

The Structure of Small Clusters and IR Spectrum Condensed Matters

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The article investigates the structure of small clusters, creating an algorithm for calculating the radii of coordination spheres in the structure of such clusters and finding the relationship between the frequencies in the IR spectrum and the characteristics of the most probable cluster in the liquid.

Keywords: Cluster, Radius of the coordination sphere, Cluster model, IR spectrum of the liquid.

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1. INTRODUCTION

At the present, there has been several approaches to modeling the structure of cluster formation in condensed matter. In quasi-crystalline theories the structure of cluster systems is modeled by lattices of cubic type (FCC, BCC, SC), and besides it is presumed that the structural properties of clusters' lattices and bulk samples coincide. In the space of coordination spheres the structure of such a cluster is represented as a system of successive coordination spheres with a single center in an arbitrarily selected atom. The researching of the structure of crystals of the cubic system allowed us to obtain the well-known rule, that proves, that the radius of the N-th coordination sphere is proportional to the square root of the number of the sphere

$$R_n = R_1 \sqrt{N} \quad (1)$$

The radius of the first coordination sphere R_1 determines the type of the crystal lattice; it is associated with the geometric dimensions (effective diameter) of the particle and the nature of the interaction among the particles in the crystal [1]

In [2] proposed analytical expressions, allowing to calculate the radii of coordination spheres and the corresponding coordination numbers for cubic lattices by number of coordination spheres. For example, for the FCC lattice the variation range is written as a formula

$$R_k = \frac{1}{\sqrt{2}} a \sqrt{k} = R_1 \sqrt{k} \quad (2)$$

where $k = 1, 2, 3, \dots$ takes the values of natural numbers, a – the lattice constant, R_1 – the radius of the first coordination sphere.

Let From the series of natural numbers, it is necessary to eliminate the numbers in accordance with the formula [2]

$$k_{excl} = 2 \left[4^q (8i - 1) \right], q = 0, 1, 2, \dots, i = 1, 2, 3, \dots \quad (3)$$

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

In [1] an algorithm for calculating the radii of coordination spheres and coordination numbers on their surface, depending on the number for the scope for the diamond is offered.

The radius of the m coordination sphere r_m is determined by the lattice parameter $a = 3.566A$ of a diamond and by direction vector $\vec{R} = \langle \mu\nu w \rangle, (\mu, \nu, w = 0, \pm 1, \pm 2, \dots)$ and is determined by formula

$$r_m = \frac{a}{4} \sqrt{\mu^2 + \nu^2 + w^2} = \frac{a}{4} R_m \quad (4)$$

where $R_m = \sqrt{4m - 1}, m = 2i - 1, i = 1, 2, 3, \dots$

According to the by authors [1] algorithm, the radii have been calculated 192 coordination spheres and the number of particles on each of them. All coordination spheres are filled.

In [3] the nanoscale objects and metal clusters is modeled with face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal density packages, besides the interconfiguration of atoms in a cluster corresponds to the structure of the bulk sample. For the FCC-lattice the radii of the successive coordination spheres are defined by the formula

$$R_n = \sigma_0 \sqrt{n} \quad (5)$$

where σ_0 – the diameter solid sphere (atom), n – the number of the coordination sphere.

For the BCC lattice:

$$R_n = \frac{\sqrt{3}}{3} \sigma_0 \sqrt{n} \quad (6)$$

The number of balls, locating on the n-th field is determined by the condition

$$u^2 + v^2 + w^2 + uv + uw + vw = n \quad (7)$$

where u, v, w – the whole numbers.

In [4] proposes a model of "double barrier of nucleation", according to which the mechanism of formation of a cluster begins with the formation of the crystalline

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core of the cluster as a unit cell of the Bravais, around which is an ordered liquid crystalline shell. The appearance of the crystal nucleus signifies the first overcome the energy barrier of nucleation. Further, there is a consistent core cell proliferation, ending with an irreversible process of crystal growth.

Different approaches to modeling the structure of cluster formations are presented in [5-7]. In all sited works [1-7] the common idea is using the principle of close packing of hard spheres, that can describe a serial arrangement of coordination spheres in real crystals and cluster formations. The replacing the solid balls by soft spheres in the model doesn't make fundamental changes in the results of the calculations, so besides the geometrical factors, it is necessary to use physical principles of coordination spheres.

2. THE PRINCIPLES OF CREATING THE SYSTEM OF COORDINATION SPHERES IN SMALL CLUSTERS

The authors of this article in [8-10] proposed a model of cluster formation in a disordered condensed medium, according to which the core of the cluster is a bound state of two particles of the medium (dimer), which is built around a system of successive coordination spheres. The result is a "shell structure" cluster. The appearance of defects in the shell structure of the cluster leads to the unification and redistribution of the mutual arrangement of the coordination spheres compared with the crystalline phase material, which determines the temperature dependence of the coordination numbers in the structure of the cluster.

The research of suggested model showed, that the formula for calculating the radius of a random coordination sphere can be represented as

$$R_n = R_1 \sqrt{pF_n} \quad (8)$$

where R_1 – the radius of the first coordination sphere, F_n – Fibonacci numbers, $p=1, 2, 3, \dots$ – natural numbers.

Relation (8) implies, that in the space of coordination spheres in a cluster formation allowed only coordination spheres with numbers matching the sequence of numbers Fibonacci $F_n = 1, 2, 3, 5, 8, 13, 21, 34, 55, \dots$, and coordination spheres with numbers $pF_i = 2, 4, 6, 10, 16, \dots$, $p=2$, other areas, whose numbers are not included in these series are not permitted by the quantization of coordination spheres

Using Binet's formula[11], it can be shown that the series of the Fibonacci numbers can be represented as a power function with the base of the golden section

$$F_n = \frac{1}{\sqrt{5}} \phi^n \quad (9)$$

Using formulas (8) and (9), we obtain the law of quantization of the radii of coordination spheres as a function of the principal quantum number

$$R_n = \frac{2}{3} R_1 \sqrt{p} (\phi)^{\frac{n}{2}} \quad (10)$$

where $n \geq 1, n=1, 2, 3, \dots$ – the principal quantum number, $\phi=1.618039\dots$ – the golden section, R_1 – the radius of the first coordination sphere, whose value is determined by the radius of a number of successive coordination spheres.

Fibonacci numbers can be expressed in terms of Chebyshev polynomials [12], or use the trigonometric interpretation of the Fibonacci series [13]

$$F_n = \prod_{l=1}^{n-1} \left(1 - 2i \cos \frac{\pi l}{n} \right) \quad (11)$$

Taken The series of Fibonacci numbers according to formula (11) is defined by two integers n and l , which can be interpreted as the principal quantum number n and the orbital quantum number l of the electron, when it moves on the surface of the coordination sphere. The relationship among the integers in the formula (11) coincides with the rules of quantization of orbital angular momentum of electrons in complex atoms: $l = 0, 1, 2, \dots, (n-1)$.

3. THE FREQUENCIES OF LIBRATION DIMERS IN THE CLUSTER'S STRUCTURE

In [8, 10], the authors obtained the ratio to calculate the frequency libration dimer in the cluster with the most probable number of particles

$$\omega_i = \sqrt{\frac{2\Delta H_{\text{dim}}}{J_{\text{dim}}}} \cdot \sqrt{\hat{Z}_i} \quad (12)$$

Equation (12) shows that the frequency librational of dimer in the cluster structure is determined by the number of particles in the cluster \hat{Z}_i , the characteristics the possible configurations of the dimer (energy of formation ΔH_{dim} , moment of inertia of the dimer J_{dim}).

During the spontaneous decay of the cluster number of particles in its composition changes and becomes equal \hat{Z}_j , then the frequencies of libration vibrations of dimer in the newly formed cluster will be

$$\omega_j = \sqrt{\frac{2\Delta H_{\text{dim}}}{J_{\text{dim}}}} \cdot \sqrt{\hat{Z}_j} \quad (13)$$

Changing the frequency is accompanied with the emission or absorption of a quantum of energy with a frequency

$$\omega_{ij} = \sqrt{\frac{2\Delta H_{\text{dim}}}{J_{\text{dim}}}} \cdot \sqrt{\hat{Z}_j} \left(1 - \sqrt{\frac{\hat{Z}_j}{\hat{Z}_{j+1}}} \right) \quad (14)$$

On the assumption that the root of the parenthesis in the formula (14) remains constant, it is possible to assign this value equal to the square root of the ongoing "golden section", i.e. $\hat{Z}_j/\hat{Z}_{j+1} = 5/8 = 0.625$, then

the formula (14) can be written as a ratio

$$\omega_{ij} = 0.2094 \sqrt{\frac{2\Delta H_{\text{dim}}}{J_{\text{dim}}}} \cdot \sqrt{F_j} \quad (15)$$

where $F_i = 1, 2, 3, 5, 8, 13, 21, 34, 55, \dots$ – the Fibonacci numbers

The set of frequencies in the IR spectra of the liquid is determined according to the formulas (12) and (15), an ordinary relation [8]

$$\omega_i = \omega_{\min,i} \sqrt{pF_i} \quad (16)$$

The existence of spectral bands in the IR spectra suggests certain rules of quantization of libration dimers in the structure of the clusters, which coincides with the quantization rules (10) or (11) of the coordination spheres in the cluster systems.

Comparing formulas (8) and (16) gives a ratio

$$\omega_i = \frac{\omega_{\min,j}}{R_1} R_i \quad (17)$$

The accepted model of the IR spectra in organic liquids allows to predict the position of the spectral bands according to the radii of of the coordination spheres in the structure of the most probable cluster with an error of about 5 %. The calculations of frequencies in the IR spectra of liquid with various molecular structure and

crystals which are created using formulas (16) and (17) have shown that in complex spectra of these objects there were always been the spectral lines corresponding with the number of cluster formations of the particles out of the Fibonacci numbers.

4. CONCLUSIONS

The distribution of the clusters of the number of particles contained in their composition suggests the existence of clusters with the most stable configuration, and with the number of particles determined by a number of the Fibonacci numbers. Consistent decay of the selected cluster number of particles from the Fibonacci series takes place according to the rule, when the newly emerged cluster has the same number of particles from the series of the Fibonacci numbers and the ratio of the number of particles in two successive transformed clusters equal to the "golden" cross-section $\phi = 0.618\dots$ remains unchanged. Changing the frequency of libration vibrations of dimer by varying the number particles in the cluster structure is accompanied with emission of a photon with a frequency proportional to the square root of the number of particles in the cluster.

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