Concentration wave method for description of all possible energy states of $A_2BC$ ordered alloy

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Abstract. The procedure for describing all possible energy states of an alloy based on the concentration wave method proposed by Khachaturian is employed to describe all possible energy states of ordered $A_2BC$ alloy based on $\mathcal{N}$-dimensional lattice. Within the framework of this method, a complete enumeration of the structures obtained by the superposition of $\mathcal{N}$ plane concentration waves with all possible wave vectors is carried out, provided that the given stoichiometry is preserved. For each such superposition, the order parameters on the first $I$ coordination spheres are calculated, thereby determining the point in the $I$-dimensional order parameter space corresponding to the given structure. For the case of $I=2$ it is shown that a complete enumeration of all structures generated by one plane concentration wave fills a non-convex figure in the space of two order parameters.

1. Introduction

It seems interesting to solve the problem of describing all possible energy states realized in a structure of a given composition for a given crystal lattice under the assumption that the energies of interatomic interactions can take any values, while taking into account the pair bonds of atoms in the first few coordination spheres. The solution of this problem will make it possible to describe possible superstructures realized in an alloy of a given stoichiometry, for a given topology of the lattice on which the atoms of the alloy are located, and for a given number of coordination spheres of pair interatomic interactions taken into account. An algorithm for solving this problem based on the method of concentration waves has been proposed in [1].

This paper proposes a simplified algorithm for determining the boundaries of variation of the order parameters for the structure of stoichiometry $A_2BC$, given on an arbitrary $\mathcal{N}$-dimensional lattice, taking into account interatomic interactions in the first $I$ coordination spheres [1]. When solving this problem, only the structural characteristics of the alloy are taken into account, and the values of the energies of interatomic interactions are not involved in consideration [2]. The algorithm is applied for ternary alloys of stoichiometric composition, taking into account the interactions of atoms in the first two coordination spheres ($I=2$) [3-7]. As examples of ternary alloys, Heusler alloys should be mentioned as materials with a number of applications [8,9].

2. Model formulation

We consider the case of a three-component alloy of the composition $A_2BC$ with the atoms of types $A$, $B$, and $C$ located in the sites of a given lattice. Interactions of atoms in the first $I$ coordination spheres
In a three-component alloy, the following coordination spheres can be written in the form

\begin{equation}
    c_A = \frac{m}{m+n+k}, \quad c_B = \frac{n}{m+n+k}, \quad c_C = \frac{k}{m+n+k}.
\end{equation}

Here \( p_{kl}^{(i)} \) denote the probability that on the \( i \)-th coordination sphere of an atom of type \( K \) there is an atom of type \( L \), where \( K, L = \{A,B,C\} \). In a three-component alloy, there are the following relationships between nine probabilities, \( p_{kl}^{(i)} \) and three concentrations \( c_A, c_B, c_C \):

\begin{align*}
p_{AA}^{(i)} + p_{AB}^{(i)} + p_{AC}^{(i)} &= 1, \quad p_{BA}^{(i)} + p_{BB}^{(i)} + p_{BC}^{(i)} = 1, \quad p_{CA}^{(i)} + p_{CB}^{(i)} + p_{CC}^{(i)} = 1, \quad c_A + c_B + c_C = 1, \\
c_A(p_{AB}^{(i)} - c_A) &= -\frac{1}{2}[c_A(p_{BB}^{(i)} + p_{BC}^{(i)}) + c_B(p_{BA}^{(i)} + 2c_A) + c_C(p_{CA}^{(i)} - 2c_A)], \\
c_B(p_{BA}^{(i)} - c_B) &= -\frac{1}{2}[c_B(p_{BB}^{(i)} + p_{BC}^{(i)}) + c_A(p_{BA}^{(i)} + 2c_B) + c_C(p_{CA}^{(i)} - 2c_B)], \\
c_C(p_{CC}^{(i)} - c_C) &= -\frac{1}{2}[c_C(p_{CC}^{(i)} + p_{CB}^{(i)}) + c_A(p_{CA}^{(i)} - 2c_C) + c_B(p_{CB}^{(i)} - 2c_C)].
\end{align*}

Let us denote by \( \phi_{KL}^{(i)} \) the binding energy of a pair of atoms of types \( K \) and \( L \) located at a distance equal to the radius of the \( i \)-th coordination sphere.

The potential energy of the structure per atom, taking into account the interaction of atoms in the first \( I \) coordination spheres can be written in the form

\begin{equation}
    E = \sum_{i=1}^{I} \frac{N_i}{2} \left[ c_A(p_{AA}^{(i)}\phi_{AA}^{(i)} + p_{AB}^{(i)}\phi_{AB}^{(i)} + p_{AC}^{(i)}\phi_{AC}^{(i)}) + c_B(p_{BA}^{(i)}\phi_{BA}^{(i)} + p_{BB}^{(i)}\phi_{BB}^{(i)} + p_{BC}^{(i)}\phi_{BC}^{(i)}) + c_C(p_{CA}^{(i)}\phi_{CA}^{(i)} + p_{CB}^{(i)}\phi_{CB}^{(i)} + p_{CC}^{(i)}\phi_{CC}^{(i)}) \right].
\end{equation}

The energy of the completely disordered state of the structure is determined by expression (6) for \( p_{AA}^{(i)} = p_{BA}^{(i)} = p_{CA}^{(i)} = c_A, \quad p_{AB}^{(i)} = p_{BB}^{(i)} = p_{BC}^{(i)} = c_B, \quad p_{AC}^{(i)} = p_{CB}^{(i)} = p_{CC}^{(i)} = c_C \), which gives

\begin{equation}
    E_{\text{disord}} = \sum_{i=1}^{I} \frac{N_i}{2} \left[ c_A\phi_{AA}^{(i)} + c_B\phi_{BB}^{(i)} + c_C\phi_{CC}^{(i)} \right].
\end{equation}

The energy of decomposition into pure components is determined by expression (6) for \( p_{AB}^{(i)} = p_{BA}^{(i)} = p_{AC}^{(i)} = p_{CA}^{(i)} = p_{CB}^{(i)} = p_{CC}^{(i)} = 0, \quad p_{AA}^{(i)} = 1, \quad p_{BB}^{(i)} = 1, \quad p_{CC}^{(i)} = 1 \), which gives

\begin{equation}
    E_{\text{decomp}} = \sum_{i=1}^{I} \frac{N_i}{2} \left[ c_A\phi_{AA}^{(i)} + c_B\phi_{BB}^{(i)} + c_C\phi_{CC}^{(i)} \right].
\end{equation}

Let us choose the energy \( E_{\text{disord}} \) as a reference point, and characterize the energy of any structure by the difference

\begin{equation}
    \Delta E = E - E_{\text{disord}} = -\sum_{i=1}^{I} \frac{N_i}{4} \left[ \alpha_{AB}^{(i)}\phi_{AB}^{(i)} + \alpha_{AC}^{(i)}\phi_{AC}^{(i)} + \alpha_{BC}^{(i)}\phi_{BC}^{(i)} \right],
\end{equation}

where the short-range order parameters

\begin{align*}
    \alpha_{AB}^{(i)} &= c_A p_{AB}^{(i)} + c_B p_{BA}^{(i)} - 2c_A c_B, \\
    \alpha_{AC}^{(i)} &= c_A p_{AC}^{(i)} + c_C p_{CA}^{(i)} - 2c_A c_C, \\
    \alpha_{BC}^{(i)} &= c_B p_{BC}^{(i)} + c_C p_{CB}^{(i)} - 2c_B c_C,
\end{align*}

and the ordering energies

\begin{align*}
    \omega_{AB}^{(i)} &= \phi_{AA}^{(i)} + \phi_{BB}^{(i)} - 2\phi_{AB}^{(i)}, \\
    \omega_{AC}^{(i)} &= \phi_{AA}^{(i)} + \phi_{CC}^{(i)} - 2\phi_{AC}^{(i)},
\end{align*}

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\( \omega_{BC}^{(i)} = \varphi_{BB}^{(i)} + \varphi_{CC}^{(i)} - 2\varphi_{BC}^{(i)} \),

are introduced.

As we see from (9), the deviation of the energy of any structure from the energy of a disordered alloy is uniquely determined by the \( N_i \) coordination numbers, by the ordering energies \( \omega_{AB}^{(i)} \), and by the parameters \( \alpha_{KL}^{(i)} \), which are Cowley short-range order parameters [10].

To determine the range of variation of the order parameters \( \alpha_i \), the method of concentration waves [1] is used, adapted for the purposes of this study as follows. A computational cell with superimposed periodic boundary conditions is considered, which, for the three-dimensional lattice \( (N=3) \) contains the \( N_x \times N_y \times N_z \) atoms. Then the following values are calculated:

\[
C_{ijl} = \sin \left( \frac{2\pi k_x^{(i)}}{N_x} + \frac{2\pi k_y^{(i)}}{N_y} + \frac{2\pi k_z^{(i)}}{N_z} + \varepsilon_i \right) \\
+ \sin \left( \frac{2\pi k_x^{(2)}}{N_x} + \frac{2\pi k_y^{(2)}}{N_y} + \frac{2\pi k_z^{(2)}}{N_z} + \varepsilon_2 \right) \\
+ \sin \left( \frac{2\pi k_x^{(3)}}{N_x} + \frac{2\pi k_y^{(3)}}{N_y} + \frac{2\pi k_z^{(3)}}{N_z} + \varepsilon_3 \right) + C,
\]

where \( 0 \leq i \times N_x, \ 0 \leq i \times N_y, \ 0 \leq i \times N_z \). The components of the vectors \( k^{(1)}, k^{(2)}, k^{(3)} \) in the expression (12) have integer values \( 0 \leq k^{(1)}_x, k^{(2)}_x, k^{(3)}_x \leq N_x, \ 0 \leq k^{(1)}_y, k^{(2)}_y, k^{(3)}_y \leq N_y, \ 0 \leq k^{(1)}_z, k^{(2)}_z, k^{(3)}_z \leq N_z \). The phase shifts \( \varepsilon_i, \varepsilon_2, \varepsilon_3 \) are introduced in order to avoid the vanishing of the \( C_{ijl} \) numbers. The constant \( C \) determines the stoichiometry of the structure of the three-component \( A_2BC \) alloy and it should be taken as

\[
C = \cos[\pi(e_B + \frac{C}{2})].
\]

Using the \( C_{ijl} \) numbers, the computational cell is filled with atoms of types \( A, B, \) and \( C \) in such a way that the node with the number \((i, j, l)\) is assigned sort \( A \) if \( C_{ijl} > 0 \) and type \( B \) if \( C_{ijl} < 0 \) and

\[
C_{ijl} \leq \cos \left( \pi \frac{C}{2} \right) - \cos(\pi \cdot c_A).
\]

In this case, when filling the computational cell with atoms, the type \( C \) is placed if the values \( C_{ijl} > 0 \) and \( C_{ijl} \geq \left( \cos \left( \pi \frac{C}{2} \right) - \cos(\pi \cdot c_A) \right) \).

After filling the cell with atoms, the observance of stoichiometry is checked and, if it is violated, this structure is not considered. For structures with stoichiometry \( A_2BC \), the short-range order parameters \( \alpha_{KL}^{(i)}, i = 1, \ldots, I \) are calculated and displayed as points in the \( I \)-dimensional \((\alpha_1, \ldots, \alpha_I)\) space. This procedure is performed for all possible vectors \( k^{(1)}, k^{(2)}, k^{(3)} \) in (12) which, for sufficiently large \( N_x, N_y \) and \( N_z \) makes it possible to get an idea of the ranges of possible changes in the order parameters of the \( \alpha_{KL}^{(i)} \).

The described algorithm is much more efficient than the method of full enumeration of the arrangement of atoms of types \( A, B, \) and \( C \) over the periodicity cell, since its application is limited by the relatively small dimensions of the cell, \( N_x, N_y \) and \( N_z \), and, which does not allow describing some of the possible structures.
Figure 1. Range of admissible values of short-range order parameters for the $A_2BC$ alloy on the bcc lattice for (a) $\alpha_{AB}^{(i)}$, (b) $\alpha_{AC}^{(i)}$ and (c) $\alpha_{BC}^{(i)}$.

As an example, the proposed algorithm is applied to the $A_2BC$ alloy on the bcc lattice. The possible ranges of the order parameters are presented in Fig. 1 for (a) $\alpha_{AB}^{(i)}$, (b) $\alpha_{AC}^{(i)}$ and (c) $\alpha_{BC}^{(i)}$.

3. Conclusions
A simplified algorithm based on the method of concentration waves is proposed, which makes it possible to determine the ranges of possible changes in the short-range order parameters $\alpha_i$ for alloys with the composition $A_2BC$, given on an arbitrary lattice of arbitrary dimension $N$. The parameters $\alpha_i$, together with the coordination numbers $N_i$ and the ordering energies $\omega_i$, determine the potential energy of the structures. The described algorithm is based on several essential assumptions. In particular, it does not take into account the deformation of the lattice upon permutation of atoms of sorts $A$, $B$ and $C$, in other words, it is assumed that atoms of different sorts have the same size. The proposed procedure works much faster than full enumeration algorithm, and, for structures on three-dimensional lattices, the gain in time will be even more significant than for two-dimensional lattices.

Methodology developed in this study can be applied to the lattices of any dimension, in particular, to the novel 2D materials [11-15].

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