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ATOMIC STRUCTURE OF ORDERED PHASES. STABILITY WITH RESPECT TO FORMATION OF ANTIPHASE DOMAINS

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It is shown in the self-consistent field approximation that a homogeneous superstructure state in alloys may be thermodynamically stable with respect to formation of an antiphase domain system (formation of antiphase domains leads to an increase of free energy) only if all superstructure sites of the reciprocal lattice coincide with "singular" points of reciprocal space of a disordered solution, these points being assumed to satisfy the E. M. Lifshitz condition. In all other cases the superstructure disintegrates into a set of antiphase domains whose geometry depends on the values of the external thermodynamic parameters, viz., temperature, composition and pressure. The respective phase states apparently correspond to the so-called periodic antiphases. A theoretical procedure for reproducing superstructures on the basis of a known star involved in ordering is discussed. Superstructures are set up in face-centered cubic and body-centered cubic substitution and interstitial solutions which are stable with respect to antiphase domain formation.

1. STABILITY OF HOMOGENEOUS SUPERSTRUCTURES AGAINST THE FORMATION OF ANTIPHASE DOMAINS

THE question of the stability of ordered phases was first considered by E. M. Lifshitz[1] within the framework of the phenomenological theory of second-order phase transitions. E. M. Lifshitz has proposed a criterion, according to which the homogeneous state of an ordered phase is stable against the formation of long-period modulations of the single-particle density distribution function of the atoms, if the point group of the wave vectors of the star with which the second order phase transition is connected contains symmetry elements that cross at one point1). The theory of[1] was subsequently developed by Dzyaloshinskiĭ[2]. It must be emphasized, however, that the analysis in[1,2] is valid only near a second-order phase transition point (this question will be considered later on in greater detail). It is shown in the present article that the Lifshitz criterion has a wider range of applicability. It can be used for phases that are far from a second-order phase transition point, regardless of the type of the phase transition. It then assumes the role of a criterion for the stability of a superstructure against the formation of antiphase domains (APD). Using the theoretical conclusions obtained in the present paper and in[3,4], which are valid in the self-consistent field approximation, we can predict the atomic structure of all substitutional and interstitial superstructures that are stable against the formation of APD and that are possible in any particular solution.

For simplicity we consider ordering in a binary solid solution having a monatomic Bravais lattice. In binary solid substitution (interstitial) solutions we can describe the distribution of the atoms over the sites (interstices) with the aid of a single-particle density function of atoms of a single component, namely the probability n(**R**) for filling the lattice sites **R** by atoms of this component. Thus, ordering in substitutional and interstitial solutions can be described within the framework of a single formalism[4]. For concreteness, however, we shall refer throughout to substitution solutions.

The thermodynamics of such solutions can be described within the framework of the self-consistent field approximation, since we are interested in cases of systems situated far from second-order phase transition points, and also in cases of system with first-order phase transition systems, for which the self-consistent field approximation is sufficiently accurate[5]. In the self-consistent field approximation, the free energy of a substitution solid solution is described by the expression[3]

$$\mathscr{F}=\frac{1}{2}\sum_{\mathbf{R}\mathbf{R}'}\tilde{V}(\mathbf{R}-\mathbf{R}')n(\mathbf{R})n(\mathbf{R}')+\varkappa T\sum_{\mathbf{R}}(n(\mathbf{R})\ln n(\mathbf{R}) \qquad (1)$$
$$+(1-n(\mathbf{R}))\ln(1-n(\mathbf{R}))),$$

where $\tilde{V}(\mathbf{R}-\mathbf{R}')$ is the energy of mixing between the sites **R** and **R**′ (for interstitial solutions, $\tilde{V}(\mathbf{R}-\mathbf{R}')$ is the potential of the interaction of two interstitial atoms located respectively at the sites **R** and **R**′); κ is Boltzmann's constant; T is the absolute temperature. The summation (1) is over all the lattice sites.

Stability of the homogeneous state of the superstructure means that any change in the atomic structure of the stable ordered phase should lead to an increase of the free energy. In particular, the APD should lead to an increase of the free energy. Since the second term in (1) (the entropy term) is a local function of the coordinates of the lattice sites, it follows that the formation APD consisting of an integer number of superstructure unit cells cannot change its values2). We can therefore

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1) A star is called an aggregate of wave vectors in the first Brillouin zone, which do not differ from one another by the reciprocal-lattice vector and are connected with one another by the rotation and reflection transformations of the crystal.

2) A certain entropy change connected with the relaxation of n(R) near the antiphase boundary (APB) is possible. But all it does is lower even more the free energy of the system with APD, and can therefore be disregarded.

assume that the change of free energy due to the formation of APD is determined by the change of the internal energy of the system

$$U=\frac{1}{2}\sum_{\mathbf{R}\mathbf{R}'}V(\mathbf{R}-\mathbf{R}')n(\mathbf{R})n(\mathbf{R}'). \tag{2}$$

The function n(**R**) can be represented in the case considered here in the form of the series

$$n(\mathbf{R})=\sum_{\mathbf{k}\in\{\mathbf{k}_{j_s}\}}{}' Q(\mathbf{k})\exp(i\mathbf{k}\mathbf{R}), \tag{3}$$

where the prime at the summation sign means that the summation is carried out over all the wave vectors $\mathbf{k}_{j_s}$ of the stars s making up the superstructure (over all the superstructure wave vectors that enter in the first Brillouin zone of the lattice $\{\mathbf{R}\}$ of the sites). The sum includes also the term Q(0) = c corresponding to the value **k** = 0 (the structure vector of the reciprocal lattice situated in the first Brillouin zone), where c is the atomic fraction of the given component. The coefficients Q(**k**) are the structure amplitudes in the superstructure sites of the reciprocal lattice $\{\mathbf{k}_{j_s}\}$ and are proportional to the long-range order parameters[1,2]. Substituting (3) in (2), we rewrite the internal energy of the superstructure in the form

$$U_0=\frac{N}{2}\sum_{\mathbf{k}}{}' V(\mathbf{k})|Q(\mathbf{k})|^2. \tag{4}$$

The probability $n_{APD}(\mathbf{R})$ of the distribution of the atoms in the system with APD can be expressed in terms of the probability n(**R**) of the distribution of the atoms in a homogeneous superstructure with the aid of the equation

$$n_{\mathrm{APD}}(\mathbf{R})=n(\mathbf{R}+\mathbf{T}(\mathbf{R}))=\sum_{\mathbf{k}}{}' Q(\mathbf{k})\exp[i\mathbf{k}(\mathbf{R}+\mathbf{T}(\mathbf{R}))], \tag{5}$$

where **T**(**R**) is a vector function equal to $\mathbf{T}_\alpha$ if the site **R** is situated in an APD of type α, where α = 1, 2, ..., z is the number of the lattice site in the unit cell of the superstructure, z is the number of atoms in the basis of the superstructure, $\mathbf{T}_\alpha$ are the disordered-solution translation vectors that are not translation vectors of the superstructure (antiphase shifts). Formula (5) can be rewritten also in another form:

$$n_{\mathrm{APD}}(\mathbf{R})=\frac{1}{N}\sum_{\mathbf{k}}{}' Q(\mathbf{k})\sum_{\boldsymbol{\tau}}S_{\mathbf{k}}(\boldsymbol{\tau})\exp(i(\mathbf{k}+\boldsymbol{\tau})\mathbf{R}), \tag{6}$$

where

$$S_{\mathbf{k}}(\boldsymbol{\tau})=\sum_{\mathbf{R}}\exp(i\mathbf{k}\mathbf{T}(\mathbf{R}))\exp(-i\boldsymbol{\tau}\mathbf{R}) \tag{7}$$

is the structure factor of the APD system; the summation over $\boldsymbol{\tau}$ in (6) is carried out over all the points of the quasicontinuum of the first Brillouin zone. For APD having the form of infinite parallel plates of thickness D, the structure factor $S_k(\tau)$ differs from zero in a small region of reciprocal space near $\tau = 0$. This region has the form of a thin infinite rod normal to the boundary of the antiphase domains, with a length on the order of $\tau \sim 1/D$. Substituting (6) in (4) we obtain

$$U=\frac{1}{2N}\sum_{\mathbf{k}}{}'\sum_{\boldsymbol{\tau}}V(\mathbf{k}+\boldsymbol{\tau})|Q(\mathbf{k})|^2|S_{\mathbf{k}}(\boldsymbol{\tau})|^2. \tag{8}$$

Since $|S_k(\tau)|^2$ is localized in a narrow region of the order of 1/D, the integration with respect to τ in (8) is actually carried out in this region near each reciprocal-lattice point of the superstructure. Within the limits of this region, the function $V(\mathbf{k}_{j_s}+\boldsymbol{\tau})$ varies little and can be expanded in powers of $\boldsymbol{\tau}$ (the expansion is actually carried out in powers of the parameter $\tau/k_{j_s} \sim a/D \ll 1$, where a is the superstructure lattice constant). Confining ourselves to the first term of the expansion, we rewrite (8) in the form

$$U=\frac{1}{2N}\sum_{\mathbf{k}}{}' V(\mathbf{k})|Q(\mathbf{k})|^2\sum_{\boldsymbol{\tau}}|S_{\mathbf{k}}(\boldsymbol{\tau})|^2+\frac{1}{2}\sum_{\mathbf{k}}{}' |Q(\mathbf{k})|^2\mathbf{V}_1(\mathbf{k})\mathbf{A}_{\mathbf{k}}(\{\mathbf{T}(\mathbf{R})\}), \tag{9}$$

where

$$\mathbf{V}_1(\mathbf{k})=\partial V(\mathbf{k})/\partial\mathbf{k}, \tag{10}$$

$$\mathbf{A}_{\mathbf{k}}(\{\mathbf{T}(\mathbf{R})\})=\frac{1}{N}\sum_{\boldsymbol{\tau}}\boldsymbol{\tau}|S_{\mathbf{k}}(\boldsymbol{\tau})|^2 \tag{11}$$

is a vector that is a functional of **T**(**R**).

Taking into account the identity $\sum_{\tau}|S_k(\tau)|^2 = N$, we can see that the first term in (9) is the energy (4) of the superstructure without the APD. The second term in (9) is the internal-energy change due to the APD described by the function **T**(**R**):

$$\Delta U=U-U_0=\frac{1}{2}\sum_{\mathbf{k}}{}' |Q(\mathbf{k})|^2\mathbf{V}_1(\mathbf{k})\mathbf{A}_{\mathbf{k}}(\{\mathbf{T}(\mathbf{R})\}). \tag{12}$$

The internal-energy change $\Delta U(\{\mathbf{T}(\mathbf{R})\})$ is also a functional of the APD distribution. Expression (11) can be rewritten in a more convenient form

$$\mathbf{A}_{\mathbf{k}}(\{\mathbf{T}(\mathbf{R})\})=\frac{1}{2N}\sum_{\boldsymbol{\tau}}\boldsymbol{\tau}(|S_{\mathbf{k}}(\boldsymbol{\tau})|^2-|S_{\mathbf{k}}(-\boldsymbol{\tau})|^2). \tag{13}$$

The stability of the homogeneous ordered phase against formation of APD means that for any APD system (any function T(R)) we have $\Delta U(\{\mathbf{T}(\mathbf{R})\}) > 0$. At the same time, it follows from (12) that we are always able to construct an antiphase domain system (a function **T**(**R**) such that $\Delta U < 0$. In fact, we choose a certain function $\mathbf{T}_1(\mathbf{R})$ satisfying the condition

$$\mathbf{T}_1(-\mathbf{R})=-\mathbf{T}_1(\mathbf{R}), \tag{14}$$

with the antiphase shifts of $\mathbf{T}_1(\mathbf{R})$ different from the antiphase shifts of $-\mathbf{T}_1(\mathbf{R})$ (they cannot be equated to the latter by adding some superstructure-translation vector). If it turns out that $\Delta U(\{\mathbf{T}_1(\mathbf{R})\}) < 0$ for the APD system, then this automatically proves the instability of the homogeneous ordered phase. On the other hand, if $\Delta U(\{\mathbf{T}_1(\mathbf{R})\}) > 0$, then we can choose a new domain structure characterized by a function $\mathbf{T}_2(\mathbf{R}) = -\mathbf{T}_1(\mathbf{R})$. From (13), after determining (7) and the property (14), it follows that

$$\mathbf{A}_{\mathbf{k}}(\{\mathbf{T}_2(\mathbf{R})\})=\mathbf{A}_{\mathbf{k}}(\{-\mathbf{T}_1(\mathbf{R})\})=-\mathbf{A}_{\mathbf{k}}(\{\mathbf{T}_1(\mathbf{R})\}). \tag{15}$$

Substituting (15) in (12) we have

$$\Delta U(\{\mathbf{T}_2(\mathbf{R})\})=\Delta U(\{-\mathbf{T}_1(\mathbf{R})\})=-\Delta U(\{\mathbf{T}_1(\mathbf{R})\})<0, \tag{16}$$

thereby proving the instability of the homogeneous state of the superstructure against formation of APD.

Thus, if the expression for ΔU, defined by (12), differs from zero, then the superstructure is always unstable against the formation of APD. In order for expression (13) to vanish identically, it is necessary to have

$$\partial V(\mathbf{k}) / \partial \mathbf{k} = 0 \tag{17}$$

for all the vectors $\{\mathbf{k}_{j_s}\}$ in the expression (3) for the probability distribution. It follows therefore that the necessary condition for the existence of a homogeneous superstructure is the requirement that the Fourier component of the mixing energy, the function $V(\mathbf{k})$, have a minimum at all reciprocal-space points corresponding to the position of the superstructure vectors of the reciprocal lattice[3]. This criterion is valid with respect to any superstructure, regardless of whether the superstructure is near or far from the ordering point. In the reciprocal lattice there are two types of minima of the function $V(\mathbf{k})$. The first can be realized in arbitrary points of reciprocal space. The positions of these minima depend on the concrete form of the interaction potential $\widetilde{V}(\mathbf{R})$. The second type of minimum is realized in "singular" points of high symmetry of the reciprocal lattice of the disordered phase. The positions of these minima are connected with the symmetry of the reciprocal lattice of the disordered phase and are therefore independent of the concrete form of the potential $V(\mathbf{R})$. Therefore small changes of the external parameters cannot lead to a displacement of minima of this type. As shown in[2,6], the values of the wave vectors $\mathbf{k}_{j_s}$ characterizing the positions of the "singular" points at which a minimum of the function $V(\mathbf{k})$ is realized are determined from the condition that the point group of the vector $\mathbf{k}_{j_s}$ contain symmetry elements that intersect at one point. This condition is fully equivalent to the criterion formulated by Lifshitz in the phenomenological theory of second-order phase transitions[1].

Using the foregoing, we can distinguish between two types of ordered phases. The first type includes those superstructure in which the positions of one or several superstructure types do not coincide with the "singular" points in the reciprocal lattice of the disordered phase satisfying the Lifshitz criterion. These superstructures cannot be in a homogeneous state, for any arbitrarily small action on the system leads to the appearance of nonzero values of the derivatives $(\partial V(\mathbf{k})/\partial \mathbf{k})|_{\mathbf{k}=\mathbf{k}_{j_s}}$, and consequently to a loss of thermodynamic stability against the formation of APD. (Unlike the APD in stable superstructure, the APD produced in this case are thermodynamically stable.) The parameters of these distributions should apparently be quite sensitive to changes of the temperature, composition, and pressure. One can assume that the APB are periodically arranged with a period $2\pi/\Delta k$, where Δk is the distance from the superstructure vector to the point at which $V(\mathbf{k})$ has a minimum. Many such long-period superstructures were observed recently[7].

The second type of superstructures includes those ordered phases in which all the superstructure reciprocal-lattice points satisfy the Lifshitz criterion. These ordered phases can be in a homogeneous state regardless of changes in the thermodynamic parameters of the system, if all these points correspond to a minimum of the function $V(K)$ (see foornote 3). In fact, the conditions under which the function $V(\mathbf{k})$ has an extremum in the "singular" points of reciprocal space are satisfied because of the symmetry of the system, and therefore cannot be disturbed by external actions. Since the number of non-equivalent "singular" points is limited, there is a realistic possibility of determining for each lattice the atomic-crystalline structure of all the ordered phases that are stable against the formation of APD.

It must be emphasized that all the deductions arrived at above for monatomic crystals remain valid also for the case of ordering in more complicated crystals with bases.

An interesting question is the relation between the present results and those of Dzyaloshinskiĭ[2]. It was concluded in[2], in particular, that superstructures that do not satisfy the Lifshitz criterion are unstable against changes of the star vectors $\mathbf{k}_{j_s}$. This conclusion is subject to no doubt near the temperature T_c of a second-order phase transition. It cannot be extended, however, to temperatures far from T_c. The reason is that the Dzyaloshinskiĭ theory[2] is based on an expansion of the free energy in a series near the vectors $\mathbf{k}_{j_s}$. This expansion is possible near T_c, but is known to be inapplicable far from T_c, where the free energy is discontinuous for all rational values of $\mathbf{k}_{j_s}$ [8]. It can be shown, in particular, that in the limiting case near T = 0°K a superstructure that does not satisfy the Lifshitz criterion is nevertheless stable against variations of the star vectors $\mathbf{k}_{j_s}$ that lead to "beats" in the distribution probability $n(\mathbf{R})$. Near T = 0°K, by virtue of the third law of thermodynamics, $n(\mathbf{R})$ takes on the two values 0 and 1. Therefore if "beats" were produced (they would be commensurate with $n(\mathbf{R})$), they would take the probability outside of its "physical" definition range $0 \le n(\mathbf{R}) \le 1$, which is impossible. Such a superstructure, however, being stable against the variations of $\mathbf{k}_j$, will nevertheless be unstable against the formation of APD.

2. DETERMINATION OF THE SUBSTITUTION AND INTERSTITIAL SUPERSTRUCTURES FROM THE KNOWN STARS

If, following[1,3], we regroup the terms in (3), gathering together those corresponding to a single star, then expression (3) can be rewritten in the form

$$n(\mathbf{R}) = c + \sum_s \eta_s \varepsilon_s(\mathbf{R}), \tag{18}$$

$$\varepsilon_s(\mathbf{R}) = \frac{1}{2} \sum_{j_s} (\gamma_s(j_s) \exp(i\mathbf{k}_{j_s}\mathbf{R}) + \text{c.c.}), \tag{19}$$

$$Q(\mathbf{k}_{j_s}) = \eta_s \gamma_s(j_s), \tag{20}$$

η_s are the long-range order parameters, the subscript s numbers the stars, and the subscript j_s numbers the wave vectors $\mathbf{k}_j$ entering in the star s. It follows from (20) that the long-range order parameters are not uniquely defined and depend on the method used to define the coefficients $\gamma_s(j_s)$. In some cases it is convenient to define the coefficients $\gamma_s(j_s)$ in such a way as to satisfy the normalization conditions[1]

$$\sum_{(j_s)} |\gamma_s(j_s)|^2 = 1. \tag{21}$$

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[3] If the function $V(\mathbf{k})$ has a maximum or a saddle point in the positions of certain superstructure vectors of the reciprocal lattice, then it can be easily shown that in this case, too, the homogeneous ordered phase is unstable against the formation of APD.

In other cases, they are so defined that in an alloy of stoichiometric composition the function n(**R**) assume the two values 0 and 1 at all $\eta_s = 1$, i.e., such that the distribution (21) describes a fully ordered distribution of the atoms at all $\eta_s = 1$.

It is shown in the Appendix that from the condition that the free energy be minimal it is possible to deduce the following condition: the coefficients $\gamma_s(j_s)$ in expressions (19) and (20) are constants independent of changes in the thermodynamic parameters of the system (temperature, composition, and pressure). Changes in the coefficients $\gamma_s(j_s)$ can occur only jumpwise on the interphase boundaries, and these changes always offer evidence of changes in the symmetry of the solid solution.

On the other hand, it was proved in[3] that the function n(**R**) must satisfy the following two necessary conditions: (I) The function n(**R**) should assume on the set $\{\mathbf{R}\}$ of all the lattice sites a number of different values exceeding by unity the total number of the long-range order parameters. (II) The sum of any two wave vectors $\mathbf{k}_{j_s}$ (including those equal to each other) in the distribution functions n(R) should, accurate to within the structure vector of the reciprocal lattice, be equal either to zero or to some third vector that is contained in this distribution.

To understand the meaning of the condition (I), we note the following. The dependence of n(**R**) on the lattice-point coordinates R means that ordering causes the lattice $\{\mathbf{R}\}$ of a disordered solution to break up into several, say t, sublattices. Each sublattice is characterized by its own probability of site occupation. Thus, the ordered state is defined, on the one hand, by the concentration c with a set of long-range order parameters η_s, and on the other hand by the set of t different values assumed by n(**R**) on the set of all points $\{\mathbf{R}\}$ Since the number of degrees of freedom of the system cannot depend on the method used to describe it, the number of parameters η_s at constant $\gamma_s(j_s)$ should be equal to t − 1 (the parameter numbered t will be the concentration c). The last conclusion is equivalent to the formulation of condition (1).

The meaning of condition (II) can be understood by noting that the vectors $\mathbf{k}_{j_s}$, which enter in the right-hand side of (18), are the principal translations of the reciprocal lattice of the ordered phase. Since the vectors $\mathbf{k}_{j_s}$ are translations of a Bravais lattice, the condition (II) reduces to the obvious property of any Bravais lattice, namely, the sum of any two translations in a Bravais lattice must be equal to some third translation in the same lattice.

So far we have discussed the case of ordering in lattices without a basis. It can be shown that in the case of complex lattices having a basis, all the results obtained above are valid with respect to each of the sublattices of this complicated structure. In this situation, the procedure of determining the structure of the ordered phase reduces to the already considered procedure of constructing an ordered distribution in a single-atom lattice, which must be carried out for one or several sublattices. The long-range order and concentration parameters will then have separate values for each of the sublattices. They can be determined from the equations of the self-consistent field[4].

The approach developed here is quite effective in a structure analysis of the ordered phases, particularly in an electron-microscope investigation of alloys by the micro-diffraction method. The latter yields directly the intersections of the reciprocal lattices of ordered phases with different planes. From these intersections one can determine the stars of the wave vectors $\{\mathbf{k}_{j_s}\}$, which determine the general form of the distribution (18), and then, using the theoretical premises described above, construct the distribution of the atoms in the investigated superstructure. Such an approach allows us to analyze the superstructures without the laborious procedure of determining the intensities of the Laue reflections (see, for example,[19]). If we are interested in the atomic structure of superstructures that are thermodynamically stable against the formation of APD, then the stars that determine the translational symmetry of the superstructures can be determined from the theoretical considerations developed in Sec. 1. We determine below all such superstructures that can arise in BCC and FCC substitution and interstitial solutions.

3. SUPERSTRUCTURES IN FCC BINARY SUBSTITUTION AND INTERSTITIAL SOLUTIONS THAT ARE STABLE AGAINST THE FORMATION OF APD

Since the ordinary FCC lattice has no basis, it follows that in FCC substitution solutions the ordered distributions of the atoms are described by expression (18). The location of the "largest" octahedral interstices are also described by a simple FCC lattice shifted by half the side of the FCC lattice cube relative to the FCC lattice of the immobile "frame" formed by the solvent atoms. The problem of ordering in an FCC interstitial solution reduces to the problem of ordering in a model FCC substitution solution made up of the interstitial atoms and their vacancies, distributed over the FCC lattice of the octahedral interstices. The ordered distribution of the interstitial atoms in the FCC interstice lattice is described by the same expression (18) as the corresponding ordered distribution of the atoms in substitution solutions. The last circumstance is the reason for the existence of a definite crystal geometry and thermodynamic isomorphism between substitution and interstitial solutions.

In the FCC lattice there are three stars satisfying E. M. Lifshitz's criterion[1]:

$$
\begin{array}{ll}
\text{a)} & (100),\ (010),\ (001);\\
\text{b)} & (\tfrac12\,\tfrac12\,\tfrac12),\quad (\bar{\tfrac12}\,\tfrac12\,\tfrac12),\quad (\tfrac12\,\bar{\tfrac12}\,\tfrac12),\quad (\tfrac12\,\tfrac12\,\bar{\tfrac12});\\
\text{c)} & (\tfrac12\ 1\ 0),\quad (\tfrac12\ 0\ 1)\quad (0\ \tfrac12\ 1),\quad (\bar{\tfrac12}\,\bar{1}\ 0),\quad (\bar{\tfrac12}\ 0\ 1),\quad (0\ \bar{\tfrac12}\ \bar{1}).
\end{array}
\tag{22}
$$

The coordinates of the wave vectors of the stars are given in the usual basis of the reciprocal-lattice vectors: $2\pi\mathbf{a}_1^*$, $2\pi\mathbf{a}_2^*$, and $2\pi\mathbf{a}_3^*$, where $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, and $\mathbf{a}_3^*$ are the reciprocal-lattice vectors, with absolute values 1/a (a are the FCC lattice constants) and directed along the axes [100], [010], and [001], respectively. Thus, the general form of the distribution describing FCC-lattice superstructures that are stable against the formation of APD is determined by expression (18) in which only the stars of (22) are present:

$$n(\mathbf{R}) = c + \eta_1 \sum_{j_1=1}^{3} \gamma_1(j_1) e^{i\mathbf{k}_{j_1}\mathbf{R}} + \eta_2 \sum_{j_2=1}^{4} \gamma_2(j_2) e^{i\mathbf{k}_{j_2}\mathbf{R}} + \frac{1}{2}\eta_3 \sum_{j_3=1}^{6} [\gamma_3(j_3) e^{i\mathbf{k}_{j_3}\mathbf{R}} + \gamma_3^*(j_3) e^{-i\mathbf{k}_{j_3}\mathbf{R}}], \tag{23}$$

where $\mathbf{R} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$; x, y, and z are the coordinates of the FCC lattice point and are equal to integers and half-integers whose sums are arbitrary integers; $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the translation vectors in the [100], [010], and [001] directions of the FCC lattice; $\{\mathbf{k}_{j_1}\}$, $\{\mathbf{k}_{j_2}\}$, and $\{\mathbf{k}_{j_3}\}$ are the vectors of stars (a), (b), and (c) in (22).

Using the conditions (I) and (II) above, we can construct quite simply all the possible functions n(**R**) describing the substitution and interstitial superstructures that are stable against the formation of APD.

By way of example, let us consider in detail first the procedure of obtaining all the superstructures that depend only on one parameter η_1 (determined by star (a) in (22)). The expression n(R) for these structures can be written in the form

$$n(\mathbf{R}) = n(x, y, z) = c + \eta_1(\gamma_1(1)e^{i2\pi x} + \gamma_1(2)e^{i2\pi y} + \gamma_1(3)e^{i2\pi z}). \tag{24}$$

We note that the vectors of the star (a) of (22) satisfy the condition (II). Substituting in (24) all the values of the lattice-point coordinates x, y, and z of the FCC lattice, we note that n(**R**) takes on four different values. Since the superstructure described by the distribution (24) depends on only one long-range order parameter η_1, it follows that by virtue of condition (I) the function n(**R**) should take on only two values from the set of all the lattice points. Choosing the coefficients $\gamma_1(j)$ to satisfy the condition (I), we arrive at the following two distribution functions:

$$n(x, y, z) = c + \eta_1\gamma_1[e^{i2\pi x} + e^{i2\pi y} + e^{i2\pi z}], \tag{25}$$

$$n(x, y, z) = c + \gamma_1\eta_1 e^{i2\pi z}. \tag{26}$$

It is easy to verify that the distribution (25) describes a substitution superstructure of the C_3Au type, namely, the probability n(x, y, z) of observing an atom of sort A at a point (x, y, z) of the FCC lattice takes on two values on the set of the lattice points: $(c + 3\eta_1\gamma_1)$ at the vertices and $(c - \eta_1\gamma_1)$ at the centers of the faces of the FCC cells (see Fig. 1a). If we regard n(x, y, z) as the probability of the distribution of the interstitial atoms in the octahedral interstices, then (25) describes interstitial superstructures either of the type Me_4X (Me represents the core atom and X the interstitial atom), or Me_4X_3. The two phases Me_4X and Me_4X_3 are equivalent (anti-isomorphic), since they can be obtained one from the other by replacing the vacancies of the interstitial atoms by interstitial atoms, and vice versa. The superstructure Me_4X is shown in Fig. 1f. Superstructures of this type (Fe_4N, Ni_4N, and V_4C_3) were observed in[9,10,11], respectively.

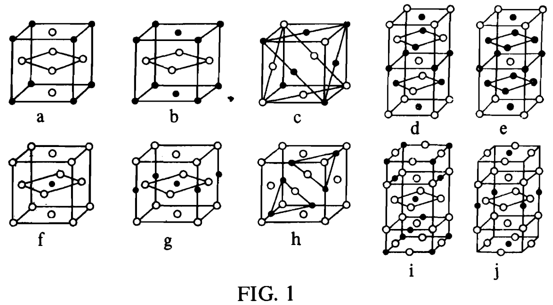

FIG. 1

The distribution (26) describes a substitution superstructure of the type $CuAu_1$: the function n(x, y, z) takes on the values $(c + \eta_1\gamma_1)$ and $(c - \eta_1\gamma_1)$ respectively in alternating (001) planes. The isomorphic interstitial superstructure described by expression (26) has a structure formula Me_2X and is shown in Fig. 1g. This phase was observed in the Ni-Fe-N system. It has a structure formula $(Ni, Fe)_2N$[10]. The coefficients γ_1 in expressions (25) and (26) are chosen in accordance with the two mentioned methods of defining the long-range order parameters. It is possible to determine similarly the remaining superstructures that are stable against the formation of APD. The corresponding distributions are

$$n(x, y, z) = c + \eta_2\gamma_2 \exp(i\pi(x + y + z)), \tag{27}$$

$$n(x, y, z) = c + \eta_2\gamma_2[\exp(i\pi(x + y + z)) + \exp(i\pi(-x + y + z)) + \exp(i\pi(x - y + z)) - \exp(i\pi(x + y - z))], \tag{28}$$

$$n(x, y, z) = c + \eta_3\gamma_3[\cos\pi(z + 2x) + \sin\pi(z + 2x)], \tag{29}$$

$$n(x, y, z) = c + \eta_1\gamma_1[e^{i2\pi x} + e^{i2\pi y} + e^{i2\pi z}] + \eta_2\gamma_2[e^{i\pi(x+y+z)} + e^{i\pi(-x+y+z)} + e^{i\pi(x-y+z)} + e^{i\pi(x+y-z)}], \tag{30}$$

$$n(x, y, z) = c + \eta_1\gamma_1(e^{i2\pi z} + \eta_2\gamma_2(e^{i\pi(x+y+z)} + e^{i\pi(x+y-z)}), \tag{31}$$

$$n(x, y, z) = c + \eta_1\gamma_1 e^{i2\pi z} + \eta_3\gamma_3 \cos\pi(z + 2y). \tag{32}$$

The distribution (27) corresponds to a superstructure of the CuPt type, the unit cell of which is shown in Fig. 1c, and its isomorphic interstitial superstructure of the Me_2X type, shown in Fig. 1h. The distribution (28) corresponds to complex superstructures of the type AB and Me_2X, containing 32 and 48 atoms per unit cell. The distribution (29) describes a tetragonal substitution superstructure, the unit cell of which is shown in Fig. 1d. The isomorphic interstitial superstructure is shown in Fig. 1i. It has not yet been observed so far. The distribution (30) describes the substitution superstructure A_7B in a substitution solution and Me_8X in an interstitial solution. The corresponding substitution superstructure $CuPt_7$ was observed in[12], and the interstitial superstructure Fe_8N in[9], while its anti-isomorphic interstitial superstructure V_8C_7 was observed in[13].

The distribution (31) describes the substitution superstructure A_3B. The corresponding superstructure Pt_3Cu was observed in[14]. The distribution (32) corresponds to a tetragonal substitution superstructure having a formula A_3B (Fig. 1e), a tetragonal interstitial superstructure having a formula Me_4X, and its anti-isomorphic superstructure Me_4X_k (Fig. 1j). The corresponding substitution phases Al_3Ti and Ni_3V were observed in[15] and[16], and the interstitial phases Ni_4N_3 and V_4N_3 were observed in[17] and[18]. This list of superstructures is complete. It includes all the substitution and interstitial superstructures that can be stable against spontaneous decay into a system of APD.

4. SUPERSTRUCTURES STABLE AGAINST APD FORMATION IN BINARY BCC SUBSTITUTION AND INTERSTITIAL SOLUTIONS

Since the BCC lattice is a Bravais lattice, the distribution of the atoms in an ordered BCC substitution solid solution is described by the same formula (18) as the distribution of the atoms in FCC substitution solutions. The situation, however, is more complicated if we are interested in interstitial BCC solutions. In such solutions there exist two types of crystallographically non-equivalent interstices, octahedral and tetrahedral. They form, respectively, three and two mutually-penetrating BCC sublattices, each of which is a primitive Bravais lattice. Thus, with respect to the formation of interstitial solutions in octahedral and tetrahedral interstices, the BCC lattice is a complex lattice having a basis consisting of 3 and 6 sites, respectively. In this situation, the interstitial superstructures that are isomorphic to the substitution superstructures are constructed with the aid of the procedures described above (see the conclusion of Sec. 2). For brevity, we shall henceforth discuss only those interstitial superstructures in which the interstitial atoms occupy only one BCC sublattice of octahedral interstices. It must be borne in mind, however, that each such interstitial phase can be set in correspondence with isomorphic interstitial phases in which the interstitial atoms are distributed in exactly the same manner in one or several octahedral or tetrahedral BCC sublattices.

Each octahedral or tetrahedral interstice in a BCC lattice has tetragonal symmetry. Therefore each concrete ordered disposition of the interstitial atoms in the BCC sublattices can be set in correspondence, in the general case, with three superstructures that differ from one another in the direction of the tetragonality axis (along [100], [010], or respectively [001]). These superstructures turn out to be crystallographically different if they cannot be transformed into one another by the symmetry transformations of the BCC lattice.

In the BCC lattice there are three stars satisfying the criterion of E. Lifshitz:

$$\begin{aligned}&\text{a)}\ (111),\\ &\text{b)}\ (\tfrac{1}{2}\,\tfrac{1}{2}\,0),\quad (\tfrac{1}{2}\,\tfrac{1}{2}\,0),\quad (\tfrac{1}{2}\,0\,\tfrac{1}{2}),\quad (\tfrac{1}{2}\,0\,\tfrac{\bar{1}}{2}),\quad (0\,\tfrac{1}{2}\,\tfrac{1}{2}),\quad (0\,\tfrac{\bar{1}}{2}\,\tfrac{1}{2}),\\ &\text{c)}\ (\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}),\quad (\tfrac{\bar{1}}{2}\tfrac{1}{2}\tfrac{\bar{1}}{2}).\end{aligned} \tag{33}$$

Just as in the case of the ordering in the FCC lattice, the coordinates of the star vectors are given in the usual basis of the reciprocal-lattice vectors: $2\pi\mathbf{a}_1^*$, $2\pi\mathbf{a}_2^*$, and $2\pi\mathbf{a}_3^*$.

In analogy with the case of the FCC lattice, we can show that out of the stars (33 a–c) it is possible to construct only six distribution functions satisfying the conditions (I) and (II). These are

$$n(x, y, z) = c + \eta_1\gamma_1 e^{i2\pi(x+y+z)}, \tag{34}$$

$$n(x, y, z) = c + \eta_2\gamma_2 e^{i\pi(x+y)}, \tag{35}$$

$$n(x, y, z) = c + \eta_3\gamma_3[\cos\pi(x+y+z) + \sin\pi(x+y+z)], \tag{36}$$

$$n(x, y, z) = c + \eta_1\gamma_1 e^{i2\pi(x+y+z)} + \eta_2\gamma_2(e^{i\pi(x+y)} + e^{i\pi(x-y)}), \tag{37}$$

$$\begin{aligned} n(x, y, z) = c + \eta_1\gamma_1 e^{i2\pi(x+y+z)} + \eta_2\gamma_2(e^{i\pi(x+y)} + e^{i\pi(x-y)} + e^{i\pi(x+z)}\\ + e^{i\pi(x-z)} + e^{i\pi(y+z)} + e^{i\pi(y-z)}),\end{aligned} \tag{38}$$

$$n(x, y, z) = c + \eta_1\gamma_1 e^{i2\pi(x+y+z)} + \eta_3\gamma_3 \sin\pi(x+y+z). \tag{39}$$

In expressions (34)–(39), x, y, and z are the coordinates of the BCC lattice points (they are either all integers or all half-integers). The function (34) describes a substitution superstructure of the type AB(B_2), such as CuZn, CuBe, FeAl, CuPd, AuZn, etc. Its isomorphic interstitial phase has a stoichiometric composition (Me_2X). The distribution (35) describes a substitution superstructure AB consisting of (110) planes filled with atoms of sort A alternating with (110) planes filled with atoms of sort B (Fig. 2a). Its isomorphic interstitial phase Me_2X is shown in Fig. 2e. The corresponding phase Ta_2O was observed in[19], and the isomorphic hydrides and deuterides Ta_2H and V_2D, in which the interstitial atoms are arranged not in an octahedral but in a tetragonal sublattice, were observed in[20,21].

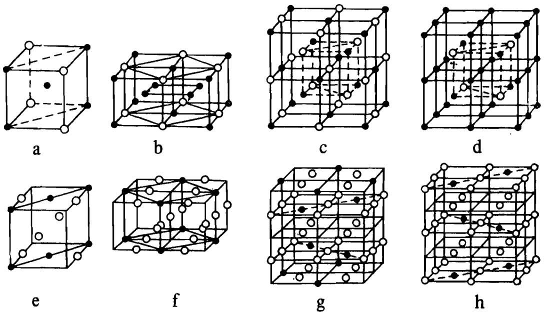

FIG. 2

The distribution (36) describes the substitution superstructure B_{32} shown in Fig. 2c. Such a lattice is possessed by the phases NaTl, LaAl, etc. Figure 2g shows the isomorphic interstitial phase Me_2X. The distribution (37) describes the substitution superstructure A_3B shown in Fig. 2b. Its isomorphic interstitial superstructure Me_4X is shown in Fig. 2f. The phase Ta_4O with such a unit cell was observed in[19]. The distribution (38) describes the order phase A_7B. In this phase, the atoms B form a BCC lattice having a lattice constant twice as large as the initial BCC lattice. The remaining points of the initial BCC lattice are occupied with atoms of type A. The isomorphic A_7B interstitial superstructure has a formula Me_8X. The interstitial atoms X in Me_8X lie in octahedral interstices and also form a BCC lattice with a constant double that of the BCC made up by the metal atoms. The distribution (39) describes a superstructure A_3B of the Fe_3Al type (Fig. 2d). Its isomorphic interstitial superstructure Me_4X is shown in Fig. 2h.

APPENDIX

MINIMIZATION OF THE FREE ENERGY WITH RESPECT TO THE PARAMETERS $\gamma_s(j_s)$

Minimizing the free energy (1) with respect to $\gamma_s(j_s)$ and recognizing that the internal energy (2) does not depend on $\gamma_s(j_s)$, by virtue of the normalization condition (21), we obtain

$$\delta\mathscr{F} = -\varkappa T\sum_{\mathbf{R}}\mathscr{L}(\mathbf{R})\exp\{i\mathbf{k}_{j_s}\mathbf{R}\}\delta\gamma_s(j_s) = 0, \qquad \mathscr{L}(\mathbf{R}) = \ln\frac{n(\mathbf{R})}{1-n(\mathbf{R})}, \tag{A.1}$$

where $\delta\gamma_s(j_s)$ is the variation of the coefficients $\gamma_s(j_s)$. Since the symmetry of the function $\mathscr{L}(\mathbf{R})$ coincides with the symmetry of the function $n(\mathbf{R})$, we can represent $\mathscr{L}(\mathbf{R})$ in the same form (18) as $n(\mathbf{R})$:

$$\begin{gathered}\mathscr{L}(\mathbf{R}) = \tilde{c} + \sum_s \tilde{\eta}_s\tilde{\varepsilon}_s(\mathbf{R}),\\ \tilde{\varepsilon}_s(\mathbf{R}) = \sum_{j_s}\Gamma_s(j_s)\exp(i\mathbf{k}_{j_s}\mathbf{R}), \qquad \sum_{j_s}|\Gamma(j_s)|^2 = 1.\end{gathered} \tag{A.2}$$

Here $\tilde{\eta}_s$ and $\Gamma(j_s)$ are certain effective "long-range-order parameters" and normalized Fourier coefficients that depend on the true long-range-order parameters η_s and the normalized Fourier coefficients $\gamma_s(j_s)$. Substituting (A.2) into (A.1), we obtain

$$\sum_{j_s} \Gamma_s^*(j_s)\,\delta\gamma_s(j_s) = 0. \tag{A.3}$$

The equality (A.3) can be interpreted as the scalar product $(\Gamma_s^*, \delta\gamma_s)$ of the multidimensional generalized vector $\Gamma_s^* = \{\Gamma_s(1), \Gamma_s(2), \ldots\}$ and $\delta\gamma_s = \{\delta\gamma_s(1), \delta\gamma_s(2), \ldots\}$. The vanishing of this scalar product denotes orthogonality of the vectors Γ_s^* and $\delta\gamma_s$. Since the extremum of the free energy is sought under the additional condition (21), we get the identity

$$(\gamma_s^*, \delta\gamma_s) \equiv 0, \tag{A.4}$$

where $\gamma_s = \{\gamma_s(1), \gamma_s(2), \ldots\}$.

Equation (A.4) means that the generalized vectors γ_s^* and $\delta\gamma_s$ are also orthogonal. Since the vector $\delta\gamma_s$ can assume arbitrary values and remain at the same time in the hyperplane normal to the vector γ_s^*, the equality (A.3) – $(\Gamma_s^*, \delta\gamma_s) = 0$ denotes that the vector Γ_s^* is orthogonal to the same hyperplane, and consequently is collinear with the vector γ_s, or $\Gamma_s = \lambda\gamma_s$. The proportionality coefficient λ is equal to unity, since $(\Gamma_s^*\Gamma_s) = (\gamma_s^*\gamma_s) = 1$ and the right-hand side of (A.2) is a real function. Thus, from the condition that the free energy have an extremal value we get

$$\Gamma_s = \gamma_s \quad \text{или} \quad \Gamma(\mathbf{k}_{j_s}) = \gamma(\mathbf{k}_{j_s}). \tag{A.5}$$

Consequently, we can rewrite (A.2) in the form

$$\mathscr{L}(\mathbf{R}) = \tilde{c} + \sum_s \tilde{\eta}_s(\eta_1, \eta_2, \ldots \eta_s, \ldots;\ \gamma_1, \gamma_2, \ldots \gamma_s, \ldots)\,\varepsilon_s(\mathbf{R}). \tag{A.6}$$

Expanding the coefficient $\tilde{\eta}_s(\eta_1, \eta_2, \ldots \eta_s, \ldots;\ \gamma_1, \gamma_2, \ldots \gamma_s, \ldots)$ in a series in the long-range order parameters $\eta_1, \eta_2, \ldots, \eta_s, \ldots$, we separate from (A.6) the term proportional to η_s^3. This term is of the form

$$\eta_s^3 a(\gamma_s)\,\varepsilon_s(\mathbf{R}) = \eta_s^3 a(\gamma_s) \sum_{j_s} \gamma_s(j_s)\, e^{i\mathbf{k}_{j_s}\mathbf{R}}, \tag{A.7}$$

where $a(\gamma_s)$ is the expansion coefficient.

On the other hand, the same term can be obtained by raising the function $\eta_s\epsilon_s(\mathbf{R})$ to the third power and separating from it the terms proportional to the exponentials $\exp(i\mathbf{k}_{j_s}\cdot\mathbf{R})$. If we take the normalization condition (18) into account, this term can be represented in the form

$$6\eta_s^3 \sum_{j_s} \left[1 - \frac{1}{2}\,|\gamma_s(j_s)|^2\right] \gamma_s(j_s)\, e^{i\mathbf{k}j_s\mathbf{R}}. \tag{A.8}$$

In order for (A.8) to assume the same formula (A.7), which follows from the condition that $\mathscr{F}$ be a minimum, it is necessary that all the moduli of the nonzero coefficients $\gamma(\mathbf{k}_{j_s})$ belonging to each star s be equal to each other.

To find the phase factors $\exp(i\varphi_{j_s})$ of the coefficients $\gamma(\mathbf{k}_{j_s})$, it is convenient to separate from (A.6) the term proportional to η_s^{m+1}, where m is the smallest possible natural number by which any vector of a star $\{\mathbf{k}_{j_s}\}$ must be multiplied in order to obtain the disordered-phase reciprocal-lattice vector multiplied by 2π. This term is of the form

$$\eta_s^{m+1} a_{m+1}(\gamma_s)\,\varepsilon_s(\mathbf{R}). \tag{A.9}$$

On the other hand, the same term can be obtained by raising the function $\eta_s\epsilon_s(\mathbf{R})$ to the power m + 1 and separating from $\eta_s^{m+1}(\epsilon_s(\mathbf{R}))^{m+1}$ the terms proportional to the exponential $\exp(i\mathbf{k}_{j_s}\cdot\mathbf{R})$. The last procedure, if we take into account the already-obtained result $|\gamma_s(1)| = |\gamma\ (2)| = \ldots = |\gamma_s|$, and consequently $\gamma_s(j_s) = |\gamma_s| e^{i\varphi_s(j_s)}$, yields

$$\eta_s^{m+1} \sum_{j_s} [\alpha + \beta e^{im\varphi_s(j_s)})\,\gamma_s(j_s)\, e^{i\mathbf{k}_{j_s}\mathbf{R}}. \tag{A.10}$$

Expression (A.10) coincides with expression (A.9) only if

$$\varphi_s(j_s) = \pi\nu / m \ (\nu = 0, 1, \ldots, 2m - 1). \tag{A.11}$$

Thus, the coefficients $\gamma_s(j_s) = |\gamma_s| \exp\{i\pi\nu_{j_s}/m\}$ in expression (18) are constants that do not depend, within the limits of the single-phase region, on the thermodynamic parameters of the system, namely the temperature, the composition, and the pressure. The coefficients $\gamma_s(j_s)$ can change only jumpwise on the boundaries of the single-phase region. Each such change leads to a change of the crystallographic symmetry of the phase.

We note in conclusion that all the obtained conclusions remain valid also in the general case, and not only within the framework of the given model. In the general case the function $\mathscr{L}(\mathbf{R})$ should be replaced by the function $\psi(\mathbf{R}) = \delta\mathscr{F}/\delta n(\mathbf{R})$ and to apply the same reasoning with respect to $\psi(\mathbf{R})$.

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