

THE GEOMETRICAL CRITERIONS OF NANOPARTICLES

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Abstract: The structure of the bulk crystals allow to determine the habit of the nanocrystales on their base only as a source point. It is impossible to neglect the size, form and influence of surface. The liquids surface relatively quickly passes to equilibrium form when free energy is minimum. Debye's temperature is rather arbitrary parameter. Its determination is based on some approach. However this parameter is introduced to the reference books and is broadly used in the crystal physics. Proposed strategy allows defining habit maximum size of nanoparticles on the base well known physics representations. The L -value is determined the bounder between sizes where it can be done value description and where it's necessary to take into account the particle sizes.

KEYWORDS: NANOPARTICLES, NANOCRYSTALES, THE STRUCTURE OF THE BULK CRYSTALS, DEBYE'S TEMPERATURE

1. Introduction

The structure of the bulk crystals allow to determine the habit of the nanocrystales on their base only as a source point. It is impossible to neglect the size, form and influence of surface. The liquids surface relatively quickly passes to equilibrium form when free energy is minimum. For crystals both theoretical calculation and experimental determination of coefficient of the surface tension (γ) are very difficult especially if it needs to know $\gamma = \gamma[uvw]_{hkl}$ where $[uvw]_{hkl}$ is crystallographic direction in plane (hkl) , and this crystallographic plane forms the crystals surface which is a face of crystal.

2. Investigation

Concept of surface tension is applicable to any atomic-molecular condensation state [1-3]. This tension changes a structure of matter in the nearest to surface atomic layers. F.e. it was confirmed experimentally for MgO crystal [4]. In this book it is shown that adsorption of water vapor by crystal brings about the expansion of lattice and absence of water films ensures its compression. If there are defects in crystal in this case the atoms can displace from inner parts of crystal to its surface. These defects can appear in the failure of big crystal. Consequently characteristics of crystallites and nanocrystals depend on not only from characteristic of source material as well as from its dispersion. It was experimentally investigated for layer silicates [5].

The atoms of surface layer in crystal have power condition which different from conditions of inner atoms. The surface atoms can displace from their ideal position and these changing propagate to any near surfaces atomic layers. In particular for halogenade of alkaline metals their crystals are possible to consider as ideal commencing only with the sixth layer from the crystal surface. In the near surface atomic layer the difference of atoms location from ideal position can be considered as appearance of surface deformation under surface tension action [6-11]. This layer is named as Bailby layer or skin-layer. The atoms mobility in this layer increases. For any size of crystallite their polyhedral habit may be saved but in nanocrystals the surface tension begins to play highly essential role and relaxation processes can proceed vastly quicker. The must forms of nanoparticles becomes not polyhedron. The form of nanoparticles is more smoothing without denominated edges and flat faces. The symmetry of the external crystalline form must be described by the point group witch is subgroup of holohedral group point symmetry of corresponding syngony. Structural factor $F^2(hkl) = F(hkl) \cdot F^*(hkl)$ where $F(hkl)$

- structural amplitude consequently the crystallographic planes

(hkl) and (\overline{hkl}) have the same crystalloenergecal parameters and the correctness form of nanocrystal must have the center of symmetry. The stable forms of nanocrystal depend on the symmetry of starting bulk crystals. These forms for cubic crystals are sphere. They are for crystals middle syngonies (tri-, tetra- and hexagonal) are rods ($c < a$) or plates ($c > a$). These forms for crystals with the lower symmetry (rombohedral, monoclinic and triclinic) are triages ellipsoid but they may have another forms, f.e. igles, rod or plates. If depends on relations between parameters of cells. The sharp border between external changed skin-layer and internal ones with three dimensional structure is absent. But there is intermediate layer (see fig. 1). For determination the sizes of these nanoparticles and the evaluation of limiting nanoparticle size are necessary to use the known tabulated parameters [12-19].

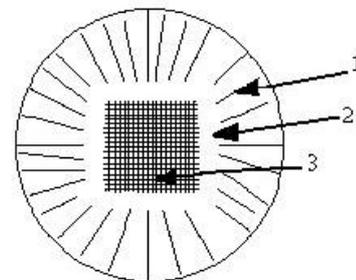


Fig. 1. The structure of nanoparticle. 1–Bailby layer (skin–layer); 2–intermediate layer; 3–crystal-structural base

3. Results

Physical characteristics of material such as density, electric and heat conduction, electrical resistance, heat capacity and etc. are usually considered for big volume materials. These parameters are presented in the different sort tables. But it is known that properties of materials in microparticles with the small quantity of atoms are distinguished from three dimensional objects that is illustrated by the drawing (see fig.2). On this drawing it is conditionally brought changing of certain P-characteristic depending on the size of particle l. P_0 -value corresponds P-value for volume sample.

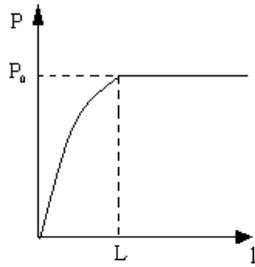


Fig. 2. Dependency of P-characteristic of material from its l-size

Characteristics particles under $l > L$ are the same as characteristics of three-dimensional (volume) crystal if $l < L$ then it is necessary to speak on the nanoparticle exactly. Since its characteristics are distinguished for characteristics of bulk phase from which this nanoparticle was received or in which it will go in further growing process if it will be realized. Calculation L-value is possible to conduct with using a Debye's temperature [1].

The heat capacity under constant volume (C_v) on the Debye's theory base has of the next form

$$C_v = \frac{d}{dT} \left[\frac{3\hbar}{2\pi^2 \cdot V_0^3} \int_0^{\omega_m} \frac{\omega^3}{\exp\left[\frac{\hbar\omega}{kT}\right] - 1} d\omega \right] = \frac{d}{dT}(U), \quad (1)$$

U – internal energy, \hbar, k – Planck's and Boltzmann's constants accordingly, V_0 – velocity of the normal fluctuation spreading, ω – frequency, moreover

$$\omega = V_0 \cdot k_v, \quad (2)$$

k_v is a wave vector, ω corresponds a condition when full number of normal fluctuation modes are $3n$, where n is density of atoms. If $\hbar\omega/kT = x$ the equation (1) is possible written as

$$C_v = \frac{d}{dT} \left[\frac{3k^4 T^4}{2\pi^2 \hbar^3 V_0^3} \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \right]. \quad (3)$$

Upper limit is

$$x_m = \frac{\hbar\omega_m}{kT} = \frac{\theta_D}{kT}. \quad (4)$$

This conditions defines Debye's temperature (θ_D) and as it follows from said θ_D depends on the composition and the structure of matter. When temperatures are low the x -values are sufficiently great. In this case integral in equation (3) has magnitude

$$\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}, \quad (5)$$

and C_v (see (1), (3)) can be written as

$$C_v = \left(\frac{2 k^4 \cdot \pi^2}{5 \hbar^3 V_0^3} \right) T^3 = const \cdot T^3. \quad (6)$$

Formula (6) is known as Debye's law. The maximum value of wave vector in (2-4) is connected with number of atoms (N) by formulas (4-6)

$$(k_v)_{max} = (6\pi^2 N)^{1/3}, \quad (7)$$

then

$$V_0 = \frac{\omega_m}{(6\hbar^2 N)^{1/3}}. \quad (8)$$

The formula (6) with provisions of (3) and (7) takes type

$$C_v = 2,4\pi^4 Nk \left(\frac{T}{\theta} \right)^3 = 234 \cdot Nk \left(\frac{T}{\theta} \right)^3 = 3,23 \cdot 10^{-21} N \left(\frac{T}{\theta} \right)^3. \quad (9)$$

If the temperature of the crystal is sufficiently high then $\hbar\omega/kT$ has little value. The expression of $\exp(\hbar\omega/kT)$ in (1) may be expended into a series. After variable about only two members of expansion into series the internal energy has form of

$$U = \frac{3\hbar}{2\hbar^2 V_0^3} \int \frac{\omega^2 \cdot kT}{\hbar} d\omega, \quad (10)$$

and (see (1))

$$U = const \cdot T. \quad (11)$$

As it follows from expressions (1) and (11) the specific heat capacity becomes non depended on the temperature. It is the classic law of Dulong and Petit.

About low temperature of crystal the C_v is related from temperature as in equality (9). The Debye's temperature is bound between classic and quantum description of the crystal properties. Debye's temperature relates with Debye's energy (E_D) and Debye's impulse (P_D) (see (4) and (8))

$$E_D = k\theta_D = k\hbar\omega_m = kV_0(6\hbar^2 N)^{1/3}, \quad (12)$$

and

$$(P_D)_i = \left(\frac{2E_D \cdot m}{3} \right)^{1/2}, \quad (13)$$

where i is index of the coordinate axes and $i=1, 2, 3$.

The mechanical displacement of atomic nuclear brings about excitation of electron. The energy of this excitation is equal energy of phonon, sense m -value in formula is mass of electron. Debye's impulse is a border value for using different physics theory (nano- or bulk theory). When it takes the small crystalline the distribution of phonons energies are different from ones and bulk crystal. It is obviously that phonons with wavelength more $\lambda = 2l$ can not exit. Here l is the particle size. For determination of bound between nanoparticle and microparticle with volume (bulk) property (L) it must take the uncertainly relation

$$P_D \cdot L = h. \quad (14)$$

From equations (13, 14) it follows

$$L = \frac{h \cdot \sqrt{3}}{\sqrt{2mk}} \cdot \theta_D^{-1/2} = 230 \cdot \theta_D^{-1/2} \text{ [nm]}. \quad (15)$$

Debye's temperature is rather arbitrary parameter. Its determination is based on some approach. However this parameter is introduced to the reference books and is broadly used in the crystal physics.

The θ_D -value is calculated on formula (9) coming from experimental velocity of sound and then it is corrected by relation

Table 1. Debye's temperatures (θ_D) and maximum sizes (L) of nanoparticles of some unielement

№	1	2	3	4	5	6	7	8	9
matter	Ne	Pr	Ar	Tl	Pb	Hg	K	In	Bi
θ_D (k)	63	74	85	89-96	88-94,5	60-100	100	109-129	117-120
L(nm)	29,0	26,7	25,0	24,0-23,5	24,5-23,6	29,7-23,0	23,0	22,0-20,3	21,2
№	10	11	12	13	14	15	16	17	18
matter	La	Gd	Na	Au	Sn (white)	Sb	Sn (gray)	Ag	Ca
θ_D (k)	132	152	150-165	168	170-189	200	200-212	215-225	219-230
L(nm)	20,0	18,7	18,8-18,0	17,7	17,7-16,7	16,3	16,3-15,8	15,7-15,3	15,5-15,2
№	19	20	21	22	23	24	25	26	27
matter	Pt	Ta	Zn	Ga	Nb	Zr	V	Pb	Ti
θ_D (k)	229	231	234-308	240	252	270	273	275	278
L(nm)	15,2	15,1	15,0-13,1	14,8	14,5	14,0	13,9	13,8	13,8
№	28	29	30	31	32	33	34	35	36
matter	As	Cd	W	Ge	Mg	Cu	Ni	Co	Mn
θ_D (k)	285	220-300	270-379	366	318-406	315-445	375-456	385	400
L(nm)	13,6	15,6-13,3	14,0-11,8	12,0	12,9-11,4	12,9-10,9	11,9-10,8	11,7	11,7
№	37	38	39	40	41	42	43	44	45
matter	Li	Mo	Al	Cr	Fe	Si	Be	B	C(diamond)
θ_D (k)	400	380-425	394-418	402-460	420-467	625-658	100-1160	1250	1850
L(nm)	11,5	11,8-11,1	11,6-11,2	11,5-10,7	11,2-10,6	9,2-9,0	7,3-6,8	6,5	5,3

The Debye's temperatures and limit sizes of nanoparticles of some halogenides of metals are brought in table 2.

Table 2. The Debye's temperature (θ_D) and maximum sizes (L) for some halogenides

№	1	2	3	4	5	6	7
matter	RbI	KI	RbBr	AgBr	NaI	RbCl	KBr
θ_D (k)	103	131	131	150	154	165	173
L(nm)	22,7	20,1	20,1	18,8	18,5	18,0	17,5
№	8	9	10	11	12	13	14
matter	NaBr	KCl	NaCl	KF	LiCl	NaF	LiF
θ_D (k)	224	231	320	336	422	492	730
L(nm)	15,4	15,1	12,8	12,5	11,2	10,4	8,5

4. Conclusions

Proposed strategy allows to define habit maximum size of nanoparticles on the base well known physics representations. The L-value is determined the bounder between sizes where it can be done value description and where it's necessary to take into account the particle sizes.

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