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Geometry of lead sulfide nanoparticles with a NaCl-type structure

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The analysis of X-ray diffraction patterns showed that the geometry of PbS nanoparticles with a structure of NaCl is a nonlinear function of particle size for PbS particles smaller than 82 nm.

The shape control of nano- and microcrystals is important for materials chemistry[1] because different particle shapes can introduce different electronic, optical and magnetic properties.[2,3] Here, we used an example of a narrow-gap semiconductor crystal of lead sulfide (PbS)[†] to show that a dramatic increase in the fraction of surface atoms with particle sizes decreased to several nanometers led to a change in the particle geometry.

The X-ray phase analysis showed that all PbS samples have a cubic $B1$ type crystal structure of $Fm\bar{3}m$ space group. Analysis of diffraction reflex broadening $\beta(2\theta)$ by the Williamson–Hall method[6,7] revealed no microstrain in nanoparticles. Hereinafter, nanoparticles are referred to as coherent scattering regions with parameters determined from the analysis of the diffraction patterns.

With the use of the Scherrer formula or a more general method of Williamson–Hall, the particle size is determined by the size of a single value of the entire set of all reflections in the diffraction pattern. In this case, it is assumed that in different *hkl* directions, the sizes of the three-dimensional particles are the same. Thus, an ideal undistorted particle is a polyhedron inscribed in a sphere; *i.e*., it has the same dimensions in all *hkl* directions. In the cubic structure, the particle shape differs from a perfect cube. Thus, the shape of particles is determined by various sizes in different *hkl* directions.

To appreciate the size and shape of PbS nanoparticles we propose an approach based on the Scherrer–Selyakov formula.[8,9] First, we determined the relations $K_{hkl} = S_{hkl}/S_{\text{tot}}$, where S_{hkl} is the area (integrated intensity) under the *hkl* reflection, and S_{tot} is the area under all reflections. For the ideal structure, the value of K^{id}_{hkl} was determined[10] as the ratio of the intensity of the *hkl* reflection to the total intensity of all reflections in a given range of angles. To determine the experimental values of K^{exp}_{hkl}, the area under the peaks was calculated by fitting each diffraction reflection pseudo-Voigt function, which is especially important in the case of overlapping peaks. Second, the aspect ratio was defined as $A_{hkl} = K^{\text{exp}}_{hkl}/K^{\text{id}}_{hkl}$. If A_{hkl} is close to 1, the contribution of scattering from the *hkl* planes of the test particle is proportional to the scattering contribution of the ideal structure. In this *hkl* direction, the particle size is commensurate to the face-centered crystal size, and the Scherrer formula can be used to determine the particle size $D_0 \equiv D_{hkl}(A_{hkl} \cong 1) = \lambda/\beta_{hkl}\cos\theta_{hkl}$, where λ is the wavelength of radiation, β_{hkl} is the full width at half maximum of *hkl* reflection, and θ_{hkl} is the incidence angle. The error in determining the size was 0.5%. The size of the nanoparticles in the *hkl* directions, where A_{hkl} differed from 1, was defined by the formula $D_{hkl} = A_{hkl}D_0$. Finally, similarly to the method of constructing particles described elsewhere,[11] on the nominal center of the particle with the cube symmetry the line segments with $D_{hkl}/2$ lengths were plotted in the forward and backward *hkl* directions; the ends of the segments were joined to give a certain image of the particle shape [Figure 1(*a*),(*b*)].

To assess the role of PbS particle surfaces, we used the Madelung constant α to characterize the ionic character of bonds and to measure the deviation of the surface atoms bonds from those in the bulk of particles. In this case, the Madelung constant is persistent for atoms in an infinitely extended crystal; for structures such as NaCl, it is $\alpha_{\text{NaCl}} = 1.74756$. In the particle of a finite size, this parameter ranges for each atom; thus, to be correct, we will talk about the Madelung parameter, which as well as the Madelung constant is $\alpha_i = \sum_j \pm R_0/r_{ij}$, where i, j are the numbers of the atoms, '–' in the case of the same charges, '+' in the case of opposite charges, r_{ij} is the distance between the ith and jth atoms, and R_0 is the distance between the neighbouring atoms in the crystal. Given the parameters of the structure of NaCl and setting $R_0 = 1$, $r_{ij} = [(m_i - m_j)^2 + (n_i - n_j)^2 + (p_i - p_j)^2]^{1/2}$, where m, n, p are the coordinates of the atom (anion or cation) in the Cartesian system, and $\alpha_i = \sum_j (-1)^{r_{ij}^2+1}/r_{ij}$. In spite of the compact algorithm, the calculation of the Madelung parameter for all atoms of the particle is extremely time-consuming even for small particle sizes. Therefore, for a qualitative assessment of the calculation, we have restricted ourselves by Madelung parameter calculation for atoms on the cut of the cube face diagonal, *i.e*., at the (110) cross-section, passing through the vertices of the cube. Madelung parameter calculation and visualization were performed using the Igor Pro 6.2 software [Figure 1(*c*)].

Figure 1 shows the diffraction patterns, geometric shapes of PbS nanoparticles, and the calculations of the Madelung parameters for the cross section (110) of cubic particles with a NaCl structure. As a unified dimensional characteristic of the particles, we use the average size obtained from the Scherrer formula for the (111) (200) (220) directions using the aspect ratio (Table 1). Thus, the particle size of PbS ranged from 7 to 82 nm. The particle shape varied strongly with particle size mainly due to the deformation of the edges and the center of the face. Particles with a size of 7 nm have slightly convex faces centers and concave edges. The edge distortion angle, *i.e*., the angle formed by its two halves, is 188°. When the size is 13 nm, the edges become nearly flat (the distortion angle is 178°), the particle takes the form of an almost perfect cube. At the larger sizes, the edges become more convex; the angle of distortion increases up to 159° at a

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[†] The PbS nanoparticles were produced using the aqueous solutions of lead(II) acetate and sodium sulfide with initial concentrations of 0.025–0.25 mol dm^{-3}. To suppress hydrolysis, trilonate or citrate ions were added to the Pb(AcO)$_2$ solution[5] at pH 4.75–6.25. The X-ray measurements were performed on a Shimadzu automated diffractometer using Bragg–Brentano in CuK$\alpha_{1,2}$ radiation in a 2θ angle range from 18 to 90° with a step of $\Delta(2\theta) = 0.03°$; the exposure time was 10 s for each data point.

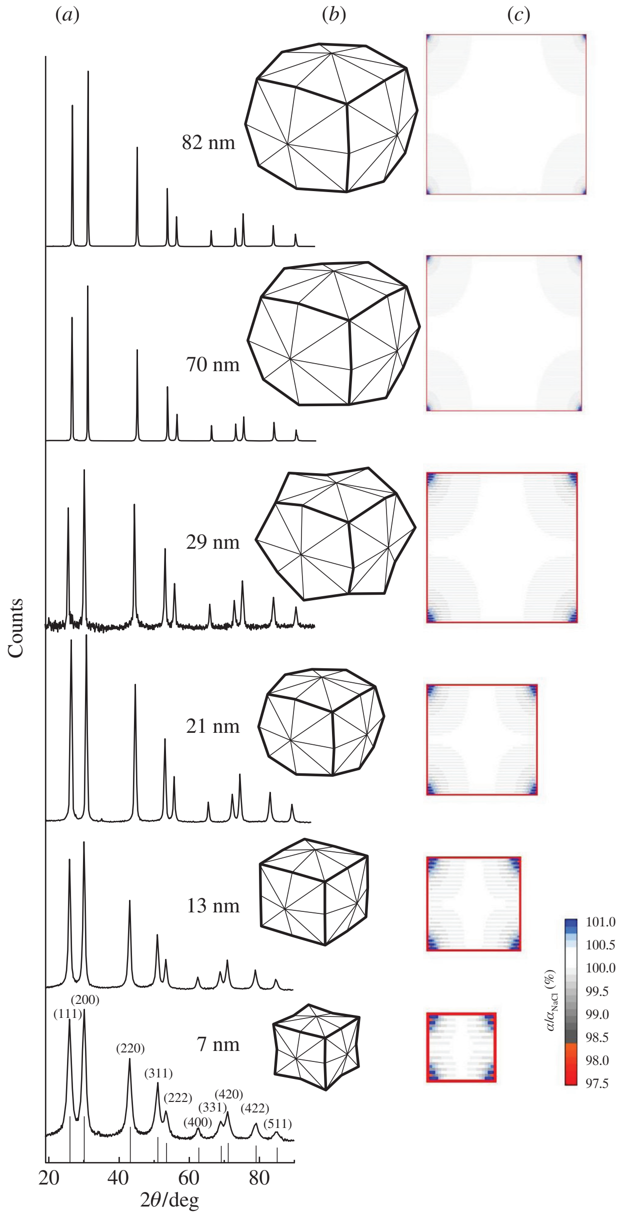

Figure 1 (*a*) Diffraction patterns of PbS nanostructured powders; (*b*) shape of nanoparticles according to X-ray diffraction analysis; and (*c*) Madelung parameter for the cross section of the cubic particles with a NaCl structure with an edge length close to the corresponding PbS particle.

Table 1 Particle size of PbS in different *hkl* directions according to an analysis of the diffraction patterns of PbS nanopowders.

Sample	*hkl*	Aspect ratio in the direction *hkl*	Particle size in the direction *hkl*/nm		Mean particle size considering to aspect ratio/nm
			From the Scherrer formula	With aspect ratio (L_{111}, L_{200}, L_{220})	
1	(111)	1.0625	6.8	7.3	7
	(200)	0.8867	7.4	6.1	
	(220)	0.9857	6.9	6.8	
2	(111)	0.9951	13.1	13.1	13
	(200)	0.9389	13.6	12.3	
	(220)	1.0130	12.7	13.3	
3	(111)	0.9151	21.7	19.8	21
	(200)	0.9198	21.6	19.9	
	(220)	1.0827	20.6	23.5	
4	(111)	0.8513	23.3	26.3	29
	(200)	0.8554	30.9	26.4	
	(220)	1.1447	29.8	35.4	
5	(111)	0.8962	57.2	65.1	70
	(200)	0.9252	72.6	67.2	
	(220)	1.0868	62.3	78.9	
6	(111)	0.9173	65.5	77.5	82
	(200)	0.9427	84.5	79.7	
	(220)	1.0650	74.8	90.0	

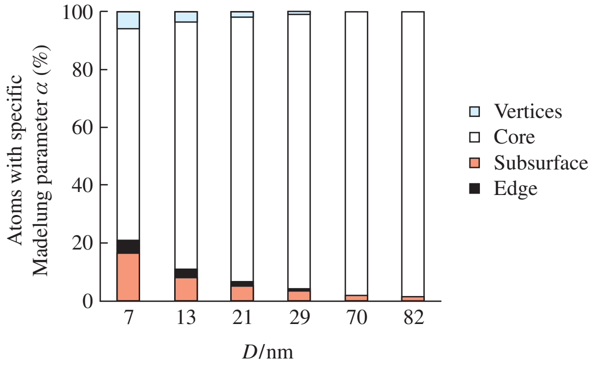

Figure 2 Fraction of atoms in the cross section of the particle with a NaCl structure [Figure 1(*c*)] with Madelung parameters characterizing the energy structure of the particle.

particle size of 21 nm. When the particle size is 29 nm, the edges fracture, and the angle of distortion reaches a maximum of 142°. Further size increasing leads to the reduction of the distortion angle: 156 and 162° at 70 and 82 nm, respectively. The shape of these particles becomes a medium between the cube and polyhedron inscribed in the sphere.

The Madelung parameter characterizes the distribution of the electrostatic potential in this section, and it has a value of 1.74756 for the fully ionic crystal. It indicates the amount of the electron density and its distribution. The gradient of Madelung parameter in different directions corresponds to the preferential direction of the electron clouds. The parameter α characterizes the energy minimum: the higher the parameter at this point, the higher the energy stability of the atom position. There are four main areas in the distribution of the Madelung parameter for a section of cubic particles: (*1*) a 'core', $\alpha_{\mathrm{NaCl}} = 1.74756$, and the deviation from it in both directions by 0.5%, *i.e.*, from 99.5 to 100.5% of α_{NaCl}; (*2*) a 'subsurface region' with parameter α between 98.5 and 99.5% of the α_{NaCl}; (*3*) 'vertices' with the parameter α up 100.5% from α_{NaCl}; and (*4*) a 'border' with the parameter α below 98.5% of α_{NaCl} [see areas of different colours and tints in Figure 1(*c*)]. The fractions of these areas with respect to all atoms on the particle cross-section are shown in Figure 2.

Calculation of the Madelung parameter confirms the idea of the increasing contribution of the surface energy with decreasing particle size. First, the strong decrease in the Madelung parameter on the borders of the cube shows the instability of the surface of the particle. Second, diminishing the particle size of the 'core' is greatly reduced by increasing the 'subsurface region'. The values of the Madelung parameter near the vertices of a cube are unexpectedly high. These vertices have an increased stability, and with a decrease in particle size the fraction of vertex contribution increases slightly faster than the fraction of the contribution of the surface (Figure 2). Thus, decreasing particle size leads to competing of two energy parameters: (1) destabilizing the particle due to growth of the surface and (2) stabilizing the particle due to the increase in the vertex energy input.

In the general case, the growing surface influence on the structure and morphology of the particles can be characterized by the ratio of surface fraction to volume one *S*/*V*. We consider four different models of cubic particles. For a perfect geometric cube, this ratio depends on its edges as follows: $S/V = 6/a$. Cubic particles with the NaCl structure may be compared with cube consisting of N^3 discrete atoms. The number of atoms on the surface of the cube is $S = 6N^2 - 12N + 8$, and the number of atoms in the bulk is $V = N^3 - S$. For PbS particles with sophisticated geometric shapes presented in Figure 1(*b*), the area is

$$S = 6\left[\frac{1}{3}L_{111}^2L_{220}^2 + \frac{2}{3}L_{200}^2L_{111}^2 + \frac{1}{2}L_{220}^2L_{200}^2 - 2\frac{L_{111}L_{200}L_{220}}{\sqrt{6}}\left(\frac{L_{111}}{\sqrt{3}} + L_{200}\right)\right]^{1/2};$$

the volume of such particles is $V = L_{111}L_{200}L_{220}/\sqrt{6}$ (Table 1). We analyzed this ratio for the cross section of cubic particles with calculated Madelung parameter, highlighting as the energy surface the ‘border’ and ‘subsurface region’, and as the volume – the ‘core’ and ‘vertices’.

Figure 3 shows curves that characterize the ratio S/V for the above models at $S/V = 1$ for a particle size of 7 nm. Thus, the general trend of S/V varying is reducing the surface fraction with increasing the particle size. Surface contribution decreases most rapidly for the atomic model of a cube and model based on Madelung parameters. For PbS particles with a geometry defined from X-ray data, the surface fraction decreases even more slowly than for a perfect cube. The greatest variation for different models is observed for a particle size of 29 nm.

In conclusion, the principal difference between the bulk state and nanostate is negligible influence of the particle surface on its properties including geometry. The bulk state for PbS is limited below the minimum particle size of about 82 nm. With smaller size the proportion of surface atoms increases dramatically and the ionic character of the interatomic bonds varies strongly. Thus, size area of less than 82 nm can be characterized as a nanostate of PbS, in which the geometry of the particle and its energy stability are entirely determined by the particle size. In PbS nanoparticles geometry dependence on the size is non-linear. The increase in the proportion of the surface of the particles is due to the formation of vertices, near which there are areas to compensate for the distortion of the electron density near the surface. For a particle size of 70–82 nm, the role of the faces begins to raise, but the contribution of vertices is still low. When reducing the particle size to 29 nm, the distortion of edges and faces becomes so significant that their fractures form new vertices of the particle. With further reduction of the size to 13 nm, the stabilizing contribution of the eight cube vertices increases, and their influence on the shape of the particle becomes basic at 7 nm.

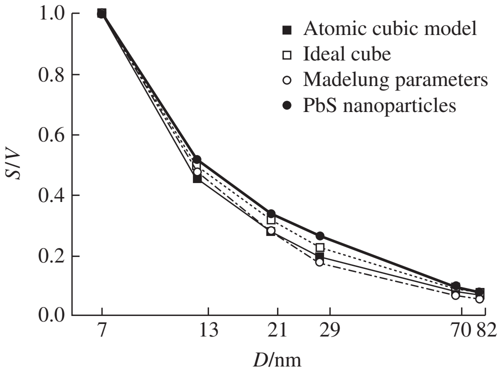

Figure 3 Dependence of the ratio S/V on particle size for different models: the ideal geometry of the cube, cubic particle with NaCl structure; PbS particle with size and geometry according to X-ray diffraction analysis [Figure 1(*a*), (*b*)]; section of the particle with a calculated Madelung parameter.

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