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## Semiempirical calculation of cadmium chalcogenide clusters

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**Abstract.** The electronic structure of cadmium chalcogenide clusters is calculated within the molecular orbital framework using the extended Hückel technique with charge self-consistency. The size of clusters calculated corresponds to one to three elementary cells (the largest cluster is  $\text{Cd}_{54}\text{S}_{63}$ ). The results of the calculation show the tendency towards semiconductor-like band-structure formation. Explicit bands in the energy spectrum appear for clusters containing more than 100 atoms. There is good correspondence to experimental features of clusters in the optical and x-ray photoelectron spectra. The relative stability of clusters with different geometries and sizes is evidence of possible structure transformations in the case of small clusters. Most stable structures of small clusters are distinct from the bulk.

### 1. Introduction

Theoretical investigation of ultrafine semiconductor and metal particles is a rather complicated problem because they include many heavy atoms. Such particles are intermediate between molecules and bulk solids. Consideration of the electronic structure of small particles is possible by means of quantum-chemical methods, explicitly using the atomistic and molecular structure representation. Together with the more widely used approach to small-semiconductor-particle energetics by methods of solid state physics, e.g. the effective-mass approximation (EMA), the quantum-chemical technique can be considered as more universal, since the calculation results can include, in principle, complete information about particle properties. Quantum-chemical calculations have been used both for band-structure determination and also for cluster calculations within the molecular orbital (MO) framework [1–9]. In the case of the quantum-chemical approach (some studies have been devoted to calculations of  $\text{Pb}_x\text{I}_{2x+y}$ ,  $\text{Bi}_x\text{I}_{3x+y}$ ,  $\text{Ga}_x\text{As}_x$ ,  $x, y \leq 6-10$ ), a semiconductor particle is considered as a molecular cluster (isolated or bounded), in which MOs are formed from the basis of atomic orbitals (AOs). In this case, occupation of the energy levels of MOs and wavefunctions can serve as a description of the different properties of the cluster. The geometry of model clusters may be arbitrary in the general case; it can be very distinctive compared with that of bulk compound, which is often observed for different ultrafine substances. On the other hand, the electronic structure analysis based on translational symmetry of the many-atom system, e.g. the EMA [10, 11], the lattice pseudopotential method [12], and the tight-binding method [13], cannot in all cases give a true solution of the problem. The main cause of this disadvantage is connected with the evident role of boundary conditions for small particles. The cluster MO approach is also applicable for large particles; however, enormous computational difficulties arise.

In the case of *ab initio* quantum-chemical methods the real possibilities of computers are restricted to the region of tens of heavy atoms, but semiempirical methods allow one to carry

out more capacious calculations that permit analysis of the molecular-to-bulk transition with cluster size increase. Use of the semiempirical extended Hückel (EH) scheme in this paper can be justified by the unavoidably large size of the basis for the problem under consideration which make a successful application of more sophisticated methods impossible. We must take at least nine AOs of each cadmium atom in the basis ( $s^1 + p^3 + d^5$ ) in order to provide a true model of chemical bond formation. Although approximations used by the EH method cannot be valid in all cases, however, it can show true qualitative regularities of electronic structure formation taking into account atomic parameters (exact, from spectroscopy) and empirical parameters (adjustable for certain problems). In every case this MO method may not be less valid than the one-electron approach (e.g. EMA) or tight-binding calculations. It should be noted that the simple Hückel method, which is 'marginally' semiempirical, reflects correctly as a whole the tendency to energy level system evolution with size [5, 14]. Also, analytical correlations obtained on the basis of the simple Hückel method are fruitful for a clear illustration of the nature of energy spectrum quantization in small clusters.

In the present paper we use the EH method with charge self-consistency which allows one to calculate a rather large cluster in order to show the evolution of the cluster properties with size. Recently it was used successfully for transition-metal complexes and metal particles [15–21]. We consider the results of calculations of energy characteristics and optical properties of cadmium chalcogenide clusters (CdS, CdSe and CdTe). These compounds have been thoroughly investigated in many experimental studies of their formation, optical spectra, luminescence and non-linear optical properties [22]. The properties of semiconductor particles do show many peculiarities at sizes less than 5–10 nm (the so-called quantum-size particles).

## 2. Calculation technique

We calculate a number of model clusters (figure 1) of different sizes which are fragments of sphalerite and wurtzite lattices (point groups  $T_d$  and  $C_{3v}$ , respectively) and other more symmetrical configurations ( $D_{4h}$  and  $O_h$ ). Owing to the high symmetry, we attained† sizes of calculable clusters more than 1 nm including more than 100 atoms ( $Cd_{54}S_{63}$ ). No macroscopic parameters of semiconductors were used within the MO framework in contrast with EMA calculations. Our parametrization was performed according to atomic characteristics, data of atomic spectroscopy and thermodynamic values for binding energies of corresponding chemical bonds. The AO parameters (Cd 4d, 5s, 5p; S 3s, 3p; Se 4s, 4p; Te 5s, 5p) from [24] were used. Off-diagonal matrix elements of the Hamiltonian were determined by the Wolfsberg–Helmholz formula in which the constant  $K$  was fitted to the thermodynamic data: for CdS,  $K = 1.8$ ; for CdSe,  $K = 2.0$ ; for CdTe,  $K = 1.9$ . The calculated energies and wavefunctions were analysed from the viewpoint of relative stability, possible electronic transitions, charge distributions at atom sites, AO contributions in bond formation, etc.

## 3. Calculation results and discussion

Most of the structures under consideration (table 1) are stable clusters with binding energies of more than 1 eV (per pair of chalcogen and cadmium atoms) excluding the very non-stoichiometric cubic CdS fragments (with relation to an atom number of 4–14). Somewhat

† The program of the EH method with charge self-consistency and reduction of the eigenvalue problem due to symmetry was used for the calculations. In this program, total matrices are divided into blocks of smaller size according to irreducible representations of the cluster symmetry group [23].

**Table 1.** Relative stabilities of different clusters  $(\text{CdX})_n$  estimated from total electron energies. To compare  $E_{\text{total}}$  for clusters with different numbers of Cd and S atoms we take the pairs of clusters with the same structure (unbounded) :  $\text{Cd}_x\text{S}_y + \text{Cd}_y\text{S}_x$ .

Cluster	Symmetry group	$E_{\text{total}}/n$ (eV)
$\text{Cd}_6\text{S}_8 + \text{Cd}_8\text{S}_6$	$O_h$	272.04
$\text{Cd}_6\text{S}_9 + \text{Cd}_8\text{S}_9$	$O_h$	271.69
$\text{Cd}_8\text{S}_8$	$D_{4h}$	273.76
$\text{Cd}_{12}\text{S}_{12}$	$D_{4h}$	271.67
$\text{Cd}_4\text{S}_6 + \text{Cd}_6\text{S}_4$	$T_d$	272.43
$\text{Cd}_4\text{S}_{10} + \text{Cd}_{10}\text{S}_4$	$T_d$	270.05
$\text{Cd}_4\text{S}_{14} + \text{Cd}_{14}\text{S}_4$	$T_d$	267.33
$\text{Cd}_{12}\text{S}_{14} + \text{Cd}_{14}\text{S}_{12}$	$O_h$	270.56
$\text{Cd}_{14}\text{S}_{14}$	$D_{4h}$	269.60
$\text{Cd}_{14}\text{S}_{16} + \text{Cd}_{16}\text{S}_{14}$	$T_d$	272.55
$\text{Cd}_{54}\text{S}_{54}$	$O_h$	269.50
$\text{Cd}_{54}\text{S}_{63} + \text{Cd}_{63}\text{S}_{54}$	$O_h$	268.44
$\text{Cd}_7\text{S}_{14} + \text{Cd}_{14}\text{S}_7$	$D_{6h}$	270.97
$\text{Cd}_{17}\text{S}_{10} + \text{Cd}_{10}\text{S}_{17}$	$C_{3v}$	271.82
$\text{Cd}_{12}\text{Se}_{12}$	$D_{4h}$	272.45
$\text{Cd}_{12}\text{Te}_{12}$	$D_{4h}$	264.60

higher values of binding energies appear for the model clusters  $\text{Cd}_6\text{S}_8^{4-}$  and  $\text{Cd}_8\text{S}_8$ , which do not correspond to fragments of known bulk stable crystal lattices. This could mean that similar clusters are more probable than bulk lattice fragments for clusters consisting of a few atoms. The high stability of bulk structures with elementary cells with  $T_d$  and  $C_{3v}$  point groups for higher atom numbers could be associated with the long translational ordering and fewer boundary atoms.

Consideration of the calculated data for MO coefficients for clusters of different symmetries ( $\text{Cd}_6\text{S}_8^{4-}$ ,  $\text{Cd}_6\text{S}_9^{6-}$  ( $O_h$ ),  $\text{Cd}_4\text{S}_6^{4-}$ ,  $\text{Cd}_4\text{S}_{10}^{12-}$ ,  $\text{Cd}_4\text{S}_{14}^{20-}$  ( $T_d$ ) and  $\text{Cd}_8\text{S}_8$  ( $D_{4h}$ ) figure 1) indicates the essential difference in bond character through the difference in AO contributions in the basis. The dominating contribution of p and d orbitals of Cd and p AO of S atoms with a small contribution from  $sp^2$  hybrid states occurs for HOMO coefficients in sphalerite lattice fragments (figure 1(a)–(c)). In the case of the model cluster  $\text{Cd}_6\text{S}_8^{4-}$  with the cubic FCC lattice the cadmium AO contribution consists mainly of a single d orbital of cadmium and  $sp^n$  hybrid orbitals of sulphur. Interaction of the  $d_{xz}$  and  $d_{yz}$  orbitals of cadmium and a pair of sulphur AO  $p_x$  and  $p_y$  occur for all the above clusters of approximately the same size. On the other hand, in the clusters ( $\text{Cd}_4\text{S}_{10}^{12-}$  and  $\text{Cd}_4\text{S}_{14}^{20-}$ ) based on sphalerite, the  $d_{xy}$  AO of Cd contributes together with  $p_z$ , and different S atoms are bounded owing to different p AOs with a small s contribution. In the case of  $O_h$  symmetry clusters ( $\text{Cd}_6\text{S}_8^{4-}$ ), s contributions of both atoms are very small. Contributions of cadmium p orbitals are also small, and different d orbitals take part in the binding with all sulphur p AOs. Such interaction of AOs gives a more uniform electronic density distribution at different atom sites with more explicit localization along bonds on the cube faces. One additive sulphur atom in the centre ( $\text{Cd}_6\text{S}_9^{6-}$ ) leads to the appearance of  $d_{z^2}-p_z$  overlapping  $\sigma$  and AOs of the central atom contribute only in high MOs. For  $\text{Cd}_4\text{S}_{10}^{12-}$  and  $\text{Cd}_4\text{S}_{14}^{20-}$  clusters, a bond forms owing to certain pairs of orbitals:  $d_{xz}$  and  $d_{yx}$ ,  $p_x$  and  $p_y$ . For the truncated sphalerite elementary cell  $\text{Cd}_4\text{S}_6^{4-}$ , in contrast, one can see participation in the bond formation of all AOs with no explicit localization along any direction.

The cluster  $\text{Cd}_8\text{S}_8$  has an essentially different structure from the usual CdS elementary cells and possesses somewhat increased stability and uniform charge distribution with little bond polarity (charges at S and Cd less than i.e. (figure 1(e)). This could be caused by

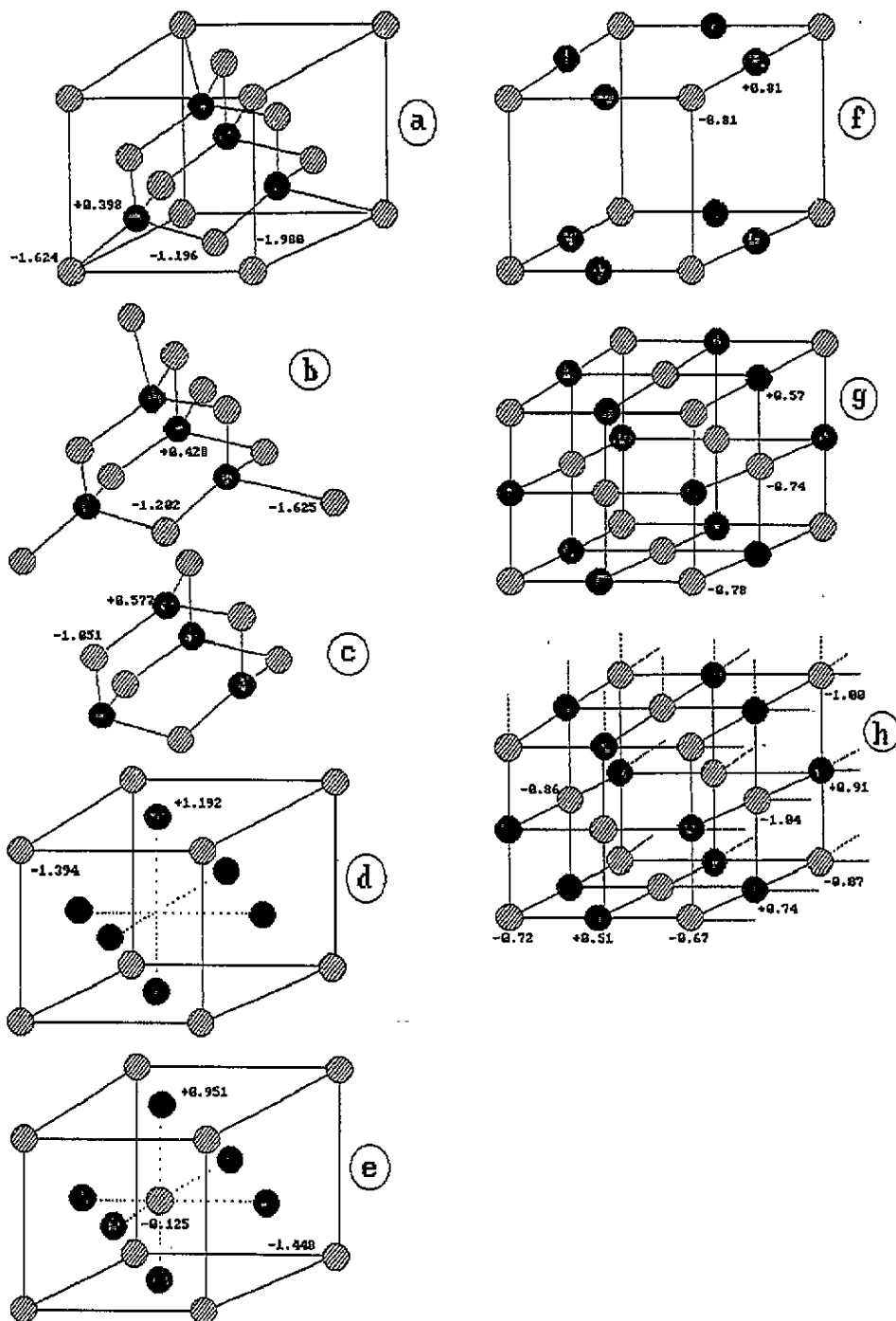


Figure 1. Structures of model clusters with calculated atom charges: ●, Cd atoms; shaded circles, chalcogen atoms. (a) Sphalerite elementary cell ( $a = 0.582$  nm); (b), (c) structures are obtained by removing some S atoms from (a) with the same interatomic distances. (d)–(g) Model structures with the same value of  $a$ , and structure for largest clusters  $\text{Cd}_{54}\text{X}_{63}^{18-}$  (or  $\text{Cd}_{63}\text{X}_{54}^{18+}$  under interchange of Cd atom sites with X atom sites) is obtained from (h) by continuation along the three directions on one period.

a larger Cd-S interatomic distance in such a model cluster (0.291 nm) than in the above sphalerite fragments (0.252 nm in  $\text{Cd}_4\text{S}_{10}^{12-}$ ). Thus, more stability of compact clusters is evidence in support of possible contraction of the optimal interatomic distance in the clusters compared with the bulk substance. In these  $\text{Cd}_8\text{S}_8$  clusters, atoms of both elements have the same AO contributions as well as in high-symmetry  $\text{Cd}_6\text{S}_8^{4-}$  and include  $d_{yz}$  orbitals of Cd which form bonds with  $p_z(\text{S})$  and pairs of  $d_{xy}(\text{Cd})$  and  $p_y(\text{Cd})$  binding with  $p_x$ - $p_y$  of S.

For the sphalerite-based clusters  $\text{Cd}_4\text{S}_x^{(8-2x)}$  for  $x = 10$ , one can expect more stability and a more uniform electron density distribution (figure 1(b)) owing to the tetrahedral arrangement of S around Cd specific to bulk Cd lattices (both wurtzite and sphalerite). However, in contrast with the undistorted tetrahedral arrangement for S and Cd in bulk lattices, in  $\text{Cd}_4\text{S}_{10}^{12-}$  the sulphur and cadmium appear in different environments (Cd has four nearest neighbours of S, and S has one or two nearest Cd atoms). From this point of view the structure of  $\text{Cd}_6\text{S}_8^{4-}$  ought to be more stable. Each Cd atom in it is surrounded by four nearest S atoms, and each S atom by three nearest Cd atoms. The electronic density distribution is more symmetrical in such a cluster. This is because of the lower Cd-S bond polarity (according to atom charge values (figure 1)) in  $\text{Cd}_6\text{S}_8^{4-}$  clusters. Cadmium atoms are located at cube faces in the latter, but in  $\text{Cd}_4\text{S}_{10}^{12-}$  and  $\text{Cd}_4\text{S}_{14}^{20-}$  they are in sites with tetrahedral surroundings. Apex atoms in  $\text{Cd}_4\text{S}_{10}^{12-}$  and  $\text{Cd}_4\text{S}_{14}^{20-}$  carry a considerable charge (about  $1.6e$ ), which can be reflected in their chemical properties. Meanwhile, the small difference in the AO contributions for  $\text{Cd}_4\text{S}_{10}^{12-}$  and  $\text{Cd}_6\text{S}_8^{4-}$  and also the values of the MO energies can provide easy structure transformations during the growth of  $(\text{CdS})_x$  particles. The coexistence of isomeric forms of cadmium chalcogenide clusters with near atom numbers will also be possible, in particular, taking into account the high mobility of ions in solutions where they can be formed.

One general result of the calculations for different clusters is the indication of the beginning of bulk-like band-structure formation, in the case of 10–20 atom clusters (figure 2). Nearly located energy levels are merged into bands (quasi-continuous), and the inter-level difference ( $\Delta$ ) between the HOMO and the LUMO contracts with increasing cluster size (it is shown by an arrow in the schematic diagrams).  $\Delta$  can serve as the analogue of the band-gap value  $E_g$  in bulk semiconductors. The schematic diagrams of the energy levels shown in figures 2 and 3 reflect clear variations in the electronic structures of different cadmium chalcogenides and clusters with different atom numbers, which correspond to one to three cubic elementary cells. They explicitly show the  $\Delta$ -value contraction in the row CdS, CdSe, CdTe.  $\Delta$  contracts also at the transition from  $\text{Cd}_{12}\text{S}_{14}^{4-}$  to  $\text{Cd}_{54}\text{S}_{63}^{18-}$ . The data obtained can be used to predict the optical properties of the clusters; they correlate with known values of the optical transition energies in systems containing  $(\text{CdS})_x$  clusters [5, 25–28]. For example, the near-edge maximum in the absorption spectrum specific to many semiconductors (it is interpreted as excitonic within the EMA framework), probably corresponds to the HOMO-LUMO transition. For  $\text{Cd}_{54}\text{S}_{63}^{18-}$ ,  $\Delta = 3.15$  eV; for  $\text{Cd}_{12}\text{S}_{14}^{4-}$ ,  $\Delta = 4.75$  eV, which is consistent with the observed location of the  $(\text{CdS})_x$  absorption band; there is a high-energy shift of about 1 eV for clusters with sizes 1–1.5 nm and up to 2–3 eV for sizes of less than 1 nm compared with the inter-band edge absorption of bulk CdS (2.5 eV). The size of clusters under consideration is from 0.5 nm for  $\text{Cd}_4\text{S}_x$  up to about 1 nm for  $\text{Cd}_{54}\text{S}_{63}$ . Thus, these model structures enter the range of cluster sizes which are minimal for possible certain experimental identification.

Comparing the calculation results with the above spectroscopic data, one can differentiate between clusters of various stoichiometries which correspond to compounds really formed under certain experimental conditions. For example, since a structure with an

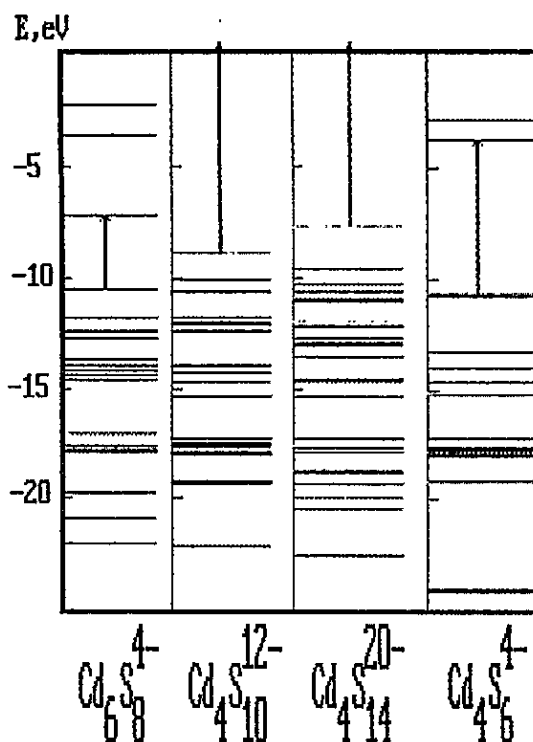


Figure 2. Schematic diagram of the energy levels calculated for small cubic clusters and HOMO-LUMO transitions.

exact geometry may be constructed with an abundance of either S or Cd in binary compounds by the type of CdX, we can select for  $O_h$  symmetry large clusters  $\text{Cd}_{54}\text{S}_{63}^{18-}$  or  $\text{Cd}_{63}\text{S}_{54}^{18+}$  or  $\text{Cd}_{54}\text{S}_{54}$  (figure 1(h)). However, only the  $\Delta$ -value corresponds to the optical data for  $\text{Cd}_{54}\text{S}_{63}^{18-}$  and, for  $\text{Cd}_{54}\text{S}_{54}$  and  $\text{Cd}_{63}\text{S}_{54}^{18+}$ ,  $\Delta < 1$  eV. Hence, one can suppose that, for the stabilized colloid formation process of  $(\text{CdS})_x$  particles [11, 24, 28], significant adsorption of excess sulphur occurs, leading to stabilization of clusters (additional sulphur was determined quantitatively in the case of clusters with organic ligands  $(\text{CdS})_x\text{-SR}$  [27, 28]).

The electron density distribution in the clusters under consideration (shown in figure 1 as atom charges) corresponds to a rather high ionicity of the Cd-S bond; in clusters with Se and Te it is lower. There is a tendency for higher charges at atoms with decreasing size. In the row of clusters  $\text{Cd}_{12}\text{X}_{14}^{4-}$  ( $\text{X} = \text{S}, \text{Se}$  or  $\text{Te}$ ) with different chalcogens, one can see very similar arrangements of energy levels (figure 2(a)). A HOMO of the  $T_{2u}$  type is formed in the main by p orbitals of chalcogen, and it shifts upwards in the row  $\text{Cd}_{12}\text{S}_{14}^{4-}$ ,  $\text{Cd}_{12}\text{Se}_{14}^{4-}$ ,  $\text{Cd}_{12}\text{Te}_{14}^{4-}$ . AO contributions of occupied MOs in clusters from this row show less mixing than in clusters with fewer atoms which indicates band-structure formation (p band in the given case). Analysis of the density of states for occupied orbitals (figure 4) and its correlation with the x-ray photoelectron spectrum for the valence band of  $(\text{CdS})_x$  1–2 nm particles immobilized in a polymer film [29] allow one to observe the true general tendency of the calculated data for  $\text{Cd}_{54}\text{S}_{63}^{18-}$ . Figure 4 clearly shows the formation of three bands of states in the energy spectrum of this cluster. Agreement with the location of experimental peaks is also reasonably correct. This is evidence of the general adequacy of the calculation, in particular taking into account the non-monodispersity of particles in samples for an x-ray

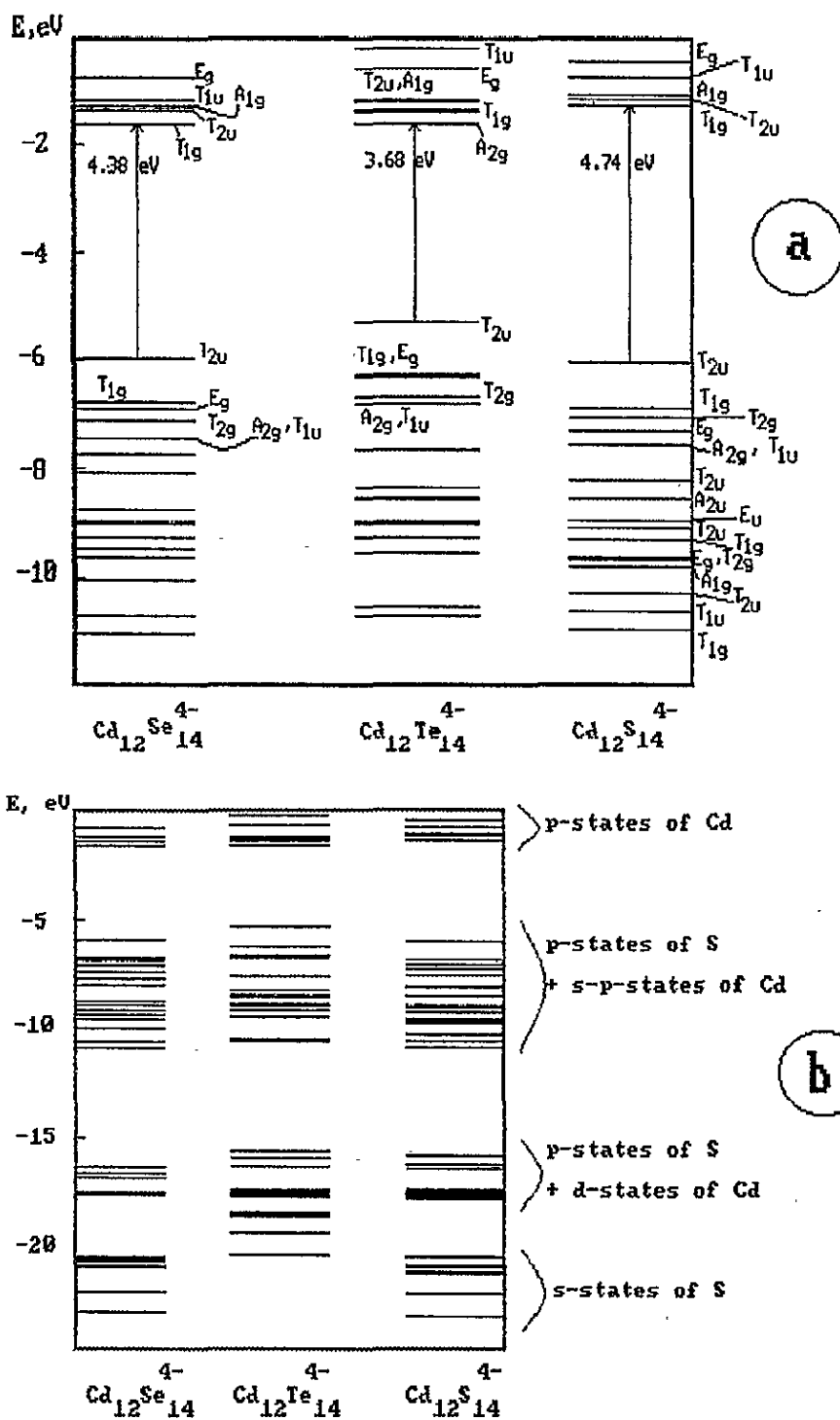


Figure 3. Schematic diagram of the energy levels calculated for  $\text{Cd}_{12}\text{X}_{14}^{4-}$  clusters and HOMO-LUMO transitions: (b) full and (a) with highest levels only, indicating the symmetry types of the orbitals.



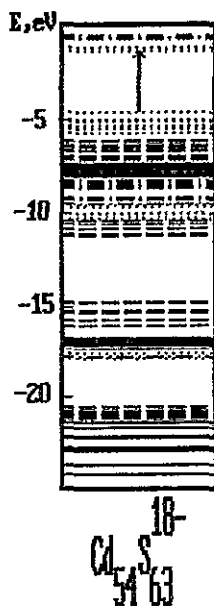


Figure 4. Schematic diagram of the energy levels calculated for the largest  $\text{Cd}_{54}\text{S}_{63}^{18-}$  clusters and the HOMO-LUMO transition.

photoelectron spectroscopy study.

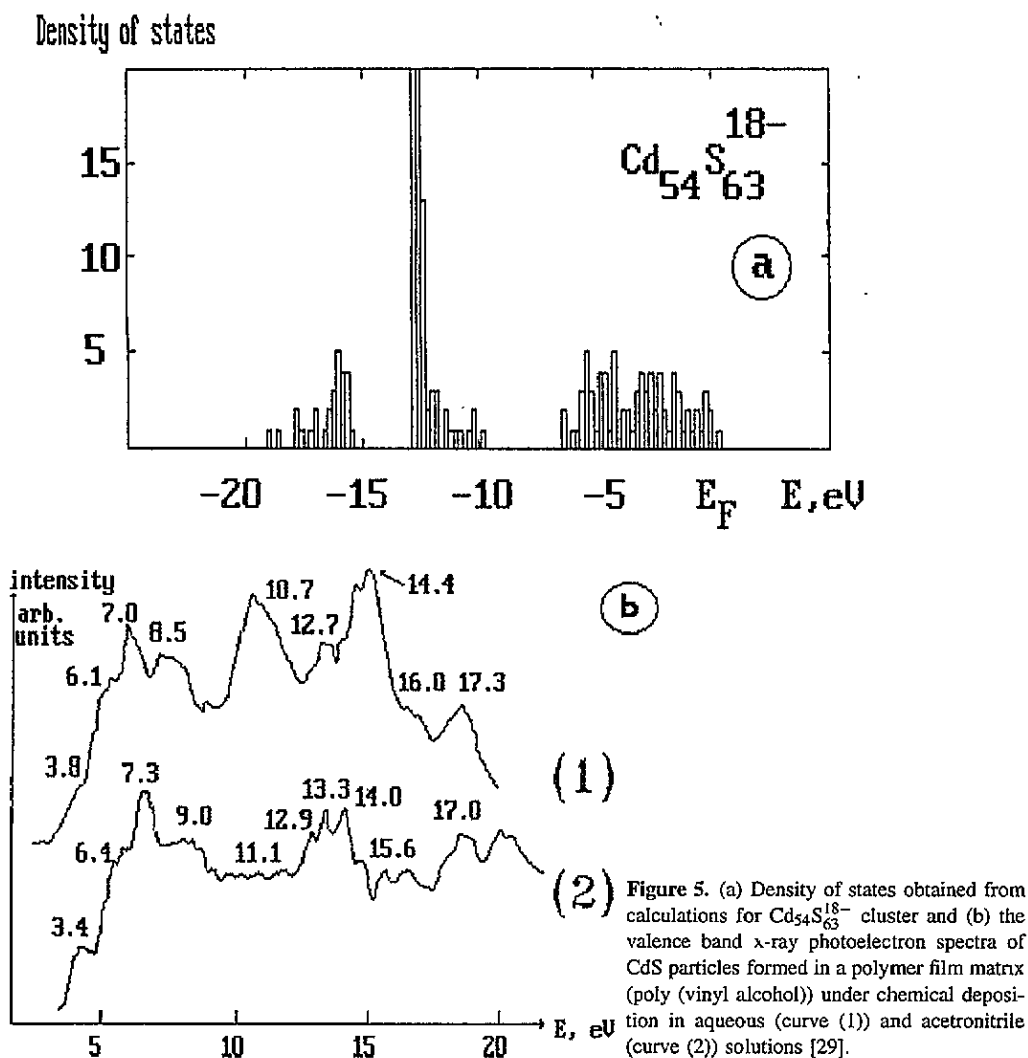
It should be noted that clusters of the type considered in this paper can form many geometrical configurations of approximately the same sizes with close energy stability, and each configuration could give specific lines in the spectrum. Consequently, monodispersity is very significant for possible comparison of calculations and experimental data.

The well known fact of the non-monotonic variation in the properties of metal clusters (e.g. even-odd oscillations) with increase in size will also be inherent to semiconductor clusters, in particular for the cadmium chalcogenides considered above. This peculiarity can be obtained naturally in MO calculations but does not follow from the EMA. So, in the energy level scheme in figure 5 for cluster  $\text{Cd}_6\text{S}_8^{4-}$ ,  $\Delta$  is less than for larger clusters; however, that does not mean that  $\text{Cd}_6\text{S}_8^{4-}$  is more metallic than  $\text{Cd}_{12}\text{S}_{14}^{4-}$ . Non-monotonic energy spectrum variation evidently can be reflected in the optical properties of systems with such particles, and possible 'oscillations' of some properties can be more complicated than in the case of metal clusters owing to the variety of isomeric configurations and stoichiometries.

#### 4. Conclusions

(1) The quantum-chemical MO approach to calculations of semiconductor clusters is more universal than solid state physics methods and allows one to determine many physical properties of clusters constructed from tens of atoms.

(2) The results of calculations for cadmium sulphide clusters and in the row sulphide, selenide, telluride are consistent with the experimental observed tendency in inter-band transition energy of their optical spectra. Electronic structure data fit the x-ray photoelectron



spectra for the cadmium sulphide valence band. The stoichiometry of  $\text{Cd}_{54}\text{S}_{63}^{18-}$  clusters and calculated data on the first electronic transition indicate the higher probability of the existence of clusters with excess sulphur in colloids.

(3) Clusters of less than 100 atoms have discrete energy levels with an explicit tendency to continuous band formation, in particular for d orbitals. The values of the HOMO-LUMO difference correspond to  $E_g$  of semiconductor particles.

(4) Of CdS clusters consisting of 10–30 atoms the structures  $\text{Cd}_8\text{S}_8$  and  $\text{Cd}_{14}\text{S}_{16}^{4-}$  are the most stable. The relative difference in stability is 1–2 eV (per pair of Cd and S atoms). In the row with the same content of  $\text{Cd}_{12}\text{X}_{14}^{4-}$  structures, cadmium selenide clusters are the most stable.

(5)  $\text{Cd}_x\text{S}_y$  clusters built on the basis of the sphalerite lattice ( $T_d$ ) have a more inhomogeneous electron density distribution than cubic FCC clusters do. This could cause the higher reactivity of  $T_d$  clusters and their lower stability.

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