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To the Problem of the Description of Ordered Structures in Binary Cubic Solid Solutions

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Within the framework of the static concentration wave method by means of the geometrically complete procedure a number of new types of ordered substitutional structures with the stoichiometric structural formulae AB, AB_3, and A_3B_5, as well as of corresponding isomorphic interstitial structures, A_2X, A_4X, and A_8X_3 (A, B, and X are the types of atoms situated at sites and interstices, respectively) are established that complete the list of all thermodynamically stable with respect to the violations of macroscopic homogeneity (Lifshitz) ordered structures arising from the disordered state of f.c.c. and b.c.c. binary solid solutions.

В рамках метода статических концентрационных волн с помощью геометрически полной процедуры установлен ряд новых типов упорядоченных структур замещения со стехиометрическими структурными формулами AB, AB_3 и A_3B_5, а также изоморфных им сверхструктур внедрения, A_2X, A_4X и A_8X_3 (A, B и X – типы атомов на узлах и в междоузлиях, соответственно), которые дополняют и, в результате, делают исчерпывающим список всех термодинамически устойчивых по отношению к нарушению макроскопической однородности (Лифшицевских) сверхструктур, образующихся из неупорядоченного состояния в бинарных твердых растворах с ГЦК и ОЦК кристаллическими решетками.

1. Introduction

The statistical description of structures with long-range order in solid solutions can be reduced to setting up Fourier series of one-particle distribution functions [1 to 6]. Therewith, the problem arises to determine the wave vectors over which the summation in these series is to be carried out.

Lifshitz [7], considering (within the Landau [8] approach) the symmetry aspect of the problem of structural phase transformations of second order, demonstrated the peculiar feature of the structures characterized by basis functions of irreducible representations (of the space symmetry group of the system at the point of the phase transformation) which correspond to the stars of wave vectors whose symmetry groups contain symmetry elements (from the crystal class of that space group) intersecting at one point.[2]) Only such structures can be thermodynamically stable with respect to violations of the macroscopic homogeneity (Lifshitz criterion). This determines the importance of finding the Lifshitz structures. By means of

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[2]) The first Brillouin zone points corresponding to such wave vectors are usually termed the high-symmetry or Lifshitz points as far as these wave vectors themselves and the superstructures corresponding to them (see Section 2) are usually termed Lifshitz vectors and Lifshitz superstructures, respectively.

the group representation method seven types of such ordered structures which can arise from the disordered state of the binary solid solution were found in the case of f.c.c., three in the case of b.c.c., and three in the case of h.c.p. crystal lattices. Therewith, the Landau condition [8] for phase transformations of second order consisting in the absence of the cubic summands in the expansion of the free energy (in terms of the long-range order parameters) was imposed.

Khachaturyan [2 to 4] proved the applicability of the Lifshitz criterion to the case of structural phase transformations of first order and proposed the static concentration wave method for the description and finding of superstructures. Therewith, in the framework of this method three types of Lifshitz superstructures were found in the case of b.c.c. solid solutions and one in the case of f.c.c. solid solutions in addition to the ones obtained by Lifshitz.

In [9, 10] the group-theory approach to the analysis of the possible types of ordering in solid solutions was developed. Within this approach two more types of superstructures in the case of b.c.c. solutions were found in [11].

In the present paper within the framework of the static concentration wave method by means of the geometrically complete procedure new types of Lifshitz superstructures arising from the disordered state of binary solid solutions with f.c.c. and b.c.c. crystal lattices are found, settling the problem of such structures.

2. The Procedure of Superstructure Finding

It is suitable to present the function which characterizes the space symmetry of the system under consideration as a series over the functions realizing the irreducible representations of the space group G_0 of the system at the point of phase transformation [7, 8, 12]. Therewith, to every irreducible representation (excluding the unity one) its own long-range order parameter is matched up. Non-zero values of these parameters make the corresponding lowering of the space symmetry of the system available.

In the framework of the lattice gas model let us describe the space symmetry of the atomic distribution in a binary solid solution by the function $P(\boldsymbol{R})$, which means the probability of finding the impurity atom [3]) at the corresponding crystal lattice position with radius vector $\boldsymbol{R}$. Let the set of all positions $\boldsymbol{R}$ form some Bravais lattice and the group G_0 be the space group of this lattice.[4]) In this case the irreducible representations of the group G_0 are numerated only by the stars $\boldsymbol{k}_s$ ($s = 1, 2, \ldots$) of the wave vectors, which belong to the first Brillouin zone of the corresponding reciprocal crystal lattice[5]), and the basis functions of the irreducible representation corresponding to some star $\boldsymbol{k}_s \equiv \{\boldsymbol{k}_{1_s}, \boldsymbol{k}_{2_s}, \ldots, \boldsymbol{k}_{l_s}\}$ ($\boldsymbol{k}_{j_s}$ are the wave vectors belonging to the same star s) are the functions [7, 12]

$$e^{i\boldsymbol{k}_{1_s}\boldsymbol{R}}, e^{i\boldsymbol{k}_{2_s}\boldsymbol{R}}, \ldots, e^{i\boldsymbol{k}_{l_s}\boldsymbol{R}}.$$

Thus, one can write the above-mentioned series in terms of the basis functions of the irreducible representations of the group G_0 in the general form

$$P(\boldsymbol{R}) = c + \sum_{s \neq 0} \eta_s \sum_{j_s} \gamma_s(j_s)\, e^{i\boldsymbol{k}_{j_s}\boldsymbol{R}}, \tag{1}$$

[3]) For clarity let the sort of atoms with the smallest concentration in a binary solid solution be termed the impurity one. Therewith, the space distribution of the atoms of the host sort, obviously, is described by the function $1 - P(\boldsymbol{R})$.

[4]) As a result, the space symmetry group of any superstructure is a subgroup of the group G_0 (in the lattice gas model).

[5]) Classification by the number of the small representation is absent.

where the summation is carried over all stars of the wave vectors from the first Brillouin zone (excluding its center: $s \neq 0$) and over all vectors of these stars; $c = n/N$ is the concentration of the impurity atoms (n and N are the total numbers of impurity atoms and of crystal lattice sites, respectively); η_s is the long-range order parameter which corresponds to the star s; $\eta_s \gamma_s(j_s)$ is the coefficient which corresponds to the wave vector $\boldsymbol{k}_{j_s}$ in the series (1). The coefficient corresponding to the "zero"-star is assumed to be equal to c, that makes the equality $P(\boldsymbol{R}) = c$ (for any $\boldsymbol{R}$) be satisfied in the disordered state of the solid solution, when all parameters of the long-range order are equal to zero. The symmetry of the function $P(\boldsymbol{R})$ is determined by the set of those stars for which the long-range order parameters η_s are not equal to zero, and by the values of the coefficients $\gamma_s(j_s)$ corresponding to these stars.

In (1) the designations adopted in the static concentration wave method [2 to 4] are used. The two following conditions are utilized for finding of superstructures within this method.

Firstly, for the unambiguous definition of the long-range order parameters one has to impose the normalization condition [8, 12]. It is conveniently chosen in the following form[6]):

Condition 1. In a completely ordered state of the solid solution (when the function $P(\boldsymbol{R})$ at any $\boldsymbol{R}$ takes only two values: zero or unity and $c = c_{st}$, where c_{st} is the stoichiometric concentration of this superstructure) all non-zero long-range order parameters should be equal to unity.

Secondly, for the expansion (1) to describe the structures with long-range order, the condition which reflects the conservation of the number of the structural degrees of freedom should be satisfied:

Condition 2. The number of non-zero long-range order parameters in (1) should be smaller by one than the total number of different values the function $P(\boldsymbol{R})$ takes at all positions $\boldsymbol{R}$ (under arbitrary allowed values of these long-range order parameters).

In this work the following procedure is used for finding (within the static concentration wave method) of the complete set of Lifshitz superstructures arising from the disordered state of cubic solid solutions.[7])

On condition that the solution is in a completely ordered state, (1) can be written for some (defined below) sites $\boldsymbol{R}_m$ for every possible combination of l ($l = 1, 2, \ldots$) Lifshitz stars (with n_s wave vectors in every star s ($s = 1, 2, \ldots, l$)) in the following general form:

$$P_m = c_{st} + \sum_{s=1}^{l} \sum_{j_s=1}^{n_s} \gamma_s(j_s)\, e^{i\boldsymbol{k}_{j_s}\boldsymbol{R}_m};$$

$$m = 1, 2, \ldots, \sum_{s=1}^{l} n_s + 1 . \qquad (2)$$

In (2) all long-range order parameters are put equal to unity, $c = c_{st}$, and the values P_m of the function $P(\boldsymbol{R})$ at corresponding positions $\boldsymbol{R}_m$ must be equal to zero or unity, in accordance with Condition 1. We choose the set of positions $\{\boldsymbol{R}_m\}$ in such a way that the

[6]) Such a normalization condition provides the coincidence of the definition of the long-range order parameters in the framework of the static concentration wave method with their classic definition in terms of the occupation probabilities (see, e.g. [13]).

[7]) Note that this procedure without any change can be used for finding of both the Lifshitz and the non-Lifshitz superstructures in binary solid solutions based on any Bravais lattice.

main determinant of the set of equalities (2), considered as a set of linear inhomogeneous equations in unknowns c_{st} and $\{\gamma_s(j_s)\}$, is not equal to zero. Solving this set of equations for all possible distributions of zeros and unities over the values of P_m, we can find the complete assemblage $\{c_{st}, \{\gamma_s(j_s)\}\}$ of those packages c_{st} and $\{\gamma_s(j_s)\}$, which satisfy Condition 1 within the chosen set $\{\boldsymbol{R}_m\}$. It is obvious that the assemblage of solutions found in the above-mentioned way must contain (as a subset in general) *all* those packages c_{st} and $\{\gamma_s(j_s)\}$, which make Condition 1 be satisfied within *all* positions $\{\boldsymbol{R}\}$.

At the final stage of the procedure we exclude those packages from $\{c_{st}, \{\gamma_s(j_s)\}\}$ which do not meet Conditions 1 and 2 within all positions $\{\boldsymbol{R}\}$. Due to the periodicity of the functions $e^{i\boldsymbol{k}_{j_s}\boldsymbol{R}}$ (and, consequently (see (1) and (2)), of the corresponding function $P(\boldsymbol{R})$) it is necessary to check for this purpose (by direct substitution of corresponding coordinates) only a finite (not large usually) number of the positions $\boldsymbol{R}$, limited by the periods of the function $P(\boldsymbol{R})$.

3. The Superstructures in Cubic Lattices

As a result of the use of the procedure described in Section 2 we found one type of superstructures in the case of f.c.c. and four types of superstructures in the case of b.c.c. crystal lattices in addition to the Lifshitz superstructures which are listed in [2 to 4]. The series (1) for the new f.c.c. superstructure can be written in the following form:

$$\begin{aligned} P_{\text{f.c.c.}}(\boldsymbol{R}) = c &+ \eta_{\text{X}}\{\gamma_{\text{X}}(1)\, e^{i2\pi x} + \gamma_{\text{X}}(2)\, e^{i2\pi y} + \gamma_{\text{X}}(3)\, e^{i2\pi z}\} \\ &+ \eta_{\text{L}}\{\gamma_{\text{L}}(1)\, e^{i\pi(x+y+z)} + \gamma_{\text{L}}(2)\, e^{i\pi(-x+y+z)} \\ &+ \gamma_{\text{L}}(3)\, e^{i\pi(x-y+z)} + \gamma_{\text{L}}(4)\, e^{i\pi(x+y-z)}\}, \end{aligned} \tag{3}$$

and for all new b.c.c. superstructures the series (1) can be represented in the following general form:

$$\begin{aligned} P_{\text{b.c.c.}}(\boldsymbol{R}) = c &+ \eta_{\text{H}}\gamma_{\text{H}}\, e^{i2\pi z} + \eta_{\text{P}}\{\gamma_{\text{P}}(1)\, e^{i\pi(x+y+z)} + \gamma_{\text{P}}(2)\, e^{-i\pi(x+y+z)}\} \\ &+ \eta_{\text{N}}\{\gamma_{\text{N}}(1)\, e^{i\pi(x+y)} + \gamma_{\text{N}}(2)\, e^{i\pi(x+z)} + \gamma_{\text{N}}(3)\, e^{i\pi(y+z)} \\ &+ \gamma_{\text{N}}(4)\, e^{i\pi(x-y)} + \gamma_{\text{N}}(5)\, e^{i\pi(x-z)} + \gamma_{\text{N}}(6)\, e^{i\pi(y-z)}\}. \end{aligned} \tag{4}$$

In expressions (3) and (4) the summations are carried out over the stars X, L of the reciprocal lattice of the disordered f.c.c. solution and over H, P, N stars of the b.c.c. solution, respectively (for the designations of the stars see, e.g., [14]). In every case x, y, and z are the orthogonal coordinates of the vector $\boldsymbol{R}$ in terms of the parameter of the corresponding crystal lattice.

The stoichiometric compositions of the superstructures which were found, the values of the coefficients in the corresponding series (3) and (4), and the references to Fig. 1 and 2 for every superstructure are given in Tables 1 and 2, respectively.[8],[9])

[8]) The characteristics are quoted only for superstructures with the stoichiometric compositions $c_{st} < 0.5$. The anti-isostructure corresponding to every superstructure (with the stoichiometric composition c_{st}) from Tables 1 and 2 can be obtained by the change of the signs of all coefficients $\gamma_s(j_s)$ of the superstructure and will have the stoichiometric compositions $1 - c_{st}$.

[9]) The structures 1 and 2 from Table 2 are equivalent to the new types of the structures found by the method of group representations in [11].

Table 1
Characteristics of the superstructure based on the f.c.c. lattice
b: Stoichiometric structural formula. c: Designations (in the corresponding figure) of lattice sites which are symmetry non-equivalent in the ordered state

b	c_{st}	$\gamma_X(1)$	$\gamma_X(2)$	$\gamma_X(3)$	$\gamma_L(1)$	$\gamma_L(2)$	$\gamma_L(3)$	$\gamma_L(4)$	Γ_X	Γ_L	P_i	ν_i	Fig.	c
A_3B_5	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$-\frac{1}{8}$	$-\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{3}{8}$	$\frac{3}{64}$	$\frac{3}{16}$	$c+\frac{1}{8}\eta_X+\frac{1}{2}\eta_L$	$\frac{3}{8}$		●
											$c+\frac{1}{8}\eta_X-\frac{1}{2}\eta_L$	$\frac{3}{8}$	1	○
											$c-\frac{3}{8}\eta_X$	$\frac{1}{4}$		⊗

Table 2
Characteristics of the superstructures based on the b.c.c. lattice
a: Number of the superstructure. b, c: The same as in Table 1

a	b	c_{st}	γ_H	$\gamma_P(1)$	$\gamma_P(2)$	$\gamma_N(1)$	$\gamma_N(2)$	$\gamma_N(3)$	$\gamma_N(4)$	$\gamma_N(5)$	$\gamma_N(6)$	Γ_H	Γ_P	Γ_N	P_i	ν_i	Fig.	c
1	AB_3	$\frac{1}{4}$	0	0	0	0	0	0	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0	$\frac{3}{16}$	$c+3/4\eta_N$	1/4	2a	●
															$c-1/4\eta_N$	3/4		○
2	AB	$\frac{1}{2}$	0	0	0	$\frac{1}{4}$	$-\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{4}$	0	0	0	$\frac{1}{4}$	$c+1/2\eta_N$	1/2	2b	●
															$c-1/2\eta_N$	1/2		○
3	A_3B_5	$\frac{3}{8}$	$\frac{3}{8}$	0	0	$-\frac{1}{8}$	$-\frac{1}{8}$	$-\frac{1}{8}$	$-\frac{1}{8}$	$-\frac{1}{8}$	$-\frac{1}{8}$	$\frac{9}{64}$	0	$\frac{3}{32}$	$c+3/8\eta_H+1/4\eta_N$	3/8	2c	●
															$c+3/8\eta_H-3/4\eta_N$	1/8		○
															$c-3/8\eta_H$	1/2		◒
4	A_3B_5	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{8}$	$-\frac{1}{8}$	$-\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{64}$	$\frac{1}{8}$	$\frac{3}{32}$	$c+1/8\eta_H+1/2\eta_P$	1/4	2d	●
															$c+1/8\eta_H-1/2\eta_P$	1/4		○
															$c-1/8\eta_H+3/4\eta_N$	1/8		⊗
															$c-1/8\eta_H-1/4\eta_N$	3/8		◒

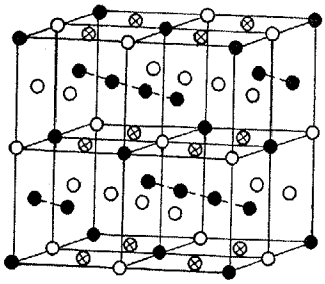

Fig. 1. Superstructure determined in Table 1

The values Γ_s,[10])

$$\Gamma_s \equiv \sum_{j_s} |\gamma_s(j_s)|^2 \tag{5}$$

(for every star s); the expressions P_i for the one-particle distribution function for every i-th sublattice ($i = 1, 2, \ldots$) which contains N_i sites symmetry equivalent in the ordered state and the values v_i,

$$v_i \equiv \frac{N_i}{N}, \tag{6}$$

where N is the total number of sites in the crystal lattice of a solution are also quoted in the tables. This additional information is sufficient for the determination of the free

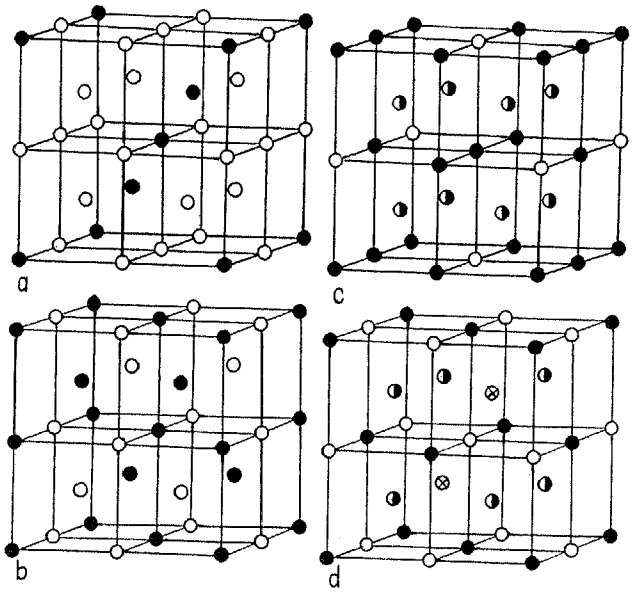

Fig. 2. Superstructures determined in Table 2

[10]) Note that it is easy to find from (1) and (5) that the sum of the values of Γ_s over all stars (with corresponding non-zero long-range order parameters) is determined by the stoichiometric composition c_{st} of the superstructure only, $\sum_s \Gamma_s = c_{st}(1 - c_{st})$.

energy F for the corresponding superstructures under the statistical-thermodynamic description. For example, within the mean-field approach [3 to 6, 15],

$$F = \frac{N}{2}\left\{\tilde{V}(0)\,c^2 + \sum_{s\neq 0}\tilde{V}(\boldsymbol{k}_s)\,\Gamma_s\eta_s^2\right\} + Nk_{\mathrm{B}}T\sum_i v_i\{P_i\ln P_i + (1-P_i)\ln(1-P_i)\}\,, \tag{7}$$

where $\tilde{V}(\boldsymbol{k}_s)$ is the value of the Fourier transform of the binary mixing potential corresponding to some star $\boldsymbol{k}_s$ of the wave vectors, T is the absolute temperature, k_{B} the Boltzmann constant.

Notice in conclusion that every substitutional superstructure in a binary solid solution based on the Bravais lattice can be put in correspondence with the isomorphic interstitial superstructure (see, e.g. [2 to 4]). Therewith, the host lattice atoms are not taken into account and an impurity atom and (interstitial) vacancy are considered as two solution components distributed within the interstitial sublattice which is isomorphic to the above-mentioned Bravais lattice.[11]) The stoichiometric composition $c_{\mathrm{st}}^{\mathrm{int}}$ of the interstitial superstructure can be obtained from the stoichiometric composition c_{st} of the isomorphic substitutional superstructure by the use of the following relation:

$$c_{\mathrm{st}}^{\mathrm{int}} = \frac{c_{\mathrm{st}}}{1 + c_{\mathrm{st}}}\,, \tag{8}$$

i.e., one can put in correspondence a definite interstitial superstructure with the stoichiometric formula $A_{n+m}X_m$ to any given substitutional superstructure — A_nB_m (A, B, and X are the designations for the types of atoms situated at sites and interstices, respectively). Thus, for all substitutional superstructures quoted in Tables 1 and 2 (with the structural stoichiometric formulae AB, AB_3, and A_3B_5) one can match up the interstitial superstructures (with the formulae A_2X, A_4X, and A_8X_3, respectively).

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[11]) In general, the assemblage of interstices forms a complex (with the basis) crystal lattice. However, the case of interstitial atom distribution predominantly within one of the interstitial sublattices only is widely observed in experiment. Such situation can be caused by both the energy non-equivalence of the (symmetry different) interstitial sublattices and the strong repulsion between the interstitial atoms which occupy neighboring (even energetically equivalent) sublattices (see, e.g., [4, 16]).

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