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Short-range order and correlations of S atoms in thin-layer PbS structures

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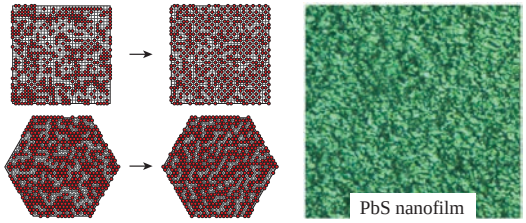
The correlations of sulfur atoms and vacancies in the planar square and hexagonal nonmetal sublattices formed by the 4(*b*) and 8(*c*) sites in thin-layer PbS films with a cubic $D0_3$ structure have been studied.



Short-range order and interatomic correlations affect considerably the structure and properties of nanocrystalline and nonstoichiometric substances.[1,2] In this work, we studied the correlations of sulfur atoms (S) and vacancies (□) in nanocrystalline thin-layer PbS films. The PbS nanofilms were deposited on a substrate by the vacuum evaporation of previously synthesized nanocrystalline PbS powder and condensation at 930 K.

Previously,[3–5] it has been demonstrated that nanostructured PbS films with particle sizes of <80 nm have a cubic (space group $Fm\bar{3}m$) structure with a disordered arrangement of sulfur atoms in octahedral 4(*b*) and tetrahedral 8(*c*) positions. This structure belongs to the $D0_3$ structure type where the non-metal lattice is separated into two sublattices, one of which is formed by the 4(*b*) sites and the other one is formed by the 8(*c*) sites. In the case of vacuum deposition, PbS films with different crystallographic orientations can be formed on the substrate surface. For the cubic $D0_3$ structure, the formation of PbS nanofilms corresponding to the (001) and (111) planes or equivalent to them is most probable. According to previous data,[6] the 8(*c*) sites in the (001) planes of the non-metal sublattice form a planar square (plane group *p*4*mm*) Kepler net of the 4^4 type [Figure 1(*a*)], and, in the (111) plane, the 4(*b*) sites of the non-metal sublattice form a planar hexagonal (plane group *p*6*mm*) net of the 3^6 type [Figurre 1(*b*)]. In the $D0_3$ structure of PbS nanofilms,[3,5] the S atoms occupy the octahedral sites 4(*b*) and tetrahedral sites 8(*c*) of the non-metal sublattice with the probabilities $P_{\text{S-octa}} = 0.84$ and $P_{\text{S-tetra}} = 0.08$, respectively. Therefore, in the (001) and (111) non-metal planes of a PbS nanofilm, a part of the sites are occupied by S atoms and the other sites are vacant.

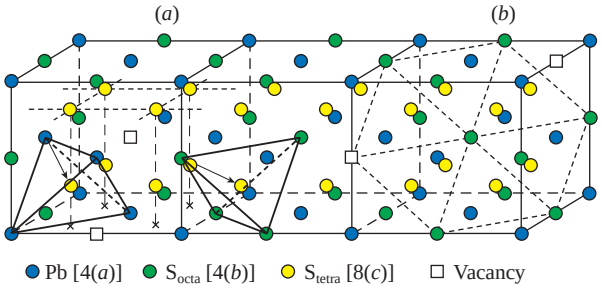


Figure 1 Positions of non-metal (*a*) square (001) and (*b*) hexagonal (111) planes in the unit cells of the cubic (space group $Fm\bar{3}m$) $D0_3$ structure of thin-layer PbS. Non-metal (001) and (111) planes pass through 8(*c*) and 4(*b*) sites, respectively.

The distribution of different atoms (or atoms and vacancies) in a crystal is characterized by long- and short-range orders.[7] We did not found superstructure reflections in the X-ray diffraction patterns of thin-layer PbS $D0_3$ structures. This indicates the absence of ordering. However, correlations between the mutual arrangement of S atoms and vacancies □ could not be ruled out. This is especially important because the relative number of vacancies in each non-metal sublattice is large and sufficient for the appearance of such correlations.

The short-range order is characterized by the short-range order parameters α_j and the correlation parameters ε_j in the *j*th coordination sphere.[7,8]

Up to now, it has not been found how many coordination spheres are covered by the short-range order appearing in the first coordination sphere.[9] Here, this problem was solved using a computer simulation of the dependence of the correlation parameters ε_j in the *j*th coordination spheres ($j \geqslant 2$) with radius R_j on the correlation parameter ε_1 of the first coordination sphere. The object of the simulation was an $S_y\square_{1-y}$ substitutional solid solution with atoms located in sites of defect planar square and hexagonal lattices: a part of the sites were occupied by sulfur atoms, and the other sites were vacant.

In the absence of a long-range order, the parameter ε_{SS} of pair correlations between two sulfur atoms S and the parameter $\varepsilon_{\square\square}$ of pair correlations between two vacancies □ are equal to each other:

$$\varepsilon_{SS}(R_j) \equiv \varepsilon_{\square\square}(R_j) \equiv \varepsilon_j = y(1-y)\alpha_j. \quad (1)$$

The parameters of unlike pair correlation of a sulfur atom and a vacancy are equal in magnitude to the pair correlation parameters of sulfur atoms (vacancies) but opposite in sign: $\varepsilon_{S\square}(R_j) \equiv \varepsilon_{\square S}(R_j) \equiv -\varepsilon_j$. In the case of a disordered distribution of atoms in an infinite lattice, the correlation parameter is zero. All probabilities were calculated for a finite lattice model without long-range order.

The probabilities of the occurrence of the pair bonds S–S, S–□, and □–□ in the $S_y\square_{1-y}$ solid solution with the atoms located at the sites of the square and hexagonal lattices were calculated for nine coordination spheres. This is sufficient to judge the

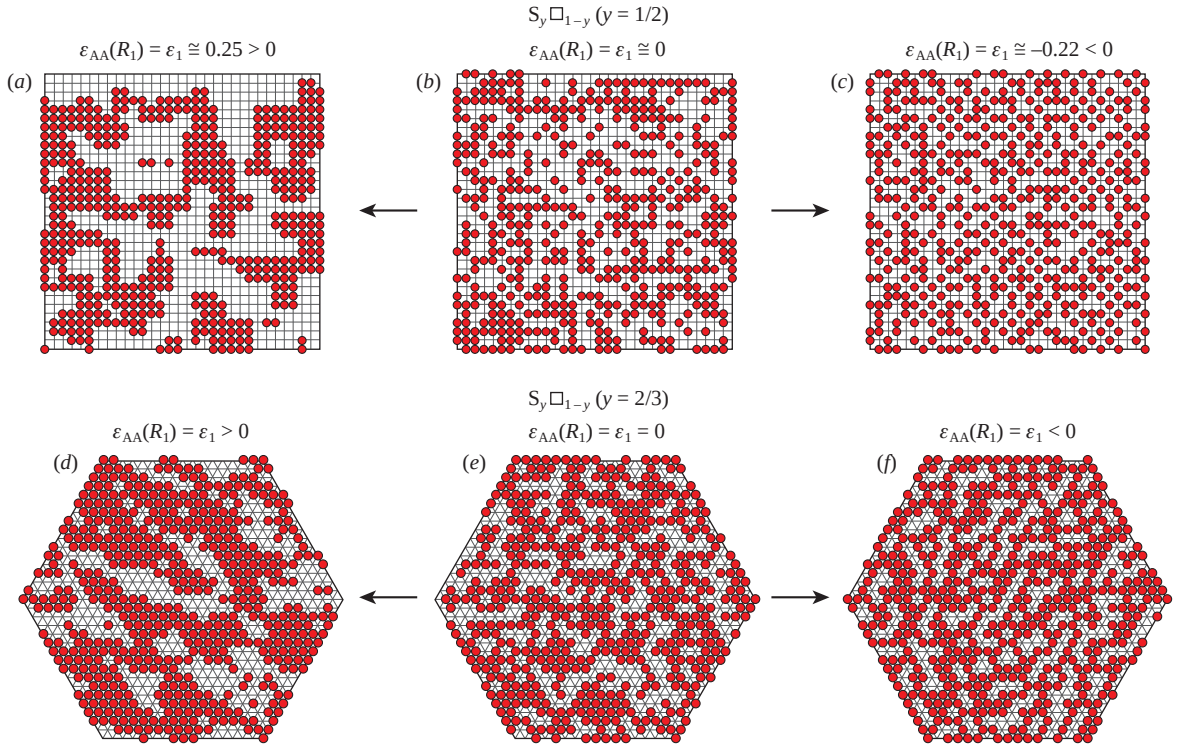


Figure 2 Model distributions of sulfur atoms in the square (plane group *p*4*mm*) lattice of the $S_y\square_{1-y}$ (y = 0.5) solid solution and in the hexagonal (plane group *p*6*mm*) lattice of the $S_y\square_{1-y}$ (y = 0.66) solid solution. (*b*),(*e*) Disordered solid solutions; (*a*),(*d*) short-range decomposition at a positive pair correlation parameter $\varepsilon_1 > 0$ in the first coordination sphere; (*c*),(*f*) short-range order formed after virtual annealing of the solid solution at a negative correlation parameter $\varepsilon_1 < 0$.

influence of the short-range order in the first coordination sphere on the pair correlation parameters in distant coordination spheres.

In the disordered infinite lattice, the correlation parameter ε_j in all coordination spheres is zero. In the case of the short-range order when the nearest coordination sphere of the S atom predominantly contains vacancies □, the correlation parameter ε_1 is negative. For the short-range decomposition, when the environment of the S atom predominantly involves S atoms (or the environment of the vacancy □ predominantly contains vacancies), the correlation is positive, *i.e.*, $\varepsilon_j > 0$.

In order to reveal the relationships between the correlation parameters in different coordination spheres, we considered two-dimensional square and hexagonal lattices of a fixed size with a specified vacancy content. The calculations were performed for 23×23 and 32×32 square lattices containing 529 and 1024 sites, respectively, and for a 33×33 hexagonal lattice containing 1089 sites.

At the first stage of the simulation of the lattice with a specified size, the computer synthesis of an $S_y\square_{1-y}$ disordered solid solution with a given quantity y, *i.e.*, with the known number of atoms and vacancies, was performed. The value of y was varied from 0.1 to 0.9 with a step of 0.1. The number of sulfur atoms necessary for the specified composition $S_y\square_{1-y}$ was introduced into the lattice with the use of a random-number generator. As a result of a statistical occupation of sites, the atoms and vacancies were distributed on the lattice in a disordered manner. The disordered state of the synthesized solution was the initial state for the subsequent simulation.

Then correlation walks of atoms were carried out over the lattice sites. For this purpose, energy fluctuations were introduced into arbitrarily chosen sites, as a result of which the atom can change to a vacant site. Only energy fluctuations sufficient for the 'jump' of an atom from its site in the crystal lattice into the neighboring vacant site were taken into account.

The virtual annealing was performed after the synthesis of the disordered lattice. An arbitrary lattice site was chosen using the Monte Carlo method. The annealing process involved displacements of atoms depending on the initial value of the correlation parameter ε_1 in the first coordination sphere. The direction of the displacement was stochastically chosen using a random-number generator.

The results of the calculations showed that there are two radically different processes: on the one hand, the decomposition of the $S_y\square_{1-y}$ solid solution occurs when the pair correlation parameter ε_1 in the first coordination shell is positive ($\varepsilon_1 > 0$); on the other hand, ordering occurs for $\varepsilon_1 < 0$ (Figure 2).

Figure 3 depicts the variation in the pair correlation parameters ε_j as a function of the relative radius R_j/a_{sq} or R_j/a_{hex} of the jth

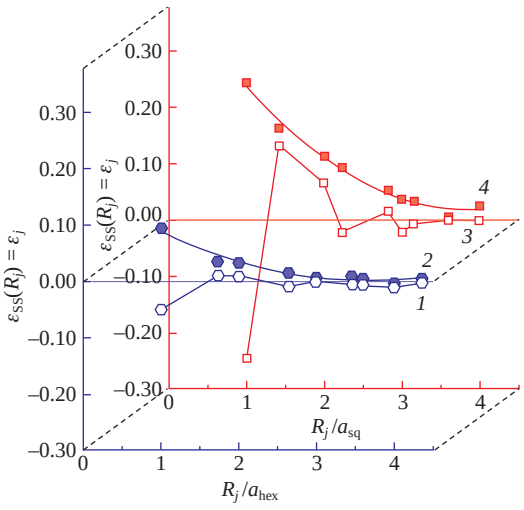


Figure 3 Pseudo-3D representation of the variation in the pair correlation parameters ε_j as a function of the relative radius of the jth coordination sphere. Parameters ε_j for the $S_{1/3}\square_{2/3}$ (y = 0.33) solid solution with the hexagonal lattice for (*1*) the short-range order with $\varepsilon_1 < 0$ and (*2*) the short-range decomposition with $\varepsilon_1 > 0$. Parameters ε_j for the $S_{1/2}\square_{1/2}$ (y = 0.5) solid solution with the square lattice for (*3*) the short-range order with $\varepsilon_1 < 0$ and (*4*) the short-range decomposition with $\varepsilon_1 > 0$.

coordination sphere for the $S_y\square_{1-y}$ solid solutions with the square and hexagonal lattices (a_{sq} and a_{hex} are the lattice constants for plane square and hexagonal lattices, respectively). The results are shown in a pseudo-3D representation. The correlations occurring in the first coordination sphere of the $S_y\square_{1-y}$ (y = 1/2) solid solution with the square lattice or the $S_y\square_{1-y}$ (y = 1/3) solid solution with the hexagonal lattice propagate (gradually decaying) up to the ninth coordination sphere; *i.e.*, they extend over a distance no shorter than $4a_{sq}$ or $4a_{hex}$. For the cubic $D0_3$ structure, $a_{sq} = a_{cub}/2$ and $a_{hex} = (\sqrt{2}/2)a_{cub}$, where a_{cub} is the lattice constant of the cubic (space group $Fm\bar{3}m$) PbS. In the case of the short-range order (open symbols), the correlation parameters ε_j oscillate, change sign, and asymptotically tend to zero in magnitude: at $\varepsilon_{SS}(R_1) \equiv \varepsilon_1 < 0$, we have $|\varepsilon_j| \to 0$ at $j \to \infty$. For the short-range decomposition at $\varepsilon_{SS}(R_1) \equiv \varepsilon_1 > 0$ (filled symbols), the correlation parameters ε_j are positive in all coordination spheres, decreasing with raising the radius of a coordination sphere, and tend to zero.

These model distributions found for sulfur atoms are useful for the determination of atomic planes that are optimal for the formation of coherent interfaces in thin-layer PbS/CdS heterostructures.

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