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Abstract

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THERMODYNAMICS OF ALMOST COMPLETELY ORDERED SOLID SOLUTIONS

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The statistical theory of solid solutions uses a number of crude model assumptions. At the same time, results pertaining to certain regions of the phase diagram can be obtained with considerably greater reliability in thermodynamic theory without using a specific model of the solution. In the case when the order—disorder transition is a second-order phase transition, for temperatures close to the ordering temperature these results were obtained in L. D. Landau's theory of second-order phase transitions ([1,2]). A thermodynamic treatment can also be carried out for temperatures much lower than the ordering temperature, when the solution is in an almost completely ordered state. In this case the "foreign" atoms on the sites of each sublattice form the corresponding dilute solution, and the free energy is not difficult to determine by arguments of the same type as in calculating the free energy of dilute solutions (see, for example, ([2])). For binary solutions A—B, having in the elementary cell n_1 sites of the first kind and n_2 sites of the second kind, whose composition is close to the stoichiometric composition $\mathrm{A}_{n_1}\mathrm{B}_{n_2}$, one obtains:

$$\begin{aligned} F = F' + \frac{n_1}{n}N\chi_1 p_{\mathrm{B}1} + \frac{n_2}{n}N\chi_2 p_{\mathrm{A}2} + kT\frac{N}{n}[n_1(p_{\mathrm{A}1}\ln p_{\mathrm{A}1} + p_{\mathrm{B}1}\ln p_{\mathrm{B}1}) \\ + n_2(p_{\mathrm{A}2}\ln p_{\mathrm{A}2} + p_{\mathrm{B}2}\ln p_{\mathrm{B}2})] + N(p_{\mathrm{B}1}^2 e_{11} + 2p_{\mathrm{B}1}p_{\mathrm{A}2}e_{12} + p_{\mathrm{A}2}^2 e_{22}). \end{aligned} \tag{1}$$

Here N is the total number of atoms in the crystal; $n = n_1 + n_2$; $p_{\alpha i}$ are the probabilities that sites of the i-th kind are occupied by atoms α, which may be expressed in terms of the atomic concentration c_A of A atoms and the degree of long-range order η by the relations

$$p_{\mathrm{A}1} = c_\mathrm{A} + \frac{n_2}{n}\eta = 1 - p_{\mathrm{B}1};$$

$$p_{\mathrm{A}2} = c_\mathrm{A} - \frac{n_1}{n}\eta = 1 - p_{\mathrm{B}2};$$

F', χ_1, χ_2, and e_{ij} depend only on temperature and volume and do not depend on the composition or on the degree of long-range order.

In expression (1), F' denotes the free energy of the completely ordered solution at temperature T (which is in a metastable state); the second and third terms take into account the change in free energy when "foreign" atoms, "localized" at specified sites, are introduced onto the sites of the crystal lattice; the fourth term takes into account the possibility of interchanging atoms on sites of each kind; finally, the last term is determined by the interaction

atoms located on foreign sites. Higher terms in the expansion of F in powers of $p_{\mathrm{B}1}$, $p_{\mathrm{A}2}$ are not taken into account. As $T \to 0$, the quantities χ_1 and χ_2 tend to finite limiting values χ_1^0 and χ_2^0.

Applying Nernst's theorem to a solid solution in a metastable state, in which the atoms on "foreign"sites are "frozen"and are "localized"(in the free energy of such a system the first three terms of expression (1) remain unchanged, the fourth term disappears, and the small last term changes), it is easy to see that the derivatives $\partial\chi_1/\partial T$ and $\partial\chi_2/\partial T$ tend to zero as $T \to 0$. In order that, at absolute zero temperature, a solution of stoichiometric composition be completely ordered, the products $p_{\mathrm{B}1}e_{1i}$, $p_{\mathrm{A}2}e_{i2}$ $(i = 1, 2)$ must be negligibly small at sufficiently low temperatures. Therefore, in the case of temperatures considerably lower than the ordering temperature, in deriving the equation for the degree of long-range order one may neglect the last term in (1). This equation is determined from the condition that the free energy be extremal with respect to variation of η, and has the form

$$\frac{\left(c_{\mathrm{A}} - \frac{n_1}{n}\eta\right)\left(c_{\mathrm{B}} - \frac{n_2}{n}\eta\right)}{\left(c_{\mathrm{A}} + \frac{n_2}{n}\eta\right)\left(c_{\mathrm{B}} + \frac{n_1}{n}\eta\right)} = \exp\left[-\frac{\chi_1 + \chi_2}{2kT}\right]. \tag{2}$$

It follows from (2) that, in the case of a solution of stoichiometric composition ($c_{\mathrm{A}} = n_1/n$), the degree of long-range order at low temperatures tends to unity according to the exponential law:

$$1 - \eta = \frac{n}{\sqrt{n_1 n_2}} \exp\left[-\frac{\chi_1^0 + \chi_2^0}{2kT}\right]. \tag{3}$$

The fact that the pre-exponential factor in formula (3) is exactly equal to $n/\sqrt{n_1 n_2}$ is connected with the absence of linear terms in the expansions of χ_1 and χ_2 in powers of T, and is a consequence of Nernst's theorem. Formula (3) is approximately valid also for solutions in which the deviation of the composition $|\Delta c_{\mathrm{A}}|$ from the stoichiometric composition is considerably smaller than the deviation $\Delta\eta$ of the degree of long-range order from the maximum value possible in a solution of the given composition. If the opposite inequality $\Delta\eta \ll |\Delta c_{\mathrm{A}}|$ is satisfied, then the degree of long-range order, upon a change in temperature, again changes exponentially, but with a twice as large exponent (corresponding to the same temperature) and a considerably larger pre-exponential factor:

$$\eta = 1 - \frac{n}{n_2}\Delta c_{\mathrm{A}} - \frac{1 - \frac{n}{n_2}\Delta c_{\mathrm{A}}}{\Delta c_{\mathrm{A}}} \exp\left[-\frac{\chi_1^0 + \chi_2^0}{kT}\right] \quad \text{for } \Delta c_{\mathrm{A}} > 0, \tag{4}$$

$$\eta = 1 + \frac{n}{n_1}\Delta c_{\mathrm{A}} + \frac{1 + \frac{n}{n_2}\Delta c_{\mathrm{A}}}{\Delta c_{\mathrm{A}}} \exp\left[-\frac{\chi_1^0 + \chi_2^0}{kT}\right] \quad \text{for } \Delta c_{\mathrm{A}} < 0.$$

If the ordering temperature is very high, then the solution is in an almost completely ordered state even at compara-

at sufficiently high temperatures (of the order of, or higher than, the Debye temperature), when the consequences of Nernst' s theorem cannot be used. In this case, in (3) and (4), instead of the constant quantity $\chi_1^0 + \chi_2^0$, there will enter a function $\chi_1 + \chi_2$ that depends only weakly on temperature (in the usual approximation of the statistical theory of ordering, it is altogether independent of it). Since at temperatures different from zero the derivative of this function with respect to T is, generally speaking, not equal to zero, the expressions preceding the exponentials in formulas (3) and (4) may differ, respectively, from $n/\sqrt{n_1 n_2}$ and $1/|\Delta c_A|$ by certain factors (usually of the order of unity).

In the general case, when the inequalities $|\Delta c_A| \ll \Delta\eta$ or $|\Delta c_A| \gg \Delta\eta$ are not satisfied, the temperature and concentration dependence of η at temperatures considerably lower than the ordering temperature, and at compositions close to stoichiometric, is determined by formula (2). At a given temperature the degree of long-range order in solutions whose composition is close to AB must be maximal at the stoichiometric composition. It is interesting to note that the elementary Gorsky—Bragg—Williams theory of ordering proves to be justified not at high, but at low temperatures (in an almost completely ordered solution, as also at temperatures considerably higher than the ordering temperature, correlations in the solution become unimportant).

It should be noted that for solutions of nonstoichiometric composition the consideration carried out becomes inapplicable not only at high, but also at very low temperatures, since in the latter case, in deriving the equation for η, one likewise cannot neglect the last terms in expression (1) (one of the probabilities p_{B1} or p_{A2} for solutions of nonstoichiometric composition tends to a constant value, while e_{ij} may increase as the temperature is lowered). At temperatures of this order the decomposition of the solution should begin into an ordered phase whose composition is closer to stoichiometric than the composition of the initial solution, and a disordered phase (or an ordered phase with another superstructure). On approaching absolute zero, the equilibrium value of the composition of the ordered phase should evidently tend to the stoichiometric composition, while the precipitating phase will be a pure metal or else a completely ordered phase of another composition. A quantitative investigation of these questions requires special consideration. The lower temperature boundary of the region of applicability of the approximation considered is lowered as $|\Delta c_A|$ decreases and is equal to zero in the case of solutions of stoichiometric composition. It lies considerably below the boundary of the region of applicability of formulas (3).

Substituting (3) and (4) into (1), it is not difficult to see that at low temperatures the configurational part of the free energy $F - F'$ is proportional to the exponential factors $\exp\left[-\frac{\chi_1^0+\chi_2^0}{2kT}\right]$ or $\exp\left[-\frac{\chi_1^0+\chi_2^0}{kT}\right]$, if, respectively, the conditions $\Delta\eta \gg |\Delta c_A|$ or $\Delta\eta \ll |\Delta c_A|$ are fulfilled. The configurational parts of the energy, entropy, heat capacity, and of the two thermodynamic functions have an exponential temperature dependence of the same type.

Since F' and the analogous terms in the other thermodynamic functions, corresponding to a completely ordered solution, increase at low temperatures with increasing temperature according to a power law, the configurational parts of the thermodynamic quantities at sufficiently low temperatures play only a small role in thermal effects. The exponential temperature dependence in the indicated cases will manifest itself in those properties of solutions which are substantially

but depend on the distribution of atoms of different kinds over the lattice sites: in studying the residual electrical resistance of an ordered alloy quenched from various temperatures, small in comparison with the ordering temperature; the intensity of diffuse scattering of X-rays or neutrons, etc.

It should be emphasized that all the results presented pertain to equilibrium states. They can be tested experimentally (with sufficiently long annealing times) in alloys which, in the almost completely ordered state at low temperatures, retain a high mobility of atoms—for example, in β-brass (especially after irradiation with fast particles, which substantially accelerates various processes in crystals), and also in alloys with high ordering temperatures (higher than the melting temperature)—such as AuZn, and in certain intermetallic compounds.

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References Cited

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2. L. D. Landau, E. M. Lifshitz, *Statistical Physics*, Moscow, 1951.

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

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