

**Renormalized interactions in truncated cluster expansions**

J. M. Sanchez

*Department of Mechanical Engineering, American University of Sharjah, Sharjah, United Arab Emirates*

(Received 25 January 2019; revised manuscript received 28 February 2019; published 24 April 2019)

It is shown that truncating the cluster expansion of the energy of alloys gives rise to renormalized effective cluster interactions that are explicit functions of the configurational variables. Such a dependence of the renormalized cluster interactions is in addition to their dependence on the volume of the alloy and on other structural parameters. The physical picture that emerges is different from the commonly used representation of the configurational energy by means of a generalized Ising-like model, which follows from the assumption that the contributions of the effective cluster interactions can be neglected beyond a relatively small cluster size. The physical picture is one in which the sum of the effective interactions contributes over long distances but the expected “near-sightedness” of the energy is preserved by the renormalized interactions. Furthermore, the cluster expansion is implemented by simultaneously fitting the volume- and configuration-dependent energy function to the zero-pressure values of the energies of formation, volumes, bulk moduli, and pressure derivatives of the bulk modulus of a set of ordered compounds. As an example of this formulation of the cluster expansion, we apply the methodology to the Cu-Au system for different types of cell-internal and cell-external relaxations.

DOI: [10.1103/PhysRevB.99.134206](https://doi.org/10.1103/PhysRevB.99.134206)**I. INTRODUCTION**

The cluster expansion (CE) method has been extensively used to describe the configurational energy of disordered alloys in terms of effective cluster interactions (ECIs), which, in turn, can be extracted from *ab initio* calculations of the total energies of a set of ordered compounds [1–6]. The consensus in the materials modeling community is that, in general, the method provides a satisfactory approximation to the energy of disordered alloys with any degree of chemical short-range order. Thus, the CE method effectively complements other approaches in alloy theory such as the single-site coherent potential approximation (CPA) [7], the generalized perturbation method (GPM) [8], and the quasirandom structures method [9].

In most implementations of the CE, it is implicitly assumed that the decay of the ECIs with the number of points and size of the cluster is sufficiently rapid so that their contributions to the configurational energy can be neglected beyond a maximum cluster size. The description that emerges from such a truncation criterion is a generalized version of the Ising model that can be conveniently used to calculate a variety of thermodynamic quantities, including temperature-composition phase diagrams [10–27]. We note that, in addition to a large number of bulk material systems, the CE has also been used to describe thermodynamic properties of thin films, surfaces, nanoparticles, and adsorbates [28–32].

Despite the apparent success of the many and diverse applications of Ising-like models to describe the configurational energy of alloys, it has been pointed out that such an approach amounts to a zeroth-order approximation of the CE formalism. In particular, it has been shown that the convergence of the CE can be improved significantly by allowing for a concentration dependence of the ECIs [5,6]. Here we show that, by considering a different criterion for truncating the CE, based on the size and range of the correlation functions

describing the short-range order in the alloy rather than on the range of the bare effective interactions, the ECIs are naturally renormalized into effective interactions that depend not only on concentration but also on the full state of short-range order of the alloy. As it is shown for the Cu-Au system, such renormalized cluster interactions result in significant improvements in the convergence, accuracy, and predictive capability of the CE.

The paper is organized as follows. In the next section, we briefly review the general formalism of the CE in order to set the terminology and notation necessary to develop, in Sec. III, the new truncation criterion. A different approach, also leading to the conclusion that the effective interactions are functions of short-range order, is followed in Sec. IV by noting that the correlation functions are specific versions of extensive thermodynamic variables which, due to Euler homogeneous functions theorem, imposes restrictions on the functional dependence of the effective interactions. The effect of both cell-internal and cell-external relaxations is the subject of Sec. V. The computation of the ECIs, which requires the inversion of a CE in which the ECIs are functions of the correlations, is addressed in Sec. VI.

**II. CLUSTER EXPANSION**

A key concept behind the theory of the CE is the existence of sets of orthogonal and complete basis functions which are defined on clusters of lattice sites and depend on occupation or spinlike variables. In particular, the lattice averages of such basis functions give rise to a set of configurational variables, commonly referred to as correlation functions, that provide a full description of the state of short- and long-range order of the alloy. These multisite correlation functions were initially introduced to calculate phase diagrams of prototype alloy systems using phenomenological Ising-like models

for the configurational energy [33–38]. The same multisite correlation functions were subsequently used by Connolly and Williams [39] to fit Ising-like models to the total energies of ordered compounds, obtained within density functional theory (DFT), thus suggesting an approach that could bridge *ab initio* energy calculations with the configurational thermodynamics theory of alloys.

The formal theory of the CE establishing the orthogonality and completeness of a particular basis set was developed by Sanchez *et al.* in 1984 [1]. In what follows, we will refer to such basis as the SDG basis. Subsequently, an infinite number of orthogonal and complete basis sets were introduced in order to conveniently capture the concentration dependence of the ECIs [2–5]. Although there are advantages in using different basis sets to carry out the CE, we note that most implementations of the CE to date have almost exclusively used the correlation functions in the SDG basis [5,6].

In what follows, we limit our discussion to binary systems in which two types of atoms decorate a periodic lattice of  $N$  sites  $\mathbf{p}$ . In general, the reference undecorated lattice can be described by a set of unit cell vectors and, in the case of a nonprimitive unit cell, by an additional set of base vectors. We will denote the structural parameters defining the undecorated lattice by  $\mathbf{a}_{uc}$ . The configuration of the lattice is then determined by a set of spinlike operators  $\sigma_{\mathbf{p}}$  that take values  $+1$  for  $A$  or  $-1$  for  $B$  atoms and, therefore, a given configuration is described by one of  $2^N$  vectors in configurational space of the form  $\boldsymbol{\sigma} = \{\sigma_{\mathbf{p}_1}, \sigma_{\mathbf{p}_2}, \dots, \sigma_{\mathbf{p}_N}\}$ . Furthermore, for a given phase of the alloy, we assume that atomic displacements relative to the undecorated lattice can be described by a set of  $N$  vectors  $\mathbf{u} = \{\vec{u}_1, \vec{u}_2, \dots, \vec{u}_N\}$ . Thus, in general, any physical property of a binary alloy, such as the energy of formation, will depend on a full set of structural and configurational variables  $\{\mathbf{a}_{uc}, \mathbf{u}, \boldsymbol{\sigma}\}$ .

To proceed with the CE we construct, for a given undecorated lattice, a set  $2^N$  distinct clusters of lattice points  $\mathbf{p}$  ranging from the empty cluster to the largest cluster that includes all  $N$  points in the lattice. Elements of the set of  $2^N$  clusters will be denoted by  $\boldsymbol{\alpha}$ . In turn, each  $\boldsymbol{\alpha}$  will be characterized by an index  $\eta$  that labels both the number of points and geometry of the cluster, the position of the cluster in the lattice, e.g., the point  $\mathbf{p}$  in the lattice associated to the center of mass of the cluster, and an index  $\nu$  that labels the “orientation” or orbit of the cluster; i.e.,  $\boldsymbol{\alpha} = \{\eta, \mathbf{p}, \nu\}$ . The fundamental idea of the CE is to describe any function of the  $2^N$  configurations  $\boldsymbol{\sigma}$  in terms of a set of  $2^N$  functions  $\phi_{\boldsymbol{\alpha}}^x(\boldsymbol{\sigma})$  defined for *each* possible cluster  $\boldsymbol{\alpha}$  of lattice sites. In their most general form, the basis functions are given by  $\phi_{\mathbf{0}}^x(\boldsymbol{\sigma}) = 1$  for the empty cluster ( $\boldsymbol{\alpha} = 0$ ) and, for the remaining  $2^N - 1$  clusters, by

$$\phi_{\boldsymbol{\alpha}}^x(\boldsymbol{\sigma}) = \prod_{\mathbf{p} \in \boldsymbol{\alpha}} \frac{(\sigma_{\mathbf{p}} - x)}{\sqrt{1 - x^2}}, \quad (1)$$

where the parameter  $x$  can take any value  $-1 < x < 1$ . Therefore, varying  $x$  gives rise to an infinite number of closely related configurational basis sets. In particular,  $x = 0$  corresponds to the SDG basis, for which the mapping  $\{\boldsymbol{\sigma}\} \rightarrow \{\boldsymbol{\alpha}\}$  is the well-known Hadamard transformation [5,40].

For a given value of  $x$ , the scalar product between two generic functions of configuration  $f(\boldsymbol{\sigma})$  and  $g(\boldsymbol{\sigma})$  is defined as

$$\langle f, g \rangle_x = \sum_{\boldsymbol{\sigma}} \mathcal{K}(x, \boldsymbol{\sigma}) f(\boldsymbol{\sigma}) g(\boldsymbol{\sigma}), \quad (2)$$

where  $\mathcal{K}(x, \boldsymbol{\sigma})$  is given by

$$\mathcal{K}(x, \boldsymbol{\sigma}) = x_A^{N_A(\boldsymbol{\sigma})} x_B^{N_B(\boldsymbol{\sigma})}, \quad (3)$$

with  $x_A = 1 - x_B = (1 + x)/2$ , and where  $N_A(\boldsymbol{\sigma})$  and  $N_B(\boldsymbol{\sigma})$  are, respectively, the number of  $A$  and  $B$  atoms in configuration  $\boldsymbol{\sigma}$ . Under the definition of the scalar product of Eq. (2), orthogonality and completeness of the basis functions are expressed as

$$\sum_{\boldsymbol{\sigma}} \mathcal{K}(x, \boldsymbol{\sigma}) \phi_{\boldsymbol{\alpha}}^x(\boldsymbol{\sigma}) \phi_{\boldsymbol{\beta}}^x(\boldsymbol{\sigma}) = \delta_{\boldsymbol{\alpha}, \boldsymbol{\beta}} \quad (\text{orthogonality}), \quad (4)$$

$$\sum_{\boldsymbol{\alpha}} \mathcal{K}(x, \boldsymbol{\sigma}) \phi_{\boldsymbol{\alpha}}^x(\boldsymbol{\sigma}) \phi_{\boldsymbol{\alpha}'}^x(\boldsymbol{\sigma}') = \delta_{\boldsymbol{\sigma}, \boldsymbol{\sigma}'} \quad (\text{completeness}). \quad (5)$$

From the completeness of the basis functions, it follows that the basis sets for different values of  $x$  are related by a linear transformation of the form

$$\phi_{\boldsymbol{\alpha}}^x(\boldsymbol{\sigma}) = \sum_{\boldsymbol{\beta}} \mathcal{B}_{\boldsymbol{\alpha}, \boldsymbol{\beta}}^{x, x'} \phi_{\boldsymbol{\beta}}^{x'}(\boldsymbol{\sigma}), \quad (6)$$

where  $\mathcal{B}_{\boldsymbol{\alpha}, \boldsymbol{\beta}}^{x, x'} = \langle \phi_{\boldsymbol{\alpha}}^x, \phi_{\boldsymbol{\beta}}^{x'} \rangle_{x'}$ . The coefficients  $\mathcal{B}_{\boldsymbol{\alpha}, \boldsymbol{\beta}}^{x, x'}$  relating a basis for a given value of  $x$  to a different basis  $x'$  are given in Ref. [5].

With the above formalism, we can write the configurational energy  $E(\mathbf{a}_{uc}, \mathbf{u}, \boldsymbol{\sigma})$ , defined on a *fixed* undecorated lattice, as

$$E(\mathbf{a}_{uc}, \mathbf{u}, \boldsymbol{\sigma}) = \sum_{\boldsymbol{\alpha}} j_{\boldsymbol{\alpha}}^x(\mathbf{a}_{uc}, \mathbf{u}) \phi_{\boldsymbol{\alpha}}^x(\boldsymbol{\sigma}), \quad (7)$$

with the ECIs given by the projection of  $E(\mathbf{a}_{uc}, \mathbf{u}, \boldsymbol{\sigma})$  onto the basis functions  $\phi_{\boldsymbol{\alpha}}^x(\boldsymbol{\sigma})$ :

$$j_{\boldsymbol{\alpha}}^x(\mathbf{a}_{uc}, \mathbf{u}) = \langle E(\mathbf{a}_{uc}, \mathbf{u}, \boldsymbol{\sigma}), \phi_{\boldsymbol{\alpha}}^x \rangle_x. \quad (8)$$

The notation in Eq. (7) is purposely chosen to emphasize the fact that, in principle, a CE requires that the energies used to determine the ECIs be for configurations of the system on a *fixed* lattice. Thus, for example, if the volume of the undecorated lattice changes, a different set of energies will be required to calculate the ECIs at the volume in question which, obviously, translates into a volume dependence of the ECIs. The same is true if the undecorated lattice is subject to other cell-external or cell-internal relaxations.

We point out that, provided *all*  $2^N$  clusters  $\boldsymbol{\alpha}$  are included in the sum, Eq. (7) for the configurational energy is exact and, furthermore, for a rigid undecorated lattice the ECIs given by Eq. (8) are constant (i.e., they do not depend on concentration and/or other configurational variables). Thus, at a fixed volume and in the absence of other relaxations, it follows that an Ising-like model that includes interactions for *all* clusters  $\boldsymbol{\alpha}$  is an *exact* representation of the energy of the alloy. However, since for real alloys the structural parameters  $\mathbf{a}_{uc}$  and  $\mathbf{u}$  will in general depend on concentration and other configurational variables, the Ising-like model representation with constant ECI will necessarily break down. In the next section, we show that the Ising-like representation of the

energy also breaks down if the expansion is truncated beyond a given set of clusters.

### III. TRUNCATED CLUSTER EXPANSION

The argument commonly used to justify the truncation of the CE is that the coefficients  $j_\alpha^x$  in Eq. (7) decay sufficiently quickly with cluster size so that they can be neglected for clusters larger than a judiciously chosen maximum cluster and/or characteristic distance. While there is evidence that the ECIs indeed decay with size and/or distance, the effect of their sum over a total number of clusters of the order of  $2^N$  is important and cannot be dismissed *a priori*. As shown below, the correct criterium to truncate a CE is to include only those correlations, or equivalently configurational dependences, that arise from the basis functions of a set of relatively small clusters. Such an approach results in approximations to the configurational energy in terms of rapidly decaying renormalized effective interactions. Importantly, the approach avoids making *ad hoc* assumptions about the decay of the Ising-like interactions. In reference to the success of the commonly used Ising-like model, we note that the contributions of higher order ECIs can be masked by fitting the energies of a relatively small number of structures, which is generally achieved with a relatively small number of parameters (or ECIs). However, the contributions to the energy of the Ising-like interactions for large clusters become evident as the number of structures included in the CE increases, as has been shown previously for the Mo-Ta system [6]. We note that the same behavior is observed in the Cu-Au system. In particular, a previous application of the Ising-like model to the Cu-Au system was shown to achieve a good fit to a relatively small set of training structures with a few ECIs [41,42]. However, as shown in Sec. VII, the Ising-like model is expected to have poor predictive capabilities. Thus, using a small set of training structures actually masks the deficiencies of the Ising-like model and, furthermore, incorrectly suggests a fast decay of the bare ECIs.

In order to explore the effect of truncating the CE, we consider the representation of the energy of Eq. (7) in the SDG basis and on a rigid undecorated lattice. To simplify the notation, we do not include in what follows the dependence of the energy, or of the ECIs, on the structural parameters  $\mathbf{a}_{uc}$  and  $\mathbf{u}$ . Furthermore, we split Eq. (7), which is exact, into a sum over a set  $\{\alpha\}_s$  of “small” clusters, which includes all clusters in the truncated CE, and a sum over the set of “large” clusters  $\{\beta\}_l$ . By definition, the set  $\{\beta\}_l$  is such that (i) it does not include any cluster in  $\{\alpha\}_s$  and (ii) the union of the sets  $\{\alpha\}_s$  and  $\{\beta\}_l$  contain all distinct  $2^N$  clusters in the lattice. The set  $\{\alpha\}_s$  contains a set of maximum clusters  $\{\alpha_{\max}\}_s$ , plus all their subclusters, and includes the empty cluster. Thus, Eq. (7) can be written as

$$E(\sigma) = \sum_{\alpha \in \{\alpha\}_s} j_\alpha^0 \phi_\alpha^0(\sigma) + \sum_{\beta \in \{\beta\}_l} j_\beta^0 \phi_\beta^0(\sigma). \quad (9)$$

Note that the number of clusters in the set  $\{\alpha\}_s$ , which will be denoted by  $M_s$ , is of order  $N$ , while the number of clusters in the set  $\{\beta\}_l$  is of the order  $2^N$ . Thus, the assumption that the contribution of the second sum in Eq. (9) can be neglected is not immediately obvious.

To elucidate the nature of the second sum in Eq. (9), we note that the basis function  $\phi_\beta(\sigma)$  for *any* of the clusters in the set  $\{\beta\}_l$  can be written as a product of basis functions  $\phi_\alpha(\sigma)$  corresponding to clusters in the set  $\{\alpha\}_s$ :

$$\phi_\beta^0(\sigma) = \prod_{\alpha \in \{\alpha\}_s} \phi_\alpha^0(\sigma). \quad (10)$$

In general, and depending on the cluster  $\beta$ , the product in Eq. (10) involves two or more clusters in the set  $\{\alpha\}_s$ .

We next introduce the operation of joining two clusters  $\alpha$  and  $\alpha'$ , denoted by  $\alpha * \alpha'$ , that produces a cluster formed by the union of both clusters but eliminates all sites belonging to the intersection of  $\alpha$  and  $\alpha'$ ; i.e.,  $\alpha * \alpha'$  is the complement, with respect to  $\alpha \cup \alpha'$ , of  $\alpha \cap \alpha'$ .

With this definition, and using Eq. (10), the second sum in Eq. (9) can be written as

$$\begin{aligned} & \sum_{\beta \in \{\beta\}_l} j_\beta^0 \phi_\beta^0(\sigma) \\ &= \sum_{\alpha \in \{\alpha\}_s} \phi_\alpha^0(\sigma) \left[ \sum_{\substack{\alpha' \in \{\alpha\}_s \\ \alpha * \alpha' \in \{\beta\}_l}} j_{\alpha * \alpha'}^0 \phi_{\alpha'}^0(\sigma) \right] + \dots \quad (11) \end{aligned}$$

We emphasize that the first sum on the right-hand side of Eq. (11) is carried out over all clusters  $\alpha$  belonging to the set  $\{\alpha\}_s$ , while the second sum is carried out, for each cluster  $\alpha$ , over all distinct clusters  $\alpha'$  such that the cluster  $\alpha * \alpha'$  belongs to the set  $\{\beta\}_l$ . Contributions to the sum over the set  $\{\beta\}_l$  arising from joining three or more clusters in  $\{\alpha\}_s$  are not explicitly shown in Eq. (11).

The evaluation of the sums on the right-hand side of Eq. (11) represent a problem of significant complexity. However, for our purposes, and since the effective interactions in the CE are obtained by fitting the energies of a set ordered compounds, it is sufficient to note that (i) the sums in question are carried out only over clusters that belong to the set of “small” clusters  $\{\alpha\}_s$  and (ii) that such sums effectively renormalize the long-range bare interactions for the “large” clusters into short-range effective interactions for the “small” clusters that are to be kept in the truncated expansion. Thus, Eq. (11) can be written as

$$\sum_{\beta \in \{\beta\}_l} j_\beta^0 \phi_\beta^0(\sigma) = \sum_{\alpha \in \{\alpha\}_s} \Delta j_\alpha^0(\sigma) \phi_\alpha^0(\sigma), \quad (12)$$

with

$$\Delta j_\alpha^0(\sigma) = \sum_{\substack{\alpha' \in \{\alpha\}_s \\ \alpha * \alpha' \in \{\beta\}_l}} j_{\alpha * \alpha'}^0 \phi_{\alpha'}^0(\sigma) + \dots \quad (13)$$

Therefore, the expansion of the configurational energy, Eq. (9), becomes

$$E(\sigma) = \sum_{\alpha \in \{\alpha\}_s} j_\alpha^0(\sigma) \phi_\alpha^0(\sigma), \quad (14)$$

with  $j_\alpha^0(\sigma) = j_\alpha^0 + \Delta j_\alpha^0(\sigma)$ . Note that, for the empty cluster,  $\Delta j_0^0(\sigma) = 0$ .

Although the configurational dependence of the ECIs in a truncated CE was derived using the SDG basis, the result is

equally valid for any configurational basis since the different basis sets are related by the linear transformation  $\{\mathcal{B}_{\alpha,\beta}^{x,x'}\}$  [5]. In particular, the ECIs in a basis for any value of  $x \neq 0$  can be obtained from those in the SDG basis ( $x = 0$ ) as follows:

$$j_{\alpha}^x(\sigma) = \sum_{\beta} j_{\beta}^0(\sigma) \mathcal{B}_{\beta,\alpha}^{0,x}, \quad (15)$$

which allow us to write the truncated CE of the energy in any basis as

$$E(\sigma) = \sum_{\alpha \in \{\alpha\}_s} j_{\alpha}^x(\sigma) \phi_{\alpha}^x(\sigma). \quad (16)$$

The results expressed by Eqs. (9)–(16) explicitly show that the truncation of the CE renormalizes the original ECIs into interactions that now depend on the full state of order of the system including, of course, the concentration of the alloy. In the spirit of the CE, which ultimately fits the ECIs to the energies of a set of ordered compounds, we are not particularly interested in the exact form of the renormalized ECIs, beyond the fact that they are unknown functions of the system's configuration.

The physical picture that emerges is quite different from that assumed by generalized Ising-like representations of the energy, or from the assumption that the interactions  $j_{\alpha}^x$  can be neglected for large clusters. The new physical picture is that the interactions  $j_{\alpha}^x$  contribute over long distances, but the “near-sightedness” of the energy is preserved by assuming that the energy is a function of the correlations functions up to a maximum cluster size. As we show in the next section, this physical picture is consistent with the basic fact that the total configurational energy is an extensive function of the configurational variables.

#### IV. CLUSTER EXPANSION FOR PERIODIC SYSTEMS

The next step toward deriving a useful form of the CE is to introduce the space group symmetry of the undecorated lattice. In particular, we note that for a rigid lattice, i.e., in the absence of any type of relaxations, the ECIs for clusters related by a symmetry operation of the space group of the undecorated lattice are equal [5]. This particular property of the ECIs on a rigid lattice allows us to rearrange the CE expansion sum of Eq. (16) by collecting all the basis functions for those clusters with the same ECIs. Thus, the sum of Eq. (16), which is over clusters of the form  $\alpha = \{\eta, \mathbf{p}, \mathbf{v}\}$ , can be written as

$$E(\mathbf{a}_{uc}, \mathbf{u}, \mathbf{z}^x) = \sum_{\eta \in \{\eta\}_s} \omega_{\eta} J_{\eta}^x(\mathbf{a}_{uc}, \mathbf{u}, \mathbf{z}^x) z_{\eta}^x. \quad (17)$$

The sum is carried out over a “small” set of clusters  $\{\eta\}_s$ , indicating a truncated CE. Furthermore, we have reintroduced the structural dependence on  $\mathbf{a}_{uc}$  and  $\mathbf{u}$  into the notation and introduced the correlation functions  $\mathbf{z}^x = \{z_{\eta}^x\}$  given by

$$z_{\eta}^x = \frac{1}{N \omega_{\eta}} \sum_{\mathbf{p}=1}^N \sum_{\mathbf{v}=1}^{\omega_{\eta}} \phi_{\{\eta,\mathbf{p},\mathbf{v}\}}^x(\sigma), \quad (18)$$

where  $\omega_{\eta}$  is the number of clusters of type  $\eta$  per lattice point. For the empty cluster,  $z_{\emptyset}^x = 1$  and  $\omega_{\emptyset} = 1$ . Also, as shown in Sec. III, the ECIs depend on the same set of correlation functions  $\mathbf{z}^x$  included in the truncated CE. As is the case for the

basis functions  $\phi_{\alpha}^x(\sigma)$  [see Eq. (6)], the correlation functions in different basis are also related by a linear transformation:

$$z_{\eta}^x = \sum_{\eta' \in \{\eta\}_s} \mathbb{B}_{\eta,\eta'}^{x,x'} z_{\eta'}^{x'}. \quad (19)$$

The form of the matrix  $\{\mathbb{B}_{\eta,\eta'}^{x,x'}\}$ , in terms of the  $\{\mathcal{B}_{\alpha,\beta}^{x,x'}\}$  defined in Eq. (6), is given in Ref. [5].

It follows from Eq. (18) that the set of correlation functions  $\{z_{\eta}^x\}$  are specific versions of a set of extensive variables  $\mathbf{X}^x = \{X_{\eta}^x\} = \{N z_{\eta}^x\}$ . It also follows from Eq. (17) that the total configurational energy,  $E_N = NE(\mathbf{a}_{uc}, \mathbf{u}, \mathbf{z}^x)$ , is an extensive function of the extensive variables  $\{X_{\eta}^x\}$  and therefore must be a homogeneous function of degree 1 in these variables. Thus, from Euler's homogeneous functions theorem, the total configurational energy will be a homogeneous function of degree one *if and only if*  $E_N(\mathbf{a}_{uc}, \mathbf{u}, \mathbf{X}^x)$  is given by

$$E_N(\mathbf{a}_{uc}, \mathbf{u}, \mathbf{X}^x) = \sum_{\eta \in \{\eta\}_s} \left( \frac{\partial E_N}{\partial X_{\eta}^x} \right)_{X^x} X_{\eta}^x, \quad (20)$$

which implies that the ECIs in Eq. (17) are related to the Euler derivatives of the total configurational energy as follows:

$$J_{\emptyset}^x(\mathbf{a}_{uc}, \mathbf{u}, \mathbf{z}^x) = \left( \frac{\partial E_N}{\partial N} \right)_{X^x}, \quad (21)$$

$$\omega_{\eta} J_{\eta}^x(\mathbf{a}_{uc}, \mathbf{u}, \mathbf{z}^x) = \left( \frac{\partial E_N}{\partial X_{\eta}^x} \right)_{X^x} = \left( \frac{\partial E}{\partial z_{\eta}^x} \right)_{z^x} \text{ for } \eta \neq \emptyset. \quad (22)$$

The simple mathematical and physical arguments leading to Eqs. (21) and (22) reinforce the main conclusion of Sec. III, namely that the ECIs of a truncated CE are functions of all the configurational variables included in the CE and therefore underscore a major conceptual shortcoming of Ising-like representations of the energy that use both truncated expansions and constant ECIs. Irrespective of the ability of such Ising-like models to fit the energies of a set of ordered structures, the model carries with it the implicit and untenable assumption that the configurational energy, which presumably is a complex function of the correlation functions, is such that all its derivatives with respect to the configurational variables are constant for all possible degrees of short- and/or long-range order in the system.

#### V. CLUSTER EXPANSION OF RELAXED STRUCTURES

In order to address structural relaxations, we begin by pointing out that the formalism of the CE strictly applies to the description of the energies of alloys for arbitrary configurations that are obtained by rearranging different atomic species on a reference lattice (undecorated) with a *given and fixed space group symmetry*. Note that volume relaxations preserve the space group symmetry of the undecorated lattice and, therefore, such relaxations can be described accurately within the CE formalism. On the other hand, cell internal and/or cell external relaxations will in general destroy the symmetry of the reference lattice and, therefore invalidate the invariance of the ECIs to the space group symmetry operations of the undecorated lattice. We note that is precisely such symmetry of the ECIs that allows the transition from a

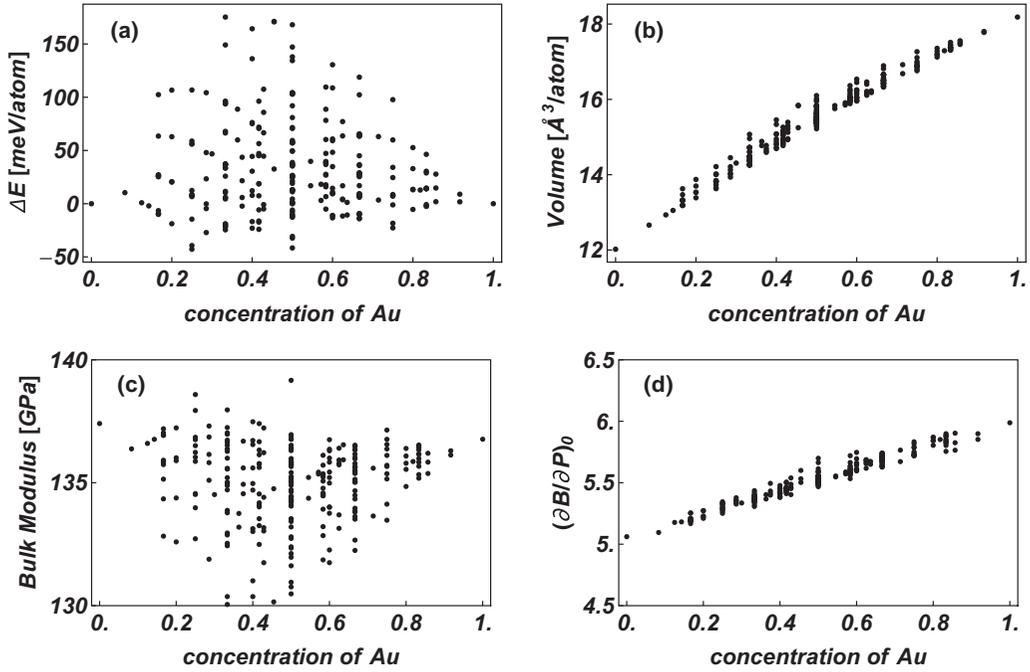


FIG. 1. Parameters for the Murnaghan's equation of state for the unrelaxed structures: (a) energies of formation, (b) volumes per atom, (c) bulk moduli, and (d) pressure derivatives of the bulk modulus.

functional dependence of the energy on the basis functions  $\phi_\alpha^x(\sigma)$ , Eq. (16), to a dependence of the energy on the correlation functions  $\mathbf{z}^x$ , Eq. (17). Thus, *using the correlation functions  $\mathbf{z}^x$  of the undecorated lattice* to describe the energy of relaxed structures with a *different* symmetry than that of the undecorated lattice introduces an additional approximation that is not generally justified within the strict formalism of the CE. In particular, such an approximation to the CE is not expected to work for structures that deviate significantly from the undecorated reference lattice. It follows from these observations that using the CE to perform ground-state analyses and/or to predict ground-state structures will not work reliably if the reference lattice of the true (and unknown) ground states deviate significantly from the reference lattice used to calculate the correlation functions  $\{z_\eta^x\}$ .

Nevertheless, the development of approximations to the CE capable of describing the configurational energy of disordered alloys that include small static and/or dynamic displacements relative to the reference lattice remains an issue of particular interest. For such relaxed structures, the parameters  $\mathbf{a}_{uc}$  and  $\mathbf{u}$  will adopt configuration dependent “equilibrium” values  $\tilde{\mathbf{a}}_{uc}(\mathbf{z}^x)$  and  $\tilde{\mathbf{u}}(\mathbf{z}^x)$ . Thus, in principle, the effect of small structural relaxations can be approximately incorporated into a dependence of the ECIs on the alloy's configuration, which is in addition to that arising from truncation; i.e., the ECIs  $J_\eta^x(\mathbf{a}_{uc}, \mathbf{u}, \mathbf{z}^x)$  in Eq. (17) become  $J_\eta^x(\tilde{\mathbf{a}}_{uc}(\mathbf{z}^x), \tilde{\mathbf{u}}(\mathbf{z}^x), \mathbf{z}^x) = \tilde{J}_\eta^x(\mathbf{z}^x)$ . As we show in Sec. VII, the additional approximation of using the correlation functions  $\mathbf{z}^x$  of the *unrelaxed* structures to describe the energies of *relaxed* structures can be controlled by eliminating from the CE those relaxed structures for which the spread in bond lengths, relative to the characteristic lengths in the unrelaxed structures, exceeds a predetermined threshold.

A truncated CE of the energy of a relaxed structure,  $\tilde{E}(\mathbf{z}^x) = E(\tilde{\mathbf{a}}_{uc}(\mathbf{z}^x), \tilde{\mathbf{u}}(\mathbf{z}^x), \mathbf{z}^x)$ , can then be approximated as

$$\tilde{E}(\mathbf{z}^x) \approx \sum_{\eta \in \{\eta\}_s} \omega_\eta \tilde{J}_\eta^x(\mathbf{z}^x) z_\eta^x. \quad (23)$$

We note that the coefficients  $\tilde{J}_\eta^x(\mathbf{z}^x)$  in Eq. (23) are far removed from the projections of the configurational energy onto the basis functions defined by Eq. (8). The coefficients in question are best interpreted as the Euler derivatives of the total configurational energy of the fully relaxed structure, which, of course, is an extensive and homogeneous function of degree 1 in the configurational variables  $\{Nz_\eta^x\}$ . In that context, we re-emphasize that the approximation introduced into the CE to describe relaxed structures consists in using correlation functions with the symmetry of the parent lattice instead of the correlation functions with the symmetry of the relaxed structures.

## VI. STRUCTURE INVERSION

The usual implementation of the CE consists of fitting the ECIs for a predetermined set of  $m$  clusters to the energies of a set of  $n$  ordered compounds. The energies of the compounds are typically calculated at their equilibrium volume at zero pressure using some version of DFT. Here, we adopt an approach that consists of fitting the configurational energy  $\mathcal{E}(v, \mathbf{z}^x)$ , properly parametrized as a function of the volume  $v$  and of the correlation functions  $\mathbf{z}^x$ , to the four quantities that define the Murnaghan [43] equation of state, i.e., the energy of formation ( $\Delta E_0^{(i)}$ ), the equilibrium volume ( $v_0^{(i)}$ ), the bulk modulus ( $B_0^{(i)}$ ), and the pressure derivative of the bulk modulus ( $B_0^{\prime(i)}$ ) at zero pressure, for a set of ordered

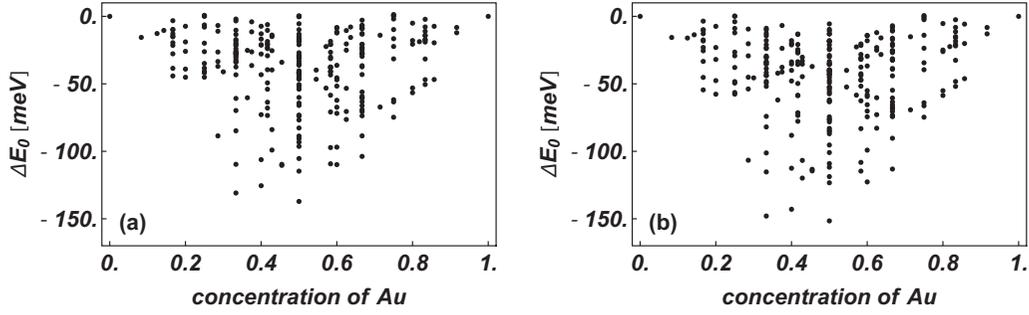


FIG. 2. Difference between the energies of formation at zero pressure of (a) the cell-internal relaxed structures minus that of the unrelaxed structures and (b) the fully relaxed structures minus that of the unrelaxed structures.

compounds. We will refer to these four quantities as the “observables” to be fitted by the function  $\mathcal{E}(v, \mathbf{z}^x)$ .

The parametrization of the configurational energy,  $\mathcal{E}(v, \mathbf{z}^x)$ , is carried out by means of a Taylor expansion of the energy about a reference state for which all the correlation functions vanish identically. Note that in a configurational basis  $\{\phi_\alpha^x(\sigma)\}$ , as defined by a given value of the parameter  $x$ , such reference state corresponds to the random alloy with an atomic concentration given by  $c_A - c_B = x$ . For example, if the CE is carried out in the SDG basis, the reference state for the Taylor expansion is the random alloy at 50:50 concentration since, in that basis, the correlation functions in the random state are given by  $z_\eta^0 = (z_1^0)^{|\eta|}$ , with  $|\eta|$  being the number of points in the cluster  $\eta$ , and at the 50:50 concentration  $z_1^0 = c_A - c_B = 0$ .

In general, the Taylor expansion of the configurational energy is given by

$$\mathcal{E}(v, \mathbf{z}^x) = \mathcal{E}_0^x(v) + \sum_{\eta \neq 0} \left( \frac{\partial \mathcal{E}}{\partial z_\eta^x} \right)_{v,0} z_\eta^x + \frac{1}{2} \sum_{\eta \neq 0, \eta' \neq 0} \left( \frac{\partial^2 \mathcal{E}}{\partial z_\eta^x \partial z_{\eta'}^x} \right)_{v,0} z_\eta^x z_{\eta'}^x + \dots, \quad (24)$$

where, at  $T = 0 K$ , the derivatives in Eq. (24) depend only on the volume per atom of the alloy.

From Eq. (24), it follows that a Taylor expansion in the SDG basis to first order in the correlation functions  $\{z_\eta^0\}$  in which, furthermore, the volume dependence of the coefficients of the Taylor expansion is neglected, reduces the energy

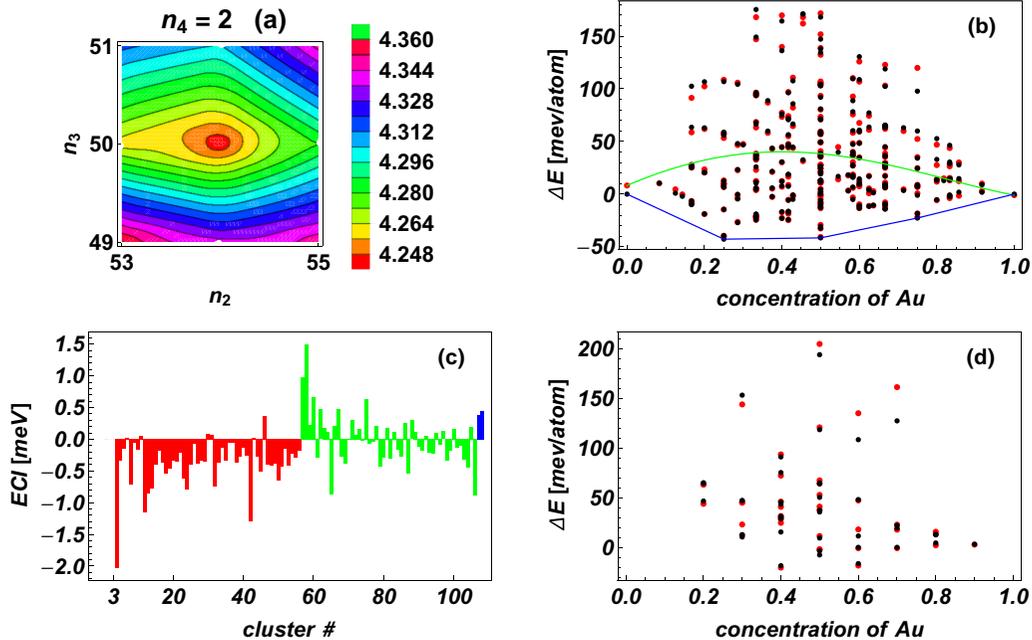


FIG. 3. Generalized Ising-model approximation. (a) Contour plots for constant cross-validation scores; (b) energies of formation of the training structures (black symbols) compared to the energies predicted by the Ining-like model (red symbols); and (c) ECIs for pairs (red), triangles (green), and tetrahedra (blue). Not shown are the ECIs for the empty cluster (38.4 meV), the point cluster (17.7 meV), and the nearest-neighbor pairs (33.9 meV). (d) Energies of formation for the test structures (black symbols) compared to the energies predicted by the Ining-like model (red symbols).

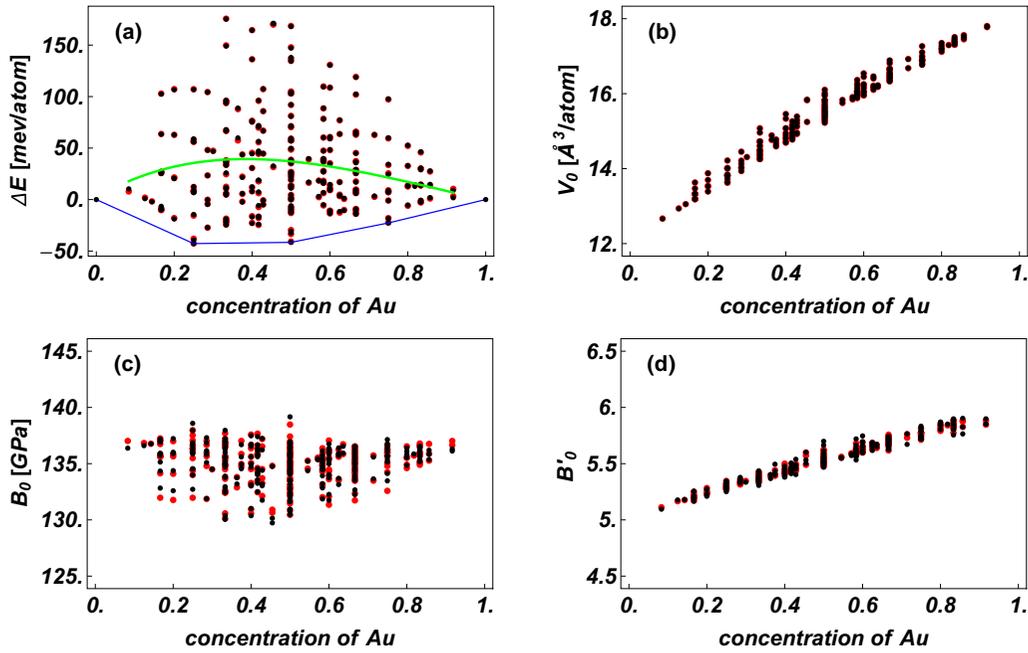


FIG. 4. Results of the CE with volume-dependent interactions. Corrections due to truncation of the CE are not included. The minimum value of the cross-validation score for the energy of formation of 0.74 meV is found for  $n_2 = 13$ ,  $n_3 = 8$  and  $n_4 = 3$ . Black and red symbols are, respectively, the calculated values shown in Fig. 1 and those obtained with the CE.

of formation to an Ising-like model with constant ECIs. Thus, the commonly used Ising-like representation, or Connolly-Williams method, is *strictly equivalent* to a Taylor expansion of the energy to first order in the correlation functions in the SDG basis about the random state at 50:50 concentration. In this context, the Ising-like model for the energy of alloys is a zeroth-order approximation of the CE method.

In order to parametrize of the energy of formation, the coefficients of the Taylor expansion are written as polynomials of degree  $m_v$  in the volume  $v$ . Thus, the set of coefficients defining such polynomials, which we will collectively call  $\mathbf{K}^x$ , fully define the function  $\mathcal{E}(v, z^x)$  and, therefore, they are the model parameters to be fitted to the observables  $\mathcal{O}$ . We note that for each compound  $i$  with correlation functions  $z_i^x$  and

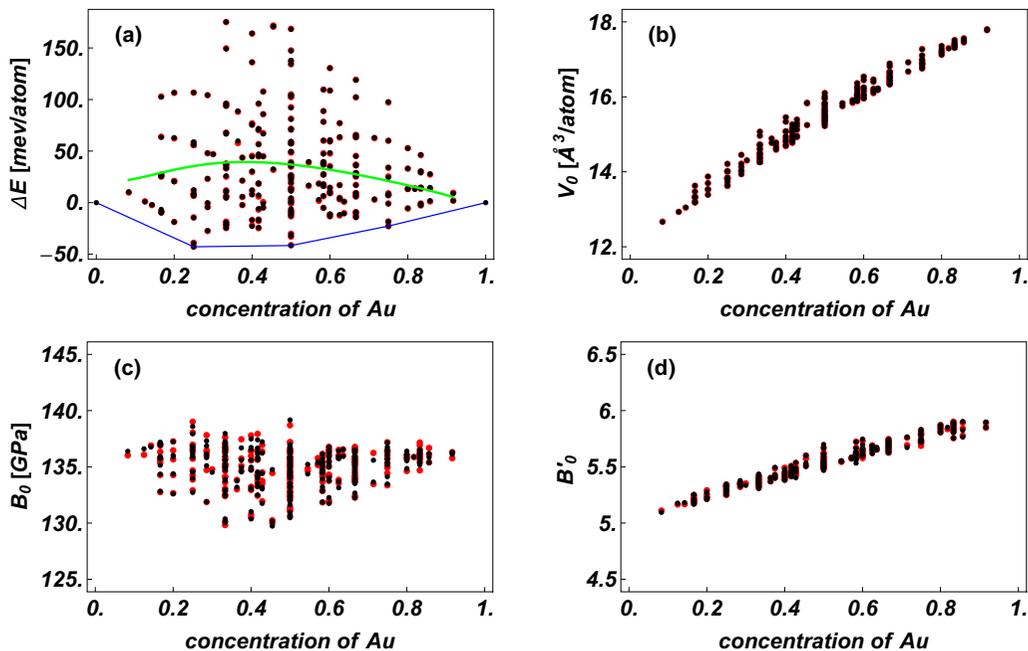


FIG. 5. Cluster expansion with volume-dependent and renormalized interactions due to truncation. The minimum value of the cross validation score for the energy of formation of 0.87 meV is found for  $n_2 = 6$ ,  $n_3 = 4$ , and  $n_4 = 0$ . Black and red symbols are, respectively, the calculated values shown in Fig. 1 and those obtained with the CE.

TABLE I. Comparison of the different approximations of cluster expansion of structures with only volume relaxations. The columns labeled CVS, rms, and max. error give, respectively, the cross-validation score, the root-mean-square error, and the maximum fitting error of each of the parameters in the Munagham equation of state for the 265 structures in the training set. The last two columns give the root-mean-square error and maximum fitting error for the 40 structures in the test set. Units for  $\Delta E$ ,  $V_0$ , and  $B_0$  are meV/atom,  $\text{\AA}^3/\text{atom}$ , and GPa, respectively. The column labeled no. of ECIs gives the number of pairs, triangles, and tetrahedra used in the expansion, which correspond to the minimum in the cross-validation score.

Method	CVS (training)	rms (training)	Max. err. (training)	No. of ECIs { $n_2, n_3, n_4$ }	rms (test)	Max. err. (test)
	$\Delta E_0/V_0/B_0/B'_0$	$\Delta E_0/V_0/B_0/B'_0$	$\Delta E_0/V_0/B_0/B'_0$		$\Delta E_0/V_0/B_0/B'_0$	$\Delta E_0/V_0/B_0/B'_0$
ATAT	4.6/—/—/—	2.9/—/—/—	23.9/—/—/—	{53, 50, 3}	7.8/—/—/—	33.0/—/—/—
$J[cte]$	4.2/—/—/—	2.5/—/—/—	22.1/—/—/—	{54, 50, 2}	7.8/—/—/—	33.8/—/—/—
$J[v]$	0.74/0.004/0.35/0.04	0.68/0.004/0.29/0.02	3.2/0.01/1.2/0.00	{13, 8, 3}	0.40/0.003/0.3/0.03	1.3/0.01/1.1/0.1
$J[v, z]$	0.87/0.008/0.65/0.09	0.56/0.004/0.29/0.021	2.2/0.02/0.93/0.05	{6, 4, 0}	0.53/0.008/0.54/0.07	1.6/0.03/1.2/0.23

zero-pressure volume  $v_0^{(i)}$ , the four observables to be fitted can be expressed in terms of  $\mathcal{E}(v, \mathbf{z}^x)$  and its first three volume derivatives as follows:

$$E_0^{(i)} = \mathcal{E}(v_0^{(i)}, \mathbf{z}_i^x), \quad (25)$$

$$P = \mathcal{E}'(v_0^{(i)}, \mathbf{z}_i^x) = 0, \quad (26)$$

$$B_0^{(i)} = v_0^{(i)} \mathcal{E}''(v_0^{(i)}, \mathbf{z}_i^x), \quad (27)$$

$$B_0^{(i)} = -1 - v_0^{(i)} \frac{\mathcal{E}'''(v_0^{(i)}, \mathbf{z}_i^x)}{\mathcal{E}''(v_0^{(i)}, \mathbf{z}_i^x)}, \quad (28)$$

where the primes stand for derivatives of the energy function with respect to volume.

In general, the relationships between the observables and the parametrized energies of formation of the compounds can be cast as a linear relation of the form

$$\mathbf{O} = \mathbf{M}^x \cdot \mathbf{K}^x, \quad (29)$$

where the vector  $\mathbf{O}$  contains the observables for the  $n$  structures, the vector  $\mathbf{K}^x$  collects the unknown coefficients of the polynomials of order  $m_v$ , defining each of the coefficients of the Taylor expansion of Eq. (24), and where the matrix  $\mathbf{M}^x$  is fully determined by  $n_v$  and by the correlation functions of the compounds.

Typically, the inversion of Eq. (29) is accomplished via a least-squares fit of the unknown parameters  $\mathbf{K}^x$  to the observables  $\mathbf{O}$ . The least-squares fit, or  $\ell_2$  minimization problem,

has a unique solution provided the matrix  $\mathbf{M}^x$  is full rank; otherwise, the number of solutions is infinite. When the matrix  $\mathbf{M}^x$  is not full rank, which typically occurs when a large number of parameters are required to obtain a sufficiently accurate fit, it is possible to obtain a unique solution by including in the  $\ell_2$  minimization a regularization term that penalizes “undesirable” properties of the ECIs. We note that regularization is also a useful technique to avoid overfitting, which is a commonly encountered issue in  $\ell_2$  minimization. However, regularization introduces assumptions about the ECIs, such as minimum norm of the interactions, fast decay, etc., that cannot be easily justified *a priori*. Thus, unless explicitly indicated, we will avoid introducing such regularization schemes. Instead, the preferred approach is to increase the number of structures used in the fitting (training set), or to invert Eq. (29) by minimizing the difference in absolute values  $|\mathbf{M}^x \cdot \mathbf{K}^x - \mathbf{O}|$ . This  $\ell_1$  minimization scheme can be formulated as a linear programming problem and it may offer some advantages over  $\ell_2$  minimization, such as providing unique solutions when  $\mathbf{M}^x$  is not a full rank matrix, avoiding the common problem of overfitting, and finding sparse solutions to the optimization problem, although such solutions are not expected in the CE of the energies of alloys. However, a properly implemented  $\ell_2$  minimization that avoids overfitting is computationally more convenient and it will be used in the next section to carry out the cluster expansion of the Cu-Au system under different approximations and relaxation conditions.

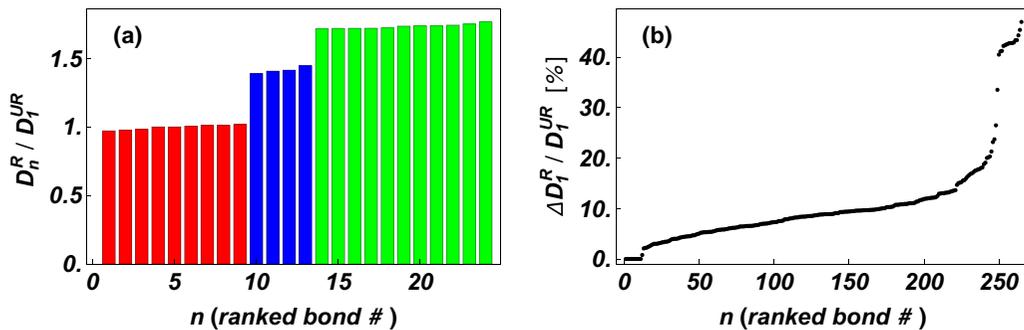


FIG. 6. (a) Pair length distribution due to cell-internal relaxations for a structure in the training set, for first (red), second (blue), and third (green) nearest neighbors in the unrelaxed structure. The pair distances are normalized to the first neighbor distance in the unrelaxed structure at the same volume as the relaxed structure. (b) Percent maximum change in the first neighbor bond lengths, relative to the unrelaxed structure, for all 265 structures in the training set.

TABLE II. Comparison of the different approximations of the cluster expansion for relaxed structures. Set 1 is the same training set of 265 structures used for the cluster expansion of the unrelaxed structures. Set 2 consists of structures for which the maximum change in the length of nearest neighbors, relative to the unrelaxed structures, is 10% or less.  $\Delta E_{\text{cvs}}$ ,  $\Delta E_{\text{rms}}$ , and  $\Delta E_{\text{max}}$ , are, respectively, the cross-validation score, the root-mean-square error, and the maximum fitting error in units of meV/atom for the structures in the training set. The last two columns give the root-mean-square error and maximum fitting error for the structures in the test set. The column labeled no. of ECIs gives the set of pairs, triangles, and tetrahedra used in the expansion, which correspond to the minimum in the cross-validation score.

Method	$\Delta E_{\text{cvs}}$	$\Delta E_{\text{rms}}$	$\Delta E_{\text{max}}$	No. of ECIs	$\Delta E_{\text{rms}}^{\text{(test)}}$	$\Delta E_{\text{max}}^{\text{(test)}}$
Volume and cell internal relaxations						
$J[v, \mathbf{z}]$ (set 1)	3.5	1.9	6.6	{5, 4, 2}	5.5	22.0
$J[v, \mathbf{z}]$ (set 2)	3.5	2.3	9.1	{4, 1, 3}	3.7	7.5
Fully relaxed						
$J[v, \mathbf{z}]$ (set 1)	4.6	2.7	11	{4, 4, 3}	8.61	38.4
$J[v, \mathbf{z}]$ (set 2)	5.9	4.5	14.9	{3, 0, 2}	4.1	8.1

The standard procedure to select the correlations to be included in the CE consists of determining a set of clusters that minimizes the cross-validation score [14–16]. In the case of the Cu-Au system, to be discussed in the next section, we limit the search for the minimum cross-validation score to clusters consisting of two, three, and four points, arranged hierarchically by the number of points in the cluster and, for clusters with the same number of points, by a measure of compactness defined as the sum of the distances between any two points in the cluster.

As mentioned in previous sections, truncation of the CE and/or structural relaxations introduces a dependence of the ECIs on the configuration of the alloy. To address such configuration dependence, we refer to the fact that the ECIs are the Euler derivatives of the energy of formation [see Eqs. (21) and (22)]. Therefore, assuming we have an analytical expression for the energy of formation as a function of volume and the correlation functions, say  $\mathcal{E}(v, \mathbf{z}^x)$ , the ECIs for nonempty clusters follow directly from Eq. (22),

$$J_{\eta}^x(v, \mathbf{z}^x) = \frac{1}{\omega_{\eta}} \left( \frac{\partial \mathcal{E}}{\partial z_{\eta}^x} \right)_{v, \mathbf{z}^x}, \quad (30)$$

while the ECI for the empty cluster is given by Euler's homogeneous function theorem:

$$\begin{aligned} J_0^x(v, \mathbf{z}^x) &= \mathcal{E}(v, \mathbf{z}^x) - \sum_{\eta \neq 0} \left( \frac{\partial \mathcal{E}}{\partial z_{\eta}^x} \right)_{v, \mathbf{z}^x} z_{\eta}^x \\ &= \mathcal{E}(v, \mathbf{z}^x) - \sum_{\eta \neq 0} \omega_{\eta} J_{\eta}^x(v, \mathbf{z}^x) z_{\eta}^x. \end{aligned} \quad (31)$$

As will be shown in Sec. VII, for the Cu-Au system, a significant improvement over the Ising-like model, or zeroth-order approximation, can be achieved by using a Taylor expansion about the random state at 50:50 concentration up to second order in the correlation functions in the SDG basis. Carrying out the Taylor expansion to at least second order brings into evidence the concentration and configuration dependence of the effective interactions that arise naturally from the truncation of the CE and/or relaxations of the lattice. However, a potential shortcoming is the expected slow convergence of the Taylor expansion for dilute alloys or compounds with concentrations that deviate significantly from 50:50. In fact, the approach should break down for the pure elements

for which the absolute values of all correlations  $\{z_{\eta}^0\}$  are equal to 1 and, therefore, the Taylor expansion of Eq. (24) does not converge. Thus, the pure elements will be excluded from the set of training structures.

Although it will not be implemented here, it is expected that expanding the energy in powers of the correlation functions  $\{z_{\eta}^x\}$  in the so-called variable basis cluster expansion [5,6] (VBCE) should address the issue of describing the configurational energy for concentrations that deviate

TABLE III. Coordinates of the clusters used with the method  $J[v]$  described in Sec. VII 2 and Table I. The positions of each point in the clusters are given in Cartesian coordinates by  $\vec{r}(n_1, n_2, n_3) = \frac{1}{2}[n_1, n_2, n_3]$ . The column labeled  $\omega_n$  gives the degeneracy of each cluster.

Cluster no.	Cluster type	$\omega_n$	$n_1, n_2, n_3$	$n_1, n_2, n_3$	$n_1, n_2, n_3$	$n_1, n_2, n_3$
1	Empty	1				
2	Point	1	0,0,0			
3	Pair 1	6	0,0,0	0, 1, 1		
4	Pair 2	3	0,0,0	0, 0, 2		
5	Pair 3	12	0,0,0	1, 1, 2		
6	Pair 4	6	0,0,0	0, 2, 2		
7	Pair 5	12	0,0,0	0, 1, 3		
8	Pair 6	4	0,0,0	2, 2, 2		
9	Pair 7	24	0,0,0	1, 2, 3		
10	Pair 8	3	0,0,0	0, 0, 4		
11	Pair 9	12	0,0,0	1, 1, 4		
12	Pair 10	6	0,0,0	0, 3, 3		
13	Pair 11	12	0,0,0	0, 2, 4		
14	Pair 12	12	0,0,0	2, 3, 3		
15	Pair 13	12	0,0,0	2, 2, 4		
16	Triangle 1	8	0,0,0	1, 0, -1	1, 1, 0	
17	Triangle 2	12	0,0,0	0, 0, 2	0, 1, 1	
18	Triangle 3	24	0,0,0	1, -1, -2	1, 0, -1	
19	Triangle 4	6	0,0,0	0, 1, 1	0, 2, 2	
20	Triangle 5	24	0,0,0	2, -1, -1	2, 0, 0	
21	Triangle 6	24	0,0,0	1, 1, -2	1, 2, -1	
22	Triangle 7	24	0,0,0	0, 1, 1	0, 1, 3	
23	Triangle 8	48	0,0,0	2, 0, -2	2, 1, -1	
24	Tetrad 1	2	0,0,0	1, 1, 0	1, 0, 1	0, 1, 1
25	Tetrad 2	12	0,0,0	0, 0, 2	0, -1, 1	1, 0, 1
26	Tetrad 3	12	0,0,0	1, -1, 0	1, 0, 1	0, 1, 1

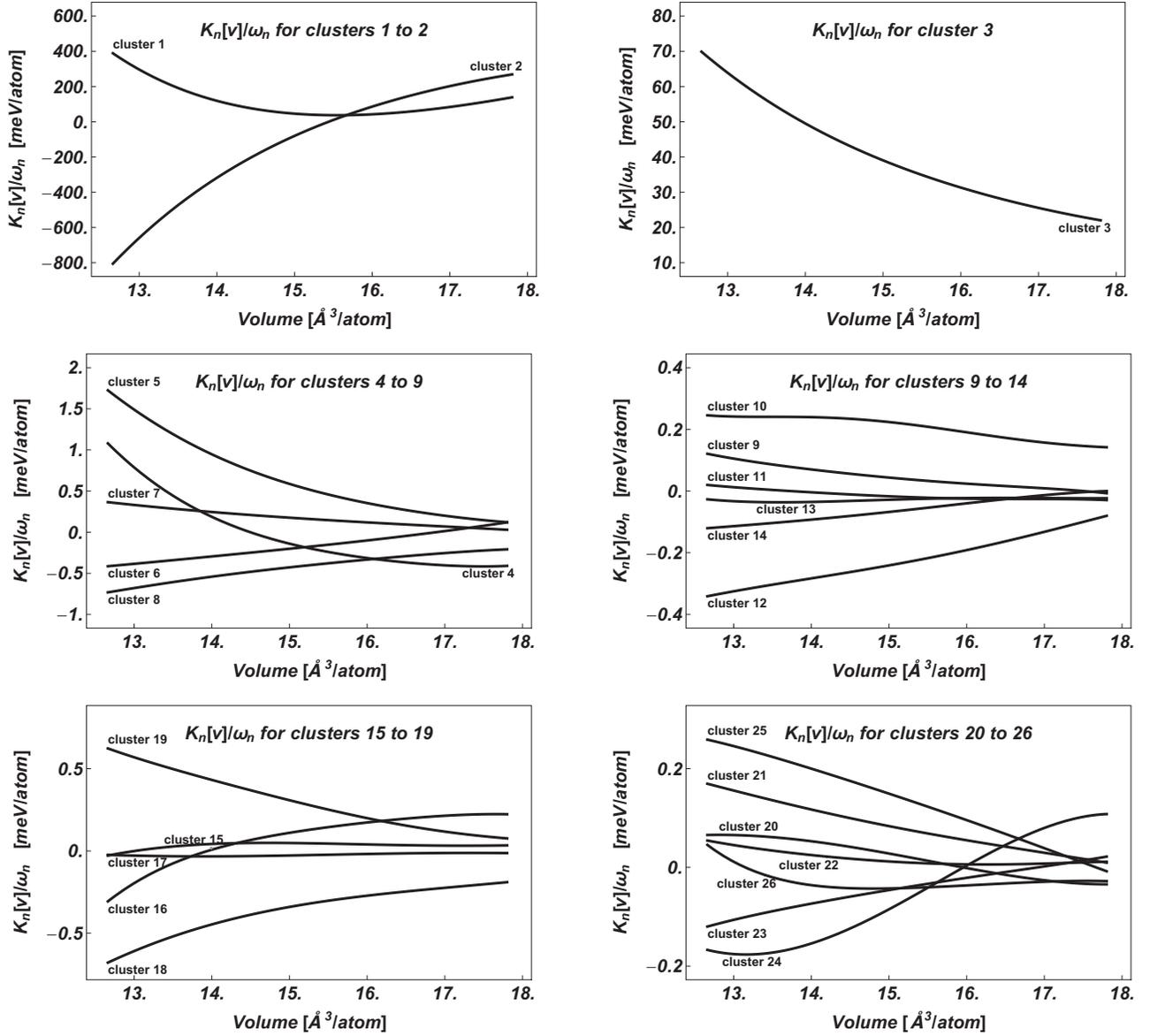


FIG. 7. Volume dependence of the coefficients  $K_n[v]$  of the Taylor expansion to first order in the correlation functions, normalized by the degeneracy  $\omega_n$  of the corresponding cluster. The clusters are labeled following Table III.

significantly from  $x = 0$ . In the VBCE, the value of  $x$  in Eq. (1), which defines the basis to be used in the CE, is chosen to be equal to the difference in concentrations of  $A$  and  $B$  atoms in the alloy, i.e.,  $x = c_A - c_B$ . Thus, different basis sets  $\{\phi_\alpha^x(\sigma)\}$  are used to describe alloys of different concentrations. In this approach, the standard state for the Taylor expansion is the random alloy at concentration  $x$ , for which all correlations  $z_\eta^x$  for the nonempty clusters vanish identically. Furthermore, the correlation functions of the pure elements for  $\eta > 0$  are also equal to zero, i.e.,  $z_\eta^x \rightarrow 0$  when  $x \rightarrow \pm 1$ , thus eliminating from the functional form of the energy the fictitious dependence of the energy of the pure elements on the correlations functions seen in Ising-like models.

## VII. IMPLEMENTATION OF THE CE: THE Cu-Au SYSTEM

In order to illustrate the results developed in previous sections, we begin by applying different versions of the CE to

unrelaxed structures in the Cu-Au system. The training set for the unrelaxed structures consists of 265 binary compounds, which includes all 135 structures with up to 6 atoms per unit cell, with the remaining ones chosen at random from structures with 7, 8, and 12 atoms per unit cell. A set of test structures, consisting of 40 compounds chosen at random from structures with 10 atoms per unit cell, will be used to validate different approximations to the CE.

The energies of formation were calculated using the VASP implementation [44,45] of the projected augmented wave (PAW) method [46] with the exchange-correlation functional in the generalized gradient approximation (GGA) (PW 91 in VASP) [47]. The energy cutoff was fixed at 550 eV and, in all cases, the  $k$  mesh was determined by varying the number of  $k$  points until a relative convergence of 1 meV was achieved. The energies of formation of the compounds were determined for (i) structures with only volume relaxations,

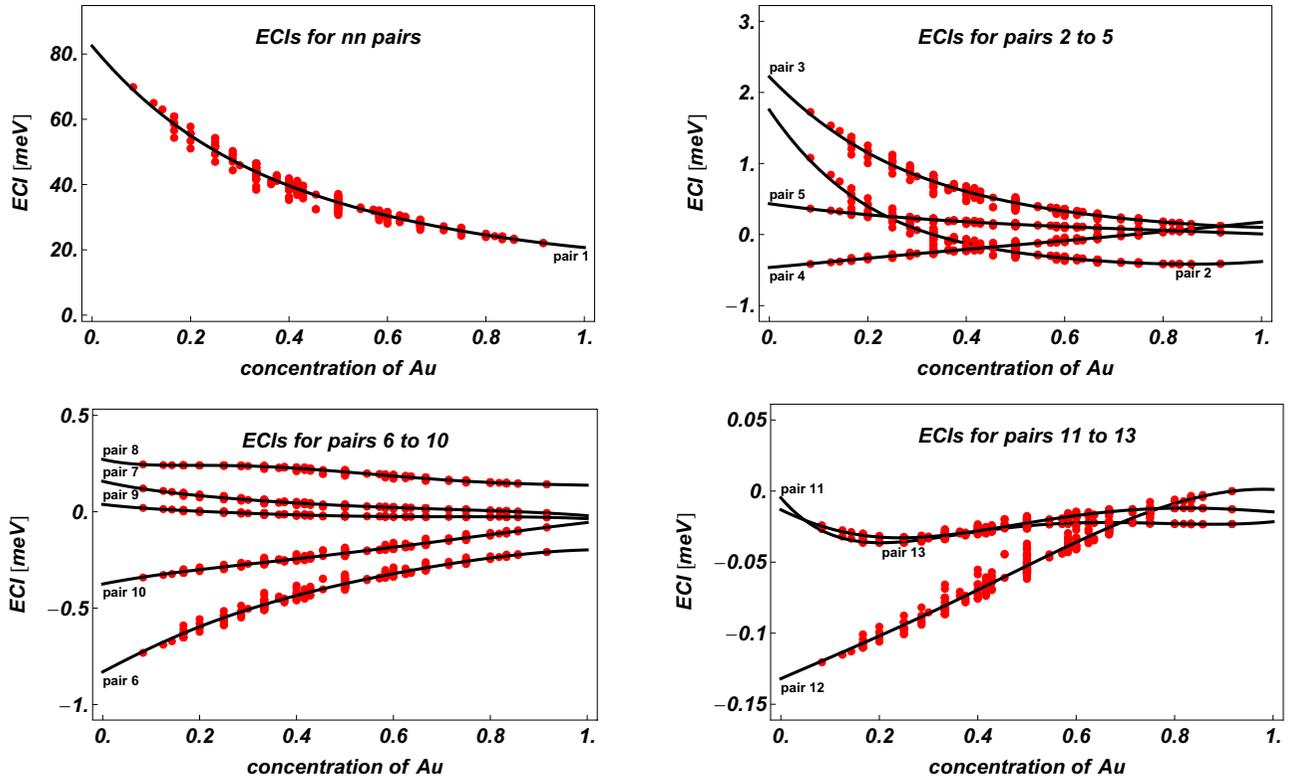


FIG. 8. Effective cluster interactions for pair clusters used with the method  $J[v]$  described in Sec. VII 2 and Table I. The coordinate of the clusters are given in Table III. The symbols correspond to the ECIs in the state of order of the compounds used in the training set, while the solid line gives the ECIs in the random state as a function of concentration.

i.e., structures for which the shape of the unit cell of the undecorated face-centered cubic (fcc) lattice and the relative ionic positions are kept constant, (ii) structures for which only volume and relative ionic positions are allowed to relax, and (iii) fully relaxed structures for which volume, unit cell shape and ionic positions are allowed to relax. We note that allowing only cell-internal relaxations of the fcc undecorated lattice is consistent with the fact that the main objective of the CE is to describe the configurational energy of the Cu-Au system in the disordered fcc phase, in which small displacements are implicitly included. The resulting approximation to the CE should also apply to the  $L1_2$  phases in Cu-Au since that phase shares the same undecorated lattice with the disordered fcc phase. However, the approximation is expected to be less reliable for the description of the  $L1_0$  phase of the Cu-Au system for which the undecorated lattice should include tetragonal distortions. Thus, a CE applicable to the  $L1_0$  phase requires that the ECIs be determined as a function of volume and  $c/a$  ratio on a tetragonal undecorated lattice.

The energies for both the unrelaxed and relaxed structures were calculated at different volumes and fitted to a Murnaghan equation of state [43]. The four parameters in the Murnaghan equation of state are shown in Fig. 1 for the unrelaxed structures. For the relaxed structures, the values at zero pressure of the volume, bulk modulus, and pressure derivatives of the bulk modulus do not change significantly relative to those of the unrelaxed structures. However, the changes in the energies of formation at zero pressure due to relaxations are significant and they are shown, relative to the

energies of the unrelaxed structures, for the structures with only cell internal relaxations [Fig. 2(a)] and for the structures that are fully relaxed [Fig. 2(b)].

### 1. Generalized Ising-like models

In order to establish a baseline for comparison with the truncated CE developed in Sec. III, we begin by fitting a generalized Ising-like model to the energies of formation of the unrelaxed Cu-Au structures. The cluster expansion for the relaxed structures will be addressed later in this section. The clusters included in the expansion consist of two-, three-, and four-point figures that are arranged hierarchically by the number of points in the cluster and, for clusters with the same number of points, by a measure of compactness defined as the sum of the distances between pairs of points in the cluster. In all cases, we search for the minimum of the leave-one-out cross validation score for the full set of 256 training structures and ensure that the solution to the  $\ell_2$  minimization is unique.

The results of the fitting procedure for the Ising-like approximation, which we will label  $J[cte]$ , are shown in Fig. 3. The cross validation scan of Fig. 3(a) shows a minimum occurring at  $n_2 = 54$  pairs,  $n_3 = 50$  triangles, and  $n_4 = 2$  tetrahedra, which is within the region where the matrix  $\mathbf{M}$  is full rank, and where the solution to the  $\ell_2$  minimization procedure is unique. The next panel, Fig. 3(b), compares the input energies of formation in the training set (black symbols) to those obtained with the Ising-like model (red symbols). Also shown in the figure are the energy of formation of the random alloy as a function of concentration (green line) and

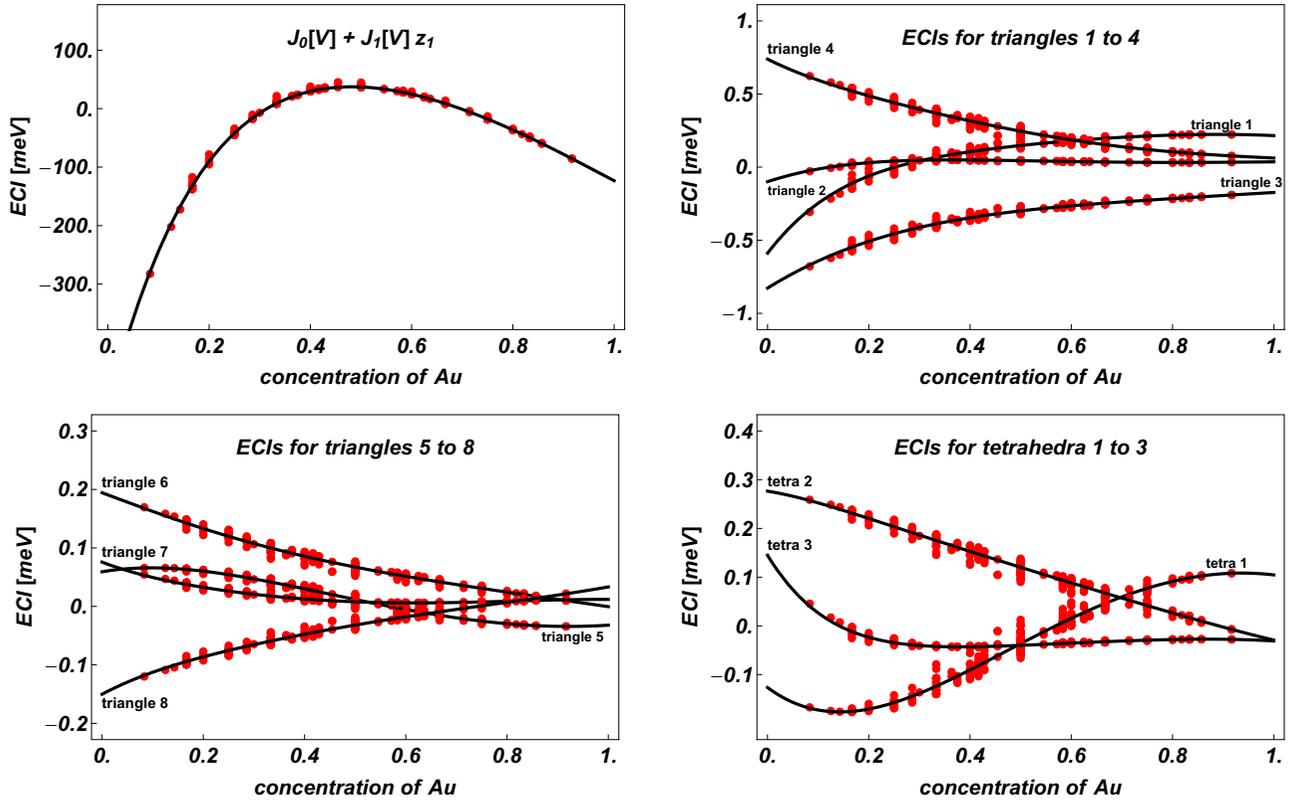


FIG. 9. Effective cluster interactions for nonpair clusters used with the method  $J[v]$  described in Sec. VII 2 and Table I. The coordinate of the clusters are given in Table III. The symbols correspond to the ECIs in the state of order of the compounds used in the training set, while the solid line gives the ECIs in the random state as a function of concentration.

the convex hull connecting the ground states (blue line). The following two panels show the constant ECIs for the Ising-like model [Fig. 3(c)], and the energies of the test set (black symbols) compared to the energies predicted by the Ising-like model (red symbols) [Fig. 3(d)]. For the key parameters measuring the quality of the fit, we obtain a cross validation score of 4.2 meV/atom, a root-mean-square error of 2.5 meV/atom, and a maximum error for the training set of 22.1 meV/atom. We note that in most applications of the CE such values would be considered acceptable although the maximum error of 22.1 meV/atom is somewhat high given the relative accuracy of the DFT calculations. The situation is less satisfactory when it comes to the ability of the Ising-like model to reproduce the energies of formation of the 40 structures in the test set. For the test set, we obtain a root-mean-square error and a maximum error of, respectively, 7.8 and 33.8 meV/atom. The same results were obtained by carrying out the cluster expansion using the Alloy-Theoretic Automated Tool Kit (ATAT) [14–16]. The ATAT package gives an Ising-like model with  $n_2 = 53$  pairs,  $n_3 = 50$  triangles, and  $n_4 = 3$  tetrahedra, and a cross-validation score of 4.6 meV/atom, root-mean-square error of 2.9 meV/atom, and maximum error of 23.9 meV/atom. For the test set, the root-mean-square and maximum errors are, respectively, 7.8 and 33.0 meV/atom. Thus, the ATAT software package and the minimization of the cross-validation scheme used here give essentially the same results with regard to the quality of the fit of the training structures, and both approaches show that the Ising model fails to predict the energies of the test set with acceptable accuracy.

## 2. Volume and truncation effects

We next consider the effect of volume relaxations without including corrections due to the truncation of the expansion. In this approximation, which we will label  $J[v]$ , the energy of formation is given by a Taylor expansion to first order in the correlation functions around the random state at 50:50 concentration. Thus, the expansion is the same as that used for the Ising-like model approximation described in Sec. VII 1, except that we now include an explicit volume dependence in the Taylor expansion coefficients  $\mathbf{K}$ . These coefficients are parametrized by a polynomial of degree 5 in the volume. For the set of training structures, the model is fitted to the four parameters of the Murnaghan equation of state shown in Fig. 1. As before, the clusters included in the expansion are given by the set of  $n_2$  pairs,  $n_3$  triangles, and  $n_4$  tetrahedra that minimize the cross-validation score for energy of formation. The minimum of such cross-validation score is 0.74 meV and occurs for  $n_2 = 13$ ,  $n_3 = 8$ , and  $n_4 = 3$ . The results of the fitting are shown in Fig. 4. We note that, since volume relaxations preserve the space group symmetry of the undecorated lattice, the only effect that is not being explicitly addressed in this approximation is the truncation of the CE discussed in Sec. III.

The next level of approximation of the CE for structures with only volume relaxations can be achieved by explicitly including a volume and a configurational dependence in the ECIs. We will label this approximation  $J[v, z]$ . As discussed in Sec. III, this configurational dependence emerges from

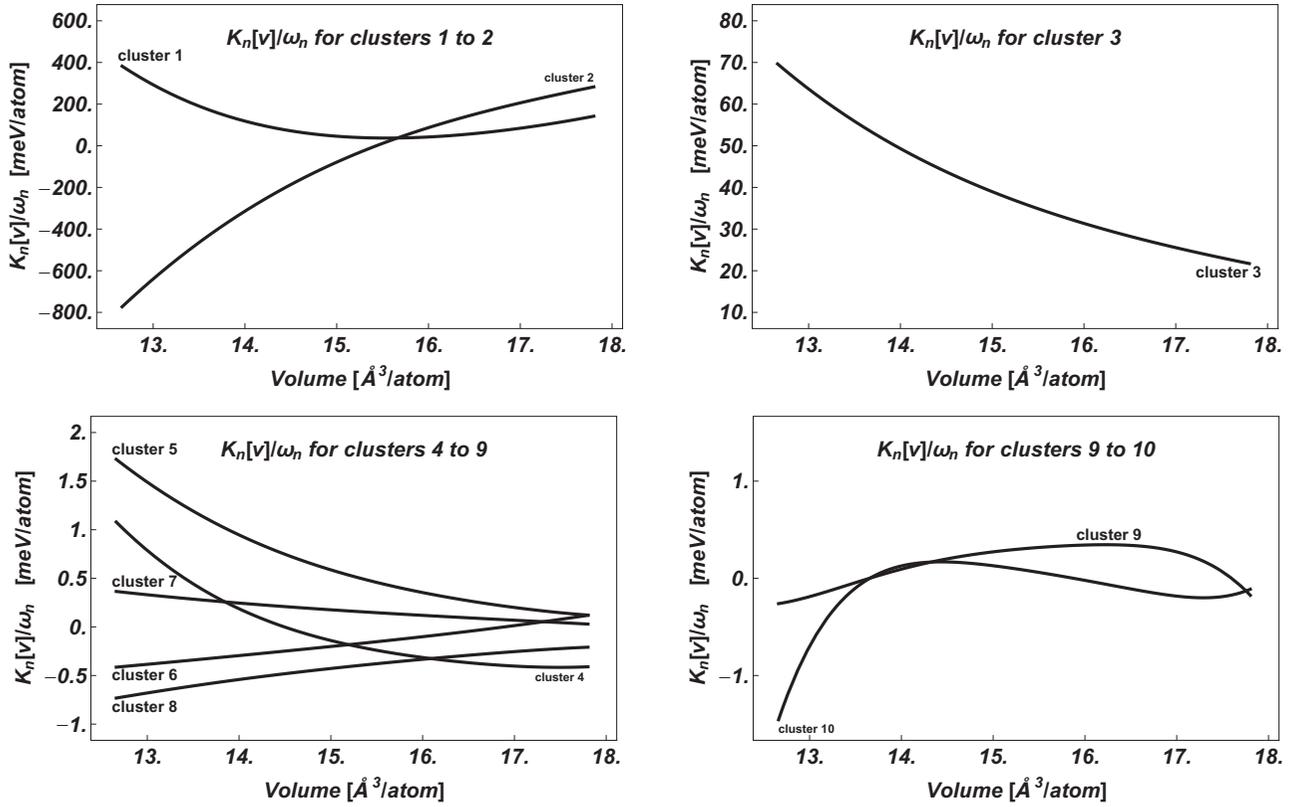


FIG. 10. Volume dependence of the first-order coefficients  $K_n[v]$  of the Taylor expansion of the energy in the method  $J[v, z]$ . The coefficients are normalized by the degeneracy  $\omega_n$  of the corresponding cluster, and the clusters are labeled following Table IV.

the renormalization of the ECIs due to the truncation of the expansion. The fitting parameters are then the coefficients of a Taylor expansion of the energy about the random state at 50:50 concentration which, to differentiate it from the previous case ( $J[v]$ ), should be of order greater than 1 in the correlation functions in the SDG basis. As in the previous case, the ECIs are given by the Euler derivatives of the resulting energy function. In the present case, the energy is expanded to second order in the correlation functions and the volume dependence of coefficients of the Taylor expansion is also parametrized with polynomials of degree 5. The minimum cross validation for the energy of formation equals 0.87 meV/atom and is found for  $n_2 = 6$ ,  $n_3 = 4$ , and  $n_4 = 0$ . Figure 5 shows the comparison of the results of the cluster expansion in the  $J[v, z]$  approximation to the calculated zero pressure values of  $\Delta E$ ,  $V_0$ ,  $B_0$ , and  $B'_0$  for all the structures in the training set. We note that since the Taylor series does not converge for  $|z_\eta| \rightarrow 1$ , we have excluded the pure elements from the fitting procedure.

The results obtained with the different approximations are summarized in Table I. Clusters, coefficients of the Taylor expansions as a function of volume, and the resulting ECIs are given in the Appendix for both methods labeled  $J[v]$  and  $J[v, z]$  in Table I. As shown in Table I, there is a significant decrease in the range of interactions when going from the  $J[cte]$  approximation that place the minimum in the cross-validation score at  $\{n_2 = 54, n_3 = 50, n_4 = 2\}$  to the  $J[v, z]$  approximation with the minimum located at  $\{n_2 = 6, n_3 = 4, n_4 = 0\}$ . Furthermore, we see that both the  $J[v]$  and  $J[v, z]$

methods reproduce the calculated values of the Murnaghan equation of state for the structures in the test set with the same level of accuracy obtained for the structures in the training set. On the other hand, the Ising-like approximation ( $J[cte]$ ) gives less than acceptable errors for the test structures.

The following observations are in order with regard to the significant difference in the range of effective interactions for the approximations used here, namely  $J[cte]$ ,  $J[v]$ , and

TABLE IV. Coordinates of the clusters used with the method  $J[v, z]$  described in Sec. VII 2 and Table I. The positions of each point in the clusters are given in Cartesian coordinates by  $\vec{r}(n_1, n_2, n_3) = \frac{1}{2}[n_1, n_2, n_3]$ . The column labeled  $\omega_n$  gives the degeneracy of each cluster.

Cluster no.	Cluster type	$\omega_n$	$n_1, n_2, n_3$	$n_1, n_2, n_3$	$n_1, n_2, n_3$
1	Empty	1			
2	Point	1	0,0,0		
3	Pair 1	6	0,0,0	0, 1, 1	
4	Pair 2	3	0,0,0	0, 0, 2	
5	Pair 3	12	0,0,0	1, 1, 2	
6	Pair 4	6	0,0,0	0, 2, 2	
6	Pair 5	12	0,0,0	0, 1, 3	
6	Pair 6	4	0,0,0	2, 2, 2	
7	Triangle 1	8	0,0,0	1, 0, -1	1, 1, 0
8	Triangle 2	12	0,0,0	0, 0, 2	0, 1, 1
9	Triangle 3	24	0,0,0	1, -1, -2	1, 0, -1
10	Triangle 4	6	0,0,0	0, 1, 1	0, 2, 2

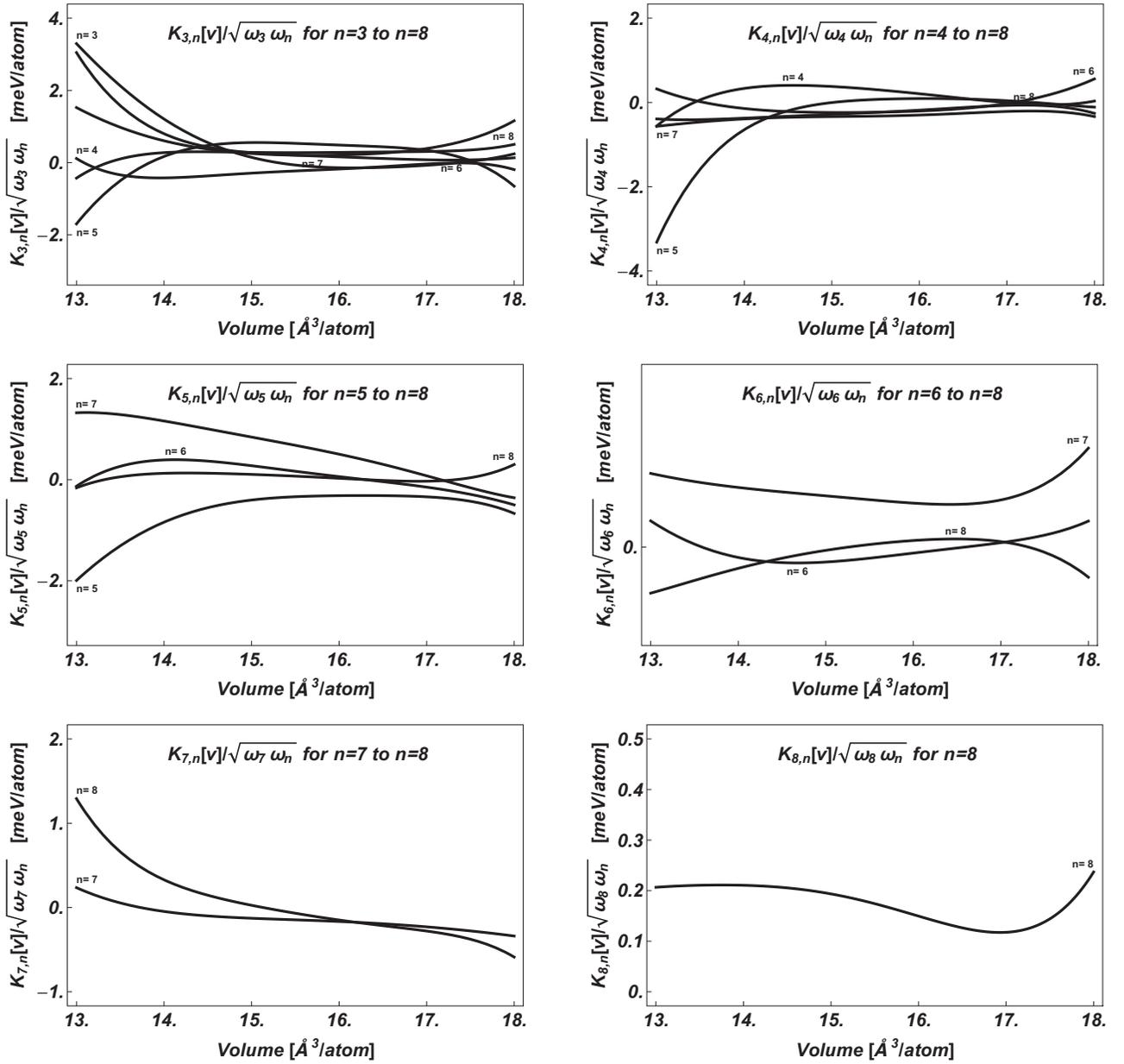


FIG. 11. Volume dependence of the second-order coefficients  $K_{n,n}[v]$  of the Taylor expansion of the energy in the method  $J[v, z]$  for all pairs used in the approximation. The coefficients are normalized by the degeneracies  $\sqrt{\omega_n \omega_n}$  of the corresponding clusters and the clusters are labeled following Table IV.

$J[v, z]$ . The long range of interactions observed for the case  $J[cte]$  is a direct consequence of the fact that, although the ECIs decay with distance and complexity, their decay is not sufficiently fast to justify the commonly used approach of neglecting the contribution of an exceedingly large number of clusters which, as mentioned, is of the order of  $2^N$ . The existence of nonlocal interactions in the energy further ensures the nonconvergence of the Ising-like model. For example, it has been shown that the standard CE does not converge if the function being expanded contains nonlinear dependences in concentration [5]. Such nonlinear dependences are commonly encountered in many models, ranging from the regular solution model to approaches such as the Friedel model for transition-metal alloys, the CPA and the GPM.

Furthermore, such nonlinear dependences in concentration arise from nonlocal terms in the energy. In the case of the Cu-Au system, it has been shown that using a semilocal exchange-correlation functional results in significant improvement in the calculated energies of formation of Cu-Au compounds [48]. Thus, nonlocal contributions arising from nonlocal exchange-correlation functionals might further contribute to the slow convergence of Ising-like models. Also, as mentioned, most applications of the CE use a relatively small number of training structures, thus masking the deficiencies of the Ising-like model and incorrectly suggesting a fast decay of the ECIs. The end result is very poor predictability of the Ising-like model. Improvements in convergence and predictability are obtained by allowing the ECIs to depend on the volume of

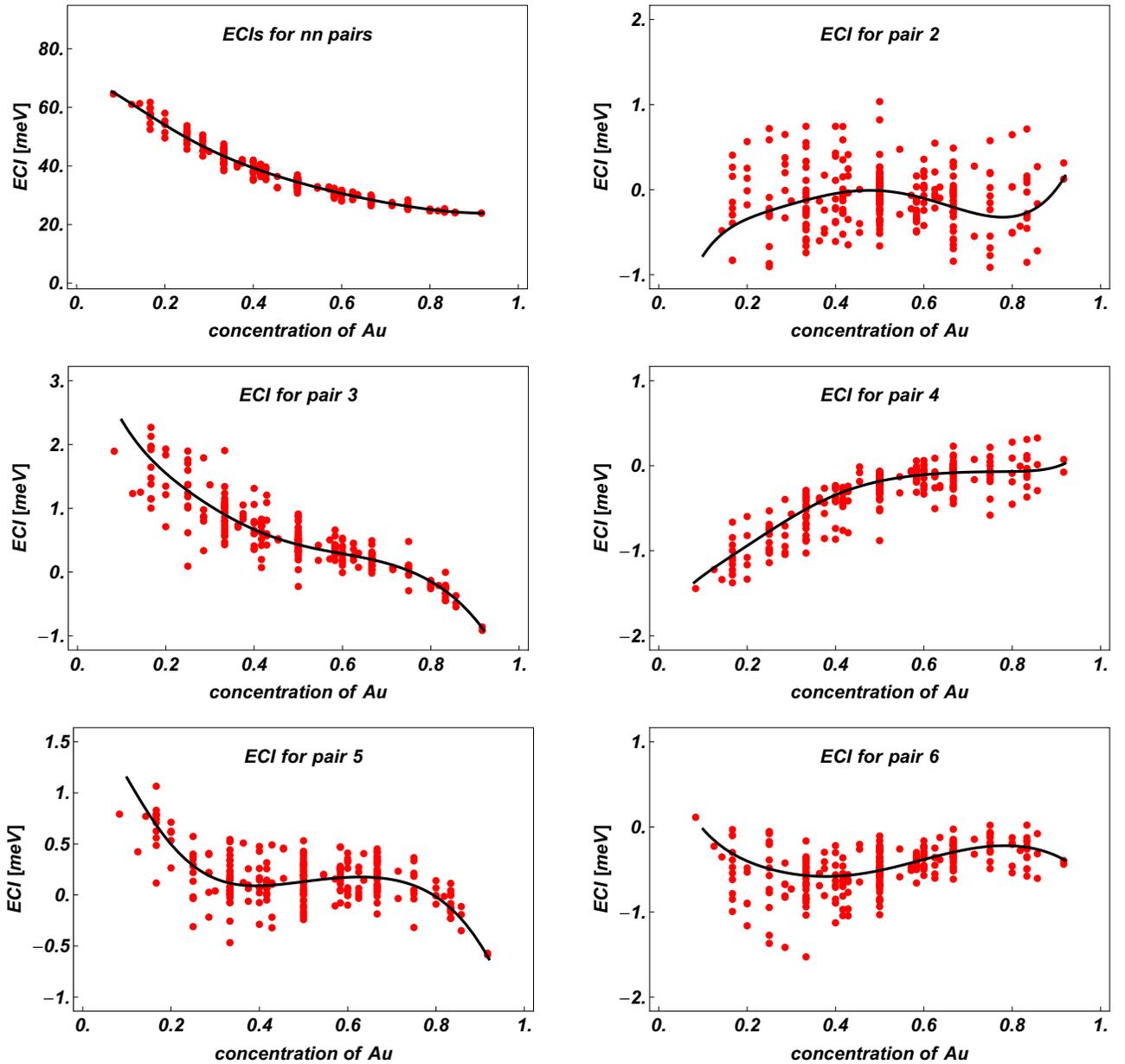


FIG. 12. Effective cluster interactions for pair clusters used with the method  $J[v, z]$  described in Sec. VII 2 and Table I. The coordinate of the clusters are given in Table IV.

the alloy, which itself is a function of the degree of order. This somewhat obvious volume dependence of the ECIs is, of course, absent in the Ising-like model. Thus, the improvement observed using the  $J[v]$  method is strictly due to the fact that the model used to fit the training structures is a more accurate description of the configurational energy of real alloys. As can be seen in the Appendix, Figs. 8 and 9, the ECIs depend strongly on concentration and, to a lesser degree, on pair and higher order correlations. Introducing truncation effects by allowing for an explicit dependence of the ECIs on the degree of order, i.e., using the method labeled  $J[v, z]$ , further reduces the range of interactions. The ECIs are now renormalized and contributions due to larger clusters are incorporated into smaller clusters. Comparing the ECIs for the case  $J[v]$  in Figs. 8 and 9 with those for the case  $J[v, z]$  in Figs. 12 and

13, we see that there is a stronger configurational dependence for the latter case.

### 3. Relaxation effects

As mentioned in Sec. V, the expansion of relaxed structures in terms of the correlation functions of the unrelaxed structures introduces an additional approximation into the CE method. The approximation arises from the fact that, in general, relaxation changes the space group symmetry of the undecorated lattice, and therefore for each cluster in the unrelaxed structures there will be a distribution of related but distorted clusters in the relaxed structures. These distorted clusters will in turn give rise to different ECIs and the critical step of going from the expansion in terms of the

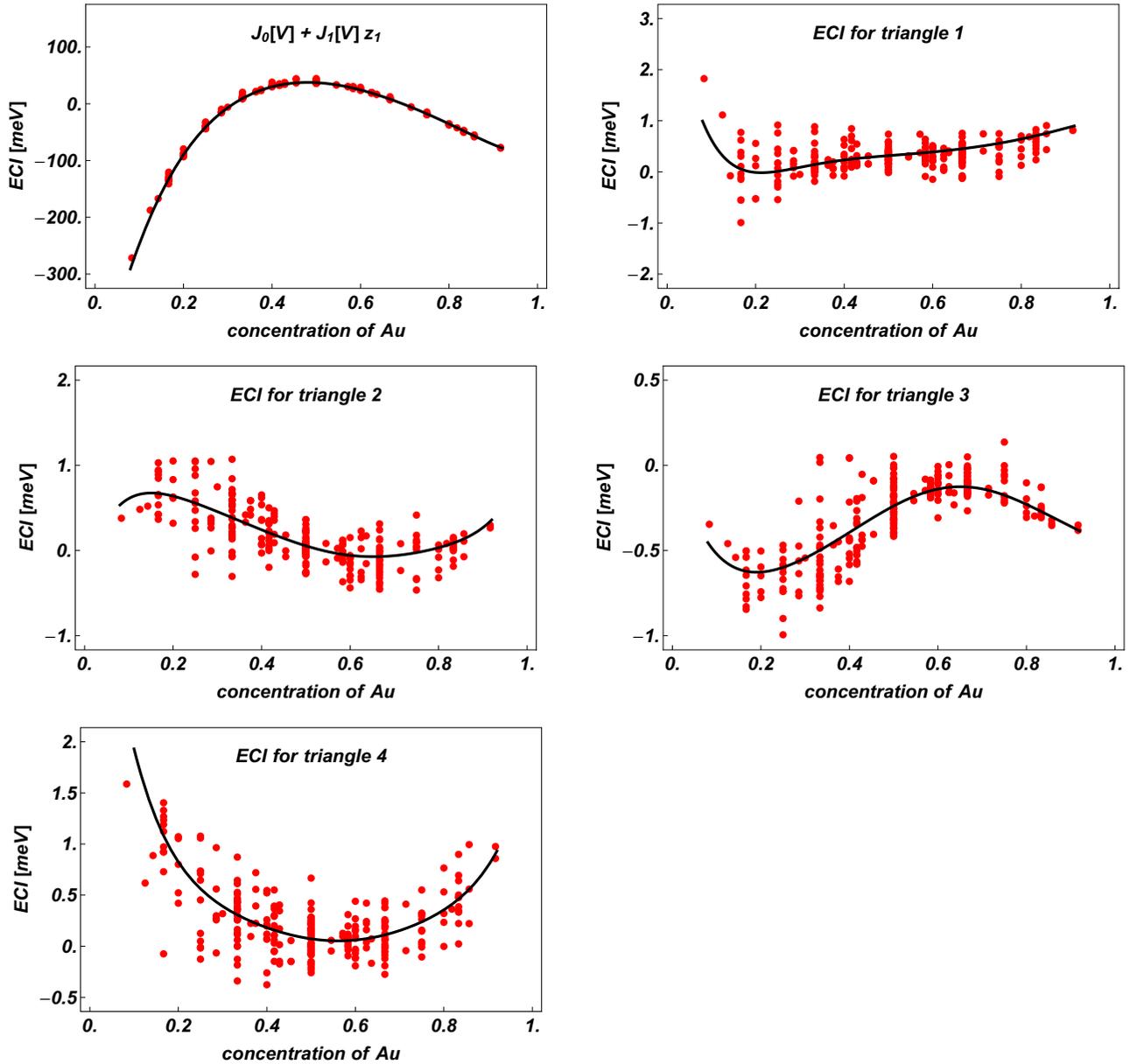


FIG. 13. Effective cluster interaction for nonpair clusters for the method  $J[v, z]$  described in Sec. VII 2 and Table I. The coordinate of the clusters are given in Table IV.

basis functions  $\{\phi_\alpha(\sigma)\}$  [Eq. (16)] to that in terms of the correlations functions  $\{z_\eta\}$  [Eq. (17)] cannot be carried out. Different approaches have been introduced in order to control this approximation [49]. Here, we use a simple approach that eliminates from the CE those structures for which the relaxation results in a distribution in bond lengths with a width exceeding a certain threshold relative to the bond lengths in the unrelaxed structures (at the same volume). Figure 6(a) shows the distribution of distances in one structure in the training set due to cell-internal relaxations for the first three pair distances in the unrelaxed structure. The relative maximum percent change in the nearest neighbor distances for all structures in the training set is shown in Fig. 6(b), where we see that the relative change in bond lengths due to cell-internal relaxations can be as large as 50%. Thus, the correlation functions of the unrelaxed structures are not expected to be

a good set of configurational variables to describe a large number of relaxed structures in the training set, as it is usually assumed in most implementations of the CE.

To illustrate this point, we carried out a cluster expansions with the ECIs functions of volume and correlations functions (i.e., the approximation referred as  $J[v, z]$ ) for the structures with volume plus cell-internal relaxations and for fully relaxed structure for two different conditions: (i) using all 265 structures in the training set (set 1) and (ii) with a reduced training set consisting of relaxed structures for which the maximum relative change in first neighbor distance is less than 10% (set 2). The results are summarized in Table II.

We see from Table II that the quality of the fit for both sets 1 and 2 are comparable and, as expected due to the additional approximation used in the expansion of relaxed structures, somewhat less accurate than the CE of unrelaxed structures

discussed previously. However, a significant difference between the two expansions is their ability to predict the energies of the structures in their corresponding test sets. For set 1, the root-mean-square and maximum errors for the energies of the test set are significantly larger than the same quantities for the set of training structures. On the other hand, for the test structures in set 2, the root-mean-square and maximum errors are comparable to the same quantities obtained for the training set.

Thus, eliminating structures with large relaxations from the training set results in a more accurate representation of the configurational energy of alloys that, on average, have the structure of the undecorated lattice. It follows from this observation that the CE is not particularly well suited to do ground-state analyses which, typically, use the CE Hamiltonian to rank the energies of a large number of configurations (or ordered structures). In fact, the actual (and unknown) ground states may undergo large cell-internal and cell-external relaxations relative to the undecorated lattice and, in principle, their energies cannot be accurately described by the correlation functions defined on a significantly different lattice. On the other hand, a judicious selection of the training structures, i.e., structures for which the relaxations are small relative to the undecorated lattice, results in a CE that provides an acceptable approximation to the configurational energy of disordered alloys with small static or dynamic displacements from a lattice that has the same structure as the undecorated lattice.

### VIII. SUMMARY AND CONCLUSIONS

The implementation of the CE, which at present requires the fitting of the configurational energy to that of a set of ordered compounds, has been reformulated on two important aspects. First, we have shown that, while the orthonormality and completeness of the cluster functions  $\{\phi_\alpha(\sigma)\}$  provide a rigorous framework for determining the configurational variables, the assumption that the ECIs can be neglected beyond a certain maximum cluster size is generally a poor approximation for real systems. Our main result is that the bare cluster interactions obtained by projecting the energy onto the basis functions can be renormalized into configuration-dependent short-range effective interactions. The renormalized interactions are related in a straightforward manner to the Euler derivatives of the configurational energy, which is a homogeneous function of degree 1 in the correlation functions. Second, in the absence of cell-internal and cell-external relaxations (other than volume), we developed an approach for the CE that simultaneously fits a parametrized form of the configurational energy to the DFT calculated zero-pressure values of the energy of formation, volume, bulk modulus, and pressure derivative of the bulk modulus of a set of ordered compounds. The approach is applied to the Cu-Au system to develop a representation of the energy in terms of short-range interactions that, at the same time, has significantly improved predictive capabilities relative to the commonly used Ising-like model. Finally, we proposed an approximate scheme to carry out the CE for relaxed structures, which consists in controlling the maximum degree of deformation of the ordered compounds included in the training set used to fit the

renormalized effective interactions. The approach is proposed to underscore the fact the using the correlations functions obtained by decorating a fixed reference lattice to describe structures that undergo significant relaxations is not justified in the context of the CE. A corollary of this observation is that the CE is not very well suited to carry out general ground-state analyses since the such ground states may undergo significant relaxations relative to the reference lattice which, in turn, introduces large errors and/or uncertainties into the energy of formation predicted by the CE.

Finally, we note that the introduction of volume- and configurational-dependent ECIs poses an additional complication for most statistical thermodynamics applications of the CE. In particular, Monte Carlo (MC) simulations using concentration- and configurational-dependent ECIs will require the calculations to be carried out self-consistently. In principle, the approach could start with ECIs for a given configuration (e.g., random or  $T \gg 0$ ), which will produce a set of ECIs, and carry out the MC simulations to equilibrium. With the new state of order, the ECIs can be reset and calculations repeated until convergence (or self-consistency) is achieved.

### ACKNOWLEDGMENTS

The author acknowledges the Texas Advanced Computing Center (TACC) at the University of Texas at Austin for providing high-performance computing resources that have contributed to the research results reported within this paper.

### APPENDIX

Table III lists the clusters used to fit the Murnaghan parameters using the method labeled  $J[v]$  in Table I. A total of 26 clusters are required to minimize the cross-validation score. Thus, in this method, the fitting parameters are 26 functions of volume  $v$ , which correspond to the coefficients of a Taylor expansion of the energy, at volume  $v$ , to first order in the correlation functions. The Taylor expansion is carried out around the random state at 50:50 concentration. The coefficients of the Taylor expansion, denoted by  $K_n[v]$ , are shown in Fig. 7. As noted in Sec. VII, the functions  $K_n[v]$  are parametrized by a polynomial of degree 5 in the volume. The corresponding ECIs, defined by Eqs. (30) and (31), are shown in Figs. 8 and 9 for the state of order of the compounds in the training set (symbols) and for the random state (solid line).

For the case  $J[v, z]$ , the Taylor expansion of the energy is carried out to second order in the correlation functions. The range of the renormalized interactions, determined by the minimum of the cross-validation score, is given by the 10 clusters listed in Table IV. The second-order expansion involves 78 coefficients that must be determined as a function of volume. As in the case  $J[v]$ , the coefficients are parametrized by a polynomial of order 5 in the volume. The volume dependences for the first-order coefficients are shown in Fig. 10, while Fig. 11 shows the second-order coefficient for all pair clusters used in the approximation. The corresponding ECIs for all 10 clusters in the approximation are shown in Figs. 12 and 13 for, respectively, the pair and the nonpair clusters.

- [1] J. M. Sanchez, F. Ducastelle, and D. Gratias, *Phys. A (Amsterdam, Neth.)* **128**, 334 (1984).
- [2] M. Asta, C. Wolverton, D. de Fontaine, and H. Dreyssé, *Phys. Rev. B* **44**, 4907 (1991).
- [3] C. Wolverton, M. Asta, H. Dreyssé, and D. de Fontaine, *Phys. Rev. B* **44**, 4914 (1991).
- [4] J. M. Sanchez, *Phys. Rev. B* **48**, 14013 (1993).
- [5] J. M. Sanchez, *Phys. Rev. B* **81**, 224202 (2010).
- [6] J. M. Sanchez, *J. Phase Equilib. Diff.* **38**, 238 (2017).
- [7] B. L. Gyorffy, *Pyhs. Rev.* **5**, 2382 (1972).
- [8] F. Ducastelle, *Order and Phase Stability in Alloys*, Cohesion and Structure, edited by F. R. de Boer and D. G. Pettifor (North-Holland, Amsterdam, 1991), Vol. 3.
- [9] A. Zunger, S. H. Wei, L. G. Ferreira, and J. E. Bernard, *Phys. Rev. Lett.* **65**, 353 (1990).
- [10] T. Mohri, K. Terakura, S. Takizawa, and J. M. Sanchez, *Acta Metall. Mater.* **39**, 493 (1991).
- [11] J. M. Sanchez, J. P. Stark, and V. L. Moruzzi, *Phys. Rev. B* **44**, 5411 (1991).
- [12] D. B. Laks, L. G. Ferreira, S. Froyen, and A. Zunger, *Phys. Rev. B* **46**, 12587 (1992).
- [13] A. Zunger, in *Statics and Dynamics of Alloy Phase Transformations (NATO ASI)* (Plenum, New York, 1994), pp. 361–419.
- [14] A. van de Walle and G. Ceder, *J. Phase Equilib.* **23**, 348 (2002).
- [15] A. van de Walle, M. Asta, and G. Ceder, *Calphad* **26**, 539 (2002).
- [16] A. van de Walle and M. Asta, *Model. Simul. Mater. Sci. Eng.* **10**, 521 (2002).
- [17] A. Zunger, L. Wang, G. L. W. Hart, and M. Sanati, *Model. Simul. Mater. Sci. Eng.* **10**, 3105 (2002).
- [18] S. Muller, *J. Phys.: Condens. Matter* **15**, R1429 (2003).
- [19] V. Blum, G. L. W. Hart, M. J. Walorskiand, and A. Zunger, *Phys. Rev. B* **72**, 165113 (2005).
- [20] R. Drautz and A. Díaz-Ortiz, *Phys. Rev. B* **73**, 224207 (2006).
- [21] A. van de Walle, *Nat. Mater.* **7**, 4558 (2008).
- [22] D. Lerch, O. Wieckhorst, G. L. W. Hart, R. W. Forcade, and S. Muller, *Model. Simul. Mater. Sci. Eng.* **17**, 055003 (2009).
- [23] T. Mohri, *J. Mater. Sci.* **50**, 7705 (2015)
- [24] X. Zhang and M. H. F. Sluiter, *J. Phase Equilib. Diff.* **37**, 44 (2016).
- [25] G. L. W. Hart, L. J. Nelson, R. R. Vanfleet, B. J. Campbell, M. H. F. Sluiter, J. H. Neethling, E. J. Olivier, S. Allies, C. I. Lang, B. Mederig, and C. Wolverton, *Acta Mater.* **124**, 325 (2017).
- [26] S.-H. Wei, L. G. Ferreira, and A. Zunger, *Phys. Rev. B* **45**, 2533(R) (1992).
- [27] R. Drautz, R. Singer, and M. Fähnle, *Phys. Rev. B* **67**, 035418 (2003).
- [28] R. Drautz, H. Reichert, M. Fähnle, H. Dosch, and J. M. Sanchez, *Phys. Rev. Lett.* **87**, 236102 (2001).
- [29] M. Fähnle, R. Drautz, F. Lechermann, R. Singer, A. Díaz-Ortiz, and H. Dosch, *Phys. Status Solidi B* **242**, 1159 (2005).
- [30] K. Yuge, *Phys. Rev. B* **84**, 085451 (2011).
- [31] L.-L. Wang, T. L. Tang, and D. D. Johnson, *Nano Lett.* **14**, 7077 (2014).
- [32] L. Cao and T. Muller, *Nano Lett.* **16**, 7748 (2016).
- [33] J. M. Sanchez and D. de Fontaine, *Phys. Rev. B* **17**, 2926 (1978).
- [34] R. Kikuchi, J. M. Sanchez, D. de Fontaine, and H. Yamauchi, *Acta Metall.* **28**, 651 (1979).
- [35] J. M. Sanchez and D. de Fontaine, *Phys. Rev. B* **21**, 216 (1980).
- [36] J. M. Sanchez and D. de Fontaine, *Phys. Rev. B* **25**, 1759 (1982).
- [37] C. Sigli and J. M. Sanchez, *Acta Metall.* **33**, 1097 (1985).
- [38] T. Mohri, J. M. Sanchez, and D. de Fontaine, *Acta Metall.* **33**, 1463 (1985).
- [39] J. W. D. Connolly and A. R. Williams, *Phys. Rev. B* **27**, 5169 (1983).
- [40] R. K. R. Yarlagadda and J. E. Hershey, *Hadamard Matrix Analysis and Synthesis with Applications to Communications and Signal/Image Processing* (Kluwer Academic, Boston, MA, 1997).
- [41] V. Ozolins, C. Wolverton, and A. Zunger, *Phys. Rev. B* **57**, 6427 (1998).
- [42] V. Blum and A. Zunger, *Phys. Rev. B* **72**, 020104(R) (2005).
- [43] F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* **30**, 244 (1944).
- [44] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- [45] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [46] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [47] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- [48] Y. Zhang, G. Kresse, and C. Wolverton, *Phys. Rev. Lett.* **112**, 075502 (2014).
- [49] A. H. Nguyen, C. W. Rosenbrock, C. S. Reese, and G. L. W. Hart, *Phys. Rev. B* **96**, 014107 (2017).