RULES FOR FILLING COORDINATION SPHERES IN CUBIC CRYSTALS WITH INTERSTICES

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A procedure for analytical description of the distribution of atomic nodes and tetrahedral and octahedral interstices in coordination spheres for cubic lattices is developed. The model is constructed by partitioning unit cells into smaller elements with basis vectors decreasing fourfold. The spatial packing of coordination spheres is defined by the vertices of seven basic polyhedra or by their combination. Examples of calculations of sphere packings by atoms and octahedral and tetrahedral positions are given. This method allows one to characterize the packings of substitution and inclusion structures and superstructures.

In interstitial solid solutions, solute atoms lie at the interstices of the crystal lattice of the solvent. Such interstitial solutions are formed by H, C, N, and O atoms in transition metal lattices [1]. In cubic (fcc, bcc) lattices, inclusion atoms can occupy interstices of two types: octahedral and tetrahedral positions. In the fcc lattice, there is one octapore and two tetrapore per atom. The bcc lattice has a higher density of interstices: three octapores and six tetrapore per atom (Fig. 1). As in the case of substitution solutions, ordered inclusion phases are formed at definite concentrations of a solute. For example, a stoichiometric phase PdH is formed from an fcc metal lattice with completely occupied octahedral interstices [2].

Possible existence of superstructures with seven inclusion phases of stoichiometric composition $M_mX_p$ ($m$, $p$ are the concentrations of components in a solid solution of stoichiometric composition) was proven by Khachaturyan [3] who used the statistical concentration wave method; analogous inclusion phases are formed from bcc lattices of transition metals.

Determination of the maximal possible set of superstructures from component concentrations demands solving the problem of interatomic interactions in many coordination spheres. This problem is easily solved for several first coordination spheres only. Therefore, it is important to construct an algorithm to establish rules for filling an arbitrary number of coordination spheres by atoms and interstices. Here we solve this problem for cubic lattices.

The problem of spatial distribution of atoms in coordination spheres was solved by us for simple cubic (sc), bcc, and fcc monoatomic lattices [4-7]. The analytical rules for determining the occupation of an arbitrary coordination

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Fig. 1. Site distribution in 1/8 of the unit cell of the bcc (a) and fcc (b) lattices. • — sites occupied by atoms (A), ○ — octahedral interstices (B), ◦ — tetrahedral interstices (C), × — positions of E type.
sphere near the atom chosen as a reference were derived by shortening the basis vectors of the bcc and fcc lattices by a factor of two. In that model, the unit cell of an fcc or bcc lattice was represented as eight sc unit cells with a lattice parameter \( a_{sc} = 1/2a_{bcc} = 1/4a_{fcc} \) (Fig. 1). It is set that the sc lattice sites coinciding with the atomic sites of fcc or bcc lattices are occupied by atoms (A), and the additional sites of sc lattices are occupied by interstices (B). Thus large unit cells of fcc and bcc lattices were represented by inclusion superstructures AB and AB3. It is easy to sample octapore distribution in coordination spheres by the procedure of [5, 6]. However, the positions corresponding to the tetrahedral sites lie in the basis of vectors that are twice as small as the basis vectors of the sc lattice. Let us diminish the sc lattice parameter by a factor of two (let us call this cell a small simple cubic (ssc) cell with a parameter \( a_{ssc} = 1/4a_{fcc} = 1/4a_{bcc} \)). In this case, each fcc and bcc lattice is a packing of 64 ssc unit cells.

The ssc sites falling at tetrahedral interstices of fcc and bcc lattices will be regarded as filled by the third component C. Thus the fcc lattice is represented as a superstructure ABC2. The bcc lattice is modeled as a three-component superstructure AB2C6. Some symmetry positions of ssc cells do not fall under A, B, or C categories. Since the effective volume of these sites is extremely small, their filling by inclusion atoms is unlikely; let us consider these sites vacant or empty (E). The fcc and bcc lattices are eventually represented as ordered sites of four types: A, B, C, and E. The fcc lattice is represented as alternating packings of ssc lattices, AE6C and AE6B, i.e., the greatest number of sites (12) are empty sites (E). The unit cell of the bcc lattice is two ssc packings: AE7 and BC2E5.

In ordered inclusion phases based on cubic lattices, there are sites of three types: A, B, and C; they are regarded as reference centers of coordination spheres. For each reference center, there are three sets of coordination spheres corresponding to the packing types A, B, and C. For any type of site chosen as a center, the radius of a coordination sphere is represented as

\[
r = a_{ssc}(x_{ex} + y_{ey} + z_{ez}),
\]

where \( x, y, z \) are certain integers defining the coordinates (indices) of sites in an orthonormal basis set \((e_{x}, e_{y}, e_{z})\). As in the case of method [6], we introduce the following numbering of coordination spheres using site indices \([x, y, z]\) called an index sequence (IS):

\[
n_{IS} = x^2 + y^2 + z^2.
\]

In this case, there is a simple relationship between the radius and index of the coordination sphere:

\[
r = a_{ssc}\sqrt{n_{IS}} = a_{ssc}(x^2 + y^2 + z^2)^{1/2}.
\]

However, a series of numbers, for example, 7, 15, 23, 28, ..., may not be represented as a sum of the squares of three integers. For conveniently keeping sequence (2) similar to (3), the spheres not obeying the rule of the sum of the squares of three integers are called O-spheres [6].

It follows from the symmetry properties of cubic lattice packings that the coordinates of the \([x, y, z]\) site indices of packings according to coordination spheres form groups differing between each other in the sets of their numbers proportional to 2, 4 (the numbers proportional to 2 form a separate group), odd numbers, and zeroes. An analysis of the distribution of the coordination indices according to groups of numbers gives the following rules for selecting the A, B, C, and E sites for the inclusion phases based on the fcc lattice with respect to the reference center at site A:

\[
\begin{array}{c|c|c|c|c}
A & B & C & E \\
4n, 0, 0 & 4n, 4m, 2p & 2n-1, 2m-1, 2p-1 & 2n-1, 0, 0 \\
4n, 4m, 0 & 2n, 0, 0 & 4(2)n, 2m-1, 2p-1 & 2n-1, 2m-1, 0 \\
4n, 4m, 4p & 4n, 2m, 0 & 4(2)n, 4(2)m, 2p-1 & 2n, 2m-1, 0 \\
2n, 2m, 0 & 2n, 2m, 2p & 4(2)n, 2m-1, 2p-1 & \\
4n, 4m, 2p & & & 
\end{array}
\]

For structures based on the bcc lattice, the distribution rules are as follows:

\[
\begin{array}{c|c|c|c|c}
A & B & C & E \\
4n, 0, 0 & 4n, 4m, 2p & 2n-1, 2m-1, 2p-1 & 2n-1, 0, 0 \\
4n, 4m, 0 & 2n, 0, 0 & 4(2)n, 2m-1, 2p-1 & 2n-1, 2m-1, 0 \\
4n, 4m, 4p & 4n, 2m, 0 & 4(2)n, 4(2)m, 2p-1 & 2n, 2m-1, 0 \\
2n, 2m, 0 & 2n, 2m, 2p & 4(2)n, 2m-1, 2p-1 & \\
4n, 4m, 2p & & & 
\end{array}
\]

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