Exploring the configurational space of binary alloys: Different sampling for different cell shapes

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In many areas of alloy theory, such as determination of the $T=0$ ground state structures or calculation of finite-T alloy thermodynamics, one needs to enumerate and evaluate the $\sim 2^N$ configurations σ created by different substitutions of atoms A and B on the N sites of a unit cell. These configurations consist of M_{ICS} "inequivalent cell shapes" (ICS's), each having M_{SSS} "same-shape structures" (SSS's). Exhaustive evaluation approaches attempt to compute the physical properties $P(\sigma)$ of *all* SSS's belonging to *all* ICS's. "Inverse band structure" approaches sample the physical properties of all SSS's belonging to a *single* inequivalent cell shape. We show that the number M_{ICS} of ICS's rises only as BN^{α}, whereas the total number of SSS's scales as $Ae^{\gamma N}$. Thus, one can *enumerate* the former (i.e., calculate all) and only *sample* the latter (i.e., calculate but a few).

approach is possible only when $P(\sigma)$ is easily calculable and even then this is practically limited to small N (often $N \leqslant 20$). This approach has been applied extensively to ground state searches of Ising-like Hamiltonians,[14–16] and is robust and safe. However, due to the fast rise of 2^N with N, this approach is limited in practice to rather small N for many applications.[17–19] In the *sampling approach* only a few $P(\sigma)$ are evaluated and the space is sampled iteratively by methods that look for special values. This can be accomplished by simulated annealing[5,20] (SA) or via genetic algorithm[17,18,21,22] (GA). However, these sampling approaches work best for a fixed cell shape, so the search is often limited to all SSS's of a *given* ICS group (see Fig. 1). Such sampling approaches were previously applied in the context of IBS where the SSS's corresponding to a given ICS are surveyed by, e.g., SA (see Ref. 5) or GA (see Ref. 22).

Here, we show that it is possible to combine the advantages of the exhaustive evaluation and sampling approach methods by performing a *sampling* on the N_{SSS} same-shape structures (e.g., via GA), and *repeating this explicitly* for each of the N_{ICS} ICS's. This "different sampling for different (cell) shapes" (DSDS) approach is what we will describe in this paper. This approach can extend the applicability of exhaustive evaluation methods from $N \approx 20$ to larger N in the 2^N problem.

The remainder of the paper is organized as follows. In Sec. II, we discuss the structure of the configurational space of the binary alloys, showing the hierarchy into which the crystal configurations are organized. We also present the algorithm to determine the configurations that are contained in the space. In Sec. III, we discuss the direct enumeration based "exhaustive evaluation" and the "sampling search," and in Sec. IV, we combine direct enumeration and sampling procedures to introduce the different sampling for different (cell) shape (DSDS) search method. In Sec. V, we apply this method to the search for the ground state configurations in the metallic alloy Au-Pd and Mo-Ta. In this case we use as $P(\sigma)$ the cluster expansion (CE) expression for the formation energy $\Delta H_{CE}(\sigma)$. We find that searching by DSDS structures with up to $N=20$ atoms gives the same result as exhaustive

In the fcc case we require for the vectors $\mathbf{a}_i$ (for the bcc lattices multiply N by 2 here and in all the formulas of this section)

$$\mathbf{a}_1 \times \mathbf{a}_2 \cdot \mathbf{a}_3 = 2N \qquad (1)$$

and, with no loss of generality,

$$a_3^2 \geqslant a_2^2 \geqslant a_1^2. \qquad (2)$$

Since adding to or subtracting from $\mathbf{a}_2$ a multiple of $\mathbf{a}_1$ does not change the lattice, we require

$$(\mathbf{a}_2 \pm \mathbf{a}_1)^2 \geqslant a_2^2 \quad \text{or} \quad a_1^2 \geqslant 2\mathbf{a}_1 \cdot \mathbf{a}_2 \geqslant 0. \qquad (3)$$

One may also add any integer combination of $\mathbf{a}_1$ and $\mathbf{a}_2$ to $\mathbf{a}_3$ without changing the lattice, so that we also require

$$\mathbf{a}_3 = t\mathbf{a}_1 + u\mathbf{a}_2 + z\mathbf{a}_1 \times \mathbf{a}_2, \qquad (4)$$

given composition $A_n B_{N-n}$, the symmetry-reduced number $\widetilde{N}_{\text{SSS}}^{(I)}(N, x_n)$ of SSS's will be lower than $\binom{N}{n}$ and will depend on the Ith cell shape:

$$\widetilde{N}_{\text{SSS}}^{(I)}(N, x_n) = D_{N,n}^{(I)} \binom{N}{n},\qquad (14)$$

where $D_{N,n}^{(I)} \leq 1$ represents the reduction factor due to the application of the symmetry operations. Given the number N of atoms per cell and the composition x_n, the symmetry reduction factor $D_{N,n}^{(I)}$ will depend on the shape of the Ith ICS.

It is interesting to calculate for the Ith ICS containing N atoms the *total* number of SSS's obtained summing over *all* the allowed compositions. In case symmetry is not used, the total number of SSS's is

$$T_{\text{SSS}}(N) = \sum_{n=1}$$

convergence of the expansion with respect to the length of interaction makes a truncated expansion a satisfactory ap-

definition of this quantity) of these ground states relative to the tie line is, however, very small, i.e., 0.1 meV/atom, so that the ground state line appears almost unchanged with respect to that obtained considering structures with no more than 20 atoms per cell. 0.1 meV/atom depth relative to the tie line of the neighboring ordered structures is indeed small, but within the numerical precision of the cluster expansion. Note that this is not the depth with respect to the random alloy which decides T_c. At concentration $x=3/8$ the structure obtained is not a superlattice, while at concentration $x=1/6$ we obtain the superlattice (310) $(AB_4)(AB_5)(AB_6)(AB_5)$. Finding a superlattice along the (310) direction is in agreement with the picture that the exhaustive evaluation[23] suggested for this region, which is characterized by the so-called "adaptive" structures. Such structures allow an efficient adaptation to infinitely small changes in the concentration within a fairly large range of alloy compositions.hchara(ompha(omph)-d23814.5arisres)814.5frtom)814.5(he)814.5balanche   the   sttai

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