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Short Communication

Cluster probabilities in binary alloys from diffraction data

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Abstract. — A method is proposed which permits us to calculate, from diffuse scattering data, the probabilities for various clusters of atoms to appear in substitutional disordered alloys. It leads to simple, Taylor-like expressions for these probabilities in terms of experimentally measured short-range order parameters. Explicit calculations are performed for two clusters, nearest-neighbour triangle and tetrahedron, on the face-centered cubic lattice. The results obtained agree well with those of other approaches. The applicability of the Kirkwood superposition approximation to alloys is discussed.

Description of local order in disordered state is a major problem in the alloy theory (for a review, see [1, 2]). From the quantitative point of view the state of order is characterized by probabilities of finding various clusters (pairs, triangles, tetrahedra, etc.) of atoms in an alloy. The pair probabilities or, equivalently, the Warren-Cowley short-range order (SRO) parameters can be extracted with sufficient accuracy from the X-ray or neutron diffuse scattering data, while no efficient method exists to measure cluster probabilities (CPs) beyond the pair ones [1, 2]. At the same time, information about CPs is essential in a number of problems in alloy physics, such as nucleation, diffusion of interstitials, Mössbauer effect, positron annihilation, etc.

Several methods for estimating the CPs from the experimentally determined SRO parameters have been proposed. In the framework of the Gehlen-Cohen (CC) simulation procedure [3] the CPs can be obtained by directly counting the corresponding configurations in a particular computer-generated alloy pattern compatible with the mixed set of several near-neighbour SRO parameters. The probability variation method (PVM) [4, 5] is based on the maximization of the entropy-like function with respect to the unknown CPs provided that the concentration and the SRO parameters are kept fixed; in the PVM it is supposed that the energy does not depend on the CPs of order higher than pair, i.e. only pair interactions are assumed. These

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methods yield mutually consistent numerical results [4], but fail to give explicit expressions for the higher-order CPs in terms of the pair ones. From the point of view of practical applications it would be highly desirable for such expressions to be available.

This goal can be achieved by using the Kirkwood superposition approximation (SA) [1, 4]. It consists in approximating 3-site, 4-site, etc., CPs by a normalized product of proper pair probabilities. However, the serious shortcoming of this method is that it works well only for weakly correlated systems while becoming inapplicable in the case of developed SRO [4]. Furthermore, the SA suffers from an ambiguity [4] and does not lead to an exact result for 3-site CPs in the case of equiatomic alloy [6].

The aim of the present paper is to develop a new scheme capable of overcoming the above difficulties in calculating the CPs. Recently, the present authors have put forward the theory of SRO in disordered state [7] based on the $\gamma$-expansion method (GEM) [8] which gives accurate values of SRO parameters via fairly simple calculations. Its accuracy has also been demonstrated in the solution of the "inverse" problem of determining pair potentials from a given SRO intensity [7, 9]. In the problem under consideration GEM leads to explicit approximate expressions for the CPs in terms of the experimentally measured SRO parameters. These relations are obtained in the framework of the Ising model for binary alloys and follow from the pair character of interaction between atoms in the model.

The $s$-site CP is defined as

$$ p_{1}^{i_1 \cdots i_s} = \langle p_{1}^{i_1} \cdots p_{s}^{i_s} \rangle $$

(1)

where the angular brackets denote ensemble averaging, $p_{n}^{i}$ is the occupation number: $p_{n}^{i} = 1$ if the site $n$ is occupied by the atom of the $i$-th kind, and $p_{n}^{i} = 0$ otherwise. The CPs corresponding to different occupations of a particular set of the lattice sites are not completely independent because of the sum rule

$$ \sum_{i} p_{n}^{i} = 1 $$

In the case of a binary alloy it is therefore convenient to introduce spin variables $\sigma_{n}$ via the relation

$$ p_{n}^{i} = \frac{1}{2} (1 \pm \sigma_{n}), $$

(2)

where the upper (lower) sign corresponds to the A(B) atom, and to express all the CPs in terms of spin averages [10]. The latter, in turn, can be written as sums of all possible products of cumulant averages, or cumulants [11]. Cumulants are introduced here in order to consider only connected diagrams of the perturbation theory and can be calculated using the fact that the logarithm of the partition function with the source field is their generating functional [11]. To realize the program formulated above, we renormalize the series expansion for the partition function in such a way that lines in diagrams correspond to the matrix elements of the exact PCF. With the help of this procedure basic self-consistent equations for the first- and second-order cumulants (the concentration and the PCF) have been derived [7, 8]. The expressions for the higher-order ones can be obtained in exactly the same way:

$$ \langle \sigma_{n_1} \cdots \sigma_{n_s} \rangle_{c} = \sum_{m_1} \cdots \sum_{m_s} \partial^{s} \ln R[\varphi] / \partial \varphi_{m_1} \cdots \partial \varphi_{m_s} \bigg|_{\varphi = 0} \times G_{m_1 \ n_1} \dots G_{m_s \ n_s}, \ s \geq 3, $$

(3)

where the subscript "c" denotes cumulant averaging, $R[\varphi]$ is the generating functional for the $S$-matrix, $G_{mn}$ the matrix element of the PCF:

$$ G_{mn} = \langle \sigma_{m} \sigma_{n} \rangle_{c} = 4c(1 - c)\sigma_{mn}, $$

(4)
$c$ the concentration, and $\alpha_{mn}$ the Warren-Cowley SRO parameter. The $\ln R[\varphi]$ is the “connected part” of the $R[\varphi]$; its derivatives in equation (3) are the amputated Green functions in the field-theoretical language [12]. Using the renormalized expansion for these derivatives leads to expressing the cumulants (and, therefore, the spin averages and the CPs) as infinite series in powers of the SRO parameters (see Eq. (4)). Low-order contributions in $\gamma$, where $\gamma$ is the small parameter of the theory, can then be easily identified [7, 8].

In the present paper only two simple clusters on the face-centered cubic lattice, namely nearest-neighbour (NN) triangle and tetrahedron, will be considered because of both particular simplicity of the corresponding expressions and existence of results for these clusters in the literature. After straightforward but somewhat lengthy calculations we have

$$C_{\text{tri}} \equiv \langle \sigma_1 \sigma_2 \sigma_3 \rangle_c = a_2 \alpha_1^2 + a_3 \alpha_1^3 + o (\gamma^3),$$
$$a_2 = -6m (1 - m^2), \quad a_3 = 2m (5 - 9m^2),$$

and

$$C_{\text{tet}} \equiv \langle \sigma_1 \sigma_2 \sigma_3 \rangle_c = b_3 \alpha_1^3 + o (\gamma^3),$$
$$b_3 = -8 (1 - m^2) (1 - 9m^2),$$

where $\alpha_1$ is the NN SRO parameter, $m \equiv \langle \sigma_n \rangle = 2c - 1$, and subscripts of spin variables enumerate the vertices of the clusters considered. These cumulants are of order $\gamma^2$ and $\gamma^3$, respectively ($\alpha_1$ is of order $\gamma$, as explained in [7]). More generally, it turns out that an upper order-of-magnitude estimate for the cumulant average of $s$ different spin variables is $\gamma^{s-1}$.

Expressions for the corresponding spin averages are obtained immediately using connection between averages and cumulants [11]:

$$S_{\text{tri}} \equiv \langle \sigma_1 \sigma_2 \sigma_3 \rangle = A_0 + A_1 \alpha_1 + A_2 \alpha_1^2 + A_3 \alpha_1^3 + o (\gamma^2),$$
$$A_0 = m^3, \quad A_1 = 3m (1 - m^2), \quad A_2 = -6m (1 - m^2), \quad A_3 = 2m (5 - 9m^2),$$

and

$$S_{\text{tet}} \equiv \langle \sigma_1 \sigma_2 \sigma_3 \rangle = B_0 + B_1 \alpha_1 + B_2 \alpha_1^2 + B_3 \alpha_1^3 + o (\gamma^3),$$
$$B_0 = m^4, \quad B_1 = 6m^2 (1 - m^2), \quad B_2 = 3 (1 - m^2) (1 - 9m^2), \quad B_3 = -8 (1 - 15m^2 + 18m^4).$$

Now the probabilities of appearance of different NN triangles and tetrahedra in alloy can be easily calculated by inserting relations (2) into the definition (1) and subsequent using equations (5) and (6). It is to be noted that equation (5) satisfies the exact result $S_{\text{tri}} = 0$ at $c = 0.5$ (i.e. $m = 0$) [6] term by term.

Thus, very simple, Taylor-like formulae have been (or can be) derived in the framework of the GEM for all quantities of interest: the cumulants, the spin averages, and the CPs. On the basis of our previous experience in calculating transition temperatures [8, 13], SRO parameters [7, 8], and pair potentials [7, 9] we expect sufficiently high accuracy of these expressions. To illustrate this, we compare our results with those of other authors. Unfortunately, as far as we know, very few data on the CPs have been published so far. In figure 1 successive GEM approximations for $S_{\text{tri}}$ and $S_{\text{tet}}$, according to equations (5) and (6), are shown for the Cu$_3$Au alloy at different temperatures, along with the corresponding GC values calculated from the data of Bardhan and Cohen [14]. Results for the CPs itself are not shown here simply in order to save space since they are completely determined by $S_{\text{tri}}$ and $S_{\text{tet}}$ provided that $c$ and $\alpha_1$ are kept fixed. The bars in the figures are connected with the nonuniqueness of determining two spin averages from the five 4-site CPs given in [14]. The temperature dependence of the experimental SRO parameters is not monotonous; the data at 450 °C were taken from [15] and differ substantially from those of [14]. This leads to the similar behaviour of the spin
averages considered. Equations (5) and (6) have been derived in the framework of the pair interaction model. Clapp [4] stated, however, that the GC procedure is implicitly based on the same assumption. This point of view appears to be confirmed by the comparison presented here and the good agreement of the GC and PVM results for 3-site CPs [4]. Nevertheless, this is still an open question.

![Graphs](image)

Fig. 1. — Spin averages (a) $S_{\text{tri}}$ and (b) $S_{\text{tet}}$ for the Cu$_3$Au alloy at different temperatures as calculated from the GC 4-site CPs [16] (crosses) and in the framework of GEM (dots). Zero-, first-, second-, and third-order GEM approximations (short-dashed, long-dashed, chain, and full lines, respectively) have been used (see Eqs. (5) and (6)). Connecting lines are guides to the eye. $T_c$ is the Cu$_3$Au transition temperature [16].

In figure 2 GEM results for the NN tetrahedron probabilities as functions of temperature in equiatomic alloy with NN interaction, in comparison with those of the cluster variation method (CVM) in the tetrahedron-octahedron (TO) approximation [16], are presented. The minor disagreement between GEM and TO-CVM results occurs only just above first-order transition temperature $T_c$. In the case under consideration the probability of finding the NN tetrahedron of four identical atoms must be strongly suppressed at approaching $T_c$ due to a tendency to ordering. This suppression is slightly overestimated in our approximate calculations, so negative GEM values of this quantity appear at sufficiently low temperatures; the situation, however, is significantly improved with increasing the order of approximation. In general, rapid convergence of the sequence of GEM approximations and the good agreement with other methods have been demonstrated. More detailed comparison with the GC procedure, the corrected TO-CVM [17], and especially with the Monte Carlo method would be highly desirable.

Our approach allows us also to estimate the validity of the Kirkwood SA. Clapp [4] has used this approximation in the following general form:

$$P_{1s}^{i_1 \ldots i_s} = C \prod_{1 \leq n < m \leq s} P_{n \rightarrow m}^{i_n \ldots i_m},$$

where normalization factor $C$ is chosen to make the sum of the $s$-site CPs unity. Another definition is also possible [18]; namely,

$$P_{123}^{ijk} = P_{12}^{ij} P_{18}^{ik} P_{23}^{jk} / p_1 p_2 p_3$$

(8)
for 3-site CPs,

\[ P_{1234}^{ijkl} = P_{12}^{ij} P_{13}^{ik} P_{14}^{il} P_{23}^{jk} P_{24}^{jl} P_{34}^{kl} \left( P_1^i P_2^j P_3^k P_4^l \right)^2 \]  

(9)

for 4-site CPs, etc. These two definitions differ in normalization; the former provides the sum of the CPs to be unity, whereas the latter leads to a correct expression in the limit of complete disorder. The right-hand sides of equations (7)-(9) can be rewritten in terms of SRO parameters. Subsequent comparison with their GEM counterparts shows that equation (7) is incorrect even in the zeroth order in \( \alpha \) (since in this order the CP is a product of proper concentrations), while the second definition of the SA (Eqs. (8) and (9)) is correct only to the first order in \( \alpha \), i.e. it is a reasonable approximation only in the case of weakly correlated systems (see above and Ref. [4]).

![Graph](image_url)

Fig. 2. — NN tetrahedron probabilities versus reduced temperature \( t = k_B T / V_1 \) in the case of equiatomic alloy with NN interaction (\( k_B \) is the Boltzmann constant, \( T \) the absolute temperature, \( V_1 \) the NN interaction potential). Dots are TO-CVM results [18], curves denote different GEM approximations as in figure 1. \( T_c \) is the reduced TO-CVM transition temperature [18]. In the case of 3-1 occupation (middle group of curves) zero- and first-order GEM approximations give identical results.

To conclude, we have proposed a general procedure of calculating the CPs and the spin averages in disordered state leading to very simple analytic expressions in terms of experimentally measured quantities. Our numerical results are in good agreement with those of other methods.
References