The quantization of the radii of coordination spheres cubic crystals and cluster systems

G Melnikov¹, S Emelyanov¹, N Ignatenko¹ and G Ignatenko¹

¹Kursk, 305040, Russia, South-West State University (SWSU)

E-mail: inmkstu@bk.ru, melnikovga@mail.ru

Abstract.

The article deals with the creation of an algorithm for calculating the radii of coordination spheres and coordination numbers cubic crystal structure and cluster systems in liquids. Solution has important theoretical value since it allows us to calculate the amount of coordination in the interparticle interaction potentials, to predict the processes of growth of the crystal structures and processes of self-organization of particles in the cluster system. One option accounting geometrical and quantum factors is the use of the Fibonacci series to construct a consistent number of focal areas for cubic crystals and cluster formation in the liquid.

Introduction

The calculation of the radii of coordination spheres in the crystals is needed to construct the theory of many-atomic interactions, to decrypt X-ray patterns of crystal having complex structures, and of solid solutions with embedded interstitial atoms [1, 2]. In theoretical terms in the lattice theory and cluster model of liquid to describe the intermolecular interaction it is necessary to calculate the sum of the characteristic [3, 5]. For disordered condensed media the application of thermodynamic relations for the calculation of the pressure in a system of interacting particles is also related with the calculation of the radii of successive coordination spheres and coordination numbers [6].

In quasicrystalline theories the structure of cluster systems is modeled by lattices of cubic type (fcc, bcc, SC), and it is believed that structural properties of arrays of clusters and bulk samples are similar. In coordination spheres the structure of such a cluster, or of a cubic crystal lattice is represented as a system of successive coordination spheres with single center in a randomly selected atom [8].

Studies of the structure of cubic system crystals allowed us to obtain the well-known rule that says that the radius of the N-th coordination sphere is proportional to the square root of the number of this sphere

\[ R_n = R_1 \sqrt{N} \]  

The radius of the first coordination sphere \( R_1 \) defines the type of the crystal lattice, it is related with the geometric size (effective diameter) of the particles and the nature of the interaction between the particles in the crystal.

From the series of natural numbers \( N = 1, 2, 3, \ldots \) it is necessary to exclude the numbers that correspond to the terms of extinction in the analysis of X-ray diffraction measurements. One of the
main problems of theoretical crystallography is to find an algorithm for calculating the radii of coordination spheres in crystal structures and cluster systems.

**Algorithms for calculating the radii of coordination spheres in crystals**

The paper [7] proposed analytical expressions that allow us to calculate the radii of coordination spheres and corresponding coordination numbers for cubic lattices by the number of coordination spheres. For the fcc lattice the variation range is written as

\[ R_k = \frac{1}{\sqrt{2}} a \sqrt{k} = R_1 \sqrt{k} \]  \hspace{1cm} (2)

where \( k = 1, 2, 3, ... \) takes the values of natural numbers, \( a \) - is the lattice constant, \( R_1 \) - is the radius of the first coordination sphere.

From the series of natural numbers it is necessary to eliminate the numbers in accordance with the formula [7]

\[ k_{\text{excl}} = 2^{\left( q \right)} (8i - 1), \quad q = 0, 1, 2, ..., \quad i = 1, 2, 3, ... \]  \hspace{1cm} (3)

In an ideal fcc lattice there is no coordination spheres with numbers \( k_{\text{excl}} = 14, 30, 46, 62, 78, 94, ... \) (with \( q = 0 \)).

The radii of the coordination spheres of an ideal SC-lattice are written in the

\[ R_k^{\text{SC}} = a \sqrt{k} = R_1 \sqrt{k} \]  \hspace{1cm} (4)

From the series of natural numbers the coordination spheres with the following numbers should be excluded:

\[ k_{\text{excl}}^{\text{SC}} = 4^{\left( q \right)} (8i - 1), \quad q = 0, 1, 2, ..., \quad i = 1, 2, 3, ... \]  \hspace{1cm} (5)

In an ideal SC lattice there are no coordination spheres with numbers:

\( k_{\text{excl}}^{\text{SC}} = 7, 15, 23, 28, 31, 39, 47, ... \)

In [8] an algorithm was suggested to calculate the radii of coordination spheres and coordination numbers on their surface depending on the sphere number for diamonds. The suggestion was made based on experimentally obtained facts that in the direction [211] the diamond lattice has cubic three-layer package with a period 0.728A, and in the direction [111] there is a periodicity with a constant of 2.059A.

The radius \( m \) of the coordination sphere \( r_m \) are determined by the diamond lattice parameter \( a = 3.566A \) and the direction vector \( \vec{R} = \langle \mu \nu \omega \rangle, (\mu, \nu, \omega = 0, \pm 1, \pm 2, ...) \) and are defined as

\[ r_m = \frac{a}{4} \sqrt{\mu^2 + \nu^2 + \omega^2} = \frac{a}{4} R_m, \]  \hspace{1cm} (6)

where \( R_m = \sqrt{4m}, \quad m = 2(i - 1), \quad i = 1, 2, 3, ..., \quad R_m = \sqrt{4m - 1}, \quad m = 2i - 1, \quad i = 1, 2, 3, ... \)

According to the proposed algorithm, the authors of [8] calculated the radii of 192 coordination spheres and the number of particles on each of them. All coordination spheres are considered filled [9]. Location of the nearest neighbors in the amorphous carbon film is similar to the arrangement of them in the diamond lattice, but the distribution of layers over coordination numbers is seriously disrupted [10].
Principles of quantization of the radii of coordination spheres in cluster systems

Currently, there are several approaches to modeling the structure of cluster formations in condensed matters. Quasicrystal models represent the structure of a cluster by means of cubic lattices or lattices of the diamond type. Quasicrystal models give good results in modeling the structure of metal clusters and can identify the most stable cluster formations with the "magic" number of particles in their composition [11].

The paper [12] proposes a model of "double barrier of nucleation", according to which the mechanism of formation of the cluster begins with the formation of the cluster crystalline core in the form Bravais unit surrounded by liquid crystalline shell. The appearance of the crystal nucleus means overcoming the first energy barrier of nucleation. Then there is a consistent core cell proliferation that ends in an irreversible process of crystal growth.

In [13] the structure of nanoscale objects and metal clusters is modeled by face-centered cubic (fcc), body-centered cubic (bcc) or hexagonal close packings, and inter-configuration of atoms in a cluster corresponds to the structure of the bulk sample. For fcc lattice the radii of successive coordination spheres are defined by the formula

$$ R_n = \sigma_0 \sqrt{n} $$

(7)

where \( \sigma_0 \) - the diameter of a solid sphere (atom), \( n \) - the number of the coordination sphere.

For the bcc lattice:

$$ R_n = \frac{\sqrt{3}}{3} \sigma_0 \sqrt{n} $$

(8)

The number of balls that are located on the \( n \)-th sphere is determined by the condition

$$ u^2 + v^2 + w^2 + uv + uv + vw = n $$

(9)

where \( u, v, w \) are integers.

The model of the close packing of hard balls in the ideal crystal lattices with cubic structure cannot describe the sequential arrangement of coordination spheres in real crystals. The replacement of solid balls by soft spheres in the model does not basically change the calculation results, so geometrical factors should be supplemented physical principles of the quantization of coordination spheres.

In their studies [14-16] the authors of this article proposed a model of cluster formation in a disordered condensed media. According to this model the core of the cluster is a dimer around which a system of successive coordination spheres is built up. The result is a "shell structure" of the cluster. The appearance of defects in the cluster shell leads to unification and redistribution of the mutual arrangement of coordination spheres in comparison with crystalline phase of matter and determines temperature dependence of coordination numbers in the structure of the cluster. The studies of the suggested model showed that quantization process must be taken into account when the radius of the coordination sphere is changed in the structure of the cluster, similar to the quantization process of electron orbits in complex atoms.

For a system of successive coordination spheres of spherical particle the radius of such spheres can be represented by the ratio

$$ R_n = R_1 \sqrt{pF_n} $$

(10)

where \( R_1 \) - the radius of the first coordination sphere, \( F_n \) - Fibonacci numbers, \( p = 1, 2, 3, ... \) - natural numbers.

Now based on de Moivre-Binet formula (Binet's formula), that allows us to present a series of Fibonacci numbers as the power function of the base of the golden section \( \phi = 1.618039... \) [17].
Using formulas (10) and (11) we'll obtain the law of quantization of the radii of coordination spheres as a function of the principal quantum number.

\[ R_n = \frac{2}{3} R_1 \sqrt{p(\phi)^n} \]

where \( n \geq 1, n = 1, 2, 3, ... \) - principal quantum number, \( \phi = 1.618039... \) - golden section, \( R_1 \) - the radius of the first coordination sphere, the value of which determines the radius of the number of successive coordination spheres.

In [18, 19] the ratio is suggested that gives trigonometric interpretation of the Fibonacci series of numbers.

\[ F_n = \prod_{i=1}^{n} \left(1 - 2i\cos \frac{\pi l}{n}\right) \]

According to formula (13) Fibonacci series is defined by two integers \( n \) and \( l \) that can be regarded as principal quantum number \( n \) and orbital quantum number \( l \) of the electron as it moves on the surface of coordination sphere. The relationship between the integers \( n \), and \( l \) in formula (13) coincides exactly with the rules of the quantization of orbital angular momentum of electrons in complex atoms: \( l = 0, 1, 2, ..., (n - 1) \). However, formula (13) eliminates quantum state with quantum numbers \( n = 1 \) and \( l = 0 \) in the second coordination sphere (and subsequent ones); the electron is just in excited state. Fibonacci numbers can be expressed in terms of Chebyshev polynomials [19, 20].

The results of the calculations. Discussion

Direct verification of relation (10) for disordered condensed media can be based on the analysis of radial distribution function (RDF) of particles. Table 1 shows the results of calculating the radii of nine consecutive coordination spheres for argon near its melting point and compares these values with experimental data [21]. The calculation error is substantially does not exceed 5%, which proves the applicability of formula (10) for predicting radii of coordination spheres in liquid noble gases.

Calculating the radius of the coordination spheres in benzene, the molecules of which are structured on benzene ring, agree with experimental data for coordination spheres radii that were derived from the construction of radial distribution function [22, 23].

Papers [10, 24, 25] provide some data on the radii of three successive coordination spheres in n-paraffins series. The data was obtained from the RDF analysis and specify the width of the peaks corresponding to these radii. Coordination spheres radius calculation based on formula (10) for liquid n-hexane near its melting temperature demonstrated the applicability of this formula for predicting sequential arrangement of coordination spheres in the structure of this class of liquids.

Conclusion

In The authors have shown that it is possible to consider two factors - geometric and physical in a model that takes into account "golden" section in the location of successive coordination spheres and allows us to formulate the rule of formation of space coordination spheres: the radius of the n-th coordination sphere reduced to the radius of the first coordination sphere is equal to the square root of the Fibonacci number that stands at the \( (n + 1) \) - th place in the Fibonacci series: 1, 1, 2, 3, 5, 8, 13, 21, 34, 55,...
The formulated rule of the formation of coordination spheres in cluster systems means that the ratio of the radius of a subsequent coordination sphere to the radius of the previous sphere remains constant and is equal to the "gold" section square root: \( R_{n+1} / R_n = \sqrt{1.618...} = 1.272... \).  

Quantization process of coordination spheres follows from the trigonometric representation of Fibonacci numbers and the square root of these numbers. According to formula (13) Fibonacci series is defined by two integers \( n \) and \( l \) that can be regarded as the principal quantum number \( n \) and orbital quantum number \( l \) of the electron as it moves on the surface of the coordination sphere. The relationship between the integers \( n \) and \( l \) in the formula (13) conforms exactly with the rules of quantization of the orbital angular momentum of an electron in complex atoms and molecules.

**Table 1.** The radii of coordination spheres in liquid argon (85K) derived from the RDF and the calculated through Fibonacci numbers (\( p=1 \)).

| Sphere number | \( F_i \) | \( R_n = R_n \sqrt{pF_n} \) |
|---------------|----------|-----------------|
| Argon (T=85 K) |          | Experiment      |
| 1             | 1        | 3.677           |
| 2             | 2        | 5.200           |
| 3             | 3        | 6.37            |
| 4             | 5        | 8.22            |
| 5             | 8        | 10.40           |
| 6             | 13       | 13.26           |
| 7             | 21       | 16.85           |
| 8             | 34       | 21.44           |
| 9             | 55       | 27.27           |

Analysis of the results of applying Fibonacci numbers and the proposed rule (10) for calculating the radii of successive coordination spheres for crystals with fcc structure and liquids with different molecular structure leads to the conclusion that the universalism of rule (10) is connected with general properties of supramolecular structure of condensed matters.

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