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Abstract

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ON THE THEORY OF ORDERING IN ALLOYS

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As is known, when long-range order in a binary alloy is considered, all lattice sites are divided into two classes (1 and 2). The presence of long-range order is then characterized by the fact that the probability of finding an atom of type A at sites of one of the classes (for example, 1) is greater than at sites of the other class. To describe long-range order, the parameter

$$\eta = P_A^{(1)} - P_A^{(2)}, \tag{1}$$

is introduced. Here $P_A^{(1)}$ is the probability that an atom A is located at a site of class 1, and $P_A^{(2)}$ at a site of class 2.

The presence of long-range order, as a rule, leads to a change in the character of the neighboring atoms relative to one another. This change can be described by means of a short-range-order parameter:

$$\sigma = \frac{N_{AA}^0 - N_{AA}}{N_{AA}^0 - N_{AA}^1}. \tag{2}$$

Here N_{AA}^0 is the number of pairs of type AA in complete disorder, N_{AA} is the number in the state under consideration, and N_{AA}^1 is the number in complete order.

In the absence of correlation, when the probability of finding an atom at a given site depends only on the class to which this site belongs and does not depend on the ratio of the number of A and B atoms around this site, σ is a single-valued function of η.

It can be shown, for example, that for the case of an equiatomic composition and a lattice in which the sites of the first class are surrounded only by sites of the second class and vice versa, the simple relation holds:

$$\sigma = \eta^2. \tag{3}$$

Fig. 1

Figure 1: Fig. 1

However, in the general case, in an alloy characterized by the long-range-order parameter η, correlation occurs. Such correlation is indeed observed experimentally (^{1,2}). If, for a given η and in the absence of correlation, $N_{AA} = N^1_{AA}$, then in the presence of correlation, for the same η, $N_{AA} \neq N^1_{AA}$. Let us assume that, in the general case, $N_{AA} = N^1_{AA}(1-x)$, where x will be the correlation parameter. For those cases in which relation (3) is valid, on the basis of (2) we obtain:

$$\sigma = \eta^2 + x(1-\eta^2). \tag{4}$$

For clarity, let us illustrate the above graphically. In a crystal, we shall single out a linear chain of sites in which sites of classes 1 and 2 alternate with one another. We shall lay off along the axis of or-

the ordinate is the probability of finding an atom A at these sites (at the origin of coordinates is site 1, at which atom A lies), and along the abscissa is the distance. Then long-range order without correlation ($\eta \neq 0,\ x = 0$); long-range order in the presence of correlation ($\eta \neq 0,\ x \neq 0$), and short-range order ($\eta = 0;\ x = \sigma$) may be schematically represented, respectively, by the graphs a, b, and v in Fig. 1.

From graphs b and v it is seen that the distribution of atoms in the immediate neighborhood of a given atom will be the same for the cases $\eta = 0$ and $\eta \neq 0$ (if $r < r_0$). In this case the long-range order itself (independently of the correlation) manifests itself at distances greater than the "radius" of action of the correlation r_0. Therefore, in what follows, when long-range order is considered, it is assumed that the volume of the crystal is considerably greater than r_0.

Fig. 1

In most theoretical works devoted to ordering processes, the energy is considered in the approximation of taking into account the interaction of nearest neighbors. In this approximation the configurational energy of the alloy has the form:

$$E = E_0 + V\sigma. \tag{5}$$

Here E_0 is a term independent of the order, and

$$V = NK\left(V_{\mathrm{AB}} - \frac{V_{\mathrm{AA}} + V_{\mathrm{BB}}}{2}\right)$$

(N is the total number of atoms; K is a constant depending on the composition and coordination number; $V_{\mathrm{AA}}, V_{\mathrm{AB}}$, and V_{BB} are the energies of pairs of the types AA, AB, and BB).

As is seen from relation (4), one and the same short-range order ($\sigma = \mathrm{const}$) corresponds to different parameters η, including $\eta = 0$. Therefore it is obvious that specifying the parameter σ does not uniquely determine the long-range order. Consequently, it is doubtful that, by means of an energy that is a single-valued function of σ (see relation (5)), it would be possible to describe the long-range order in an alloy.

Moreover, in the approximation under consideration the least free energy under the condition $\sigma = \mathrm{const}$ corresponds to a state in which long-range order is absent. Thus, for a given short-range order, the equilibrium state of the alloy will be a state without long-range order. Indeed, it is quite obvious that the presence of the additional constraint imposed by the condition $\eta \neq 0$ leads to a decrease in the entropy of the alloy. Since at $\sigma = \mathrm{const}$ we have $E = \mathrm{const}$, the free energy $F = E - TS$ in this case for $\eta = 0$ will be less than for $\eta \neq 0$. Let us note-

in that an additional accounting for the interaction of atoms located in several shells around a given atom, and not only in the first shell, introduces nothing fundamentally new into our reasoning.

For clarity let us dwell on a concrete example. Consider the quasi-chemical theory of ordering developed widely in recent years by Fowler and Guggenheim (^{3}). In this theory individual pairs of atoms are treated as independent units, so that the number W of different configurations of the system is assumed proportional to the number of ways in which the total number of pairs can be divided into a prescribed number of pairs of the types AA, AB, BB, and BA. After some additional assumptions W is given by the relation:

$$W(\sigma,\eta) = \frac{N^{(1)}!}{(N^{(1)}p_A^{(1)})!(N^{(1)}p_B^{(1)})!} \cdot \frac{N^{(2)}!}{(N^{(2)}p_A^{(2)})!(N^{(2)}p_B^{(2)})!} \times \\ \times \frac{\left(\frac{N_{A'B}}{Z/2}\right)! \left(\frac{N_{B'A}}{Z/2}\right)! \left(\frac{N_{A'A}}{Z/2}\right)! \left(\frac{N_{B'A}}{Z/2}\right)!}{\left(\frac{N_{AB}}{z/2}\right)! \left(\frac{N_{BA}}{z/2}\right)! \left(\frac{N_{AA}}{z/2}\right)! \left(\frac{N_{BB}}{z/2}\right)!} \tag{6}$$

Here $N^{(1)}$ and $N^{(2)}$ are, respectively, the number of sites of classes 1 and 2; the prime on the index indicates the state with absence of correlation ($x = 0$), z is the coordination number.

It is easy to show that, under the condition $\sigma = \mathrm{const}$, as the long-range order parameter η decreases, the number of configurations W increases. Therefore $W(\sigma, 0) > W(\sigma, \eta)$, and hence $S(\sigma, 0) > S(\sigma, \eta)$. Thus in the present case as well we arrive at $(F\sigma, 0) < F(\sigma, \eta)$.

On the basis of the foregoing one may draw the general conclusion: **to describe the emergence of long-range order (for $\sigma \neq 1$ and sufficiently large crystal volumes) by means of an approximation that takes into account only the direct interaction of nearest neighbors is fundamentally impossible.**

The emergence of long-range order is essentially a cooperative phenomenon associated with the crystal as a whole. The cooperative character of the nature of the ordering energy was considered by Slater (^{4}). The author connects the energetic advantage of long-range order with a lowering of the Fermi energy (the energy of the generalized electrons) due to the appearance of new Brillouin zones. This approach enables him to explain the emergence of long-range order for the case of the alloy CuPt, in which long-range order does not lead to a change of the neighborhood in the first coordination shell.

It is important to emphasize that theories taking into account only the energy of nearest-neighbor interaction for the most part ignore not only the electronic theory of metals, but also Landau' s general thermodynamic considerations (^{5}) concerning the role of symmetry in ordering processes. A treatment that takes into account the specific energy of long-range order, however, may be closely connected both with the electronic theory of metals and with Landau' s theory.

It must be noted that in the first works on ordering (^{6},^{7}) the energy of the alloy was specified as a function only of the long-range order parameter:

$$E = E_0 + U\eta^2. \tag{7}$$

However, after Bethe' s work (^{8}), expression (5) began to be used predominantly for the energy.

Since in the general case in an alloy one must take into account both the energy of nearest-neighbor interaction and the specific energy associated with long-range order, the energy should be regarded as a function of the parameter σ and the parameter η.

If one assumes that the specific energy of long-range order does not depend on the correlation and uses relations (5) and (7), then for the energy of the alloy one can write the following expression:

$$E = E_0 + U\eta^2 + V\sigma. \tag{8}$$

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Note: Figure translations are in progress. See original paper for figures.