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Cluster distribution and long-range ordering in multicomponent interstitial alloys

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Formulae determining the long-range order parameters and the population of clusters of interstitial atoms were derived from low-temperature approximation of fundamental principles. The size of the clusters, the range of interactions and the number of the alloy components were not limited. The method proposed is not sensitive to the kind of a crystal structure and thus can be used for real systems.

1. Introduction

The ordering of interstitial atoms in solid solutions is, from the formal point of view, analogous to that in substitutional alloys. However, detailed consideration of the systems imposes several rigorous and hard to fulfil conditions. For instance, the potentials of configurational interactions are usually of long-range nature and, according to the estimations presented elsewhere [1], they may expand up to distances of many coordination spheres. From our previous analysis [2] it appears that the interaction range may be even longer, and in some crystallographic direction it may reach up to 6 lattice constants. This stems from the fact that besides the short-range potentials of chemical origin, long-range deformational potentials exist which are created by the lattice deformation around an occupied interstitial site. This is the main difficulty in the theoretical study of a condensed system on a microscopic level, taking into account simultaneous interactions with many neighbouring systems.

The magnitude of the configurational potentials, e.g. in a substitutional alloy such as CuZn, is of the order of 350 K [3]. Interactions of the same order of magnitude are observed also in other systems, for example, in magnetic materials exhibiting Curie or Neel points below 1000 K. However, according to theoretical calculations [1, 2, 4] some values of configurational potentials in the Fe–C system are of the order of 3000–25 000 K. Therefore, the ratio V_{ij}/kT is much more than 1 over the whole temperature range in which this phase exists. The condition mentioned above renders useless all methods based, for instance, on a high-temperature diagram expansion.

In the systems of interest, strongly bonded, durable clusters should exist. At present, the most frequently used method is cluster expansion, first introduced by Coniglio *et al.* [5, 6, 7]. This method can easily be obtained from Mayer's mathematical cluster. The Mayer's functions, however, have singularities at 0 K, and therefore they cannot be applied for a very low-temperature regime ($V_{ij}/kT \gg 1$). Attempts to use a low-temperature approximation in systems with an Ising-like Hamiltonian, encounter serious difficulties when the interactions with remote neighbours are taken into account, and practically, they do not work beyond the first- and second-neighbour interactions [8]. Historical development of the most important methods is reviewed elsewhere [9].

Evidence from experimental studies [10], indicates that in the interstitial solid solutions, apart from the two-particle clusters, three-particle clusters can also be formed. In addition, the existence of multicomponent clusters cannot also be a priori excluded. In our previous paper [11], we proposed a low-temperature expansion approach. However, in practice, consideration of larger than two-particle configuration, is extremely tedious. Interstitial alloys may contain several different impurity atoms in the interstitial sites. If, in addition, such a system contains different substitutional elements around which the additional clusters of interstitial atoms may be formed, then phenomena of short-range ordering can be very complex. Such a situation occurs fairly commonly in all iron alloys being used for practical purposes. Therefore, for a theoretical consideration of such systems it is important to be able to take into account a sufficiently large number of components.

To fulfill this requirement, we developed a new approach, which is proposed in the present paper. The combination method in the calculation of the configurational entropy is adopted. This allows the entropy of the system to be expressed as an explicit function of the ordering parameters and simplifies the form of the final formulae describing the thermodynamics. This may play a decisive role in the consideration of real systems, characterized by a large number of short-order parameters. Such a situation occurs when the interactions with many coordination shells are taken into account, especially, in multicomponent alloys. A way of obtaining a configurational entropy refers to the works by Bethe and Wills [12], Cowley [13–16] and Khachaturyan [13]. This method was also applied in our previous works [3, 11, 19, 20] where probabilities of the formation of different atomic configurations were taken into account. In our last paper [2], we presented for the first time the preliminary

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foundation of a cluster model, limited to one alloying component in the absence of long-range order. The present paper is aimed at the generalization of ideas developed previously [2].

2. Formulation of the problem

Following [19] the most general form of the Hamiltonian of a multicomponent substitutional alloy is

$$H = \Sigma_{(n)}\, 1/n!\, \Sigma_{(\mu\nu \dots \lambda)} \Sigma_{(ij \dots k)} V_{(ij \dots k, \mu\nu \dots \lambda)} \\ C_{(i\mu)} C_{(j\nu)} \cdots C_{(k\lambda)} \tag{1}$$

where $V_{(ij \dots k, \mu\nu \dots \lambda)}$ are n-particle irreducible potentials between the atoms of the sort $\mu\nu \dots \lambda$, which are disposed over the lattice sites $ij \dots k$; $C_{(i\mu)}$, $C_{(j\nu)}$, $\dots$ $C_{(k\lambda)}$ are operators of the respective concentrations. For example, $C_{(i\mu)}$ is a stochastic function that is equal to unity when a μ sort of atom is located at point i of the crystal lattice, and is equal to zero otherwise, an analogous rule holding true for the remaining subscripts.

The Hamiltonian (Equation 1) can be applied to describe the interactions in multicomponent interstitial alloys, by treating an empty interstitial site as if it is occupied by an atom of another kind. Then, as in substitutional alloys, in each lattice point, an obvious identity is satisfied

$$\Sigma_{(\mu)} C_{(i\mu)} = 1 \tag{2}$$

This means, that a number of mutually independent values of $C_{i\mu}$ is exactly equal to the number of real atomic components in the interstitial sites.

Let us consider a partition function of Gibbs ensemble

$$Z = \exp(-H/kT) \tag{3}$$

where k and T are Boltzmann's constant and the absolute temperature. For a specified three-particle cluster of fixed suffixes i, j and k, the factor representing this cluster in the partition function is

$$Z_{(ijk, \mu\nu\lambda)} = \exp[-(V_{(ij, \mu\nu)} C_{(i\mu)} C_{(j\nu)} \\ + V_{(jk, \nu\lambda)} C_{(j\nu)} C_{(k\lambda)} + V_{(ik, \mu\lambda)} C_{(i\mu)} C_{(k\lambda)} \\ + V_{(ijk, \mu\nu\lambda)} C_{(i\mu)} C_{(j\nu)} C_{(k\lambda)})/kT] \tag{4}$$

If all sites i, j and k are occupied ($C_{(i\mu)} = C_{(j\nu)} = C_{(k\lambda)} = 1$), Equation 4 is equivalent to

$$Z_{(ijk, \mu\nu\lambda)} = \exp(-V'_{(ijk, \mu\nu\lambda)} C_{(i\mu)} C_{(j\nu)} C_{(k\lambda)}/kT) \tag{5a}$$

where

$$V'_{(ijk, \mu\nu\lambda)} = V_{(ij, \mu\nu)} + V_{(jk, \nu\lambda)} + V_{(ik, \mu\lambda)} + V_{(ijk, \mu\nu\lambda)} \tag{5b}$$

Thus, the total equivalent potential in a three-particle cluster is equal to the sum of the potentials of all two-particle interactions plus potential $V_{(ijk, \mu\nu\lambda)}$ accounting for a change of two-particle potentials as a result of the presence of the third atom. An identical result holds for a cluster of arbitrary size; it is necessary to sum possible interaction potentials of the highest possible order and of all other lower orders. Accounting for Equation 5, we shall present the partition function (Equation 3) in the form

$$Z = Z_{(ij, \mu\nu)} Z_{(ijk, \mu\nu\lambda)} \dots Z_{(ij \dots k, \mu\nu \dots \lambda)} \cdots \tag{6}$$

where $Z_{(ij, \mu\nu)}$, $Z_{(ijk, \mu\nu\lambda)}$, $\dots$ $Z_{(ij \dots k, \mu\nu \dots \lambda)}$ represent the contributions of successive two-, three-, $\dots$ n-particle clusters.

At absolute zero, Equation 6 is simplified in a natural way. For a one-component alloy, all clusters except that with the lowest binding energy, disappear; the cluster with the lowest binding energy is the most favourable energetically. In such a case, only this one factor, associated with a unique configuration, participates in the partition function in Equation 6. It is identical in all components of the partition function ($\Delta Z_{(ij \dots k, \mu\nu \dots \lambda)} = 0$). The situation is analogous for a larger number of dopant components. If the chemical composition does not satisfy a cluster stoichiometry of the lowest binding energy, then the excess atoms form additional clusters to satisfy the route leading to the absolute minimum free energy of the system. In each real case the situation is unambiguous: the number of clusters is finite and the fluctuation of each $Z_{(ij \dots k, \mu\nu \dots \lambda)}$) factor is equal to zero.

Making use of an identical transform of the partition function Z

$$Z \equiv [\exp(S/k)]\, Z \exp(-S/k) \equiv [\exp(S/k)] \langle Z \rangle \tag{7}$$

where S is the entropy of the Gibbs ensemble, we obtain the following expression for the internal energy, U [11]

$$U = -kT \ln \langle \exp(-H/kT) \rangle \tag{8}$$

By replacing all these factors with their thermodynamic mean values, we obtain an expression for the internal energy

$$U = 1/2\, \Sigma'_{(ij, \mu\nu)} V'_{(ij, \mu\nu)} \langle C_{(i\mu)} C_{(j,\nu)} \rangle \\ + 1/3!\, \Sigma'_{(ijk, \mu\nu\lambda)} \langle C_{(i\mu)} C_{(j\nu)} C_{(k\lambda)} \rangle + \dots \\ + 1/n!\, \Sigma'_{(ij \dots k, \mu\nu \dots \lambda)} V'_{(ij \dots k, \mu\nu \dots \lambda)} \\ \langle C_{(i\mu)} C_{(j\nu)} \cdots C_{(k\lambda)} \rangle + \dots \tag{9}$$

where Σ' means that in each such sum, all lattice sites taking part in the formation of the clusters of other orders are excluded. The lattice sums of Equation 9 include only those components for which, simultaneously, all factors $C_{(j\mu)}$, $C_{(j\nu)} \dots C_{(j\lambda)} = 1$. By summing we obtain

$$U = N \Sigma_{(\alpha)} V_\alpha C_\alpha (\Sigma_{(\mu 1)} n_{(\mu, \alpha 1)}) \tag{10}$$

where N is the total number of lattice sites, $V_\alpha = V'_{(ij \dots k, \mu\nu \dots \lambda)}/n_\alpha$, n_α is the number of atoms in cluster α, C_α the probability of the existence of cluster α, and $n_{(\mu, \alpha 1)}$ the number of atoms a sort μ belonging to cluster α, located in the sublattice 1.

Taking into account the law of conservation of the total number of particles in the system, we obtain

$$\Sigma_\alpha C_\alpha n_{(\mu, \alpha 1)} = C_{(\mu, 1)} \tag{11}$$

where $C_{(\mu, 1)}$ is the atomic concentration of impurity μ in the sublattice 1.

In fact, Equation 10 represents an expansion of internal energy over the contributions of corresponding isolated clusters and this way is a cluster method. This is a result of low-temperature approximation and, in particular, of neglecting fluctuations of factors $\Delta Z_{(ij\ldots k,\,\mu\nu\ldots\lambda)}$.

3. Entropy

The entropy, S, can be expressed as [3]

$$S = S_{\mathrm{L}} + S_{\mathrm{sh}} \tag{12}$$

where S_{L} is the entropy connected with long-range ordering, and S_{sh} the entropy connected with short-range ordering, in our case with clusters. Adapted for a multicomponent interstitial, the expression for entropy S_{L}, according to [20], is

$$\begin{aligned} S_{\mathrm{L}} = & -k[\Sigma_{(\mu,1)} C_{(\mu,1)} \ln C_{(\mu,1)} \\ & + (1 - \Sigma_{(\mu,1)} C_{(\mu,1)}) \ln (1 - \Sigma_{(\mu,1)} C_{(\mu,1)})] \end{aligned} \tag{13}$$

Let us calculate the entropy S_{sh}, unlike S_{L}, by the combination method. It is easy to calculate that the total number of clusters of type α is NC_α. Let us calculate the total number of sites in the crystal, allowed by the given crystallographic structure, possible to be occupied by such a cluster. By translating a given cluster over the whole crystal we obtain N such possibilities. Moreover, there are R_α possibilities of transforming a given cluster into another one, equivalent crystallographically. R_α takes into account only those clusters which cannot be obtained from the remaining clusters by a translation manner. In addition, in the case of multicomponent alloys, q_α possible ways of mutual replacement of the potentials V_α must be taken into account. As a final result, a given cluster configuration can be accomplished in the crystal in $NR_\alpha q_\alpha$ ways. Omitting technical details of calculations, the total configuration entropy of the system can be written as

$$\begin{aligned} S_{\mathrm{sh}} = & -kN\Sigma_{(\alpha)} n_\alpha \{C_\alpha \ln [C_\alpha/(R_\alpha q_\alpha - C_\alpha)] \\ & + R_\alpha q_\alpha \ln [(R_\alpha C_\alpha - C_\alpha)/R_\alpha q_\alpha]\} \end{aligned} \tag{14}$$

Treating parameters C_α as variation parameters, from the condition of the minimum of the free energy $F = U - TS$, we obtain, after differentiation, the equilibrium values of these parameters

$$C_\alpha/(R_\alpha q_\alpha - C_\alpha) = N_1/\exp[-V_\alpha/(kT)] \tag{15}$$

Normalization constants N_1 appears in Equation 15 as a result of taking into account the law of conservation of the total number of particles in the system. Values of this constant can be found numerically by substituting the actual values of atomic concentration $C_{(\mu,1)}$ into Equation 10. In the case of one sublattice in a one-component alloy, if condition $R_\alpha q_\alpha \gg C$ is satisfied, which is usually the case because $R_\alpha \geq 1$, then approximately

$$N_1 = C/\Sigma_{(\alpha)} R_\alpha \exp(-V_\alpha/kT) \tag{16}$$

In this approximation,

$$C_\alpha/C_\beta = R_\alpha q_\alpha \exp[(-V_\alpha + V_\beta)/kT]/(R_\beta q_\beta) \tag{17}$$

is valid, while all atoms in Equation 17 belong to the same sublattice 1. The Equation 15 along with the conditions given by Equation 11 enable the numerical values of short-range order parameters, i.e. the cluster population, to be determined. The same condition of free-energy minimum allows the equilibrium values of long-range order parameters to be ascertained. The numerical evaluation of these values gives no technical troubles.

4. Discussion

The actual expressions for the probability of the existence of clusters of α kind, C_α, make it possible to estimate the temperature range of the applicability of the obtained solutions, the necessary condition being $|V_\alpha/kT| \gg 1$ at least for one type of cluster. The determination of low-temperature cluster expansion was the main purpose of the present work. Apart from the values of C_α, values of long-range order parameters, which determine the impurity concentrations in particular sublattices, were also found. The method can be applied to any kind of system, provided the Hamiltonian of these systems can be described by Equation 1 of the Ising-like type.

There are no a priori limitations concerning the range of interactions and the type and size of clusters. In this case, inevitably, the problem of the large number of clusters arises. These clusters differ from each other with regard to size, topology and, in multicomponent alloys, also to the chemical composition. Equation 17 enables a rough selection to be made, relying on the choice between all populations of the clusters that are meaningful in the theoretical model. A sole criterion of such a selection is the value of binding energy shared by a single atom, V_α.

Moreover, the developed method does not refer directly to a particular crystalline structure. All structural information, necessary to solve the ordering problem, is simply comprised in the values of R_α and q_α coefficients, in Equation 14. Accordingly, it can be easily applied to other interstitial alloys and to other types of crystallographic structure. In the case of practical applications, a crucial point is the knowledge of the potentials $V_{(ij\ldots k,\,\mu\nu\ldots\lambda)}$. However, this is a separate problem, which is outside the scope of the present work.

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