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# First-principles study of structures and electronic properties of cadmium sulfide clusters*

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The lowest-energy structures and the electronic properties of $Cd_nS_n$ ($n = 1-8$) clusters have been studied by using density-functional theory simulating package DMol$^3$ in the generalized gradient approximation (GGA). The ring-like structures are the lowest-energy configurations for $n = 2, 3$ and the three-dimensional spheroid configurations for $n = 4-8$. The three-dimensional structures may be considered as being built from the $Cd_2S_2$ and $Cd_3S_3$ rings. Compared to the previous reports, we have found the more stable structures for $Cd_nS_n (n = 7, 8)$. Calculations show that the magic numbers of $Cd_nS_n$ ($n = 1-8$) clusters are $n = 3$ and 6. As cluster size increases, the properties of $Cd_nS_n$ clusters tend to bulk-like ones in binding energy per CdS unit and Mulliken atomic charge, obtained by comparing with the calculated results of the wurtzite and zinc blende CdS for the same simulating parameters.

**Keywords:** GGA, DMol$^3$, energy gap, binding energy
**PACC:** 3640, 3640B, 7115M

## 1. Introduction

The special properties of II–VI semiconductors make them suitable in special applications, such as optical sensitizers, photovoltaic solar cells, photocatalysts, and quantum devices etc. In the past decade, the properties of these materials have been investigated[1−8] both experimentally and theoretically. The study of physical properties of these clusters is an important part of the theoretical research. As we know, the properties of clusters will change as their size increases from molecular level to a bulk. Large clusters have bulk-like properties, and may be used to simulate an infinite large system. Therefore, the study in this field is growing rapidly. Many experimental and theoretical studies have been focused on the clusters of various compositions that have important and promising applications. For the binary clusters, there have been a lot of theoretical studies devoted to the properties of cadmium sulfide clusters, due to the variation of their electronic properties as a function of system size. Nevertheless, the fact that the characterization of cluster and nanoparticle becomes technologically possible has made clusters especially interesting. Joswig *et al*[9] investigated the structure of $Cd_nS_n$ using a simplified LCAO–DFT–LDA scheme. Trave *et al*[10] calculated CdS microclusters in sodalite by using the first principles local density function (LDF) methods. Troparevsky and Chelikowsky[11] studied the ground state structures of $Cd_nS_n$ ($n = 2-8$) clusters by using ab initio pseudopotentials constructed with the local density approximation (LDA). Maroulis and Pouchan[12] presented conventional *ab initio* and density functional theory results for the static dipole (hyper) polarizability of $(CdS)_n$ ($n = 1, 2$, and 4). So far, the study of cadmium sulfide clusters in the generalized gradient approximation (GGA)[13−15] method has not been reported. In the present work, we study the lowest-energy structures and electronic properties of $Cd_nS_n$ ($n = 1-8$) clusters by using the GGA method.

## 2. Method of calculation

The density-functional electronic structure calculations of $Cd_nS_n$ ($n = 1-8$) clusters have been performed by using the first principles DMol$^3$ package.[16−19] We adopted PW91[20] as the exchange–correlation functional with a double-

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numerical basis including a polarization p-function, and performed all electron spin-unrestricted calculations. The density functional is treated by using the GGA method. Self-consistent field calculations are done with a convergence criteria of $1.0\times10^{-5}$ a.u. and $1.0 \times 10^{-6}$ a.u. (atomic unit) for the total energy and electron density. We use convergence criteria of $2.0 \times 10^{-4}$ nm for the gradient and $5.0 \times 10^{-4}$ nm for the displacement. In order to compare with the zinc-blende and wurtzite CdS crystal, we have calculated electronic properties of the two bulk CdS crystals using the same simulating parameters.

We present a series of low-energy structural isomers for each cluster size by using a simulated annealing procedure. In this method, the cluster is heated to a high temperature and then slowly cooled down to room temperature. Initially, the cluster samples exist in numerous configurations without regard to the corresponding structural energy. As the cluster is cooled down, only energetically favourable structures are sampled. The structures obtained from the empirical simulations are then fully optimized using the density function theory (DFT) to locate the lowest-energy configuration. The essential idea here is to divide the phase space into several regions and find a locally stable isomer to represent each region. Although the energies and structural parameters of these isomers may not be described very accurately by the empirical potential, these minima may give a reasonable sampling of the phase space and can be further optimized by DFT. If there is no significant difference between the DFT result and empirical phase space, the lowest energy structure at the GGA level should be obtained by the combination of simulated annealing technique and GGA minimization.

# 3. Results and discussion

## 3.1. Structures of cadmium sulfide

The lowest-energy structures and low-lying isomers of $Cd_nS_n$ $(n = 1-8)$ clusters are shown in Fig.1. The lowest-energy structures obtained from our calculation are denoted by $Cd_nS_{n-1}$. In order to condense the article, we only analyse the lowest-energy structures of $Cd_nS_n$ $(n = 1 - 8)$ clusters. In Table 1, we list the Cd–S bond lengths ($R$), S–Cd–S angles ($\alpha$), symmetry group, binding energy per CdS unit ($E_b$), HOMO–LUMO energy gap or band gap ($E_{gap}$) and

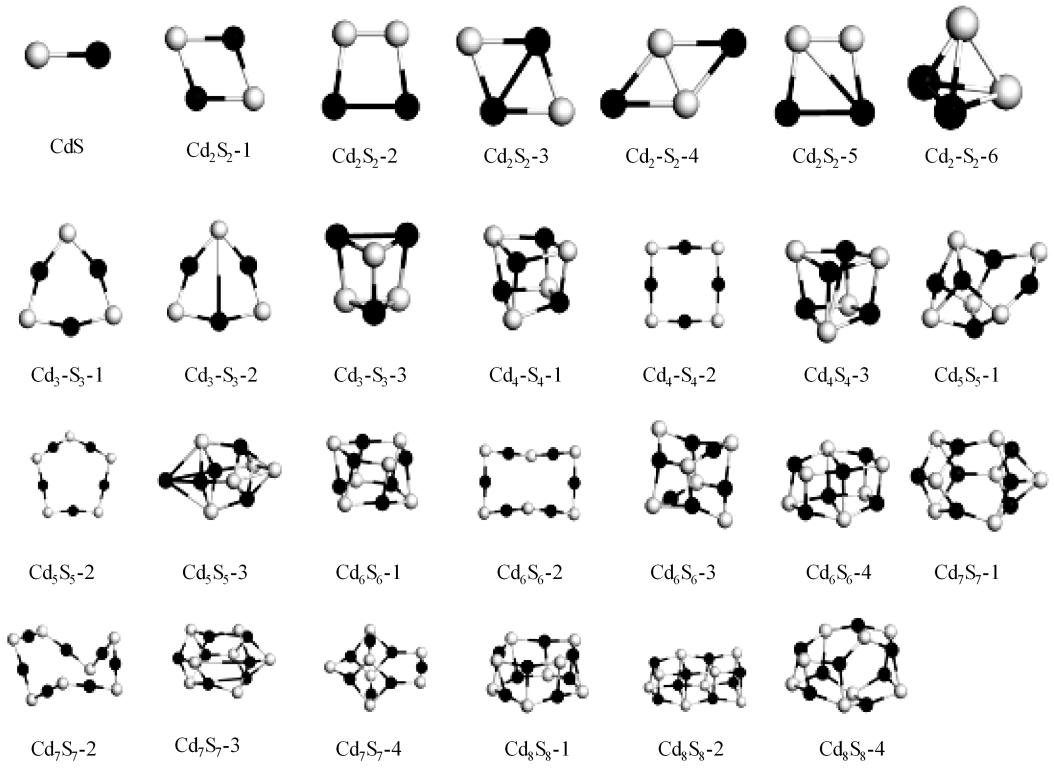



**Fig.1.** Some of the isomers found in $Cd_nS_n$ $(n = 1 - 8)$ clusters. The black balls refer to cadmium atoms and the white ones refer to sulfide atoms.

**Table 1.** Some parameters for CdS: $R$/nm, Cd–S bond lengths; $\alpha/(^\circ)$, S–Cd–S angles; symmetry group; $E_b$/eV, binding energy per cadmium sulfide unit; $E_{gap}$/eV, energy gap or band gap; and Mulliken atomic charges.

| $n$ | $R$(Cd–S)/nm | $\alpha$(S–Cd–S)/(°) | symmetry-group | $E_b$/eV | $E_{gap}$/eV | Mulliken-atomic-charges/e | |
|---|---|---|---|---|---|---|---|
| | | | | | | Cd | S |
| 1 | 0.236 | | Cinfv | –1.557 | 0.262 | 0.460 | –0.460 |
| 2 | 0.250 | 110.6 | $D_{2h}$ | –3.358 | 1.215 | 0.571 | –0.571 |
| 3 | 0.243 | 156.4 | $D_{3h}$ | –4.215 | 2.544 | 0.538 | –0.538 |
| 4 | 0.261 | 103.4 | Td | –4.345 | 2.157 | 0.608 | –0.608 |
| 5 | 0.239–0.265 | 152.4–101.2 | Cs | –4.473 | 1.653 | 0.536–0.599 | –0.558–0.601 |
| 6 | 0.253–0.271 | 99.7–142.0 | $D_{3d}$ | –4.728 | 2.405 | 0.588 | –0.588 |
| 7 | 0.252–0.260 | 98.2–131.7 | $C_{3v}$ | –4.725 | 2.220 | 0.587–0.612 | –0.582–0.614 |
| 8 | 0.251–0.274 | 98.1–157.8 | $D_{4d}$ | –4.775 | 2.489 | 0.553 | –0.553 |
| blende CdS | 0.253 | 109.5 | F-43M | –5.668 | 1.660 | 0.620 | –0.620 |
| wurtzite CdS | 0.258–0.259 | 109.1–109.8 | P63MC | –5.752 | 1.578 | 0.643–0.644 | –0.643–0.644 |

Mulliken atomic charges of the CdS clusters and crystals. From Fig.2, we can discover that ring-like structures correspond to the lowest-energy configurations at $n = 2$ and 3, and three-dimensional spheroids correspond to those at $n = 4 - 8$. And the latter configurations can be imagined as being built from the two smaller ring-like clusters, which is consistent with the reported $Zn_iS_i$ $(i = 1 - 9)$ clusters.[21]

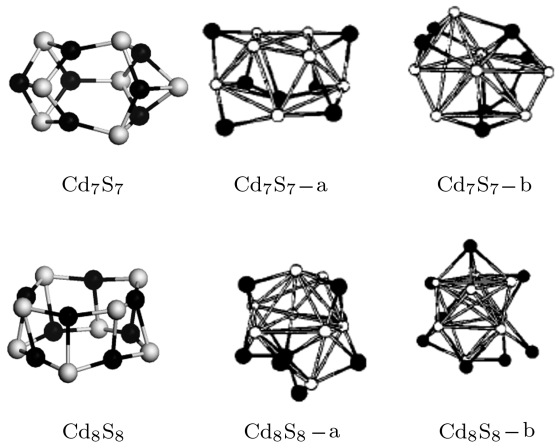



**Fig.2.** Lowest-energy structures for $Cd_nS_n$ $(n = 7, 8)$ reported in Ref.[11].

For CdS dimers, our GGA calculation predicts the bond length to be $R = 0.236$ nm, binding energy per CdS unit $E_b = -1.557$ eV, and symmetry group Cinfv. Our result is much closer to the experimental result ($R = 0.252$ nm)[22] comparing to LDA result (about $R = 0.214$ nm) in Ref.[11].

For $Cd_2S_2$, the calculated global minimum structure has been found to be a parallelogram. The bond length obtained is 0.250 nm, which is very close to the experimental data (0.257 nm). The S–Cd–S angle is 110.6°, and the symmetry group is $D_{2h}$. From Table 1, it seems logical that the $Cd_2S_2$ ring is the most energetically stable structure, since it contains the favourable Cd–S bond length, S–Cd–S angle, and atomic charges. However, our results demonstrate that the lowest-energy $Cd_3S_3$ ring is more stable than the $Cd_2S_2$ cluster. The detailed discussion will be given in the following analysis.

For $Cd_3S_3$, the calculated ground state structure of the $Cd_3S_3$ cluster is planar. In contrast with the CdS crystal supercell or cell in Fig.3, we find that the two known crystal structures in $Cd_3S_3$ cluster are zinc-blende and wurtzite CdS. As can be seen in Table 1, the Cd–S bond length in $Cd_3S_3$ is 0.007 nm shorter than in $Cd_2S_2$, and the S–Cd–S angle is much more open. This ring structure has a $D_{3h}$ symmetry and is a very important one.

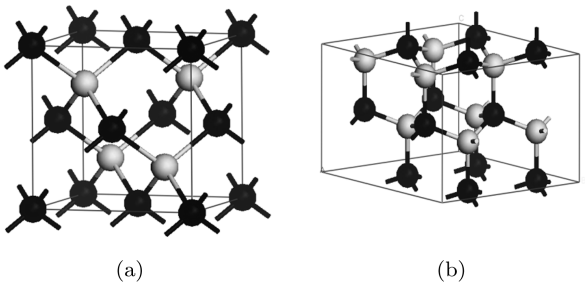



**Fig.3.** Supercell of wurtzite structure CdS (a) and crystal cell of blende structure CdS (b). The black balls refer to cadmium atoms s and the white ones refer to sulfide atoms.

For $Cd_4S_4$, the ground state structure is interesting. Firstly, it is the first nonplanar structure found. Secondly, it can be viewed as being built from

six equivalent units of an earlier presented structure $Cd_2S_2$ rings. This global minimum structure has a $T_d$ symmetry, with 0.261 nm Cd–S bond length and 103.4° S–Cd–S angle, which are consistent with those of the $Cd_4S_4$ clusters reported in Ref.[11].

For $Cd_5S_5$, our calculation predicts the global minimum structure of $Cd_5S_5$ cluster is a three- dimensional spheroid configuration, composed of four $Cd_2S_2$ and two $Cd_3S_3$ rings. We can regard the ground state $Cd_5S_5$ as a structure composed of two joint rings of $Cd_2S_2$ and $Cd_3S_3$. The Cd–S bond lengths and S–Cd–S angles have been found in a wide range from 0.239 to 0.256 nm and 101.2° to 152.4°, respectively. This lowest-energy structure has $C_s$ symmetry, which seems to be like a chair.

For $Cd_6S_6$, its structure is similar to that of $Cd_4S_4$ and $Cd_5S_5$, and it can be envisioned as made of smaller building blocks: $Cd_2S_2$ and $Cd_3S_3$ rings. It is formed by two bent $Cd_3S_3$ rings, which are linked together by $Cd_2S_2$ rings. Comparing the ground state $Cd_6S_6$ structure with wurtzite CdS supercell, we find that the wurtzite CdS crystal can be viewed as being built from the lowest-energy $Cd_6S_6$ cluster. The bond lengths and S–Cd–S angles are found in a wide range from 0.253 to 0.271 nm, and 99.7° to 142.0°, respectively. The resulting structure has $D_{3d}$ symmetry and this lowest-energy structure is consistent with that of $Cd_6S_6$ clusters reported in Ref.[11].

For $Cd_7S_7$, its three-dimensional structure is interesting, because of the reappearance of the building blocks considered. $Cd_7S_7$ may be viewed as a polyhedron formed by three long faces composed of $Cd_3S_3$ rings that are inverted on the next face. The polyhedron is closed on the top and the bottom by six $Cd_2S_2$ rings, with bond lengths and S–Cd–S angles ranging from 0.252 to 0.260 nm, and 98.2° to 131.7°, respectively. The global minimum structure has $C_{3v}$ symmetry. It is worthwhile to point out that this lowest-energy structure is not consistent with the reported ground state structure of $Cd_7S_7$-a and $Cd_7S_7$-b in Fig.2. So, we have also calculated these $Cd_7S_7$ isomers by using our GGA method. The obtained results show that the total energies of the $Cd_7S_7$ isomers are higher by about 2 eV than our lowest-energy $Cd_7S_7$ structure.

For $Cd_8S_8$, the three-dimensional structure of it has been found to be the ground state structure. The lowest-energy $Cd_8S_8$ structure may be treated as a polyhedron formed by two 'quasiplanar' $Cd_4S_4$ rings bonded together by eight $Cd_2S_2$ rings. The bond lengths and S–Cd–S angles are in wider range from 0.251 nm to 0.274 nm, and 98.1° to 157.8°, respectively. This resulting structure has $D_{4d}$ symmetry. In Fig.2 we also give the ground state structure of $Cd_8S_8$ reported by Troparevsky.[11] Our results obtained show that the total energies of the $Cd_8S_8$ isomers are higher by about 2eV than those of the lowest-energy $Cd_8S_8$ structure we obtained.

From the above discussion, there are two basic building blocks found in the construction of the most stable large clusters, i.e. $Cd_2S_2$ and $Cd_3S_3$ rings. When we analyse the two crystal structures of cadmium sulfide, zinc-blende and wurtzite, depicted in Fig.3, we find that both structures have the same building block, $Cd_3S_3$ rings. Different arrays of $Cd_3S_3$ rings will result in the cubic structure (zinc-blende) and the hexagonal structure (wurtzite). The geometry of the rings is the same in both crystals, with Cd–S bond lengths ranging from 0.253 nm to 0.259 nm and S–Zn–S angle is 109°. We can compare these values with the geometries of the $Cd_3S_3$ rings in the calculated lowest energy structures, given in Table 1. As the cluster size increases, the observed ring geometry of $Cd_3S_3$ shows somewhat contraction so that it approaches the bulk structures: the angles are closer to each other and the bond lengths are very similar.

## 3.2. Electronic properties of cadmium sulfide

We show the second difference of cluster energies defined by $\Delta_2 E_{(n)} = E_{(n+1)} + E_{(n-1)} - 2E_{(n)}$ in Fig.4, which is a sensitive quantity that characterizes the stability of clusters[23−26] as a function of cluster size. Local maximum peaks for $\Delta_2 E(n)$ are found at $n = 3$ and 6, indicating that the clusters with these values may be more stable than their neighbouring clusters.

Moreover, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the global minima of $Cd_nS_n$ ($n = 1-8$) indicates that the magic numbers for these $Cd_nS_n$ clusters are at $n = 3$ and 6, too. In Fig.5(a), we present the energy gap as a function of cluster size. The local maximal energy gap has been found to be at $n = 3$ and 6. Generally, a higher energy gap implies that the cluster is more stable.[27] It is noteworthy that $n = 3$ and 6 were found to be the magic numbers for $Cd_nS_n$ ($n = 1 - 8$) clusters. Figure 5(b) presents the energy gap for previous LDA

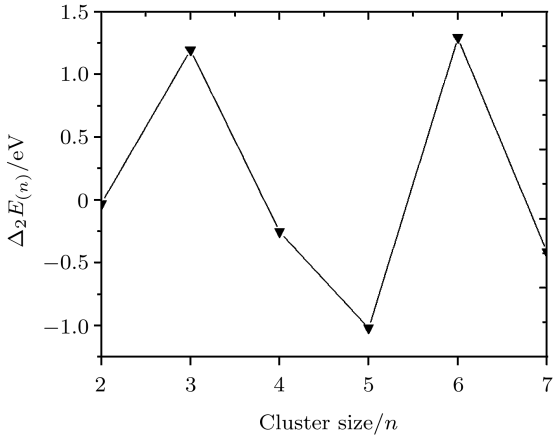



**Fig.4.** Second difference of cluster energies $\Delta_2 E_{(n)} = E_{(n+1)} + E_{(n-1)} - 2E_{(n)}$ as a function of cluster size $n$ for $n = 1 - 8$. The magic number effect of the electron shell at 3, 6 can be identified.

calculations.[11] It is noteworthy that $n = 3$ and 6 (i.e. number of atoms 6 and 12) are also found to be the magic numbers for $Cd_nS_n$ clusters. But, this curve is a little different from our calculation, which descends at $n = 8$ in Fig.5 (b). The reason is that the structures of $Cd_7S_7$ and $Cd_8S_8$ clusters are not the lowest-energy structures for $Cd_nS_n$ clusters ($n = 7, 8$).

The binding energy ($E_b$) per CdS unit of $Cd_nS_n$ clusters as a function of cluster size $n$ is plotted in Fig.6. The cluster binding energy increases with cluster size rapidly up to $n = 6$ and keeps nearly stable at $n \geq 7$. Such a behaviour can be related to the appearance of more highly coordinated structures. The binding energy $E_b$ per CdS unit of hexagonal wurtzite structure CdS and blende structure CdS is listed in Table 1, too. Comparing the $E_b$ of $Cd_nS_n$ clusters with two CdS crystals, we observe that the discrepancy between $Cd_8S_8$ cluster and the CdS crystals is less than 1.0 eV. Just as in Fig.5, the curve is not consistent with that reported in Ref.[11]. The reason is that the structures of $Cd_7S_7$ and $Cd_8S_8$ clusters are not the ground state structures for $Cd_7S_7$ and $Cd_8S_8$ clusters in former report.

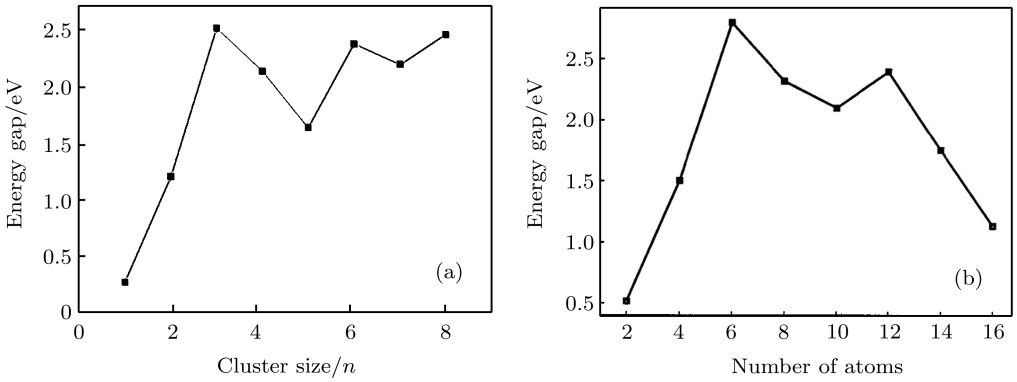



**Fig.5.** (a) The calculated energy gap (HOMO–LUMO) of cadmium sulfide clusters. (b) HOMO–LUMO energy gaps versus the number of atoms in the $Cd_nS_n$ clusters.[11]

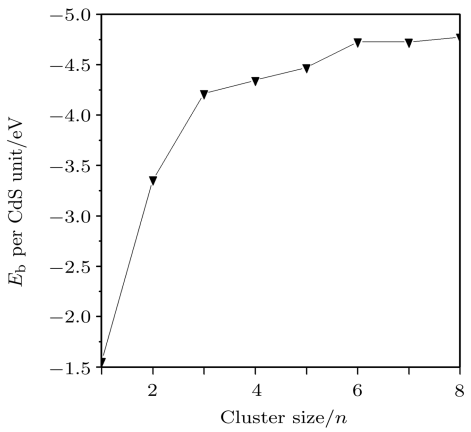



**Fig.6.** The binding energy per cadmium sulfide unit $E_b = (nE_{Cd} + nE_S - E_{(CdS)_n})/n$, where $n$ is the number of cadmium sulfide units, of CdnSn clusters is charted.

# 4. Conclusions

In summary, the global minima structures, binding energies per CdS unit, energy gap, and Mulliken atomic charges of $Cd_nS_n$ ($n = 1 - 8$) clusters have been obtained by GGA calculations in density functional theory combined with the simulated annealing. The following conclusions can be drawn: (A) the lowest energy structures of $Cd_nS_n$ are planar for $n \leq 3$; (B) the lowest energy structures of $Cd_nS_n$ clusters are the three-dimensional for $n = 4 - 8$, which can be regarded as being built from $Cd_2S_2$ rings and $Cd_3S_3$ rings; (C) the magic numbers of $Cd_nS_n$ clusters are $n = 3$ and 6.

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