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The Symmetry of Interatomic Lattice Potentials in General Crystal Structures. 1. Basic Theory

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Abstract

Within the framework of a generalized model of a multicomponent lattice gas, the symmetry properties of many-particle interatomic potentials are investigated. The relations of the invariance (with respect to the symmetry transformations) for the potentials and the relationships between their Fourier components are represented in a form convenient to check the symmetry adequacy of microscopic model potentials in real as well as in reciprocal space. The method of statistical-thermodynamic description of multicomponent solid solutions is suggested, taking into consideration the symmetry changes of interatomic potentials due to the structural phase transformations.

1. Introduction

The statistical-thermodynamic description of a multicomponent solid solution is feasible when the energy parameters of interatomic interactions in a given solid solution are known. However, for the clarification of the structural (*i.e.* connected with the space distribution of particles) aspect of this problem, the basic information is the space-symmetry-related properties of the energy parameters. The power of the symmetry arguments in the study of phase transformations was demonstrated by the great success of the Landau phenomenological theory and also of the latest statistical-thermodynamic theories of structural instabilities connected with the phase transformations (*e.g.* de Fontaine, 1979; Khachaturyan, 1978, 1983).

The common shortcoming of well known theories of structural phase transformations in solid solutions is still that the symmetry properties of interatomic potentials are being postulated without factual grounds. For instance, in Krivoglaz & Smirnov (1964) and Sanchez, Gratias & de Fontaine (1982), isotropy of the interatomic potentials is assumed. The changes of interatomic potential symmetry due to the structural phase transformations are not usually taken into consideration in statistical-thermodynamic analysis. Similar changes, however, can cause the essential specific features of the phase diagrams of the solid solutions, such as the change of the phase transformation order and the alteration of the stability region of the ordered phase (*e.g.* Golosov & Ushakov, 1976).

The importance of pure symmetry examination of interatomic potential changes under structural phase transformations has been demonstrated in a number of studies where the symmetry criteria of the stabilization of non-stoichiometric ordered structures forming as a result of step-by-step phase transformations were formulated (branching scheme) (*e.g.* Somenkov, 1972; Bugaev & Ryzhkov, 1979). Similar symmetry considerations concerning the polymorphic reconstructive phase transformations with the structure changes, both in impurity and in matrix subsystems of interstitial alloys, have been performed by Somenkov, Irodova & Shil'shtein (1978). In all the above-mentioned studies, however, the sequential methods for obtaining the interatomic potential symmetry properties are not yet elaborated.

The aim of the present work is to establish the general symmetry requirements on interatomic potentials (including the many-particle ones) in a multicomponent solid solution under the condition that its space symmetry (*i.e.* the symmetry of the component distribution functions) is given. The application of the general symmetry concept to resolve the stated problem allows one to avoid both the detailed statistical-thermodynamic analysis of the system evolution under the variation of the external thermodynamic parameters and the necessity to specify the microscopic nature of the interatomic interactions.

In §2, the general expression for the configuration energy of the multicomponent solid solution within the framework of the lattice gas model is obtained, taking into account the contributions from many-particle interactions.

In §3, the symmetry properties of the mixing potentials of a solid solution with any given space distribution of its particles are analyzed.

In §4, the definition of the Fourier components matrix of many-particle mixing potentials is given and the relationships between the elements of this matrix are obtained.

In §5 and §6, the symmetry properties of the injection potential and the binary mixing potential are taken up separately, owing to their wide use in statical-thermodynamic theories of solid solutions.

In §7, the plausible applications of the symmetry relations obtained in this work to statistical-thermodynamic considerations of multicomponent solid solutions are discussed.

2. Energy of a multicomponent solid solution within the lattice gas model

In the general case, the energy E of some arbitrary classical system that consists of $\mathcal{R}$ interacting particles in the external field can be written as

$$\begin{aligned} E &= E_0 + \sum_{\mathbf{X}} E_1(\mathbf{X}) + (1/2!) \sum_{\mathbf{X}_1 \neq \mathbf{X}_2} E_2(\mathbf{X}_1, \mathbf{X}_2) \\ &\quad + \ldots + E_{\mathcal{R}}(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n) \\ &= E_0 + \sum_{n=1}^{\mathcal{R}} (1/n!) \sum_{\mathbf{X}_1 \neq \mathbf{X}_2 \neq \ldots \neq \mathbf{X}_n} E_n(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n), \end{aligned} \tag{1}$$

where $E_n(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n)$ is the energy of interaction between n chosen particles placed at positions $\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n$ and vectors $\mathbf{X}_i$ under the summation over the positions, fixed at some moment, of all $\mathcal{R}$ particles of the system. In (1), it is supposed to be impossible to separate out from E_0 any additive component that is a function of coordinates only and also to separate out from any n-particle interaction energy $E_n(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n)$ the additive component of the form $E_s(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_s)$ with $s < n$.

In the case of the multicomponent solid solution (MSS) within the lattice gas model,* the particles of types $\alpha = \alpha_1, \alpha_2, \ldots, \alpha_z$ that form the MSS can occupy, by definition, only the positions $L \equiv (p, \mathbf{R})$ of some space lattice (in general, with basis), which are specified by the vectors

$$\mathbf{X}(L) = \mathbf{X}(p, \mathbf{R}) = \mathbf{R} + \mathbf{h}_p, \tag{2}$$

where $\mathbf{R}$ is the radius vector of the basis and $\mathbf{h}_p$ $(p = 0, 1, \ldots, \nu)$ are the components of the lattice basis $(\mathbf{h}_0 \equiv 0)$.

In general, all sublattices are allowed and prohibited for particles of definite types.† Therefore, let us specify every sublattice p by the set $\{\alpha^p\} \equiv \{\alpha_0^p, \alpha_1^p, \ldots, \alpha_{Z_p}^p\}$ of the types of particle for which the sublattice p is allowed to be occupied. Describing the momentary space distribution of the MSS particles by the set of functions

$$C_\alpha(L) \equiv \begin{cases} 1 & \text{if the position } L \text{ is occupied by an} \\ & \quad \alpha\text{-type particle} \\ 0 & \text{in the opposite case} \end{cases} \tag{3}$$

and taking into account the condition

$$C_\alpha(L) = C_\alpha(p, \mathbf{R}) \equiv 0 \quad \text{if} \quad \alpha \not\subset \{\alpha^p\} \tag{4}$$

from the above-mentioned reasons for allowed and prohibited sublattices, one can rewrite the energy (1) for the case of the MSS under consideration in the form*

$$\begin{aligned} E = \sum_{n=1}^{N} (1/n!) \sum_{\alpha_1, \alpha_2, \ldots, \alpha_n} \sum_{\substack{L_1, L_2, \ldots, L_n \\ L_i \neq L_j}} E_n^{\alpha_1 \alpha_2 \ldots \alpha_n}(L_1, L_2, \ldots, L_n) \\ \times C_{\alpha_1}(L_1) C_{\alpha_2}(L_2) \ldots C_{\alpha_n}(L_n), \end{aligned} \tag{5}$$

where the summation over α_i is carried out over Z types of atoms of the MSS and the summation over $L_i \equiv (p_i, \mathbf{R}_i)$ is carried out over N lattice positions available for atoms under the restricting condition $L_i \neq L_j$, which means that only summands with different variables L_1, L_2, ... are present in (5); $E_n^{\alpha_1 \alpha_2 \ldots \alpha_n}(L_1, L_2, \ldots, L_n)$ is the n-particle interaction potential of the particles of the types $\alpha_1, \alpha_2, \ldots, \alpha_n$ that occupy the positions $L_1, L_2, \ldots, L_n$, respectively.

Let us eliminate the condition $L_i \neq L_j$ under the summation in (5) completing the definition of the n-particle interaction potentials by the requirement

$$E_n^{\alpha_1 \alpha_2 \ldots \alpha_n}(\ldots, L_i, \ldots, L_j, \ldots) \equiv 0 \quad \text{if} \quad L_i = L_j, \tag{6}$$

i.e. setting $E_n^{\alpha_1 \alpha_2 \ldots \alpha_n}(L_1, L_2, \ldots, L_n) \equiv 0$ if even one pair of the positions among the space variables coincides. The requirement (6) is connected with the above-mentioned irreducibility of the given many-particle energy of any order to other ones of lower orders. It is easy to be convinced of this, making use of (5) and taking into consideration the relationship

$$[C_\alpha(L)]^s = C_\alpha(L) \tag{7}$$

$(s = 1, 2, \ldots)$, which follows from (3).

Using the condition

$$\sum_{\alpha=\alpha_1}^{\alpha_Z} C_\alpha(p, \mathbf{R}) = \sum_{\alpha=\alpha_0^p}^{\alpha_{Z_p}^p} C_\alpha(p, \mathbf{R}) = 1, \tag{8}$$

which is valid for any $(p, \mathbf{R})$ and reflects the fact that any position of the lattice can be occupied by only one particle, we exclude all quantities $C_{\alpha_0^p}(p, \mathbf{R})$ in (5). Then, in the general case, for every sublattice p the corresponding α_0^p types of particle must be eliminated.

Since the choice of the excluded type of atom for every sublattice is arbitrary [see (8)], the corresponding procedure can be realized in accordance with the reasons concerning the convenient statistical-thermodynamic description of an alloy. For example, in the case of the MSS based on metals, all sublattices can be divided into

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* In such a model, the averaging over the electron and phonon degrees of freedom is supposed to be performed due to the higher rate of the processes related to these degrees of freedom in comparison with the rates of atomic redistribution among the positions of the lattice.

† For example, in interstitial solutions, the interstitial impurity cannot be placed at the sites of the matrix lattice. Other examples are chemical compounds of ceramic type in which an atom of every type occupies its own sublattice only.

* Within the lattice gas model, the quantity E_0 in (1) is a non-configuration part of the energy, which we set equal to zero adopting E_0 as the origin.

two groups: substitutional and interstitial sublattices. It is convenient to choose the type of metal whose concentration in the MSS is the greatest and whose atoms can occupy all substitutional sublattices as the excluded one for each of these sublattices. In the case of interstitial sublattices, the (interstitial) vacancies are always present among the types of interstitial (the presence of a vacancy in some position means a lack of any particle in this position). Thus, it is convenient to choose the vacancy as an excluding type for all interstitial sublattices.

The energy of the MSS, after excluding all quantities $C_{\alpha_0^p}(p, \mathbf{R})$ in the right-hand part of (5) and taking (6) into account, can be represented in the form

$$E = V_0 + \sum_{n=1}^{N} (1/n!) \times \sum_{\substack{\alpha_1,\alpha_2,\ldots,\alpha_n \\ \alpha \neq \alpha_0^p}} \sum_{L_1,L_2,\ldots,L_n} V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1, L_2, \ldots, L_n) \times C_{\alpha_1}(L_1) C_{\alpha_2}(L_2) \ldots C_{\alpha_n}(L_n), \tag{9}$$

where the notation $\alpha \neq \alpha_0^p$ means that the indices α_i $(i = 1, 2, \ldots, n)$ under the summation cannot take the values corresponding to those types of particle that are numerated as α_0^p. The quantities V_0 and $V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1, L_2, \ldots, L_n)$ in (9) are the linear combinations of $E_s^{\alpha_1\alpha_2\ldots\alpha_s}(L_1, L_2, \ldots, L_s)$ with different s and different sets of α and L.* For example, when just the same type α_0 is excluded at all sublattices,† these quantities are defined by the expression

$$V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1, L_2, \ldots, L_n) = \sum_{\substack{s=n \\ (s\neq 0)}}^{N} \sum_{t=s-n}^{s} A_{nst} \times \sum_{L_{n+1},L_{n+2},\ldots,L_s} E_s^{\alpha_1\alpha_2\ldots\alpha_{s-t}\alpha_0\ldots\alpha_0}(L_1, L_2, \ldots, L_s), \tag{10}$$

where

$$A_{nst} \equiv \frac{(-1)^{n-s+t} n!}{(s-t)!(n-s+t)!(s-n)!}, \tag{11}$$

$n = 0, 1, \ldots, N$. In particular,

$$V_0 = \sum_{n=1}^{N} (1/n!) \sum_{L_1,L_2,\ldots,L_n} E_n^{\alpha_0\ldots\alpha_0}(L_1, L_2, \ldots, L_n) = \sum_{L} E_1^{\alpha_0}(L) + (1/2!) \sum_{L_1,L_2} E_2^{\alpha_0\alpha_0}(L_1, L_2) + \ldots, \tag{12}$$

$$V_1^{\alpha}(L) = \sum_{n=1}^{N} [1/(n-1)!] \sum_{L_2,\ldots,L_n} [E_n^{\alpha\alpha_0\ldots\alpha_0}(L, L_2, \ldots, L_n) - E_n^{\alpha_0\ldots\alpha_0}(L, L_2, \ldots, L_n)] = [E_1^{\alpha}(L) - E_1^{\alpha_0}(L)] + \sum_{L_2} [E_2^{\alpha\alpha_0}(L, L_2) - E_2^{\alpha_0\alpha_0}(L, L_2)] + \ldots, \tag{13}$$

$$V_2^{\alpha_1\alpha_2}(L_1, L_2) = \sum_{n=2}^{N} [1/(n-2)!] \sum_{L_3,\ldots,L_n} [E_n^{\alpha_1\alpha_2\alpha_0\ldots\alpha_0}(L_1, L_2, \ldots, L_n) - 2E_n^{\alpha_1\alpha_0\ldots\alpha_0}(L_1, L_2, \ldots, L_n) + E_n^{\alpha_0\ldots\alpha_0}(L_1, L_2, \ldots, L_n)]$$
$$= [E_2^{\alpha_1\alpha_2}(L_1, L_2) - 2E_2^{\alpha_1\alpha_0}(L_1, L_2) + E_2^{\alpha_0\alpha_0}(L_1, L_2)] + \sum_{L_3} [E_3^{\alpha_1\alpha_2\alpha_0}(L_1, L_2, L_3) - 2E_3^{\alpha_1\alpha_0\alpha_0}(L_1, L_2, L_3) + E_3^{\alpha_0\alpha_0\alpha_0}(L_1, L_2, L_3)] + \ldots. \tag{14}$$

Let us call the quantities $V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1, L_2, \ldots, L_n)$ the n-particle mixing potentials of the MSS.* Their physical meaning follows from (9). Thus, the quantity V_0 is the energy of the system, which consists only of the particles with the fixed type α_0^p at every sublattice p, and the addend to V_0 in E is connected with the dissolution of the particles of types $\alpha \neq \alpha_0^p$. The quantity $V_1^{\alpha}(p, \mathbf{R})$ is the effective one-particle energy of the injection of the particle $\alpha \neq \alpha_0^p$ into the position $(p, \mathbf{R})$ and the quantities $V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1, L_2, \ldots, L_n)$ define the effective interactions of n particles of the types $\alpha \neq \alpha_0^p$, which are injected into corresponding positions of the crystal lattice.

The model of the lattice gas for the MSS considered above is the generalization of the Izing model. It differs from the conventional Izing model by the multicomponency of the solid solution, by taking into consideration any-order many-particle interactions and by the lack of limitations on the radii of these interactions.

3. Symmetry of mixing energies

The space group G of the MSS at a given structural thermodynamic equilibrium state within the framework of the model under consideration is the common symmetry group of the set of functions $\{P_\alpha(L)\}$ $(\alpha = \alpha_1, \alpha_2, \ldots, \alpha_z)$, where every quantity $P_\alpha(L)$ is determined by the expression

$$P_\alpha(L) \equiv \langle C_\alpha(L) \rangle \tag{15}$$

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*Note that the quantities $V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1, L_2, \ldots, L_n)$, which by definition are the linear combinations of the quantities $E_s^{\alpha_1\alpha_2\ldots\alpha_s}(L_1, L_2, \ldots, L_s)$, similar to the latest ones, must meet condition (6).

† This case corresponds to multicomponent substitutional or interstitial alloys.

* The quantity $E_2^{AA}(L_1, L_2) + E_2^{BB}(L_1, L_2) - 2E_2^{AB}(L_1, L_2)$, which is usually called the mixing energy, can be obtained from (14) in the particular case of the binary substitutional solid solution $A - B$ $(\alpha_0 \equiv B)$ if only pairwise interactions are taken into account.

(the $\langle\ldots\rangle$ sign means the statistical average over the Gibbs ensemble) and is equal to the probability of finding an $\underset{\sim}{\alpha}$-type particle at the position L. In the general case $G \subseteq \tilde{G}$, where $\tilde{G}$ is the space symmetry group of the MSS crystal lattice that is specified by the positions L. $G = \tilde{G}$ in the case of a disordered (chaotic) distribution of the particles of every type among the allowed positions.

Let us apply some symmetry transformation $g \in G$ to the MSS. Then, every given particle will change its position L to the symmetry-equivalent position $L' \equiv gL$.* The new distribution of the particles will be characterized by the set $\{\bar{C}_\alpha(L)\}$ of functions, which are determined by the relationship

$$\bar{C}_\alpha(L) \equiv C_\alpha(g^{-1}L), \tag{16}$$

where $g^{-1} \in G$ is the reciprocal element to g. The energy E' of the space-transformed MSS can be represented [in accordance with (9)] in the following form:

$$E' = V_0 + \sum_{n=1}^{N}(1/n!) \times \sum_{\substack{\alpha_1,\alpha_2,\ldots,\alpha_n \\ \alpha\neq\alpha_0^p}} \sum_{L_1,L_2,\ldots,L_n} V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1,L_2,\ldots,L_n) \times \bar{C}_{\alpha_1}(L_1)\bar{C}_{\alpha_2}(L_2)\ldots\bar{C}_{\alpha_n}(L_n), \tag{17}$$

where the coefficients $V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1,L_2,\ldots,L_n)$ at any degrees of $\bar{C}_\alpha(L)$ are the same as the corresponding coefficients in (9) because the transformation g is an element of the space symmetry group G of the MSS and, correspondingly, sends the MSS into itself. Using (16) and changing the summation over the variables L_i in (17) by the equivalent summation over the variables $\bar{L}_i \equiv g^{-1}L_i$ (which are also denoted by L_i, taking into account the above-mentioned equivalence), we obtain

$$E' = V_0 + \sum_{n=1}^{N}(1/n!) \times \sum_{\substack{\alpha_1,\alpha_2,\ldots,\alpha_n \\ \alpha\neq\alpha_0^p}} \sum_{L_1,L_2,\ldots,L_n} V_n^{\alpha_1\alpha_2\ldots\alpha_n}(gL_1,gL_2,\ldots,gL_n) \times C_{\alpha_1}(L_1)C_{\alpha_2}(L_2)\ldots C_{\alpha_n}(L_n). \tag{18}$$

On the other hand, the MSS energy cannot change its numerical value under any transformation from the space symmetry group G, *i.e.*

$$E = E'.$$

For the realization of this condition, we must put, in (9) and (18) (which determine E and E', respectively), the coefficients of the same products of the functions $C_\alpha(L)$ to be equal. Thus, we obtain*

$$V_n^{\alpha_1\alpha_2\ldots\alpha_n}(gL_1,gL_2,\ldots,gL_n) = V_n^{\alpha_1\alpha_2\ldots\alpha_n}(L_1,L_2,\ldots,L_n), \tag{19}$$

where $g \in G, n = 1, 2, \ldots$.

Relationship (19) reflects the important fact that the mixing potentials of any two sets with the same number of particles are equal if even one symmetry transformation of the MSS which sends one set to another (under the condition that the types of corresponding particles coincide), exists.

The elements $g = \{S|\boldsymbol{\tau}(S) + \mathbf{R}_m\}$ of the MSS symmetry space group G can be found making use of the condition†

$$P_\alpha(gL) = P_\alpha(L) \tag{20}$$

(for every $\alpha = \alpha_1, \alpha_2, \ldots, \alpha_z$), where gL is the position of the lattice that can be obtained from the arbitrary chosen position $L \equiv (p, \mathbf{R})$ by the symmetry transformation g:

$$\begin{aligned}\mathbf{X}(gL) &\equiv g\mathbf{X}(L) \\ &= \{S|\boldsymbol{\tau}(S) + \mathbf{R}_m\}\mathbf{X}(L) \\ &= S(\mathbf{R} + \mathbf{h}_p) + \boldsymbol{\tau}(S) + \mathbf{R}_m.\end{aligned} \tag{21}$$

Here, in accordance with the notations of Seitz (1936) for the elements of the space group, S is the matrix representation for the element of crystal class of group G, $\boldsymbol{\tau}(S)$ is the translation vector which does not coincide with any translation period $\mathbf{R}_m$ of the group G given by the equalities

$$P_\alpha(p, \mathbf{R} + \mathbf{R}_m) = P_\alpha(p, \mathbf{R}), \tag{22}$$

which follow from (20) as a particular case under $g = \{U|\mathbf{R}_m\}$ where U is the unity matrix.

In the case of a MSS with an arbitrary type of long-range order in the distribution of the components among the positions of the crystal of lattice gas, let us choose the primitive unit cell so that the set of radius vectors $\{\mathbf{R}\}$ of the unit cells coincides with the set $\{\mathbf{R}_m\}$ of translation periods of group G. Then, assuming in (22) that $\mathbf{R}_m = -\mathbf{R}$, we obtain

$$P_\alpha(p, \mathbf{R}) = P_\alpha(p, 0) \tag{23}$$

for any α, p and $\mathbf{R}$.

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* As declared above, the group G is the subgroup of the symmetry group $\tilde{G}$ of the MSS crystal lattice. Therefore, under any transformation $g \in G$, every position L must be sent to some position $L' \equiv gL$ of the same lattice: $\mathbf{X}(L') = g\mathbf{X}(L)$.

* Note, that a similar line of reasoning was used by Maradudin & Vosko (1968) for the statement of the transformation rules for atomic force constants of the crystal. The difference lies in the fact that the mixing potentials (of any order) are scalar quantities whereas the atomic force constants form a tensor of second order.

† In the present work, the effects connected with the existence of the internal (interphase) and external surfaces of the MSS crystal are neglected and, therefore, the crystal lattice can be considered as infinite and homogeneous when performing symmetry transformations. Note that a similar line of reasoning is also valid in the case of finite and inhomogeneous MSS for the essentially massive homogeneous domains within the MSS when the surface effects can be neglected.

Assuming in (19) that $g = \{U|\mathbf{R}_m\}$, which corresponds to the pure translation symmetry transformations from group G, we obtain the property of the invariance to the translations $\mathbf{R}_m$:

$$\begin{aligned} V_n^{\alpha_1\alpha_2\ldots\alpha_n}&(p_1, \mathbf{R}_1 + \mathbf{R}_m; p_2, \mathbf{R}_2 + \mathbf{R}_m; \ldots; p_n, \mathbf{R}_n + \mathbf{R}_m) \\ &= V_n^{\alpha_1\alpha_2\ldots\alpha_n}(p_1, \mathbf{R}_1; p_2, \mathbf{R}_2; \ldots; p_n, \mathbf{R}_n), \end{aligned} \tag{24}$$

where the designation of the positions $L \equiv (p, \mathbf{R})$ is written in explicit form and the following relationships from (21) are taken into account:

$$\begin{aligned} \mathbf{X}(gL) &\equiv g\mathbf{X}(L) \\ &= \{U|\mathbf{R}_m\}\mathbf{X}(p, \mathbf{R}) \\ &= (\mathbf{R} + \mathbf{R}_m) + \mathbf{h}_p \\ &= \mathbf{X}(p, \mathbf{R} + \mathbf{R}_m). \end{aligned} \tag{25}$$

Putting $\mathbf{R}_m = -\mathbf{R}_n$ in (24) (which is available due to the corresponding choice of the unit cell), we obtain

$$\begin{aligned} V_n^{\alpha_1\alpha_2\ldots\alpha_n}&(p_1, \mathbf{R}_1 - \mathbf{R}_n; p_2, \mathbf{R}_2 - \mathbf{R}_n; \ldots; \\ &p_{n-1}, \mathbf{R}_{n-1} - \mathbf{R}_n; p_n, 0) \\ &= V_n^{\alpha_1\alpha_2\ldots\alpha_n}(p_1, \mathbf{R}_1; p_2, \mathbf{R}_2; \ldots; p_n, \mathbf{R}_n), \end{aligned} \tag{26}$$

which means that the mixing potential of the nth order depends only on $(n-1)$ space variables, *i.e.* on the radius vectors of $(n-1)$ unit cells respective to the unit cell of an arbitrary chosen particle (we give the number n to this particle for definiteness).

Rearranging the variables of the summation in (9): $\alpha_i \leftrightarrow \alpha_j, L_i \leftrightarrow L_j$ (where i and j are the numbers of two arbitrarily chosen particles) and then interchanging the multipliers $C_{\alpha_i}(L_i)$ and $C_{\alpha_j}(L_j)$, we obtain [taking into account the random character of the functions $C^{\alpha}(L)$] the next (commutative) property of the mixing potentials:

$$V_n^{\ldots\alpha_i\ldots\alpha_j\ldots}(\ldots, L_i, \ldots, L_j, \ldots) = V_n^{\ldots\alpha_j\ldots\alpha_i\ldots}(\ldots, L_j, \ldots, L_i, \ldots). \tag{27}$$

4. Properties of Fourier transforms of mixing potentials

The Fourier components of the binary mixing potentials are the basic parameters in a number of advanced theories of the atomic order (*e.g.* de Fontaine, 1979; Khachaturyan, 1978, 1983). Therefore, here we consider the symmetry properties of the Fourier transforms of mixing potentials.

The Fourier transformation according to (26) may be determined as

$$\begin{aligned} \tilde{V}_n^{\alpha_1\alpha_2\ldots\alpha_n}&(p_1, \mathbf{k}_1; p_2, \mathbf{k}_2; \ldots; p_{n-1}, \mathbf{k}_{n-1}; p_n) \\ &\equiv \sum_{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_{n-1}} V_n^{\alpha_1\alpha_2\ldots\alpha_n}(p_1,\mathbf{R}_1; p_2,\mathbf{R}_2;\ldots; p_{n-1},\mathbf{R}_{n-1}; p_n,0) \\ &\quad\times \exp\left[-i\sum_{l=1}^{n-1}(\mathbf{k}_l, \mathbf{R}_l)\right] \\ &= \sum_{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_{n-1}} V_n^{\alpha_1\alpha_2\ldots\alpha_n}(p_1,\mathbf{R}_1; p_2,\mathbf{R}_2; \ldots; p_n,\mathbf{R}_n) \\ &\quad\times \exp\left[-i\sum_{l=1}^{n-1}(\mathbf{k}_l, \mathbf{R}_l - \mathbf{R}_n)\right]. \end{aligned} \tag{28}$$

The equality is obtained by replacing the summation variables $\mathbf{R}_l$ with $\mathbf{R}_l - \mathbf{R}_n$ $(l = 1, 2, \ldots, n-1)$ and taking (26) into account.

Taking advantage of the symmetry transformation rules (21) for two sites $(p_l, \mathbf{R}_l)$ and $(p_n, \mathbf{R}_n)$, one finds

$$\mathbf{R}_l - \mathbf{R}_n = S^{-1}(\mathbf{R}'_l - \mathbf{R}'_n + \mathbf{h}_{p'_l} - \mathbf{h}_{p'_n}) - (\mathbf{h}_{p_l} - \mathbf{h}_{p_n}) \tag{29}$$

$[L' = (p', \mathbf{R}') \equiv gL = g(p, \mathbf{R})]$. Substituting this expression into (28) and using the symmetry properties of the mixing potentials (19), we obtain

$$\begin{aligned} \tilde{V}_n^{\alpha_1\alpha_2\ldots\alpha_n}&(p'_1, S\mathbf{k}_1; p'_2, S\mathbf{k}_2; \ldots; p'_{n-1}, S\mathbf{k}_{n-1}; p'_n) \\ &= \tilde{V}_n^{\alpha_1\alpha_2\ldots\alpha_n}(p_1, \mathbf{k}_1; p_2, \mathbf{k}_2; \ldots; p_{n-1}, \mathbf{k}_{n-1}; p_n) \\ &\quad\times \exp\left\{i\sum_{l=1}^{n-1}[(S\mathbf{k}_l, \mathbf{h}_{p'_l} - \mathbf{h}_{p'_n}) - (\mathbf{k}_l, \mathbf{h}_{p_l} - \mathbf{h}_{p_n})]\right\}, \end{aligned} \tag{30}$$

where the vector $S\mathbf{k}_i$ $(i = 1, 2, \ldots, n)$ is obtained from vector $\mathbf{k}_i$ as a result of the transformation described by matrix S.

From (28), we obtain the following two equalities:

$$\begin{aligned} \tilde{V}_n^{\alpha_1\alpha_2\ldots\alpha_n}&(p_1, -\mathbf{k}_1; p_2, -\mathbf{k}_2; \ldots; p_{n-1}, -\mathbf{k}_{n-1}; p_n) \\ &= \tilde{V}_n^{\alpha_1\alpha_2\ldots\alpha_n *}(p_1, \mathbf{k}_1; p_2, \mathbf{k}_2; \ldots; p_{n-1}, \mathbf{k}_{n-1}; p_n), \end{aligned} \tag{31}$$

$$\tilde{V}_n^{\alpha_1\alpha_2\ldots\alpha_n}(\ldots, p_j, \mathbf{k}_j + \mathbf{b}, \ldots) = \tilde{V}_n^{\alpha_1\alpha_2\ldots\alpha_n}(\ldots, p_j, \mathbf{k}_j, \ldots), \tag{32}$$

where $\mathbf{b}$ is the translation vector of the reciprocal lattice: $(\mathbf{b}, \mathbf{R}_m) = 2\pi K$ (K an integer) for all feasible R_m and j is an integer in the interval $[1, n-1]$. Using (27), we obtain

$$\begin{aligned} \tilde{V}_n^{\ldots\alpha_i\ldots\alpha_j\ldots}&(\ldots p_i, \mathbf{k}_i \ldots p_j, \mathbf{k}_j \ldots) \\ &= \tilde{V}_n^{\ldots\alpha_j\ldots\alpha_i\ldots}(\ldots p_j, \mathbf{k}_j \ldots p_i, \mathbf{k}_i \ldots), \end{aligned} \tag{33}$$

where i and j are any integers within the interval $[1, n-1]$.

Equations (30)–(33) give the general relationships between the Fourier components of the mixing potentials.

Within the well known models of solid solutions (de Fontaine, 1979; Khachaturyan, 1978, 1983) in consideration of the configuration energy, as a rule, only contributions from the injection and binary mixing potential are taken into account. Thus, it is advisable to examine in detail the symmetry properties of these low-order mixing energies.

5. Properties of the injection potential

From the translation properties of the mixing potentials (26), we have

$$V_1^\alpha(p,\mathbf{R}) = V_1^\alpha(p,0) \equiv \Phi_p^\alpha, \tag{34}$$

for the injection potential (unitary mixing potential), *i.e.* the potential Φ_p^α of the injection for the particle of the type $\alpha \neq \alpha_0^p$ into the position with the number p within the unit cell does not depend on the coordinates of this unit cell. Under this condition, the symmetry properties (19) lead to the following equality for the injection potentials:

$$\Phi_{p'}^\alpha = \Phi_p^\alpha, \tag{35}$$

where the set of numbers p' is given by the symmetry transformations $\mathbf{X}(p',\mathbf{R}') = g\mathbf{X}(p,\mathbf{R})$, $g \in G$.

Thus, the injection potentials of a given atom into two symmetry-equivalent positions (*i.e.* positions that can be sent from one to the other owing to the symmetry transformations from group G) are equal.

6. Properties of binary mixing potentials and their Fourier transforms

For the binary mixing potential, using (26), (27) and (19),[*] we obtain

$$\begin{aligned} V_2^{\alpha\beta}(p,\mathbf{R}_1;q,\mathbf{R}_2) &= V_2^{\alpha\beta}(p,\mathbf{R}_1-\mathbf{R}_2;q) \\ &\equiv w_{pq}^{\alpha\beta}(\mathbf{R}_1-\mathbf{R}_2), \end{aligned} \tag{36}$$

$$w_{pq}^{\alpha\beta}(\mathbf{R}) = w_{qp}^{\beta\alpha}(-\mathbf{R}), \tag{37}$$

$$w_{p'q'}^{\alpha\beta}(\mathbf{R}') = w_{pq}^{\alpha\beta}(\mathbf{R}). \tag{38}$$

Equality (38) implies that $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$, $\mathbf{R}' = \mathbf{R}_1' - \mathbf{R}_2'$, $\mathbf{X}(p',\mathbf{R}_1') = g\mathbf{X}(p,\mathbf{R}_1)$ and $\mathbf{X}(q',\mathbf{R}_2') = g\mathbf{X}(q,\mathbf{R}_2)$.

Fourier transforms of the binary mixing potentials, in accordance with (28), are determined as

$$\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{R}} w_{pq}^{\alpha\beta}(\mathbf{R}) \exp[-i(\mathbf{k},\mathbf{R})]. \tag{39}$$

From this, corresponding to (30)–(33), the following relationships between the components of the Fourier transforms (39) take place:

$$\tilde{w}_{p'q'}^{\alpha\beta}(S\mathbf{k}) = \tilde{w}_{pq}^{\alpha\beta}(\mathbf{k}) \exp[i(S\mathbf{k},\mathbf{h}_{p'}-\mathbf{h}_{q'}) - i(\mathbf{k},\mathbf{h}_p-\mathbf{h}_q)], \tag{40}$$

$$\tilde{w}_{pq}^{\alpha\beta}(-\mathbf{k}) = \tilde{w}_{pq}^{\alpha\beta *}(\mathbf{k}), \tag{41}$$

$$\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k}+\mathbf{b}) = \tilde{w}_{pq}^{\alpha\beta}(\mathbf{k}). \tag{42}$$

Equation (40) implies that $\mathbf{X}(p',\mathbf{R}_1') = \{S|\tau(S)+\mathbf{R}_m\}\mathbf{X}(p,\mathbf{R}_1)$ and $\mathbf{X}(q',\mathbf{R}_2') = \{S|\tau(S)+\mathbf{R}_m\}\mathbf{X}(q,\mathbf{R}_2)$. Furthermore, from (37) and (39),

$$\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k}) = \tilde{w}_{qp}^{\beta\alpha}(-\mathbf{k}). \tag{43}$$

The symmetry analysis of eigenvalues $\Lambda^\sigma(\alpha,\beta|\mathbf{k})$ of matrix $\|\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k})\|$, which are determined by the equations

$$\sum_q \tilde{w}_{pq}^{\alpha\beta}(\mathbf{k}) v_q^\sigma(\alpha,\beta|\mathbf{k}) = \Lambda^\sigma(\alpha,\beta|\mathbf{k}) v_p^\sigma(\alpha,\beta|\mathbf{k}) \tag{44}$$

[index σ enumerates eigenvalues $\Lambda^\sigma(\alpha,\beta|\mathbf{k})$ and eigenvectors $v_p^\sigma(\alpha,\beta|\mathbf{k})$], occupy an important place in the concentration wave method (see §7). With the aim of obtaining the general symmetry properties of $\Lambda^\sigma(\alpha,\beta|\mathbf{k})$, we rewrite (44) for the wave vector $S\mathbf{k}$:

$$\sum_q \tilde{w}_{pq}^{\alpha\beta}(S\mathbf{k}) v_q^\sigma(\alpha,\beta|S\mathbf{k}) = \Lambda^\sigma(\alpha,\beta|S\mathbf{k}) v_p^\sigma(\alpha,\beta|S\mathbf{k}). \tag{45}$$

Substituting p for p' and q for q' and using the transformation rule (40) for matrix $\|\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k})\|$, we have

$$\begin{aligned} &\sum_q \tilde{w}_{pq}^{\alpha\beta}(\mathbf{k}) \{\exp[-i(S\mathbf{k},\mathbf{h}_{q'}) + i(\mathbf{k},\mathbf{h}_q)] v_{q'}^\sigma(\alpha,\beta|S\mathbf{k})\} \\ &\quad = \Lambda^\sigma(\alpha,\beta|S\mathbf{k}) \{\exp[-i(S\mathbf{k},\mathbf{h}_{p'}) \\ &\qquad + i(\mathbf{k},\mathbf{h}_p)] v_{p'}^\sigma(\alpha,\beta|S\mathbf{k})\}. \end{aligned} \tag{46}$$

From (44) and (46), one can obtain, using a specific numeration of eigenvalues,

$$\Lambda^\sigma(\alpha,\beta|S\mathbf{k}) = \Lambda^\sigma(\alpha,\beta|\mathbf{k}). \tag{47}$$

Using the properties (41)–(43) of matrix $\|\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k})\|$ in (44), one can easily obtain

$$\Lambda^\sigma(\alpha,\beta|-\mathbf{k}) = \Lambda^\sigma(\alpha,\beta|\mathbf{k}), \tag{48}$$

$$\Lambda^\sigma(\alpha,\beta|\mathbf{k}+\mathbf{b}) = \Lambda^\sigma(\alpha,\beta|\mathbf{k}). \tag{49}$$

Thus, the eigenvalues $\Lambda^\sigma(\alpha,\beta|\mathbf{k})$ of the Fourier transforms of the binary mixing potential have the following general symmetry properties: (1) periodicity in appropriate reciprocal space; (2) invariance to inversion transformation; (3) the symmetry point group of $\Lambda^\sigma(\alpha,\beta|\mathbf{k})$ coincides with the symmetry crystal class of the MSS.

Note that the relationships (47)–(49) for the particular case of a binary disordered substitutional alloy were derived by Sanchez, Gratias & de Fontaine (1982) under the assumption of the isotropy of the pairwise interatomic potential and by Zhorovkov (1993) under the postulation of the symmetry property (38).

7. Concluding remarks

In solid solutions, a lowering of the temperature gives a sequence of phase transformations of ordering type until

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[*] The notation for the binary mixing potential is similar to those used by de Fontaine (1979), Khachaturyan (1978, 1983) and Bugaev & Tatarenko (1989).

the stoichiometric composition of the superstructure (in agreement with the Nernst principle) coincides with the composition of the system (or further evolution of the system will meet the limitations concerning the kinetic factor). Such a scheme for atomic ordering was considered, for example, by Krivoglaz (1969), Somenkov (1972) and Khachaturyan (1978, 1983). At every stage of the ordering, both the symmetry of the relative distribution of the different atom types at positions within the crystal lattice and, in general, the symmetry of the lattice itself, will change. The important generalization of the conventional lattice gas model leads to the use of symmetry-adequate interatomic potentials in every region of the phase diagram characterized by the definite space symmetry. The symmetry properties of interatomic potentials for every stage of the ordering can be stated by using the method proposed in this paper on condition that the symmetry of the corresponding ordered state is known. The information about the properties of interatomic potentials in turn could facilitate the study of structural and thermodynamic features of the MSS at a corresponding stage of the ordering and the prediction of the phase transformations of order–order type to another structural stage (including the prediction of the space symmetry of the new ordered stage).

For example, in the analysis of the thermodynamic stability of ordered structures within the concentration waves method, it is necessary to know the normal concentration modes of the structural instabilities. These modes are specified by the eigenvectors of the binary mixing-potential matrix $\|\tilde{w}^{\alpha\beta}_{pq}(\mathbf{k})\|$ (de Fontaine, 1979; Khachaturyan, 1978, 1983). It was shown, for instance, by Sanchez, Gratias & de Fontaine (1982), Khachaturyan (1978, 1983), Solov'eva & Shtern (1990) and Zhorovkov (1993) that finding the concentration modes can be realized by using the information on independent components of this matrix only. The relationships obtained in §6 make it possible to establish which components of the matrix $\|\tilde{w}^{\alpha\beta}_{pq}(\mathbf{k})\|$ can be considered as independent and also to find analytical relationships between corresponding components.

Thus, the opportunity now arises of predicting the structural types corresponding to all regions of the phase diagram of a solid solution (consistently from the disordered state at sufficiently high temperatures when the symmetry of the MSS coincides with the symmetry of the initial crystal lattice of the MSS), taking into consideration the symmetry changes of interatomic potentials due to structural transformations. In the case when the disordered state cannot take place even at sufficiently high temperatures (for instance, in some chemical compounds of the intermetallic type and also in ceramics), the above-mentioned scheme can be realized starting from the given ordered state if its structure (*i.e.* the space symmetry) is known, for example, from diffraction experiments.

The suggested method of finding the symmetry properties of interatomic potentials can also be useful in the development (within one or other microscopic theory) of such potentials for multicomponent solid solutions.

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References

BUGAEV, V. N. & RYZHKOV, V. I. (1979). *Fiz. Met. Metalloved.* **47**, 568–577.

BUGAEV, V. N. & TATARENKO, V. A. (1989). *Interaction and Arrangement of Atoms in Interstitial Solid Solutions Based on Close-Packed Metals*. Kiev: Naukova Dumka. (In Russian.)

FONTAINE, D. DE (1979). *Configurational Thermodynamics of Solid Solution, Solid State Physics*, Vol. 34, pp. 73–274, edited by H. EHRENREICH, F. SEITZ & D. TURNBULL. New York: Academic Press.

GOLOSOV, N. S. & USHAKOV, A. V. (1976). *Fiz. Tverd. Tela*, **18**, 1262–1268.

KHACHATURYAN, A. G. (1978). *Prog. Mater. Sci.* **22**, 1–150.

KHACHATURYAN, A. G. (1983). *Theory of Structural Transformations in Solids*. New York: John Wiley.

KRIVOGLAZ, M. A. (1969). *The Theory of X-ray and Thermal Neutron Scattering from Real Crystals*. New York: Plenum Press.

KRIVOGLAZ, M. A. & SMIRNOV, A. A. (1964). *The Theory of Order–Disorder in Alloys*. London: Macdonald.

MARADUDIN, A. A. & VOSKO, S. H. (1968). *Rev. Mod. Phys.* **40**, 1–37.

SANCHEZ, J. M., GRATIAS, D. & DE FONTAINE, D. (1982). *Acta Cryst.* A**38**, 214–221.

SEITZ, F. (1936). *Ann. Math.* **37**, 17–26.

SOLOV'EVA, M. I. & SHTERN, D. M. (1990). *Izv. Vuz. Fiz.* No. 6, pp. 90–94.

SOMENKOV, V. A. (1972). *Ber. Bunsenges. Phys. Chem.* **76**, 733–740.

SOMENKOV, V. A., IRODOVA, A. V. & SHIL'SHTEIN, S. S. (1978). *Fiz. Tverd. Tela*, **20**, 3076–3085.

ZHOROVKOV, M. F. (1993). *Izv. Vuz. Fiz.* No. 8, pp. 13–25.