Small clusters of II-VI materials: Zn_iS_i, $i=1-9$

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The improvements in the characterization of II-VI compound-based solar cells and the recent experimental characterization of small clusters and nanoparticles make the study of small II-VI clusters very interesting. In this work, the ground states of small Zn_iS_i clusters are studied, $i=1-9$. Ringlike structures have been found to be the global minima in the case of the smaller studied clusters, i.e., $i=1-5$, and three-dimensional spheroid structures for larger ones, $i=6-9$. This is due to the stability of obtuse S—Zn—S angles in the first case, and to the stability gained from higher coordination in the second case. The three-dimensional structures may be envisioned as being built from Zn_2S_2 and Zn_3S_3 rings, the last ring being the building block of the zinc-sulfide crystal structures, both zinc blende and wurtzite. As cluster size increases, the geometry of the Zn_3S_3 rings is closer to the one of bulk. Moreover, this structural tendency produces trends to bulklike properties in other properties such as cohesive energy and atomic charges.

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I. INTRODUCTION

Interest in II-VI compound semiconductors has grown spectacularly in recent years due to their paramount technological potential. Their special semiconductor properties make these compounds suitable for applications such as photovoltaic solar cells [1–10], optical sensitizers [11], photocatalysts [12,13], or quantum devices [14]. As can be appreciated, such important applicability has led to extensive investigation.

In addition to the importance of experimental research, theoretical studies are of great importance not only because of their ability to expand our understanding, but also because of their predictive power. Some theoretical studies of zinc sulfide have appeared in the literature [15,16]. Remarkable works are those of Muilu and Tappani [17,18], and Pollmann and co-workers [19–24]. Muilu and Pakkanen performed Hartree-Fock molecular orbital (HF-MO) calculations of small ZnS crystallites and surfaces. The smallest studied cluster was a Zn_3S_3 ring as occurring in wurtzite. They then built larger systems by adding similarly sized structures, arriving finally at a $Zn_{246}S_{240}$ structure. This was possible due to the transitional symmetry of two-electron integrals, which lowered the integral dependence from $O(N^3)$ to $O(N)$. Thus computational effort was reduced, and larger systems were analyzable. However, one of the main drawbacks of this method is that electron correlation is not taken into account.

To study bulk structures, density-functional theory (DFT) was used by Pollmann and co-workers. They investigated not only ZnS bulk structures but many II-VI combinations. First, they performed calculations at the local-density approximation (LDA) level of theory, and they found that lattice constants were adequately represented only if *d* orbitals were taken into account as valence electrons. Even in this case the obtained band energies were poor, placing the occupied *d* bands 3 eV too high. In order to overcome this shortcoming, they proposed an approach based on self-interaction-corrected pseudopotentials (SIC-PP). In this way, they improved considerably the band energies and band gaps, and demonstrated that these calculations are a valid tool in order to quantitatively study well-ordered, clean semiconductor surfaces.

In studying bulk and surface properties of crystals, cluster models are and have been widely used. Cluster properties change from molecular to bulk properties as size increases. Large enough clusters have bulklike properties, and may be used to simulate infinite systems. Nevertheless, the fact that cluster and nanoparticle characterization is becoming technologically possible have made clusters specially interesting in themselves. Therefore, the literature in the field is growing rapidly. Many experimental [25–30] and theoretical [31–36] studies have been reported concerning clusters of various compositions, which have important and interesting applications. For example, Fe_2O_3 nanoparticles can be precipitated in a gel, forming the so-called ferrogels. These compounds have electromagnetic properties, making them suitable for applications in human mobile protheses that are able to answer mental electrical messages.

Due to the interest in both II-VI compounds and clusters it occurred to us that it would be interesting to perform a theoretical study of II-VI compound clusters, fusing in this way both fields, as it is done in the case of carbon clusters such as fullerenes, which have photovoltaic applications [37,38]. In this paper calculated structure and properties of the zinc sulfide small clusters are reported. All the calculations have been performed at the Becke3 exchange potential and Lee-Yang-Perdew correlation potential (B3LYP) level of theory, combined with the Stevens, Krauss, Basch, and Jasien (SKBJ) relativistic pseudopotentials.

II. METHOD

All geometries were fully optimized using the B3LYP gradient-corrected density-functional method [39–42] analytic gradients. Harmonic vibrational frequencies were determined by analytical differentiation of gradients.

The relativistic compact effective core potentials and shared-exponent basis set [43] of SKBJ were used as the basic basis set in this study. The *d* electrons of Zn were included in the valence, and an extra *d* function was added

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TABLE I. Relative energies (kJ/mol) between two minima of the same cluster size, calculated with the three described basis sets.

	SKBJ (d)	SKBJ (exp)	TZ2P
$\Delta E\ (E_{GM^{(4)}}-E_{GM^{(4)}})$	117.27	130.62	118.32
$\Delta E\ (E_{GM^{(6)}}-E_{LM_1^{(6)}})$	38.40	35.22	42.25
$\Delta E\ (E_{GM^{(6)}}-E_{LM_2^{(6)}})$	75.15	56.52	70.29

on both Zn ($\alpha=0.3264$) and S ($\alpha=0.7$) atoms, due to their importance in the formation of bonds. We denote the final basis set used as SKBJ(d).

Because there are so many possible structures for these clusters, several starting points for these complete B3LYP/SKBJ(d) optimizations were generated using a simulated annealing approach at the Stewart semiempirical model parametrization (PM3) [44] level of theory. Of course, additional starting points were derived from simple chemical intuition.

All the geometry optimizations and frequency calculations were carried out with the GAUSSIAN94 [45] and GAUSSIAN98 [46] package. For the PM3 simulated annealing technique the HYPERCHEM [47] program was used.

A. Basis-set selection

In the previous section it was mentioned that the basis set used during these calculations was SKBJ(d). Although a larger basis set is not expected to change significantly the geometry of the obtained structures, the relative energies between them may be affected. In order to check the reliability of our SKBJ(d) basis set, single point energy calculations using larger basis sets were performed on several structures which will be detailed later. Two other basis sets were examined. The first was a simple expansion of the previously described SKBJ(d) basis. Two s and p functions (with $\alpha=1.335\,122,\ 1.120\,129$), one d ($\alpha=2.561\,376$), and one f ($\alpha=3.115\,413$) were added to the Zn basis. The SKBJ(d) basis was expanded for S as well with the two new s and p functions having exponents $\alpha=1.231\,541,\ 0.373\,393$, and the f function, $\alpha=0.593\,345$. All of these added functions were energy optimized at the second-order Moller-Plesset (MP2) level of theory using the GAMESS [48] package. As the SKBJ(d) basis set only has one d function on S, it was decided that upon the addition of another, the exponents of both should be energy optimized. The exponents for the two d functions in this expanded basis were 0.896 605 and 0.288 732. This expanded basis set will be referred to as SKBJ(exp). The second examined basis set was an all electron triple-ζ double polarization (TZ2P) basis ($14s11p6d2f/10s8p3d2f$) for Zn [49–51] and ($13s10p2d1f/6s5p2d1f$) for S [52,53]. The relative energies between two minima of each cluster size chosen is shown below in Table I.

These results demonstrate the reliability of the used SKBJ(d) basis set. The relative energies calculated using the various basis sets vary little, and the difference in CPU usage is great. Thus, we have chosen the SKBJ(d) basis to be used throughout this work.

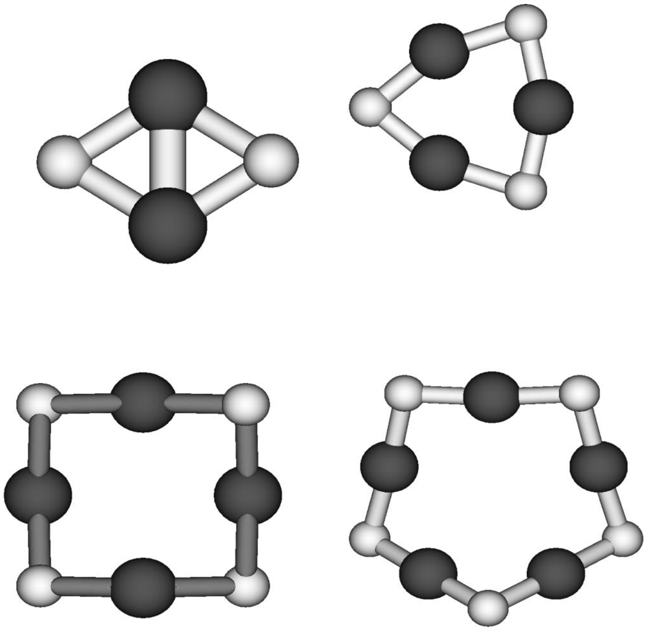

FIG. 1. Calculated global minima of Zn_iS_i, $i=2-5$, labeled, from left to right, $GM^{(2)}$, $GM^{(3)}$, and in the second row $GM^{(4)}$ and $GM^{(5)}$, respectively. The dark, larger atoms are those of Zn.

III. RESULTS AND DISCUSSION

A. Structure of the calculated minima of Zn_iS_i clusters. $i=1-9$

In this section the calculated minima are presented. Although our interest is mainly centered on global minima, structures and properties of higher-lying local minima are presented as well.

In order to show the calculated structures in a more understandable way, we have arbitrarily divided these clusters into two groups, according to the structure of the global minimum. In the first group, group 1, structures of the clusters Zn_iS_i, $i=1-5$, are included, where the global minima are planar or near-planar ringlike structures, and in the second group, group 2, the rest, $i=6-9$, are included, where the global minima are three-dimensional spheroids. A Bader analysis of all these structures has been performed as well. For that purpose the all electron 6-311G [49–50] basis for Zn and the 6-31G [54–58] basis for S were used.

The presented structures are labeled according to the following system: GM (global minimum) and LM (local minimum). The superscripts denote the number of ZnS units, and the subscripts denote the number of local minimum.

1. Group 1

As we have mentioned above, in this section we will describe the calculated structures of Zn_iS_i, $i=1-5$. The principal characteristic of the calculated global minima is that all are planar, except in the case of Zn_5S_5, which is quasiplanar. The planar Zn_5S_5 ring is a stationary point of Hessian order two, and lies 6.95 kJ/mol above the minimum. In Fig. 1 the calculated global minima of the different cluster sizes are presented, and the structures of the characterized local minima are shown in Fig. 2.

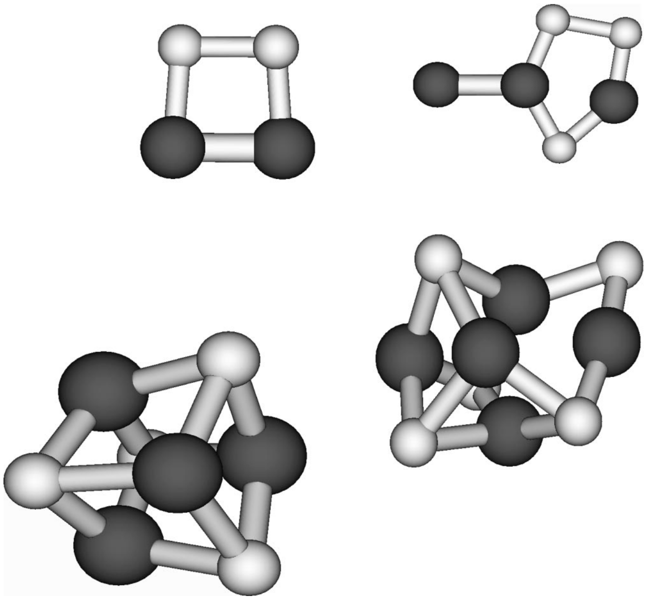

FIG. 2. Calculated local minima of Zn_iS_i, $i=2-5$, labeled from left to right, LM$^{(2)}$, LM$^{(3)}$ and in the second row LM$^{(4)}$ and LM$^{(5)}$, respectively.

A quick glance at this figure shows that while the calculated local minima of the smallest clusters, namely Zn_2S_2 and Zn_3S_3, are planar, the local minima of Zn_4S_4 and Zn_5S_5 are not. In Table II important values such as molecular geometries, energies, and the symmetry of the presented structures are shown.

TABLE II. Zn—S bond lengths, S—Zn—S angles, electronic energies, and symmetry groups of the structures of Figs. 1 and 2. For the local minima, energies relative to the corresponding global minimum are in kJ/mol.

	R(Zn—S) (Å)	α(S—Zn—S) (deg)	Point group	Electronic energies (hartree)
GM$^{(1)}$	2.09		$C_{\infty v}$	−236.229 939
GM$^{(2)}$	2.27	114.5	D_{2h}	−472.601 525
LM$^{(2)}$	2.34		C_{2v}	117.10
GM$^{(3)}$	2.21	157.8	D_{3h}	−709.004 295
LM$^{(3)}$	2.20–2.26	131.1–141.4	C_s	233.75
GM$^{(4)}$	2.19	177.4	D_{4h}	−945.365 754
LM$^{(4)}$	2.38	105.4	T_d	117.27
GM$^{(5)}$	2.18	178.9	C_s	−1181.711 233
LM$^{(5)}$	2.21–2.41	102.4–159.3	C_1	68.19

Zn_1S_1. GM$^{(1)}$ is obviously a linear structure which belongs to the $C_{\infty v}$ point group. However, while the molecular structure is trivial, the short Zn—S bond length should be pointed out.

Zn_2S_2. Both the global minimum, GM$^{(2)}$, shown in Fig. 1 and the next lower-lying local minimum, LM$^{(2)}$, in Fig. 2, have been found to be planar. LM$^{(2)}$ lies 117.10 kJ/mol above the global minimum. It seems logical that the GM$^{(2)}$ is the most energetically stable structure, since it contains the favorable cross-ring Zn-Zn interaction as well as four Zn—S bonds. Noticeable as well is the shorter Zn—S bond length of GM$^{(2)}$, while the Zn—Zn bond length is similar to that of LM$^{(2)}$. Nevertheless, Zn—S bond lengths are 0.18 Å longer than in Zn_1S_1. GM$^{(2)}$ belongs to the D_{2h} point group and LM$^{(2)}$ to the C_{2v} point group.

Zn_3S_3. GM$^{(3)}$ is depicted in Fig. 1 and LM$^{(3)}$ in Fig. 2. As in the case of Zn_2S_2 only planar structures have been found. This, of course, does not mean that the existence of nonplanar structures may be ruled out. However, all attempts to locate nonplanar local minima eventually led to planar structures.

The Bader analysis of this molecule shows a planar ring-like structure where each atom has a coordination number two; there are no Zn-Zn interactions as in GM$^{(2)}$. Nevertheless, as it may be viewed in Table II, the Zn—S bond length is 0.06 Å shorter than in GM$^{(2)}$, and the S—Zn—S angle is much more open, as allowed by the larger ring. This structure has D_{3h} symmetry. GM$^{(3)}$ is a very important structure, which will become more obvious later. Note that the two known crystal structures for zinc sulfide, both zinc blende and wurtzite, are built of Zn_3S_3 rings. LM$^{(3)}$ belongs to the C_s point group.

Zn_4S_4. The two characterized minima are shown in Fig. 1, GM$^{(4)}$, and Fig. 2, LM$^{(4)}$. This latter structure is especially interesting for two reasons. The first is that it is the first nonplanar minimum found. The second, very interesting as well, is that it can be viewed as being built from six equivalent units of an earlier presented structure: Zn_2S_2 rings as occurring in GM$^{(2)}$. The resulting structure has T_d symmetry. However, in these faces Zn—Zn bonds are not reported by the Bader analysis. The Zn—S bond is enlongered by 0.11 Å, and the S—Zn—S angle bent by 10° in comparison to GM$^{(2)}$. In this structure all the atoms have coordination number three, compared to GM$^{(4)}$, where each atom has coordination number two. Thus, one might think that the cage structure would be more stable. However, it is the planar structure that lies 117.27 kJ/mol lower in energy. This D_{4h} planar structure, compared to the already shown Zn_2S_2 and Zn_3S_3 rings, presents shorter Zn—S bond lengths, and the S—Zn—S angle is close to 180°. This tendency to form near-linear S—Zn—S angles is strong, and the geometrical constraints of the three-dimensional LM$^{(4)}$ result in a strained S—Zn—S angle of 105.4°, and therefore the planar ring is more stable.

Zn_5S_5. The two Zn_5S_5 minima characterized in this work are presented in Fig. 1, GM$^{(5)}$, and Fig. 2, LM$^{(5)}$. At this size, the strictly planar structure is not the global minimum. The structure when constricted to planarity yields a stationary point of Hessian order two; that is, it has two negative vibrational frequencies. Departing from that structure, a quasiplanar structure has been found to be the global minimum, GM$^{(5)}$, which lies 6.95 kJ/mol below the planar stationary point. Four Zn atoms are contained in the same plane, and the other, along with the two sulfur atoms bonded to it lie to one side of that plane. The remaining sulfur atoms alternate up and down around the ring. This structure allows Zn to form near linear S—Zn—S bonds, as occurring in GM$^{(4)}$.

As in the case of LM$^{(4)}$, LM$^{(5)}$ is three dimensional, and can be seen as being built from units of GM$^{(2)}$ and GM$^{(3)}$.

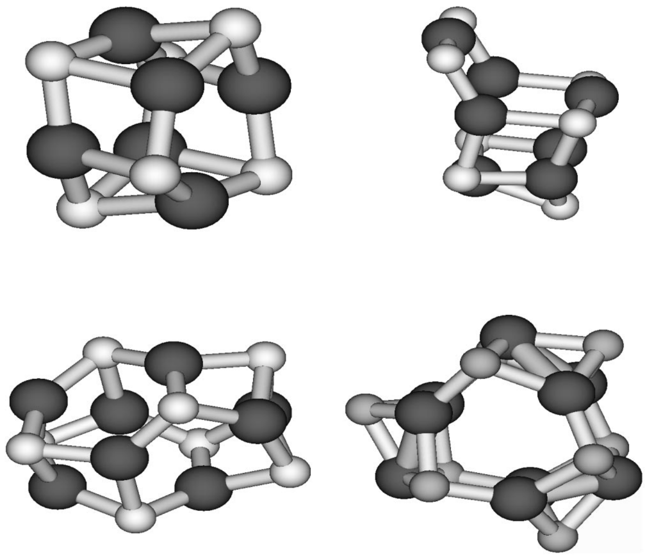

FIG. 3. Global minima of $\mathrm{Zn}_i\mathrm{S}_i$, $i=6-9$, labeled, from left to right, $\mathrm{GM}^{(6)}$, $\mathrm{GM}^{(7)}$ and in the second row $\mathrm{GM}^{(8)}$ and $\mathrm{GM}^{(9)}$, respectively.

Examining Fig. 2 one may picture $\mathrm{LM}^{(5)}$ as a structure of two joined rings of $\mathrm{Zn}_2\mathrm{S}_2$ and $\mathrm{Zn}_3\mathrm{S}_3$. In one side a $\mathrm{Zn}_2\mathrm{S}_2$ ring is contained, and in the other a bent $\mathrm{Zn}_3\mathrm{S}_3$ ring. These two structures are bonded on one extreme, where new $\mathrm{Zn}_2\mathrm{S}_2$ rings appear, and on the opposite extreme the $\mathrm{Zn}_3\mathrm{S}_3$ ring is bent. It is interesting to note that the Zn—S bond lengths are significantly longer than those of the planar structure. Various lengths are found in a wide range from 2.21 to 2.41 Å.

The global minima of the clusters in group 1 have been found to be planar rings, $\mathrm{GM}^{(1)}$, $\mathrm{GM}^{(2)}$, $\mathrm{GM}^{(3)}$, and $\mathrm{GM}^{(4)}$, or a near-planar ring, $\mathrm{GM}^{(5)}$. In these structures a strong tendency of Zn to form linear S—Zn—S bonds is seen. Nonplanar local minima have been found only for $\mathrm{Zn}_4\mathrm{S}_4$ and $\mathrm{Zn}_5\mathrm{S}_5$, and these can be pictured as being built from $\mathrm{GM}^{(2)}$- and $\mathrm{GM}^{(3)}$-like structures. Nevertheless, the internal geometry of these rings change significantly. In the three-dimensional structures Zn—S bond lengths are longer and S—Zn—S angles are more bent than in the planar and near-planar global minima.

2. Group 2

This group contains the clusters of which the global minima are nonplanar, $\mathrm{Zn}_i\mathrm{S}_i$, $i=6-9$. In Fig. 3 the global minima are shown, and in Fig. 4 the local minima are shown. In Table III the Zn—S bond lengths, S—Zn—S angles, electronic energies, and symmetry points of the presented structures are given.

Zn_6S_6. As has been mentioned already, the main difference at first sight between $\mathrm{GM}^{(6)}$ and the previously seen global minima is that $\mathrm{GM}^{(6)}$ is nonplanar. There has been a transition from a situation in which the planar ring structures were favored to a situation where three-dimensional structures are favored. Examining the trend in relative energies between the ring and three-dimensional structures for $i=4,5,6$, we find that the ring structure was more stable for $i=4$ by 117.27 kJ/mol. That difference was reduced to 68.19 kJ/mol for $i=5$, and here with $i=6$ the three-dimensional structure is finally more stable than the ring by 75.17 kJ/mol.

As in the case of the smaller three-dimensional structures, $\mathrm{GM}^{(6)}$ can be envisioned as being built up from smaller building blocks: $\mathrm{Zn}_2\mathrm{S}_2$ and $\mathrm{Zn}_3\mathrm{S}_3$ rings. In the case of $\mathrm{GM}^{(6)}$, it is formed by two bent $\mathrm{Zn}_3\mathrm{S}_3$ rings, stacked one on top of the other, which are linked together by $\mathrm{Zn}_2\mathrm{S}_2$ rings. The resulting structure has D_{3d} symmetry. Bader analysis of this molecule shows that there are no Zn-Zn interactions in this structure.

The six zinc atoms of $\mathrm{LM}_1^{(6)}$ form a octahedron. The sulfur atoms are placed as follows: two of them are found on op-

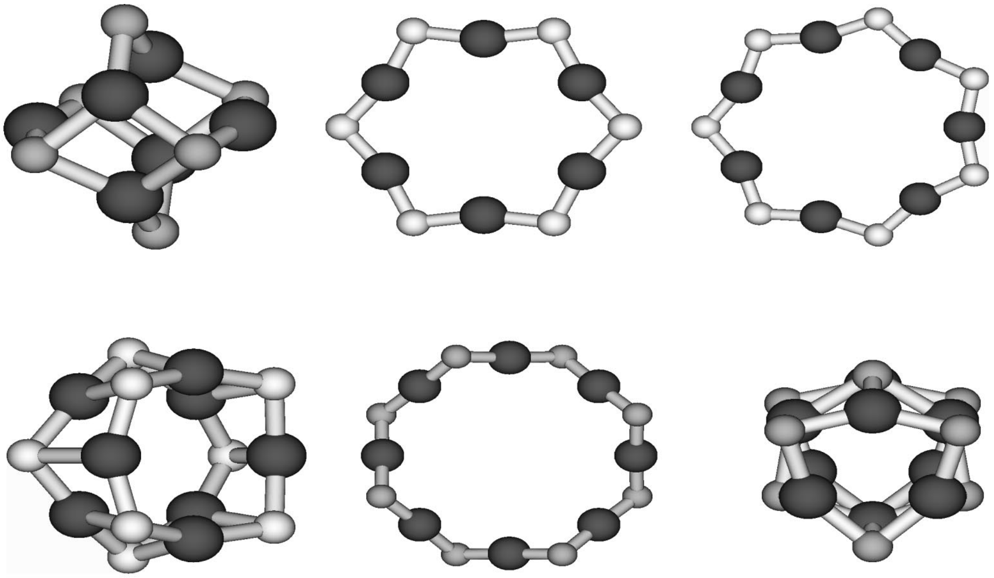

FIG. 4. Local minima of $\mathrm{Zn}_i\mathrm{S}_i$, $i=6-9$, labeled, from left to right, $\mathrm{LM}_1^{(6)}$, $\mathrm{LM}_2^{(6)}$, $\mathrm{LM}^{(7)}$ and in the second row $\mathrm{LM}_1^{(8)}$, $\mathrm{LM}_2^{(8)}$, and $\mathrm{LM}^{(9)}$, respectively.

TABLE III. Zn—S bond lengths, S—Zn—S angles, electronic energies, and point groups of the structures of Figs. 3 and 4. For the local minima, energies relative to the corresponding global minimum in kJ/mol.

	R(Zn—S) Å	α (S—Zn—S) (deg)	Point group	Electronic energies (hartree)
$\mathrm{GM}^{(6)}$	2.31–2.47	140.55	D_{3d}	−1418.072 375
$\mathrm{LM}_1^{(6)}$	2.40	96.7–155.2	D_{2d}	38.40
$\mathrm{LM}_2^{(6)}$	2.18	194.05	D_{6h}	75.15
$\mathrm{GM}^{(7)}$	2.20–2.58	97.4–175.0	C_s	−1654.415 922
$\mathrm{LM}^{(7)}$	2.18	198.30	D_{7h}	107.52
$\mathrm{GM}^{(8)}$	2.28–2.42	100.3–137.1	S_4	−1890.805 999
$\mathrm{LM}_1^{(8)}$	2.28–2.50	100.7–154.4	D_{4d}	78.94
$\mathrm{LM}_2^{(8)}$	2.18	177.79	D_{4d}	166.33
$\mathrm{GM}^{(9)}$	2.28–2.33	103.8–138.0	C_{3h}	−2127.178 171
$\mathrm{LM}^{(9)}$	2.29–2.45	92.5–147.2	D_{3d}	146.41

posite edges, and the rest are placed above the octahedral faces, two in the upper half and two in the lower half. This atomic placement leads to the formation of $\mathrm{Zn_2S_2}$ and $\mathrm{Zn_3S_3}$ rings as in previous three-dimensional structures. The resulting structure has D_{2d} symmetry.

Of course, an important question arises at this point: why is the planar structure, $\mathrm{LM}_2^{(6)}$, not the global minimum? In Table III it may be seen that the S—Zn—S angles in $\mathrm{LM}_2^{(6)}$ are far from linearity. Hence, this planar structure is not as stable as it is $\mathrm{GM}^{(4)}$ and $\mathrm{GM}^{(5)}$. Besides, the coordination number of $\mathrm{GM}^{(6)}$ is three for all atoms, while it is two for $\mathrm{LM}_2^{(6)}$. The combination of these factors makes the nonplanar $\mathrm{GM}^{(6)}$ more stable. In the case of $\mathrm{LM}_1^{(6)}$, all atoms have coordination number three, except the two sulfurs placed on the equatorial plane formed by the zincs of the octahedron. This structure is also more stable than the planar one, as can be seen in Table III.

$\mathrm{Zn_7S_7}$. As in $\mathrm{Zn_6S_6}$, nonplanar structures built from small cluster structures are found to be more stable than a ring structure. The S—Zn—S angles found in this ring structure are even further from linearity than those of $\mathrm{Zn_6S_6}$, and one may think that therefore the energy difference between $\mathrm{GM}^{(7)}$ and $\mathrm{LM}^{(7)}$ will be larger. Indeed, it is. The energy difference between $\mathrm{GM}^{(7)}$ and $\mathrm{LM}^{(7)}$ is 107.52 kJ/mol, as compared to 75.17 kJ/mol in the case of $\mathrm{Zn_6S_6}$.

$\mathrm{GM}^{(7)}$ can be seen as a structure of two joined ring structures: a $\mathrm{Zn_3S_3}$ and a bent $\mathrm{Zn_4S_4}$ ring. Half of the $\mathrm{Zn_4S_4}$ ring is linked to the $\mathrm{Zn_3S_3}$ ring, forming in this way new $\mathrm{Zn_2S_2}$ rings as in $\mathrm{GM}^{(6)}$, and a second bent $\mathrm{Zn_4S_4}$ ring.

$\mathrm{LM}^{(7)}$ is a planar ring, which belongs to the D_{7h} point group.

$\mathrm{Zn_8S_8}$. Three calculated structures of $\mathrm{Zn_8S_8}$ are presented, $\mathrm{GM}^{(8)}$ in Fig. 3, and $\mathrm{LM}_1^{(8)}$ and $\mathrm{LM}_2^{(8)}$ in Fig. 4. These structures are interesting, not only because of the reappearance of the building blocks, but also for the manner in which these blocks are used. $\mathrm{GM}^{(8)}$ may be viewed as a polyhedron formed by four long faces composed of one $\mathrm{Zn_2S_2}$ and one $\mathrm{Zn_3S_3}$ unit that are inverted on the next face. The polyhedron is closed on the top and the bottom by a $\mathrm{Zn_2S_2}$ unit. The resulting global minimum has S_4 symmetry.

$\mathrm{LM}_1^{(8)}$ is composed by two ''parallel'' $\mathrm{Zn_4S_4}$ units bonded together by $\mathrm{Zn_2S_2}$ units, as occurs in the previous structures. The resulting structure is of D_{4d} symmetry. $\mathrm{LM}_2^{(8)}$ is a ring structure with coplanar zinc atoms, where the sulfur atoms alternate up and down around the ring. This break in planarity can be understood looking at the S—Zn—S angles, which are close to 180, while if the molecule were planar, they will be far from linearity. Thus, bond lengths similar to other ring structures are found. However, the energy difference between $\mathrm{GM}^{(8)}$ and $\mathrm{LM}_2^{(8)}$ is even larger than in smaller cases, 166.33 kJ/mol, and this is due to the stability gained by the coordination number three, in a largely stable geometrical configuration.

$\mathrm{Zn_9S_9}$. The global minimum, $\mathrm{GM}^{(9)}$, is given in Fig. 3, and one local minimum, namely, $\mathrm{LM}^{(9)}$ in Fig. 4. As in the previous cases, these structures can be envisioned as being built with the same basic $\mathrm{Zn_2S_2}$ and $\mathrm{Zn_3S_3}$ blocks. In the case of $\mathrm{GM}^{(9)}$, $\mathrm{Zn_3S_3}$ units may be viewed as caps to a polyhedron joined by a ring formed of $\mathrm{Zn_2S_2}$ and $\mathrm{Zn_3S_3}$ units. The ring is formed by alternating one $\mathrm{Zn_3S_3}$ and two joined $\mathrm{Zn_2S_2}$ units. The resulting structure has C_{3h} symmetry.

$\mathrm{LM}^{(9)}$ is formed by three ''parallel'' $\mathrm{Zn_3S_3}$ rings, bonded together by $\mathrm{Zn_2S_2}$ units. It may be constructed by the addition of an extra $\mathrm{Zn_3S_3}$ unit to $\mathrm{GM}^{(6)}$. The resulting structure has D_{3d} symmetry.

It is interesting to notice that in all of these structures the coordination number of some atoms has increased from three to four.

Two main reasons have been given to explain the transition from ring global minima in group 1 to three-dimensional spheroid global minima in group 2: on one hand, the tendency to form linear S—Zn—S angles and, on the other hand, the achievement of a higher coordination number. We have seen that higher coordination is preferred when achieving that goal does not present too much of a strain on the bond angle. Three-dimensional spheroid structures have been found as well in other related compounds, i.e., zinc-oxide molecules [59].

It has been mentioned above that basically two building blocks are found in the construction of the most stable large

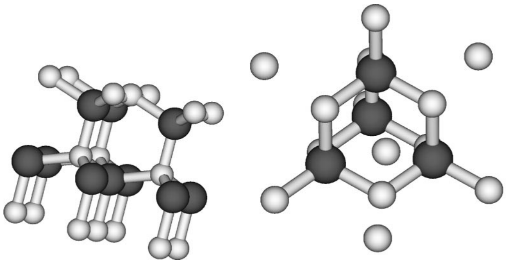

FIG. 5. Structures of wurtzite and zinc blende, respectively.

clusters, that is, Zn_2S_2 and Zn_3S_3 rings. When one analyzes the two crystal structures of zinc sulfide [60], i.e., zinc blende and wurtzite, depicted in Fig. 5, one finds that both structures have the same building block, Zn_3S_3 rings. The only difference is the form the rings are combined, resulting in a cubic structure, zinc blende, and a hexagonal one, wurtzite. In both crystals the geometry of the rings is similar, with Zn—S bond lengths of 2.34 Å and S—Zn—S angles of 109°. One may compare these values to the geometries of the Zn_3S_3 rings in the calculated global minima, given in Table IV.

As the cluster size increases, the observed ring geometry shows some convergence to that of the bulk structures; the angles are more bent and the bond lengths are already very similar. The fact that the angles are still 20° from those of the bulk may be explained by means of the coordination number. The coordination number in the bulk structures is four for all atoms, which geometrically allows a 109° angle. In the largest presented global minima, most of the atoms have coordination number three, which does not allow for such bent angles.

B. Natural charges

At this point we analyze the natural charges, which are given in Table V. The cationic nature of zinc and the anionic nature of sulfur can be observed in all the structures. The atomic charges are larger as cluster size increases, and a trend towards the charge separation in the bulk ($|1.43e|$) is seen.

C. Cohesive energy

The cohesive energy per zinc sulfide unit is calculated as $E_f = (iE_{Zn} + iE_S - E_{Zn_iS_i})/i$, where i is the number of ZnS units. The cohesive energy may be depicted versus the inverse of the cubic root of i, and then a line can be fit to the obtained points. Extrapolating it to $i^{-1/3}=0$, that is, to $i=\infty$, or the bulk, a theoretical value that can be compared to the experimental one is obtained [17,18]. We have taken that same approach. Nine points representing the cohesive energy of the studied global minima, given in Table VI, are plotted in Fig. 6. In fitting a line to the data, not all the points are representative, and only the points belonging to three-dimensional structures, i.e., $GM^{(6)}$ to $GM^{(9)}$ have been taken into account. A line was fit to the cohesive energy of $GM^{(6)}$ to $GM^{(9)}$ versus $i^{-1/3}$, and it was found to have the equation $y = 563.358 - 291.893x$. The correlation of this line is 0.998 58, which is some indication that we have properly located the global minima of such clusters. The extrapolated value, as is obvious from the linear equation, is 563.358 kJ/mol, which represents 92.73% of the experimental value 607.51 kJ/mol.

These results may be compared to those obtained by Muilu and Pakkanen [17,18]. As it has been mentioned earlier, they used a HF-MO method to study ZnS clusters. They performed calculations for clusters of different size, the largest one being of size $Zn_{240}S_{240}$. Their best extrapolated value was 520.72 kJ/mol, 85.7% of the experimental. The fact that electron correlation is taken into account in our calculations explains why we obtain results closer to the experimental value, even with smaller clusters.

TABLE IV. Geometries of the Zn_3S_3 rings in the calculated global minima and bulk structures.

	Zn—S (Å) (range)	Zn—S (Å) (average)	S—Zn—S (deg) (range)	S—Zn—S (deg) (range)
$GM^{(3)}$	2.21	2.21	157.83	157.8
$GM^{(6)}$	2.31	2.31	140.55	140.6
$GM^{(7)}$	2.20–2.33	2.28	136.5–161.9	145.0
$GM^{(8)}$	2.28–2.40	2.33	125.6–137.15	130.9
$GM^{(9)}$	2.28–2.39	2.32	127.2–138.0	130.2
Bulk		2.34		109

TABLE V. Natural charges (e) of the shown global minima.

	Zn	S
$GM^{(1)}$	0.900	−0.900
$GM^{(2)}$	1.159	−1.159
$GM^{(3)}$	1.183–1.184	−1.183–−1.184
$GM^{(4)}$	1.200	−1.200
$GM^{(5)}$	1.182–1.216	−1.174–−1.224
$GM^{(6)}$	1.270	−1.270
$GM^{(7)}$	1.194–1.269	−1.217–−1.285
$GM^{(8)}$	1.276–1.291	−1.279–−1.288
$GM^{(9)}$	1.285−1.293	−1.287–−1.297

TABLE VI. Cohesive energy E_f (kJ/mol) of characterized global minima.

	E_f (kJ/mol)
$GM^{(1)}$	99.99
$GM^{(2)}$	285.94
$GM^{(3)}$	375.21
$GM^{(4)}$	392.73
$GM^{(5)}$	394.85
$GM^{(6)}$	403.12
$GM^{(7)}$	410.21
$GM^{(8)}$	417.18
$GM^{(9)}$	423.43

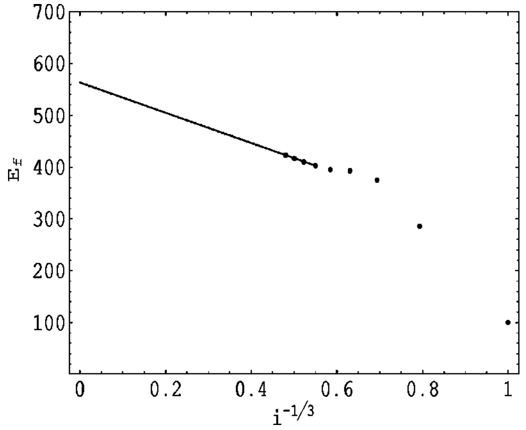

FIG. 6. Cohesive energy (kJ/mol) vs the inverse of the cubic root of ZnS units ($i^{-1/3}$).

IV. CONCLUSIONS

There are two main factors determining whether a ring or three-dimensional structure will be the global minimum for the small zinc-sulfide clusters: the stability of very obtuse S—Zn—S bond angles, and the stability gained from higher coordination. For Zn_iS_i , $i=1-5$, the first term outweighs the second and ring structures are predicted to be the global minima. For $i=6$ and greater, however, the size of the cluster allows for both obtuse S—Zn—S bond angles and higher coordination in the three-dimensional spheroid structures, making these the most stable.

These three-dimensional clusters can be envisioned as being built of smaller building blocks, basically Zn_2S_2 and Zn_3S_3 rings. The crystal structures of zinc sulfide, zinc blende and wurtzite show Zn_3S_3 rings as building blocks. The geometry of these rings in three-dimensional clusters is shown to have a trend toward bulklike geometries, even in such small clusters. This trend appears as well in other properties, such as cohesive energy or atomic charges. We find, therefore, a unequivocal trend to bulklike properties even in such small systems.

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[1] A. Kampmann and D. Lincot, J. Electroanal. Chem. **418**, 73 (1996).
[2] Y. Y. Loginov, K. Durose, H. M. Al-Allak, S. A. Galloway, S. Oktik, A. W. Brinkman, H. Richter, and D. Bonnet, J. Cryst. Growth **161**, 159 (1996).
[3] A. Niemegeers and M. Burgelman, J. Appl. Phys. **81**, 2881 (1997).
[4] K. Li, A. T. S. Wee, J. Lin, K. L. Tan, L. Zhou, S. F. Y. Li, Z. C. Feng, H. C. Chou, S. Kamra, and A. Rohatgi, J. Mater. Sci.: Mater. Electron. **8**, 125 (1997).
[5] K. Omura, A. Hanahusa, T. Arita, H. Higuchi, T. Aramoto, T. Nishio, S. Sibutani, S. Kumazawa, M. Murozono, Y. Yabuuchi, and H. Takakura (unpublished).
[6] C. Ferekides and J. Britt, Sol. Energy Mater. Sol. Cells **35**, 255 (1994).
[7] H. C. Chou, A. Rohatgi, N. M. Jokerst, S. Kamra, S. R. Stock, S. L. Lowrie, R. K. Ahrenkiel, and D. H. Levi, Mater. Chem. Phys. **43**, 178 (1996).
[8] S. Naseem, D. Nazir, R. Mumtaz, and K. Hussain, J. Mater. Sci. Technol. **12**, 89 (1996).
[9] J. Touukova, D. Kindl, and J. Tousek, Thin Solid Films **293**, 272 (1997).
[10] T. L. Chu and S. S. Chu, Solid-State Electron. **38**, 533 (1995).
[11] P. J. Sebastian and M. Ocampo, Sol. Energy Mater. Sol. Cells **44**, 1 (1996).
[12] A. J. Hoffman, G. Mills, H. Yee, and M. R. Hoffmann, J. Phys. Chem. **96**, 5546 (1992).
[13] S. Kuwabata, K. Nishida, R. Tsuda, H. Inoue, and H. Yoneyama, J. Electrochem. Soc. **141**, 1498 (1994).
[14] E. Corcoran, Sci. Am. **263** (11), 74 (1990).
[15] J. L. Martins and N. Troullier, Phys. Rev. B **43**, 2213 (1991).
[16] Y. N. Xu and W. Y. Ching, Phys. Rev. B **48**, 4335 (1993).
[17] J. Muilu and T. A. Pakkanen, Surf. Sci. **364**, 439 (1996).
[18] J. Muilu and T. A. Pakkanen, Phys. Rev. B **49**, 11 185 (1994).
[19] P. Schroer, P. Kruger, and J. Pollmann, Phys. Rev. B **47**, 6971 (1993).
[20] P. Schroer, P. Kruger, and J. Pollmann, Phys. Rev. B **48**, 18 264 (1993).
[21] P. Schroer, P. Kruger, and J. Pollmann, Phys. Rev. B **49**, 17 092 (1994).
[22] D. Vogel, P. Kruger, and J. Pollmann, Phys. Rev. B **52**, 14 316 (1995).
[23] J. Pollmann, P. Kruger, M. Rohlfing, M. Sabisch, and D. Vogel, Appl. Surf. Sci. **104/105**, 1 (1996).
[24] D. Vogel, P. Kruger, and J. Pollmann, Phys. Rev. B **54**, 5495 (1996).
[25] A. Ecker, E. Weckert, and H. Schnockel, Nature (London) **387**, 379 (1997).
[26] R. Rousseau, G. Dietrich, S. Kruckeberg, K. Lutzenkirchen, D. Marx, L. Schweikhard, and C. Walther, Chem. Phys. Lett. **295**, 41 (1998).
[27] J. Cizeron and M. P. Pileni, J. Phys. Chem. B **101**, 8887 (1997).
[28] V. S. Gurin, J. Phys. Chem. **100**, 869 (1996).
[29] B. Guo, K. Kerns, and A. Castleman, Science **255**, 1411 (1992).
[30] B. Guo, S. Wei, J. Purnell, S. Buzza, and A. Castleman, Science **256**, 515 (1992).
[31] J. E. Fowler and J. M. Ugalde, Phys. Rev. A **58**, 383 (1998).
[32] T. Qureshi and V. Kumar, e-print http://www.lanl.gob.abs/cond-mat/9806167.
[33] A. Tomasulo and M. V. Ramakrishna, Chem. Phys. **210**, 55 (1996).

[34] P. Fuentealba and O. Reyes, J. Phys. Chem. A **103**, 1376 (1999).

[35] M. Haser, U. Schneider, and R. Ahlrichs, J. Am. Chem. Soc. **114**, 9551 (1992).

[36] L. Lou, T. Guo, P. Nordlander, and R. E. Smalley, J. Chem. Phys. **99**, 5301 (1993).

[37] P. V. Kamat, I. Bedja, and S. Hotchandani, J. Phys. Chem. **98**, 9137 (1994).

[38] M. Freemantle, Chem. Eng. News **77**, 15 (1999).

[39] P. Hohemberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[40] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[41] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[42] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[43] W. J. Stevens, M. Krauss, H. Basch, and P. G. Jasien, Can. J. Chem. **70**, 612 (1992).

[44] J. J. P. Stewart, J. Comput. Chem. **12**, 320 (1991).

[45] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Allaham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN94 B.2., Gaussian, Inc., Pittsburg PA, 1995.

[46] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, B. J. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ciolowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martins, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, GAUSSIAN 98 (Revision A5), Gaussian, Inc., Pittsburgh PA, 1998.

[47] HyperChem™, Release 4.5 for Windows, Molecular Modeling System, Copyright 1994, 1995 Hypercube, Inc.

[48] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993) (GAMESS package).

[49] A. J. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).

[50] P. J. Hay, J. Chem. Phys. **66**, 4377 (1977).

[51] D. M. Hood, R. M. Pitzer, and H. F. Schaefer, J. Chem. Phys. **71**, 705 (1979).

[52] A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).

[53] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).

[54] R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **54**, 724 (1971).

[55] W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972).

[56] P. C. Hariharan and J. A. Pople, Mol. Phys. **27**, 209 (1974).

[57] M. S. Gordon, Chem. Phys. Lett. **76**, 163 (1980).

[58] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973).

[59] E. C. Behrman, R. K. Foehrweiser, J. R. Myers, B. R. French, and M. E. Zandler, Phys. Rev. A **49**, 1543 (1994).

[60] http://www.molecules.org/binarycpds.html