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Observation and Simulation of PbS Nonocrystal Formation at the Initial Steps

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SUMMARY: Ultrafine lead sulfide clusters are produced by the reaction of long-chain thiols with lead ions in non-aqueous medium, and according to X-ray diffraction (XRD) data reveal the different steps of he bulk-like rocksalt lattice growth. XRD pattern is simulated by the Debye formula for four model clusters (27, 75, 125, 729 atoms) and the correspondence of model and experimental clusters is shown that allows to estimate their size. *Ab initio* MOLCAO calculations result in energetical parameters and charge distribution for the clusters with 27 atoms. The value of energy gap indicates the true tendency of variation for the clusters of different size but left yet higher than maxima in the optical absorption at the fixed steps.

Introduction

The growing interest to quantum-size semiconductor nanocrystals promotes searching of new methods of their synthesis those provide controllable growth and determine properties of nanocrystals [1)]. For example, a protection of particles by organic groups allows to produce clusters with certain number of atoms that results in pronounced quantum-size effects in their physical properties. The controlled synthesis of the clusters with identification of crystal structure (up to 54 metal atoms) was reported recently for cadmium chalcogenides [2-5)] using protection by organic groups which stop the growth at the earlier steps. We studied formation of lead sulfide clusters in alcoholic solution using long-chain thiols as the sulfidization reagents which provide simultaneous sulfide formation and the self-protection at the different steps of the growth[6)]. The further growth of nanocrystals can proceed due to an additional sulfur source (H_2S) as fusion of primeval clusters in medium of tetrahydrofuran. In the present work additively to the experimental results on the formation process of small PbS nanocrystal mentioned above we consider their theoretical development: (1) simulation of X-ray diffraction patterns for the nanocrystals with definite number of atoms and (2) quantum chemical calculations of small lead sulfide clusters.

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Simulation of XRD pattern

X-ray scattering was simulated for model lattices with 27, 75, 125, and 729 atoms which correspond to the clusters with the fragments of PbS rocksalt lattice. The 27-atom fragment is a cube with 9-atomic face (Fig.1), the 125 atom fragment is the 27-atom cube doubled in the x,y,z-directions and has 25-atomic faces. The 75-atom fragment is a half of the latter.

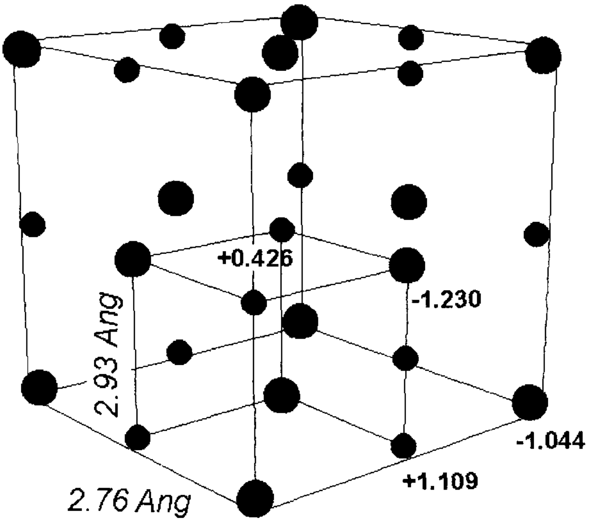

Fig. 1: $Pb_{13}S_{14}^{2-}$ cluster as the 27-atom fragment of the PbS rocksalt lattice and values of the effective charges at atoms obtained by SCF RHF calculations together with the interatomic distances of the optimized equilibrium geometry (retaining O_h symmetry).

The fragment largest for simulation is 729-atomic cube which was obtained by the x,y,z-translations of the 125-atomic one on the distance equal to the one lattice period (2.97 Å). The Debye formula for the scattered X-ray intensity was used taking into account the corresponding atomic scattering factors [7]. The results of the simulation (Fig.2) are compared with the two experimental patterns[6]. The 27-atom cluster appears too small to give the pronounced diffraction peaks, but the larger models reveal better correspondence with the experimental data. The positions of the peaks for 729-atomic fragment and their relative intensities are rather close the experimental ones. From these data one can conclude that the two steps fixed in the precipitation experiment are in correspondence with the formation of clusters in the given size range, and the cubic 125-, and 729-atomic clusters are the adequate models of ultrafine PbS particles formed due to the incomplete aggregation. Some deviations of the simulated peak positions with decrease of size can be associated with possible lattice distortion and strain that was recently pointed out for ultrafine PbS[8)].

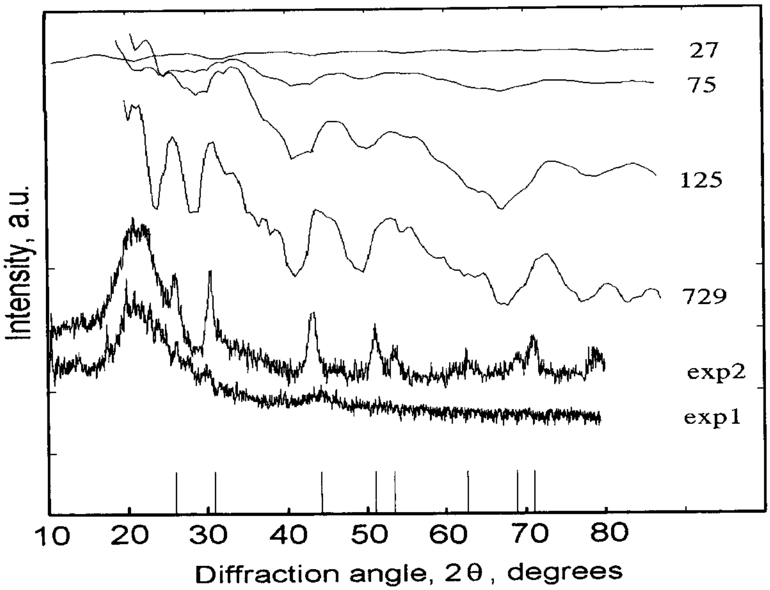

Fig. 2. Simulated X-ray diffraction for PbS clusters with the four model rocksalt lattices containing 27, 75, 125, and 729 atoms in comparison with the selected experimental XRD patterns and the reference data (JSPDS) for the bulk rocksalt PbS shown by vertical bars.

Quantum chemical calculations

Quantum chemical calculations were performed with MOLCAO scheme by SCF RHF method (*ab initio* level with effective core potential[10)]) with GAMESS package[11)] and available for the clusters with 27 and less atoms. From the point of view of the present work as the main results for comparizon with experiment we consider the value of energy difference between HOMO and LUMO which at the simplest approximation can correspond to the energy of the first optical transition of clusters. We see the pronounced tendency of decrease of this value with increase of the cluster size, and increase under the hydrogen addition. This value for $Pb_{13}S_{14}^{2-}$ is approximately twice as compared with the first maximum of the absorption spectrum observed for earlier steps of the cluster growth[6)] (~3eV). According to the calculation data this cluster (Fig.1) has no perfect cubic geometry and the sulfur atoms at the corner become more close to the center. Such distortion can be the cause of the XRD pattern deviation observed. This cluster is highly ionic with rather large excess charges at the surface atoms. In the precipitation experiments they are bounded by organic moieties which were simulated here by hydrogens (Tab.1). Its addition reduces the charge of atoms with which this hydrogen atom binds, but another atoms increase the charge (not shown in Fig. 1). Addition of hydrogen leads also to some restoration of the perfect cubic structure (difference of Pb-S interatomic distances is 0.09Å instead of 0.16Å without hydrogen).

Tab. 1. Values of the difference between highest occupied MO (HOMO) and lowest unoccupied MO (LUMO), Δ, calculated for the clusters by SCF RHF method.

Cluster	Pb_4S_4	$Pb_{13}S_{14}^{2-}$	$Pb_{13}S_{14}H_8^{6+}$	$Pb_{13}S_{14}H_{14}^{12+}$
Δ, eV	8.61	6.80	7.21	8.41

Conclusions

The theoretical development of the recent study of ultrafine lead sulfide clusters formation by the reaction of long-chain thiols with lead ions in non-aqueous media shows possibility of simulation of the early steps of cluster growth as fragments of the bulk-like rocksalt lattice. Energetic of the smallest $Pb_{13}S_{14}^{2-}$clusters calculated at the *ab initio* level shows the deviation from the experimental data on optical absorption that argues on the larger size of clusters observed.

References

1) A.P. Alivisatos, *J. Phys. Chem.* **100,** 13226 (1996); *Science* **271,** 933 (1996).
2) N. Herron, Y. Wang et al., *J. Am. Chem. Soc.* **112,** 1322 (1990); *Science* **259,** 1426 (1993).
3) T. Vossmeyer, L. Katsikas et al., *J. Phys. Chem.* **98,** 7665 (1994); *Science* **267,** 1476 (1995).
4) J. Rockenberger, L. Troger, A. Kornowski et al., *J. Phys. Chem.* **B 101,** 2691 (1997).
5) Y. Nosaka, H. Shigeno, and T. Ikeuchi, *J. Phys. Chem.* **99,** 8317 (1995).
6) V.S. Gurin, Proc. Int. Symp. *"Science and Technology of Atomically Engineered Mater."* (ed. P.Jena e.a.), 1995, World Sci., Singapore; *J.Cryst.Growth.(*1998) to pe published
7) D.T. Cromer and J.T. Waber, *Acta Cryst.* **18** (1965) 104.
8) S.B. Quadri, J.P. Yang, E.F. Skelton, and B.R. Ratna, *Appl. Phys. Lett.* **70** (1997) 1020.
9) W.J.Stevens, H.Basch, M.Krauss and P.Jasien, *Can. J. Chem.* **70,** 612 (1992).
10) M.W.Schmidt, K.K.Baldridge, J.A.Boatz et al., *J.Comput.Chem.* **14,** 1347 (1993).