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] $\alpha(x, T)$ and mixing enthalpies [10, 11].

The configurational energy $E_{\text{config}}[\{S_i\}, \{\boldsymbol{R}_i\}]$ 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 $\mathrm{Sc}_{1-x}\square_x\mathrm{S}$ (where $\square$ denotes a vacancy on the Sc site) pure A and B cannot be expressed by these finite-ranged Js. Consequently, this contribution, $E_{\mathrm{CS}}(\sigma)$, to the formation enthalpy is expressed by the last term in equation (2):

$$E_{\mathrm{CS}}(\sigma) \qquad \sum_{\boldsymbol{k}} \frac{E_{\mathrm{CS}}^{\mathrm{eq}}(x, \bar{k})}{4x(1 \quad x)} |S(\boldsymbol{k}, \sigma)|^2 F(\boldsymbol{k}), \tag{5}$$

where $\quad E_{\mathrm{CS}}^{\mathrm{eq}}(x, \bar{k})$ is the *constituent strain energy* [8,24], which is defined as the strain energy required to maintain coherency along an interface (with orientation $\bar{k}$) 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 $\bar{k}$ (formally, this is a long-period superlattice A_n/B_n with $n \to \infty$ oriented along $\bar{k}$

3.1. The constituent strain

Determining $E_{\mathrm{CS}}^{\mathrm{eq}}(x, \bar{k})$ 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 $\quad E_A^{\mathrm{epi}}$ and $\quad E_B^{\mathrm{epi}}$ is positive definite and, hence, the coherency strain of equation (7) must be positive definite.

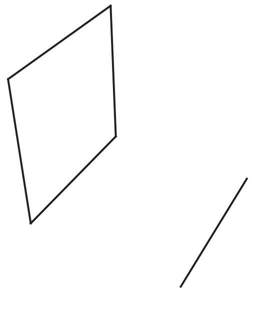
Finally, in the third step, the constituent strain energy is interpolated to arbitrary directions of $\bar{k}$ by fitting the results to an expansion of Kubic harmonics. That is, after $E^{\mathrm{eq}}_{\mathrm{CS}}(x, \bar{k})$ has been directly calculated for a set of directions using total energy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

$$E^{\mathrm{eq}}_{\mathrm{CS}}(x, \bar{k}) \quad \sum_{l\ \ 0}^{l_{\max}} b_l(a\quad)K_l(\bar{k}). \tag{8}$$

In cubic alloys, only terms with $l \quad 0, 4, 6, 8, 10, 12, \ldots$ 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. $l_{\max} \quad 8$. Figure 4 depicts $E^{\mathrm{eq}}_{\mathrm{CS}}(x, \bar{k})$ for Ni–Pt and Cu–Au as a parametric plot in all directions.

In summary, $\quad E^{\mathrm{eq}}_{\mathrm{CS}}(x, \bar{k})$ 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 $a \quad (a_A \;\square\; a \quad \square\; a_B)$, 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, $E_{\mathrm{epi}}(a\quad)$, 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 $a\quad$ 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 $H_{\mathrm{CE}}(\sigma)$ to $H_{\mathrm{LDA}}(\sigma)$, 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 $J_{\mathrm{pair}}(\boldsymbol{k})$ be a smooth function of $\boldsymbol{k}$. We define [24] a 'smoothness value' M as

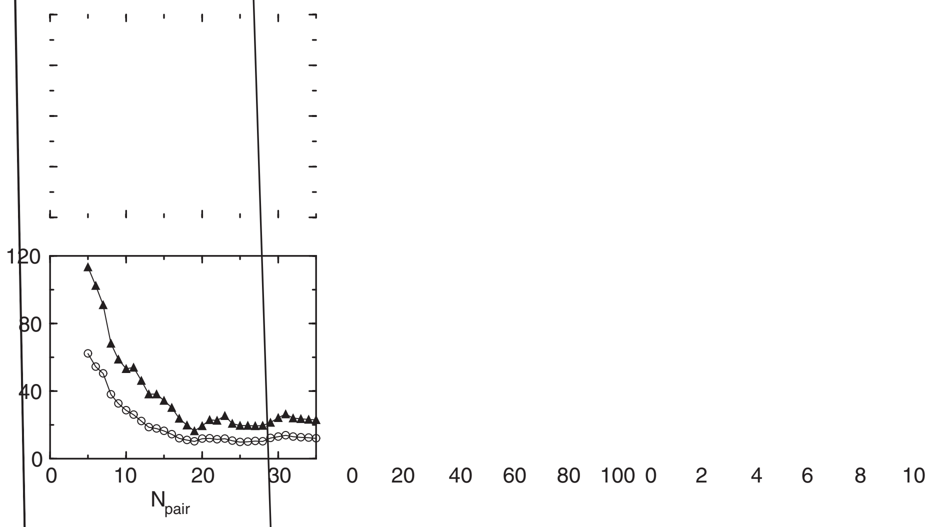
$$M \quad \frac{1}{\alpha}\sum_{\boldsymbol{k}} J(\boldsymbol{k})\left[-\;{}^{2}_{\boldsymbol{k}}\right]^{\lambda/2} J(\boldsymbol{k}), \tag{9}$$

where the exponent λ

[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*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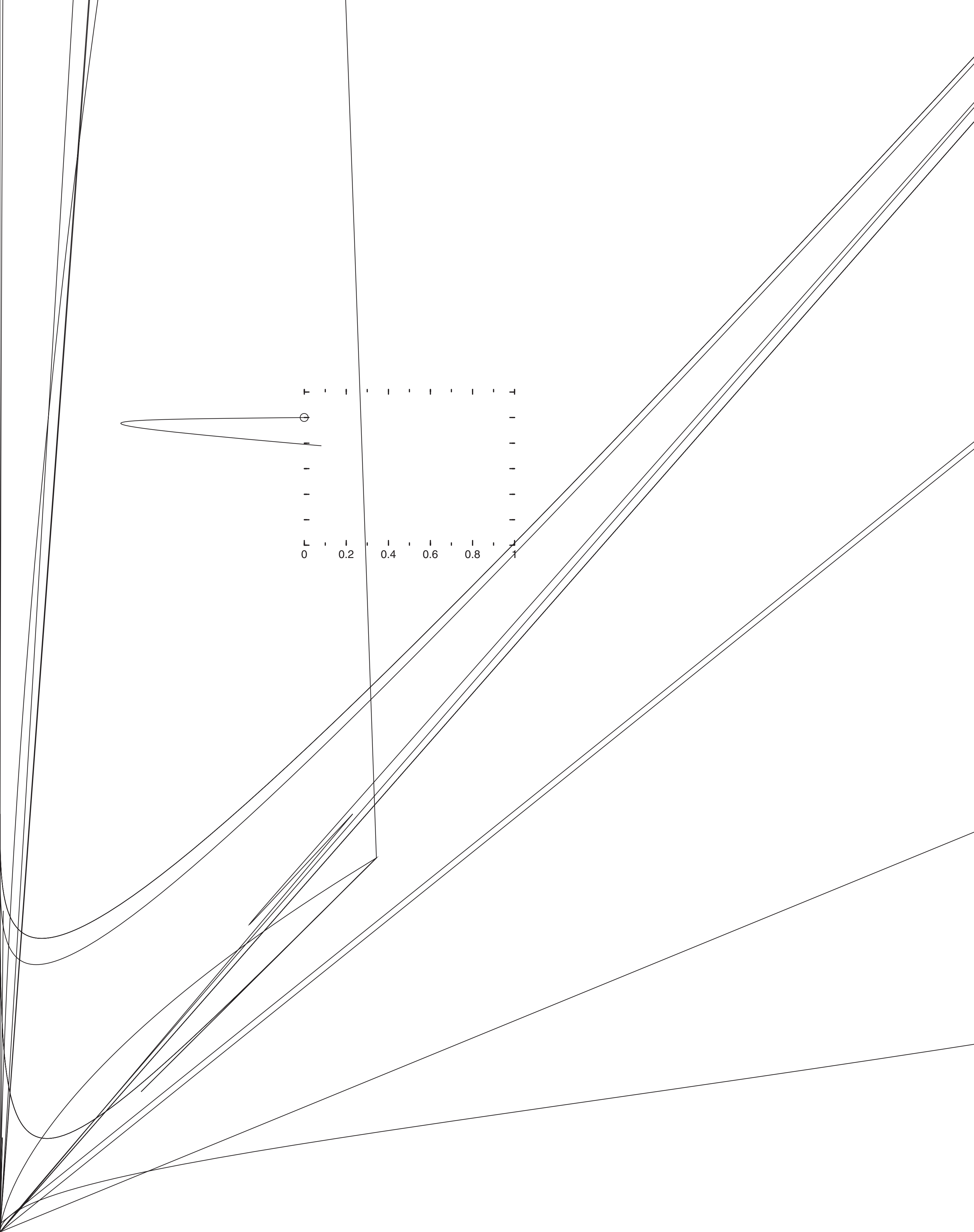
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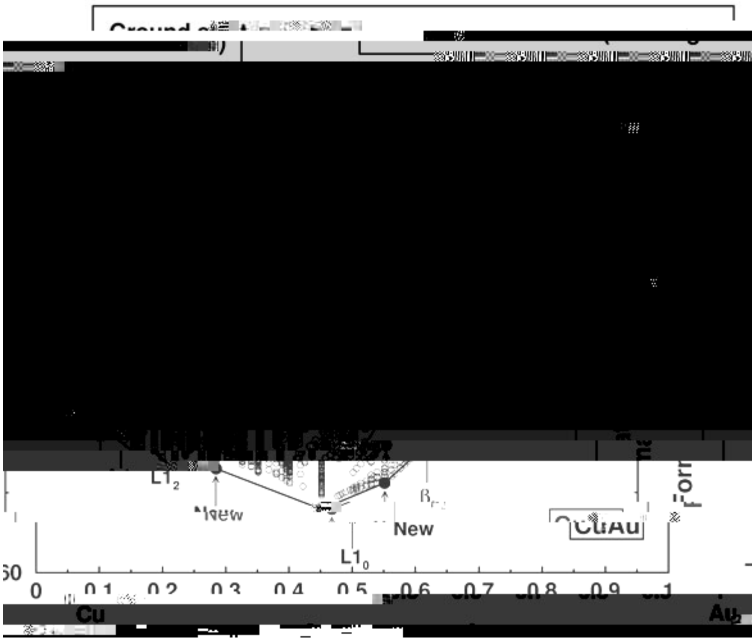
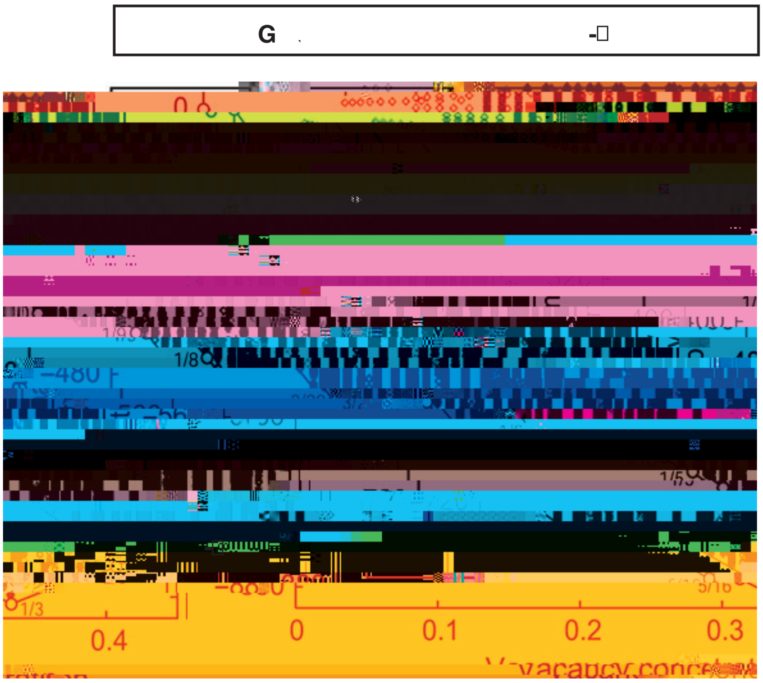
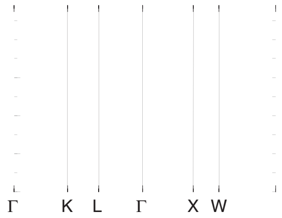


. Ground state search for Cu–Au (see caption of figure 10).



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