{DFT} = 120$ is shown in Fig. 4(b). In the CE with the CASP sampling, structures with a wide range of energies can be most precisely predicted among three sampling.
When constructing an optimal CE on the basis of WCV-AVE minimization without using the CE error estimated from the DFT energies for the structure population, the convergence of WCV-AVE should be examined using the probe structures in the same way as reported in our previous paper.\textsuperscript{7} Structures selected evenly from each group classified by CASP can be adopted as the probe structures. When the WCV-AVE evaluated with the probe structures of a trial CE converges, an optimal CE with $m$ clusters is obtained. Finally, by performing the CE for various $m$ values, the number of clusters can be determined using WCV-CASP.

IV. SUMMARY

We have proposed a CE technique that is reliable for predicting a wide range of structures including minority structures. The procedure is particularly useful when the CE errors of minority structures are larger than the average error. Such a situation occurs when we truncate CE in Eq. (1). To find an optimal CE in such a system, adequate estimation of the errors of minority structures is essential. In the proposed procedure, CASP enables us to distinguish structures and estimate the errors in each group. The accuracy of CE over a wide range of structures can be improved by optimizing CE in all the groups simultaneously by WCV-AVE minimization. This would lead to a more accurate prediction of the ground-state structures, thermodynamics, and configurational properties of multicomponent systems.

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