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Atomic ordering in non–stoichiometric solid solutions in the low-temperature range

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An expansion is found of the configurational internal energy of a system. The expansion is carried out within long-range ordering parameters and static correlation functions. The results obtained are demonstrated by a specific example – an analysis of the carbon martensite. A number of peculiarities are shown numerically for the low-temperature range related to the behaviour of short- and long-range ordering parameters and, in particular, the major role played by short-range ordering.

1. Introduction

Non–stoichiometric solid solutions are in most cases the subject of experimental investigations in the field of atomic ordering. Although there are a number of theoretical methods for their investigation [1], the problem still remains of finding a convenient and comparatively accurate theoretical method, especially when dealing with the low-temperature range.

A low-temperature approximation is known [2] in which the small parameter is the deviation from unity of the long-range ordering parameter η. However, that parameter is only justifiably small when the fluctuations of the local concentrations vanish at a temperature of absolute zero, that is, for stoichiometric solutions. For non–stoichiometric solutions the assumption of smallness may prove incorrect in the temperature range under consideration. A typical representative of such systems is the carbon martensite. On one hand, it always obtains strongly non–stoichiometric solutions. On the other hand, according to theoretical estimates [3, 4], some of the interaction potentials are enormous, attaining values up to 1 to 2 eV. As a result, the entire temperature range of its existence should be regarded as a low-temperature one, ($V_{ij}/kT \gg 1$).

This paper attempts to show some peculiarities of the atomic ordering within the low-temperature range arising from the lack of stoichiometry.

2. Low-temperature expansion of internal energy

Starting from the Gibbs ensemble, making use of an identical transformation of the partition function Z:

$$Z = \exp(S/k)[\exp(-S/k)Z] = \exp(S/k)\langle Z\rangle \tag{1}$$

where S is the entropy and k is Boltzmann's constant. We obtain the following expression for the internal energy

$$U = -kT\ln\langle Z\rangle \tag{2}$$

This expression has been used for the first time by Khachaturyan [5]. At the thermodynamic limit, when Gibbs' ensemble allows only for the existence of configurations with the same energy, the arithmetic mean in Equation 2 assumes the meaning of a thermodynamic averaging.

We will introduce an operator $\hat{X}$ according to the definition

$$\hat{X} = \frac{\hat{Z} - 1}{\hat{Z} + 1} \tag{3}$$

where $\hat{Z} = \exp(-\hat{H}/kT)$, while $\hat{H}$ is the Hamiltonian of the system. Bearing in mind the identity

$$\frac{1}{\hat{Z} + 1} = \tfrac{1}{2}(1 - \hat{X})$$

we obtain from Equation 3

$$\hat{X} = \hat{X}_1 + \frac{\langle\hat{Z}\rangle - 1}{\langle\hat{Z}\rangle + 1}(1 - 2\hat{X}_1 + \hat{X}_1\hat{X}) \tag{4}$$

where

$$\hat{X}_1 = \frac{\Delta Z}{2 + \Delta Z},$$
$$\Delta Z = \hat{Z} - \langle\hat{Z}\rangle$$

whereas the internal energy can be represented in the form

$$U = -kT[\ln\langle 1 + \hat{X} - 3\hat{X}_1 + \hat{X}_1 X\rangle - \ln\langle 1 - \hat{X} - \hat{X}_1 + \hat{X}_1\hat{X}\rangle] \tag{5}$$

There is an independence between $\hat{X}$ and $\hat{X}_1$

$$\hat{X}_1 = \frac{\hat{X} - \langle\hat{X}\rangle - \langle\hat{X}_1\rangle + \langle\hat{X}_1\hat{X}\rangle}{1 - 2\langle\hat{X}\rangle + \hat{X}\langle\hat{X}\rangle + \langle\hat{X}\hat{X}_1\rangle - X\langle\hat{X}_1\rangle} \tag{6}$$

This dependence can be obtained starting from the definition of ΔZ, as given by Equation 4, and making use of the dependences of Equations 3 and 4. Taking into account that $\langle\hat{X}_1\rangle \ll \langle\hat{X}\rangle$ a solution for $\hat{X}_1$ can be found by iteration. To a first approximation we

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obtain

$$\hat{X}_1^{(1)} = \frac{\hat{X} - \langle \hat{X} \rangle}{1 - 2\langle \hat{X} \rangle + \hat{X}\langle \hat{X} \rangle} \tag{7}$$

From Equations 5 and 6 it follows that the internal energy can be expressed as a power series depending on $\hat{X}$ alone.

We shall choose a Hamiltonian of the system in the form

$$\hat{H} = \sum_n \hat{H}_n \tag{8}$$

where $\hat{H}_n = 1/n! \sum_{ij\ldots k} \sum_{\mu\nu\ldots\lambda} V_{ij\ldots k}^{\mu\nu\ldots\lambda} \hat{C}_i^\mu \hat{C}_j^\nu \ldots \hat{C}_k^\lambda$; $V_{ij\ldots k}^{\mu\nu\ldots\lambda}$ – irreducible interaction potentials; and $\hat{C}_i^\mu$, $\hat{C}_j^\nu$, $\hat{C}_k^\lambda$ – local concentration operators which are random functions equal to 1 or 0. The suffixes i, j, k and μ, ν, λ label the crystal-lattice sites and the component types, respectively.

Making use of an obvious property of $\hat{C}_i^\mu$,

$$(\hat{C}_i^\mu)^n = \hat{C}_i^\mu + (1 - \hat{C}_i^\mu)\delta(n) \quad \text{for} \quad n \geqslant 0 \tag{9}$$

$\hat{Z}$ can be represented in the form

$$\hat{Z} = \prod_{i>j} \prod_{\mu\nu} (1 + T_{ij}^{\mu\nu} \hat{C}_i^\mu \hat{C}_j^\nu) \times \prod_{j>\ldots>k} \prod_{\lambda} (1 + T_{ij..k}^{\mu\nu\ldots\lambda} \hat{C}_i^\mu \hat{C}_j^\nu \ldots \hat{C}_k^\lambda) \times \ldots \tag{10}$$

where $T_{ij\ldots k}^{\mu\nu\ldots\lambda} = \exp(-V_{ij\ldots k}^{\mu\nu\ldots\lambda}/kT) - 1$. Equation 10 for $\hat{Z}$ can be expanded into a series in all possible products $\hat{C}_i^\mu \hat{C}_j^\nu \hat{C}_k^\lambda$:

$$\hat{Z} = 1 + \frac{1}{2}\sum_{ij}\sum_{\mu\nu} Z_{ij}^{\mu\nu} \hat{C}_i^\mu \hat{C}_j^\nu + \frac{1}{3!}\sum_{ijk}\sum_{\mu\nu\lambda} Z_{ijk}^{\mu\nu\lambda} \hat{C}_i^\mu \hat{C}_j^\nu \hat{C}_k^\lambda + \frac{1}{n!}\sum_{ij\ldots k}\sum_{\mu\nu\ldots\lambda} Z_{\underbrace{ij\ldots k}_{n}}^{\mu\nu\ldots\lambda} \hat{C}_i^\mu \hat{C}_j^\nu \ldots \hat{C}_k^\lambda + \ldots \tag{11}$$

where

$$Z_{ij}^{\mu\nu} = (1 + T_{ij}^{\mu\nu}) - 1 = T_{ij}^{\mu\nu}$$

$$Z_{ijk}^{\mu\nu\lambda} = (1 + T_{ijk}^{\mu\nu\lambda})(1 + T_{ij}^{\mu\nu})(1 + T_{jk}^{\nu\lambda})(1 + T_{ki}^{\lambda\mu}) - 1 - Z_{ij}^{\mu\nu} - Z_{jk}^{\nu\lambda} - Z_{ki}^{\lambda\mu}$$

The algorithm for constructing an arbitrary coefficient $Z_{\underbrace{ij\ldots k}_{n}}^{\mu\nu\ldots\lambda}$ is as follows: one must form all the possible products of the expressions $(1 + Z_{\underbrace{ij\ldots k}_{r}}^{\mu\nu\ldots\lambda})$ for $2 \leqslant r \leqslant n$, symmetrical in all conjugated suffixes $(i, \mu), (j, \nu) \ldots (k, \lambda)$. From the product thus obtained one must subtract unity, as well as all the possible coefficients $Z_{\underbrace{ij\ldots k}_{r}}^{\mu\nu\ldots\lambda}$ with $2 \leqslant r < n$. This way of finding the subsequent terms of the series is simpler than the diagram technique [6] frequently used. It is also very convenient for use by means of computational techniques.

Taking into account the obvious equality:

$$(1 + T_{ij\ldots k}^{\mu\nu\ldots\lambda} \hat{C}_i^\mu \hat{C}_j^\nu \ldots \hat{C}_k^\lambda)^n = 1 + T'^{\mu\nu\ldots\lambda}_{ij\ldots k} \hat{C}_i^\mu \hat{C}_j^\nu \ldots \hat{C}_k^\lambda \tag{12}$$

where

$$T'^{\mu\nu\ldots\lambda}_{ij\ldots k} = [\exp(-V_{ij\ldots k}^{\mu\nu\ldots\lambda}/2kT)]^n - 1$$

from Equations 10 and 11 it follows that

$$(\hat{Z})^n = 1 + \frac{1}{2}\sum_{ij}\sum_{\mu\nu} Z'^{\mu\nu}_{ij} \hat{C}_i^\mu \hat{C}_j^\nu + \ldots + \frac{1}{n!}\sum_{ij\ldots k}\sum_{\mu\nu\ldots\lambda} Z'^{\mu\nu\ldots\lambda}_{ij\ldots k} \hat{C}_i^\mu \hat{C}_j^\nu \ldots \hat{C}_k^\lambda + \ldots \tag{13}$$

where all the coefficients $Z'^{\mu\nu\ldots\lambda}_{ij\ldots k}$ obtain from the coefficients $T'^{\mu\nu\ldots\lambda}_{ij\ldots k}$ in precisely the same manner as $Z_{ij\ldots k}^{\mu\nu\ldots\lambda}$ in Equation 11 do so from $T_{ij\ldots k}^{\mu\nu\ldots\lambda}$. An expression for $\hat{X}$ can be obtained directly by means of Equation 13. For this purpose it suffices that Equation 3 shall be represented as a series in the powers of $\hat{Z}^n$ and summing up all terms at the same products $\hat{C}_i^\mu \hat{C}_j^\nu \ldots \hat{C}_k^\lambda$. We obtain finally:

$$\hat{X} = \frac{1}{2}\sum_{ij}\sum_{\mu\nu} X_{ij}^{\mu\nu} \hat{C}_i^\mu \hat{C}_j^\nu + \ldots + \frac{1}{n!}\sum_{ij\ldots k}\sum_{\mu\nu\ldots\lambda} X_{\underbrace{ij\ldots k}_{n}}^{\mu\nu\ldots\lambda} \hat{C}_i^\mu \hat{C}_j^\mu \ldots \hat{C}_k^\lambda + \ldots \tag{14}$$

where $X_{ij}^{\mu\nu} = -th(V_{ij}^{\mu\nu}/2kT)$,

$$X_{ij..k}^{\mu\nu\ldots\lambda} = -th[(V_{ijk}^{\mu\nu\lambda} + V_{ij}^{\mu\nu} + V_{jk}^{\nu\lambda} + V_{ki}^{\lambda\mu})/2kT] - X_{ij}^{\mu\nu} - X_{jk}^{\nu\lambda} - X_{ki}^{\lambda\mu}$$

The general expression $X_{\underbrace{ij\ldots k}_{n}}^{\mu\nu\ldots\lambda}$ is built up analogically to the coefficient $Z_{ij\ldots k}^{\mu\nu\ldots\lambda}$ in Equation 11: a normalized over $2kT$ sum is formed of all possible potentials $V_{\underbrace{ij\ldots k}_{n}}^{\mu\nu\ldots\lambda}$ for $2 \leqslant r \leqslant n$. Taking a hyperbolic tangent of this sum we then subtract all possible coefficients $X_{ij\ldots k}^{\mu\nu\ldots\lambda}$ with $2 \leqslant r < n$.

As seen above, in the final run we get an expansion of the internal energy in the parameters $X_{ij\ldots k}^{\mu\nu\ldots\lambda}$ (which are in all cases limited in value), as well as in $\langle \hat{C}_i^\mu \hat{C}_j^\nu \ldots \hat{C}_k^\lambda \rangle$. The latter represent the probabilities $p_{ij\ldots k}^{\mu\nu\ldots\lambda}$ for forming a multiparticle cluster.

3. Free energy of the carbon tetragonal martensite

The carbon martensite is a convenient example of the low-temperature expansion obtained. For a qualitative analysis, it suffices to confine ourselves to a comparatively rough approximation, approximating the internal energy (Equation 5) by the first term of the expansion

$$U \approx -2kT\langle \hat{X} \rangle \approx 2kT \sum_{ij} th(V_{ij}/2kT)p_{ij} \tag{15}$$

With this approximation for describing the atomic ordering, the long-range parameter η and the pair correlation functions g_{ij} suffice. According to experimental investigations using the neutron-diffraction method [7], the carbon atoms occupy octahedral vacancies in the iron lattice forming two sublattices: one along the z axis, which fills in predominantly (sublattice I), and the remaining ones along the x and y axes (sublattice II). Under these circumstances the sublattice concentrations can be expressed by means of the long-range ordering parameter η and the carbon concentration C in the following way

$$\begin{aligned} C_1 &= C(1 + 2\eta)/3 \\ C_2 &= C(1 - \eta)/3 \end{aligned} \qquad (16)$$

According to the approximation adopted, the short-range parameters g_{ij} are of the form g_{11}, g_{12}, and g_{22} depending on which sublattice hosts the sites i and j.

For calculating the free energy, it is necessary to have the system's entropy in addition to the internal energy, as given by Equation 15. For this purpose we shall use a general expression given in [6]. In accordance with the simplifying assumptions made there, we confine ourselves to taking the one- and two-particle terms. We obtain finally

$$\begin{aligned} S \approx\ & -k \sum_i \left[C_i \ln C_i + (1 - C_i) \ln (1 - C_i)\right] \\ & - \frac{k}{2} \sum_{ij} \left\{ (C_i C_j + g_{ij}) \ln \left(1 + \frac{g_{ij}}{C_i C_j}\right) \right. \\ & + [C_i (1 - C_j) - g_{ij}] \ln \left(1 - \frac{g_{ij}}{C_i (1 - C_j)}\right) \\ & + [(1 - C_i) C_j - g_{ij}] \ln \left(1 - \frac{g_{ij}}{(1 - C_i) C_j}\right) \\ & + [(1 - C_i)(1 - C_j) + g_{ij}] \\ & \left. \times \ln \left(\frac{g_{ij}}{(1 - C_i)(1 - C_j)}\right) \right\} \end{aligned} \qquad (17)$$

For the purpose of finding equilibrium values for all ordering parameters, we shall make use of the condition

$$\frac{\partial F}{\partial X_k} = \frac{\partial U}{\partial Xk} - T \frac{\partial S}{\partial Xu} = 0 \qquad (18)$$

where X_k are short- and long-range ordering parameters, while U and S are determined by Equations 15 and 17, respectively.

Conveniently, this differentiation can be carried out in a general form without specifying the crystallographic structure of the material. As a result we obtain

$$\begin{aligned} \frac{\partial S}{\partial Xk} =\ & -k \left\{ \sum_i \frac{\partial C_i}{\partial Xk} \ln \left(\frac{C_i}{1 - C_i}\right) + \frac{1}{2} \sum_{ij} \frac{\partial p_{ij}}{\partial Xk} \right. \\ & \times \ln \left[\frac{\left(1 + \frac{g_{ij}}{C_i C_j}\right) \left(1 + \frac{g_{ij}}{(1 - C_i)(1 - C_j)}\right)}{\left(1 - \frac{g_{ij}}{C_i (1 - C_j)}\right) \left(1 - \frac{g_i}{(1 - C_i) C_j}\right)} \right] \\ & \left. + \sum_{ij} \frac{\partial C_i}{\partial Xk} \ln \left(\frac{1 - \frac{g_{ij}}{C_i (1 - C_i)}}{1 + \frac{g_{ij}}{(1 - C_i)(1 - C_j)}} \right) \right\}, \end{aligned} \qquad (19a)$$

and

$$\frac{\partial U}{\partial Xk} = kT \sum_{ij} \frac{\partial p_{ij}}{\partial XU}\, th\, (V_{ij}/2kT) \qquad (19b)$$

The system of equations obtained in the particular case for the short-range ordering parameters has the following solution

$$g_{ij} = \frac{(1 - \alpha_{ij})(C_i + C_j - 2C_i C_j) - 1 + \sqrt{\omega_{ij}}}{2(1 - \alpha_{ij})} \qquad (20)$$

where:

$$\begin{aligned} \omega_{ij} &= 1 - 2(1 - \alpha_{ij})(C_i + C_j - 2C_i C_j) \\ &\quad + (1 - \alpha_{ij})^2 (C_i - C_j)^2 \\ \alpha_{ij} &= \exp\,[-2th\,(V_{ij}/2kT)] \end{aligned}$$

This solution does not depend explicitly on the crystallographic structure of the material, which is due to the adopted simplifying assumptions. To this approximation the correlation functions g_{ij} depend solely on the interaction potentials, the temperature, and the sublattice concentrations C_i and C_j, that is, depend parametrically on the long-range parameter η. The specific equation for finding an equilibrium value of parameter η can already be obtained by thorough accounting for the crystallographic structure of the material. In this way, the effect of that structure on the correlation functions in this case materializes indirectly via the parameter η. Taking into account the structure of martensite and carrying out summation over all sites i and j to determine η, we obtain the equation

$$\begin{aligned} \frac{\mathrm{g}}{\mathrm{NC}T} \left(\frac{\partial F}{\partial \eta}\right) =\ & 2\ln \frac{C_1 (1 - C_2)}{C_2 (1 - C_1)} + \sum_{R_\mathrm{n}} J_\mathrm{n} \left\{ \ln \left[\frac{\left(1 - \frac{g_{12}(R_\mathrm{n})}{C_1 (1 - C_2)}\right)^2}{\left(1 - \frac{g_{12}(R_\mathrm{n})}{C_2 (1 - C_1)}\right) \left(1 + \frac{g_{12}}{(1 - C_1)(1 - C_2)}\right)} \right] \right. \\ & \left. - \ln \left[\frac{1 - \frac{g_{22}}{C_2 (1 - C_2)}}{1 + \frac{g_{22}}{(1 - C_2)^2}} \right] \right\} + 2 \sum_{R_m} J_m \left\{ \ln \left[\frac{\left(1 - \frac{g_{11}}{C_1 (1 - C_1)}\right) \left(1 + \frac{g_{22}}{(1 - C_2)^2}\right)}{\left(1 + \frac{g_{11}}{(1 - C_1)^2}\right) \left(1 - \frac{g_{22}}{C_2 (1 - C_2)}\right)} \right] \right\} = 0 \end{aligned} \qquad (21)$$

TABLE I Pair interaction potentials V_n between a carbon atom situated in an octahedral site $(0\,0\,\frac{1}{2})$ and another carbon atom in an octahedral site $(x, y, z + \frac{1}{2})$, according to [3]

n	x, y, z	$V_n(x, y, z)$ (eV) A	$V_n(x, y, z)$ (eV) B	J_m
1	$0\,\frac{1}{2}\,0$	−0.83	−1.20	4
2	$\frac{1}{2}\,0\,\frac{1}{2}$	−0.114	−0.14	8
3	$\frac{1}{2}\,1\,0$	–	0.071	8
4	$\frac{1}{2}\,1\,\frac{1}{2}$	−0.0364	−0.048	16
5	$1\,\frac{1}{2}\,1$	0.168	0.010	16
6	$0\,\frac{3}{2}\,0$	0.00348	−0.043	4
7	$\frac{1}{2}\,0\,\frac{3}{2}$	−0.0666	−0.052	8
8	$1\,\frac{1}{2}\,0$	−0.028	–	8
9	$1\,\frac{3}{2}\,0$	−0.0296	−0.029	8
10	$\frac{3}{2}\,1\,\frac{1}{2}$	−0.00329	0.016	16
11	$2\,\frac{1}{2}\,0$	−0.0545	−0.030	8
12	$1\,\frac{3}{2}\,1$	0.0008	0.000	16
13	$2\,\frac{1}{2}\,\frac{1}{2}$	−0.0025	−0.001	16
14	$\frac{3}{2}\,0\,\frac{3}{2}$	0.0542	0.016	8
				J_n
15	$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$	−0.44	−0.314	8
16	0 0 1	2.04	1.35	2
17	1 0 0	−0.282	−0.191	4
18	1 1 0	−0.127	−0.020	4
19	1 0 1	−0.0276	−0.028	8
20	$\frac{3}{2}\,\frac{1}{2}\,\frac{1}{2}$	−0.0384	−0.059	16
21	$\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2}$	0.244	0.015	8
22	1 1 1	−0.0254	0.022	8
23	2 0 0	−0.0412	−0.316	4
24	0 0 2	0.224	0.13	2
25	$\frac{3}{2}\,\frac{3}{2}\,\frac{1}{2}$	−0.290	−0.015	8
26	$\frac{3}{2}\,\frac{1}{2}\,\frac{3}{2}$	−0.00605	−0.012	16
27	2 1 0	–	−0.024	8
28	0 1 2	–	−0.036	8
29	2 0 1	–	−0.018	8

J_n, J_m are the coordination numbers.

where N is the number of all octahedral sites in the crystal; J_n, J_m are the numbers of atoms in the respective coordination spheres; R_n, R_m are the radii of these spheres; and C_1, and C_2 and C are defined according to Equation 16.

4. Results of computer simulation

The form of Equations 20 and 21 is useful for a direct determination of atomic ordering by means of computional techniques. Here the interaction potentials between the carbon atoms are free theoretical parameters. From theoretical estimates [3, 4] the interaction radius in martensite is known to be large, so that to arrive at reliable results one should account for 20 to 30 coordination spheres. In our opinion, the most realistic set of interaction constants has been presented in [3], which forms the basis of our estimates. This set is listed in Table I, column A. To compare the results, we have also carried out calculations using another set of potentials (Table I, column B) taken from the same reference [3]. A large number of potentials leads to a respectively large number of variational parameters, namely 50 different g_{ij} in case A and 54 g_{ij} in case B, plus a single long-range ordering parameter η in both cases. Irrespective of the large number of variational parameters, finding their equilibrium values does not pose any serious problem.

As the correlation functions are obtained directly from Equation 20, it remains to examine the zeros of the function defined by Equation 21. As a result of the numerical analysis, we obtain the dependence of the parameter η on temperature at various carbon densities. These results are shown graphically in Fig. 1 and relate to the potential sets A and B, respectively, from Table I. From the dependences shown, it follows that in all cases the order–disorder phase transitions are first-order with hysterisis. The typical temperature dependence of the correlation functions is shown in Fig. 2 and refers to case A. From the entire set g_{ij} in Fig. 2, we show the ones with the largest absolute magnitudes, both atoms are from the first sublattice and whose interaction potentials are also the largest, that is, g_{11} (1/2 1/2 1/2) and g_{11} (0 0 1).

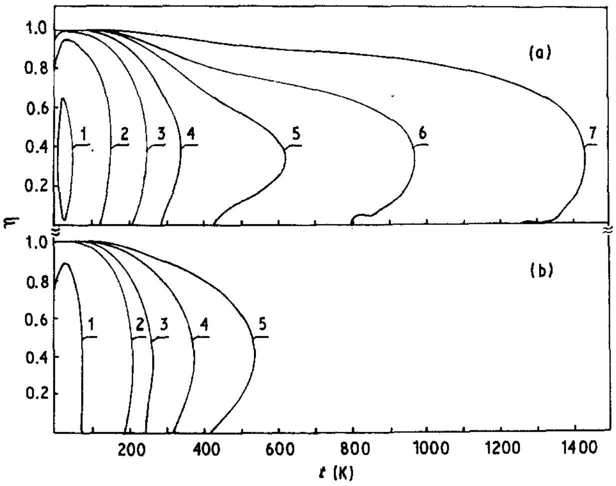

Figure 1 Temperature dependence of the long-range ordering parameter η for a set A or B of potentials according to Table I, and at different carbon concentrations. 1a to 7a correspond to 1.5, 2.5, 4, 5, 6 and 7, and 10 at % carbon; 1b to 5b correspond to 1.5, 4, 5, 7 and 10 at % carbon.

5. Discussion

The general features of the atomic ordering in stoichiometric solid solutions cited in the Introduction are to a large extent clarified. Unlike the stoichiometric solid solutions, the nonstoichiometric ones remain almost unexplored, particularly in the low-temperature

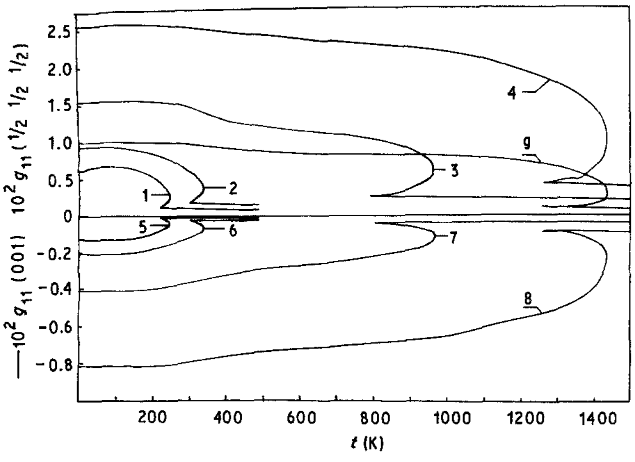

Figure 2 Temperature dependence of the correlation functions g_{11} $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and g_{11} (0 0 1) for set A of potentials V_n of Table I at different carbon atom concentrations. 1, 2, 3, 4, g_{11} $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ at C = 4, 5, 7 and 10 at % carbon; 5, 6, 7, 8, g_{11} (0 0 1) at C = 4, 5, 7 and 10 at % carbon; 9, C_1^2 at C = 10 at % carbon.

range. These problems have been considered in [3], but the authors have used an expansion in V_{ij}/kT, that is, the high-temperature approximation. Also, they have neglected the short-range ordering parameters. Thus their results differ largely from the ones presented here. This holds true for the long-range parameter η. Although the latter parameter depends strongly on the specific set of potentials V_{ij}, it follows from Fig. 1 that there are common relationships. First, the zero temperature does not imply that the parameter η should assume the ultimately allowed value $\eta = 1$; on the contrary, it can be maximal at higher temperatures. This behaviour is observed at all concentrations studied, and in particular the lower ones. (These effects are easily seen from the graphical relationships presented in Fig. 2.) At very low concentration (curve 1 in Fig. 1a), there can also exist an unordered phase along with the ordered one, the two phases being separated by a potential barrier in between. These effects do not appear in the traditional investigation carried out in [3]. Estimates for the critical temperature reported in [3] at the same interaction potentials are superior to ours by an order of magnitude. Bearing in mind the results of the neutron diffraction [7] obtained for martensite with 6.7 at % carbon and leading to $\eta \approx 0.7$, they agree with our calculations, which is not easy to explain by means of the traditional analysis.

A second peculiarity of the atomic ordering is connected with the correlation functions. The correlation functions for stoichiometric solid solutions are known to vanish at a temperature of absolute zero because the concentrations of all the sub-lattices assume external values of 0 or 1, equivalent to the disappearance of the fluctuations themselves. For nonstoichiometric solutions, there are always sublattices with concentrations different than 0 or 1. Therefore in such solutions there should in principle be non-vanishing correlation functions at zero temperature. From Fig. 2 it can be seen that their absolute values in that temperature range are maximal.

For stoichiometric solid solutions, the probability of finding two atoms in sites i and j, $p_{ij} = C_iC_j + g_{ij}$, is usually determined by the product C_iC_j (except perhaps for the critical range), while the correlation functions g_{ij} make a small contribution. In this case, p_{ij} differ several-fold by the product C_iC_j within the entire temperature range at all the concentrations considered. This implies that in this type of system short-range ordering effects dominate over long-range ones, and should not be underestimated.

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