

## Obtaining Ising-like expansions for binary alloys from first principles

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Many measurable properties of crystalline binary  $A_{1-x}B_x$  alloys, such as phase diagrams and excess thermodynamic functions, could be predicted via lattice statistical mechanics methods if one knew the ‘configurational energy’. The latter describes the energy at  $T = 0$  for each of the  $2^N$  possible occupation patterns of the  $N$  lattice sites by an  $A$  or a  $B$  atom. Traditional approaches described the configurational energy either via empirically fitted, truncated Ising Hamiltonians, or through highly approximated coherent-potential constructs. We illustrate here the alternative approach of ‘mixed-basis cluster expansion’ which extracts from a set of *ab initio* local density approximation calculations of

of the system. Finally, such simulations give directly the short-range-order parameters [8, 9]  $(x, T)$  and mixing enthalpies [10, 11].

The configurational energy  $E_{\text{config}}[.S_i, .R_i]$  can be modelled at different levels of approximation. One distinguishes between 'direct approaches' and 'cluster expansions' (CE).

and the ‘concentration wave method’ [22], which involve various approximations beyond the first-principles local density approximation (LDA) that underlies these approaches. In their various forms, these methods ignored atomic relaxation of even size-mismatched systems, approximated the total energy just by the sum of energy eigenvalues, and until recently [23], overlooked the Madelung contribution to the energy of ionic alloys. Here we will discuss how a robust CE can be obtained directly from LDA calculations on a few ordered  $A_pB_q$  structures. This ‘mixed-basis cluster-expansion’ (MBCE) approach [1, 24] builds on and extends the Connolly–Williams [25] approach. We have recently applied this method to predict thermodynamic behaviour of numerous binary alloys, including Cu–Au [26–28], Cu–Ag [26], Cu–Pt [29, 30], Ni–Au [26, 28, 31], Ag–Au [32, 33], Cu–Pd [33], Ni–V [34, 35], Ni–Pt [36], Ag–Pd [37, 38], Al–Zn [10, 39], Pd–V [34, 35], Pd–Pt [32], Cu–Al [10] and Cu–Zn [40] and some semiconductor alloys [20, 41, 42]. Such CEs are then used in Monte-Carlo simulations of the Hamiltonian. This yields phase diagrams, ground state structures, thermodynamic functions, short-range-order profiles and precipitate shapes.

In this paper, we illustrate in detail how such an expansion is constructed from LDA total energies. We focus on the technical issues of how a robust fit is achieved, how structures are chosen and how a stable expansion is obtained. We illustrate this using three systems: Ni–Pt, Cu–Au and  $\text{Sc}_{1-x}V_x\text{S}$  (where  $\square$  denotes a vacancy on the Sc site)

pure  $A$  and  $B$  cannot be expressed by these finite-ranged  $J$ s. Consequently, this contribution,  $E_{CS}(x)$ , to the formation enthalpy is expressed by the last term in equation (2):

$$E_{CS}(x) = \sum_{\mathbf{k}} \frac{E_{CS}^{eq}(x, \bar{\mathbf{k}})}{4x(1-x)} S(\mathbf{k}, x)^2 F(\mathbf{k}), \quad (5)$$

where  $E_{CS}^{eq}(x, \bar{\mathbf{k}})$  is the *constituent strain energy* [8,24], which is defined as the strain energy required to maintain coherency along an interface (with orientation  $\bar{\mathbf{k}}$ ) of bulk  $A$  and  $B$ .

To understand the necessity for this term in the CE, consider coherent phase separation, i.e. solid  $A$  and  $B$  coherently match along the crystallographic direction  $\bar{\mathbf{k}}$  (formally, this is a long-period superlattice  $A_n/B_n$  with  $n \rightarrow \infty$  oriented along  $\bar{\mathbf{k}}$



### 3.1. The constituent strain

Determining  $E_{CS}^{eq}(x, \bar{k})$  requires three steps: (i) calculating the epitaxial energies of each end point,  $A$  and  $B$  for several directions  $\bar{k}$  and in-plane lattice constant  $a$ , (ii) finding the  $a$  that minimizes the total  $A + B$  epitaxial energies for intermediate concentrations and (iii) interpolating the results of (ii) to arbitrary directions of  $\bar{k}$ .

For the first step, one calculates via LDA for pure  $A$  and pure  $B$  the total energy of several different in-plane lattice constants,  $a$  (perpendicular to  $\bar{k}$ ), and in each case, the unit cell is



five principal directions. Naturally, each of the energies  $E_A^{\text{epi}}$  and  $E_B^{\text{epi}}$  is positive definite and, hence, the coherency strain of equation (7) must be positive definite.

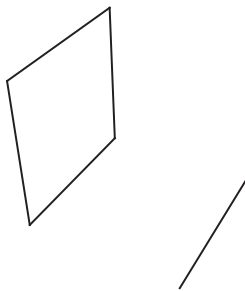
Finally, in the third step, the constituent strain energy is interpolated to arbitrary directions of  $\bar{k}$  by fitting the results to an expansion of Kubic harmonics. That is, after  $E_{\text{CS}}^{\text{eq}}(x, \bar{k})$  has been directly calculated for a set of directions using total energy methods, it is then interpolated to all directions by fitting the directly calculated results the following expression:

$$E_{\text{CS}}^{\text{eq}}(x, \bar{k}) = \sum_{l=0}^{l_{\text{max}}} b_l(a) K_l(\bar{k}). \quad (8)$$

In cubic alloys, only terms with  $l = 0, 4, 6, 8, 10, 12, \dots$  are non-zero and only these enter into the expansion. If only the first two terms are retained, then (8) reduces to well-known expression from harmonic elasticity theory (see discussion in [44]). However, our experience shows that anharmonic effects are usually significant, and so, in practice, we normally fit the data using at least four terms in equation (8), i.e.  $l_{\text{max}} = 8$ . Figure 4 depicts  $E_{\text{CS}}^{\text{eq}}(x, \bar{k})$  for Ni–Pt and Cu–Au as a parametric plot in all directions.

In summary,  $E_{\text{CS}}^{\text{eq}}(x, \bar{k})$  is determined as follows:

- (a) Epitaxial calculations are performed for each constituent of the alloy,  $A$  and  $B$ . For a series of different in-plane lattice constants  $a$  ( $a_A = a = a_B$ ), the total energy is minimized by varying the out-of-plane lattice constant (parallel to  $\bar{k}$ ) while the in-plane lattice constant





is held fixed. These values,  $E_{\text{epi}}(a)$ , are interpolated to all values between  $a_A$  and  $a_B$  by a polynomial fit.

- (b) The strain energy for any composition  $x$  is taken to be the weighted average of the epitaxial energies calculated in (a) but we choose the in-plane lattice constant  $a$  to minimize the strain energy as shown in equation (7).
- (c) The strain energy for several directions  $\bar{k}$  is determined by repeating (a) and (b) for each direction  $\bar{k}$ . In practice, we use 5–7 different  $\bar{k}$ -directions. These directly calculated  $\bar{k}$ -dependent values for the strain energy are then interpolated to arbitrary values of  $\bar{k}$  by fitting to an expansion in Kubic harmonics, as shown in equation (8). Because of anharmonic effects, we typically find it necessary to use at least four terms in equation (8).

### 3.2. The constrained CE fit

In constructing the fit of  $H_{\text{CE}}(\mathbf{k})$  to  $H_{\text{LDA}}(\mathbf{k})$ , it is advantageous to use a different number interaction energies  $J$  than the number of LDA-calculated input formation enthalpies. This is unlike the Connolly–Williams approach [25] where the number of input structures and interaction energies must be the same, so a large number of LDA calculations might be needed to obtain a converged expression. However, at the same time, we must avoid ‘over-fitting’ by using too many interaction energies which results in a very accurate *fit* but a very poor *prediction* for structures not included in the fit. To achieve these objectives, we can require that  $J_{\text{pair}}(\mathbf{k})$  be a smooth function of  $\mathbf{k}$ . We define [24] a ‘smoothness value’  $M$  as

$$M = \frac{1}{\sum_{\mathbf{k}} J(\mathbf{k})} \left[ \frac{1}{\sum_{\mathbf{k}} J(\mathbf{k})} \right]^{-2} J(\mathbf{k}), \quad (9)$$

where the exponent

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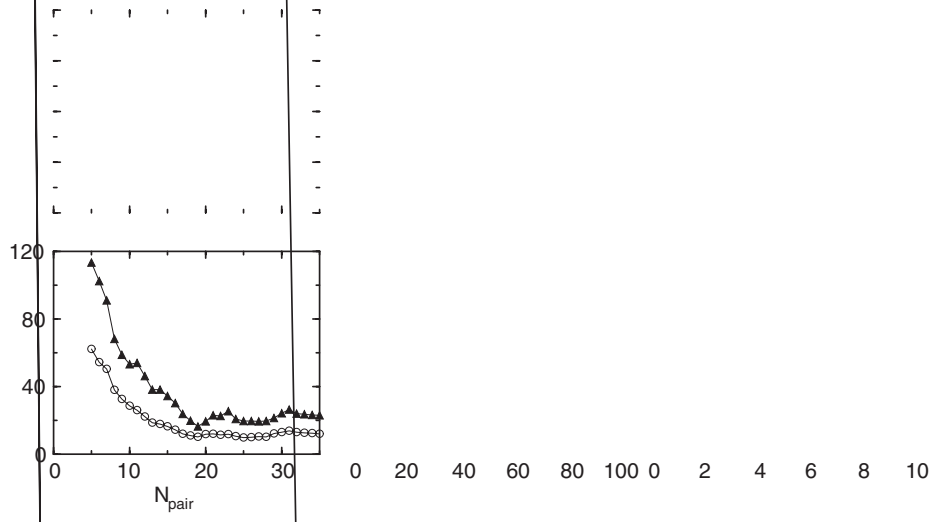
[40] and table III in [28] give a typical list of input structures. These structures need not be

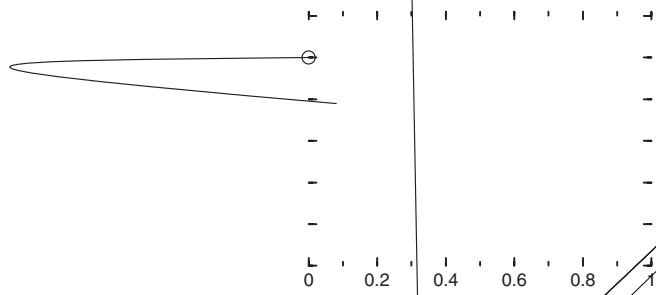
#### 4.2. Selection of the type of cluster interactions

The interaction energies  $J$  are determined by minimizing equation (10). Of course an excellent fit can be obtained by using a large number of fitting parameters but such 'over-fitting' destroys the predictive accuracy of the CE. We desire a CE which accurately fits the input structures *and*



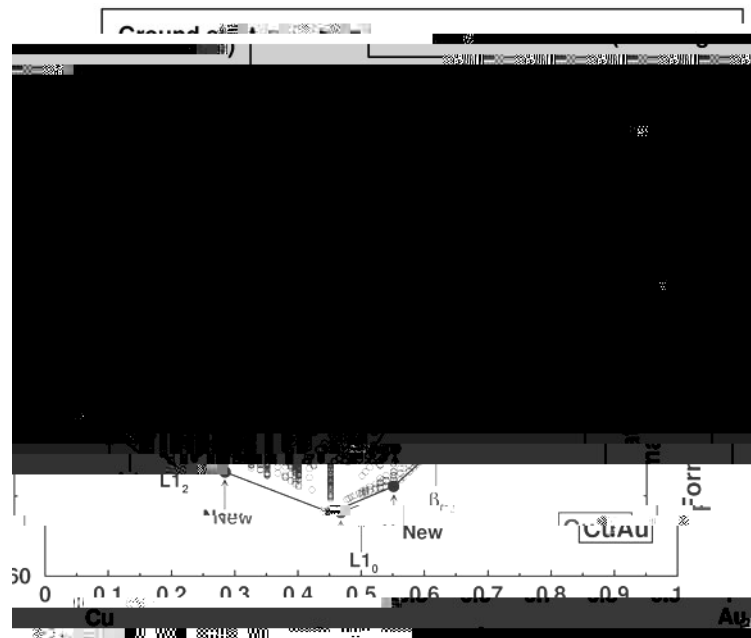




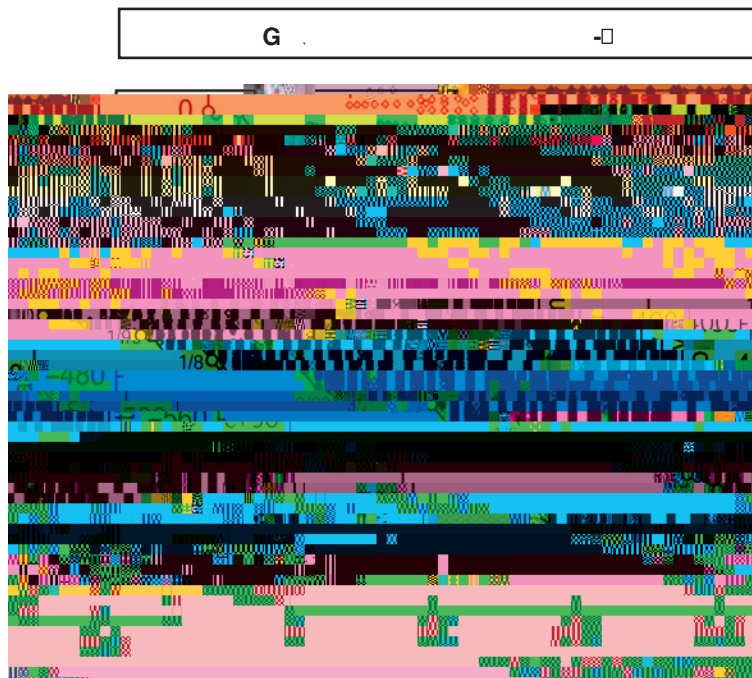








. Ground state search for Cu–Au (see caption of figure 10).



. Ground state search for  $\text{Sc}_{1-x}\text{S}_x$  (see caption of figure 10).





