

Computational Evidence of Bubble ZnS Clusters

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Energy minimized structures of $(\text{ZnS})_n$ clusters, with n ranging from 10 to 47, have been generated using simulated annealing techniques based on interatomic potentials. The clusters have “bubble” like polyhedral structures, in which all of the atoms are three coordinated, rather than the densely packed bulklike structures. Density functional theory calculations also show that the bubble clusters are more stable than the bulklike clusters.

1. Introduction

Clusters ranging in size between a small number and several thousand atoms bridge the gap between molecules and the bulk and exhibit a variety of unusual phenomena. Small clusters have been a theme of theoretical and experimental interest for many years.¹ The II–VI and III–V compound semiconductors have been extensively studied because of their wide range of applications, in photovoltaic solar cells, catalysis, quantum devices and dots; but there is still very little understanding of the structure and the properties of such clusters. Much recent research has been directed toward the realm of nanoparticle production, but no clear consensus has emerged as to the structures of the most stable clusters. Density functional theory calculations on GaN suggest the possibility for the formation of GaN nanotubes,² with electronic properties different from those of carbon nanotubes. For some systems, such as BN, there is the interesting suggestion of the possibility of forming fullerene-like structures.³ Computational techniques have been previously used to study the stability of such clusters for III–V systems,^{4,5} but only local minimization techniques were employed, which usually do not generate the most stable cluster structures. Furthermore, no comparison between the stability of the fullerene-like clusters and the bulklike clusters has yet been made. In this paper, we use a simulated annealing method to obtain the global minima of several ZnS clusters. We also report the comparison of the energies of these clusters with the energies of bulklike clusters. Calculations reveal a fascinating class of new “bubble” like clusters with surprisingly open structures.

2. Methodology

Our theoretical analysis aims to predict the geometries and energies of ZnS clusters, with a size ranging from 10 to 47 ZnS units. The simulated annealing procedure uses interatomic potentials, but *ab initio* calculations have been performed in order to check the reliability of the interatomic potentials in some key cases and to provide more accurate values of the cluster energies.

Because of the large number of possible structures that a given cluster could assume, we performed simulated annealing in order to attempt to identify the global minimum for every cluster at room temperature. A 50ps molecular dynamics simulation is run for every cluster at 3000 K (using the DL_POLY code⁶). After that, the system is cooled, running simulations of 50 ps every 10 K until the temperature is 300 K.

There is, of course, no method of calculating unambiguously the global minimum for systems; all available methods can generate local minima. We tried to minimize the possibility of reaching a local minimum by performing at least three different simulated annealing processes for each cluster. In some cases, the final cluster structure is the same regardless of the process, but in others, each simulated annealing process gives slightly different geometries. In these cases, we chose the most stable cluster configuration as the closest structure to the global minimum. The high temperature used for the initial steps of the simulated annealing has the effect of removing any possible influence that the initial configuration could have on the final structure. Indeed, we found that the same structures were obtained starting from a random arrangement of atoms or from a cluster cut from the bulk crystal.

The final cluster structures obtained with the simulated annealing procedure are then optimized employing three different methods. The first uses interatomic potentials and is carried out with the GULP code⁷ to minimize the energy of the clusters. The potential parameters were obtained by careful fitting to reproduce crystal and molecular properties of ZnS. Details of the parameters can be found in reference.⁸

Two *ab initio* methods were also employed in order to provide more accurate energies. We studied small clusters using hybrid density functional theory calculations, with the B3LYP exchange-correlation functional^{9,10} as implemented in the Gaussian 98 code.¹¹ We used the Stevens, Krauss, Basch, and Jasien (SKBJ) valence basis set,¹² with 10 core electrons modeled by effective core potentials. An extra d function was added on both Zn and S. This kind of calculation is denoted B3LYP/SKBJ(d). Previous studies on ZnS clusters have proved the reliability of this basis set.¹³ For bigger clusters, we also performed pure density functional theory calculations using the DMol³ code.^{14,15} We used the PW91 exchange-correlation functional,^{16,17} with

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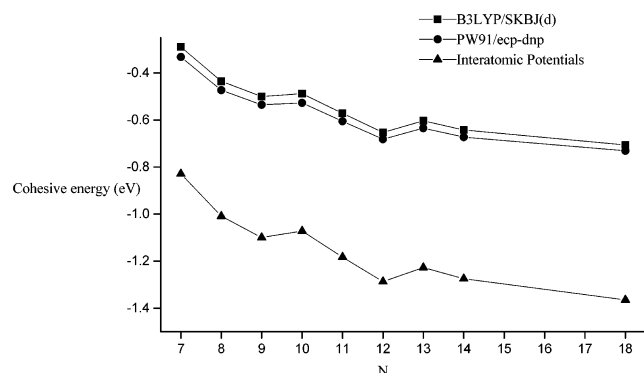


Figure 1. Cohesive energies calculated with the three methods used in our study, as a function of the cluster size. Data obtained from hybrid DFT calculations (B3LYP/SKBJ(d)) are represented by solid squares, data obtained from pure DFT calculations (PW91/ecp-dnp) by solid circles and data obtained from interatomic potential calculations by solid triangles. Energies are calculated by performing geometry optimizations (with the three methods) on the cluster structures obtained with simulated annealing.

effective core potentials and a double numerical plus polarization basis set. We denote this calculation PW91/ecp-dnp.

We checked that the three methods employed provide similar results. The interatomic potential parameters were developed to predict bulk properties, where atoms always form $(\text{ZnS})_3$ rings. Therefore, we use the energy per ZnS unit in a $(\text{ZnS})_{3\text{-ring}}$ as the reference energy for the three methods. Figure 1 shows the plot of the cluster cohesive energy as a function of the size, where this energy for a $(\text{ZnS})_n$ cluster is defined as

$$E_{\text{cohesive}} = \frac{\left\{ [E(\text{ZnS})_n]_{\text{Cluster}} - n \left[\frac{E(\text{ZnS})_{3\text{-ring}}}{3} \right] \right\}}{n}$$

It can be observed that the two ab initio methods provide remarkably similar results. Because B3LYP/SKBJ(d) are much more time-consuming calculations, PW91/ecp-dnp is the method of choice for calculating accurate cluster energies for bigger clusters. It is gratifying that the trend described by the interatomic potential calculations is the same as that calculated with ab initio methods. It suggests that they can be used to calculate the relative stability of the clusters with acceptable accuracy.

3. Results and Discussion

It has commonly been assumed that large $(\text{ZnS})_n$ clusters ($n > 20$) should have bulklike structures, with most of the atoms four coordinated. However, our studies show that up to $n = 47$, spheroidal clusters with only three coordinated atoms are more stable than the bulklike ones. We denote these spheroidal open clusters as “bubble clusters”. These clusters are formed by the spatial arrangement of 4, 6, and 8 atom rings, where all of the atoms are three coordinated. The rings are nonplanar distorted polygons; bond distances and bond angles in the same ring are unequal. The number of rings appearing in the lowest energy structure of a $(\text{ZnS})_n$ cluster can be predicted following these two formulae:

$$N_{6\text{-ring}} = n - 4 - N_{8\text{-ring}}$$

$$N_{4\text{-ring}} = 6 + N_{8\text{-ring}}$$

which can be deduced from the Euler’s Law, which states that for a closed structure formed by polyhedra the number of

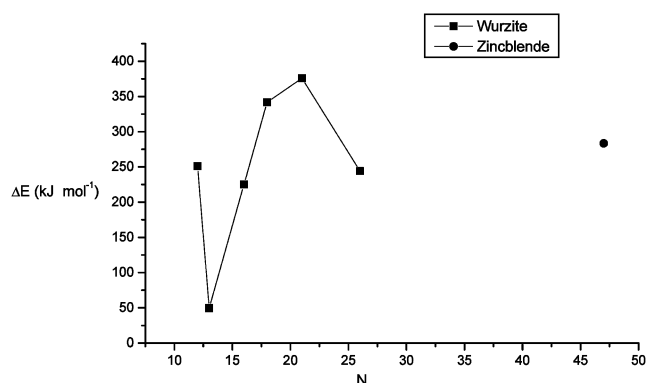


Figure 2. Difference between the energies of bulklike clusters and the energies of bubble clusters, as a function of cluster size. Energies are calculated by performing geometry optimizations of the clusters, with PW91/ecp-dnp level of theory. The zero energy level for each cluster is the energy of the bubble cluster with the same number of ZnS units, calculated with PW91/ecp-dnp as well.

vertexes plus the number of faces will always equal the number of edges plus two. We note that when there are no 8-rings, there must necessarily be six 4-rings.

Our calculations suggest that the presence of 8-rings reduces the stability of the structure. For some clusters, we obtained more than one spheroidal structure and the most stable is that with the least number of 8-rings. For example, for $(\text{ZnS})_{13}$, we obtained two local minima with 8-rings (previously reported¹⁸) but the lowest energy cluster is formed only by 4- and 6-rings. One of the two local minima has one 8-ring and is more stable than the other local minimum, which has two 8-rings. However, we note that in some cases, our simulations did generate structures with octagons. Another characteristic of the stoichiometric bubble clusters is that they cannot contain any odd numbered polygons, which would force Zn–Zn or S–S bonds, leading to high energies. Further calculations are in progress to estimate the energetics associated with nonstoichiometry.

Bulk ZnS occurs in two common polymorphs: zinc blende (or sphalerite) and wurtzite. In both structures, the atoms are tetraordinated. Zinc blende is based on a face-centered cubic array of atoms, whereas wurtzite is derived from a hexagonal close-packed array. In the two structures, the nearest neighbor connections are the same, but the distances and angles to more distant neighbors are different. To give added confidence in our results, we have cut clusters from the wurtzite and zincblende structures and compared the energies of these clusters with the energies of the bubble clusters, as shown in Figure 2. We can see that bubble clusters are always more stable than bulklike clusters. Only one with the zinc blende structure is shown, as wurtzite clusters are more stable than those based on zinc blende, as the former clusters usually have lower dipole moments than the latter. Both bulklike clusters have some two coordinated atoms. The relaxation of the structures removes in part the dipole, but some atoms remain two coordinated. On the other hand, in all of the spheroidal clusters, the total dipole is very small and there are no two coordinated atoms, which will be one factor promoting the stability of these structures.

Although atoms in bubble clusters are more stable than in bulklike clusters, they are less stable than in any of the two bulk polymorphs. We studied the possibility of forming crystals using bubble clusters as building blocks. Because the $(\text{ZnS})_{12}$ cluster has the structure of a sodalite cage, we repeated it periodically in three dimensions to build a ZnS-based material isomorphous with siliceous sodalite. The resulting crystal is based on the structure of a bubble cluster, but with all of the

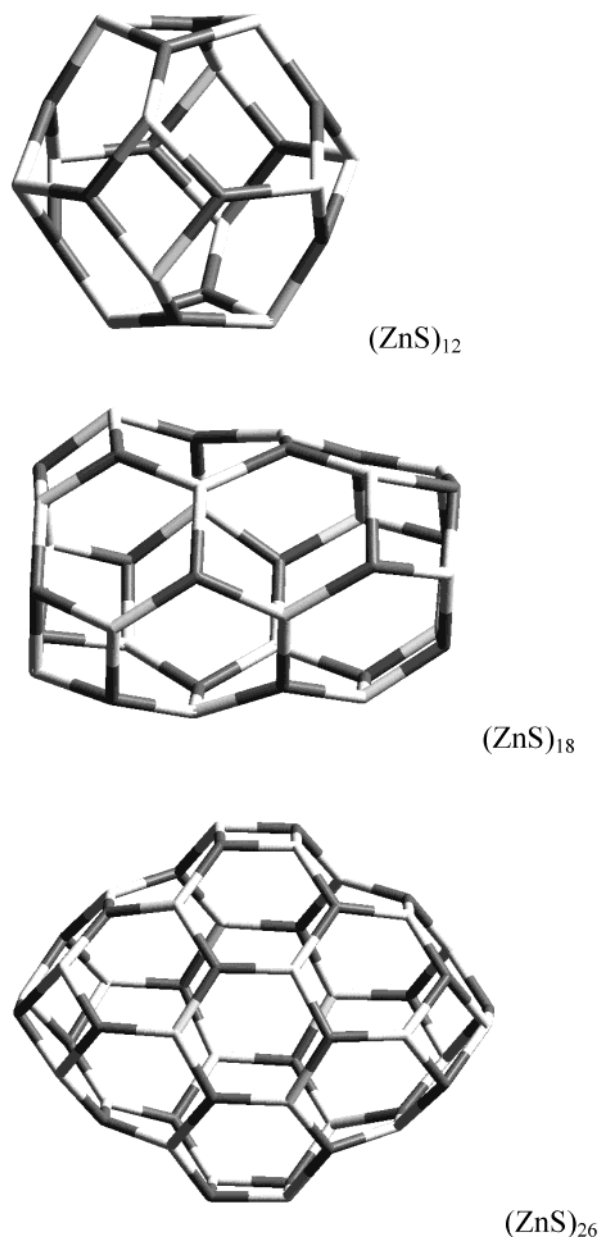


Figure 3. Structures of selected bubble clusters. Light grey sticks refer to sulfide atoms and dark grey sticks to zinc atoms.

atoms being four coordinated, which would increase its stability. PW91/ecp-dnp calculations show that this is a metastable structure compared to both zinc blende and wurtzite polymorphs (the difference in energy is around 25 kJ/mol per ZnS unit). We should also consider another interesting possible bulk structure. Because all of the bubble clusters are three coordinated, it would be useful to study the possibility of creating a bulk material in which all of the atoms are three coordinated. With PW91/ecp-dnp calculations, we found that a planar graphite-like structure (composed of layers of ZnS hexagons) is a metastable phase, which is 49.4 kJ/mol per ZnS unit less stable than the zinc blende phase. All of these features suggest that there must be some cluster size above which bubble clusters start being less stable than bulklike clusters. Global minimization techniques applied to bigger clusters than the ones we have studied in this paper could provide useful information about this transition between bubble and bulklike structures and are under way.

Figures 3 and 4 show some particularly interesting cluster structures: (ZnS)₁₂, (ZnS)₁₈, (ZnS)₂₆, and (ZnS)₄₇. (ZnS)₁₂ has

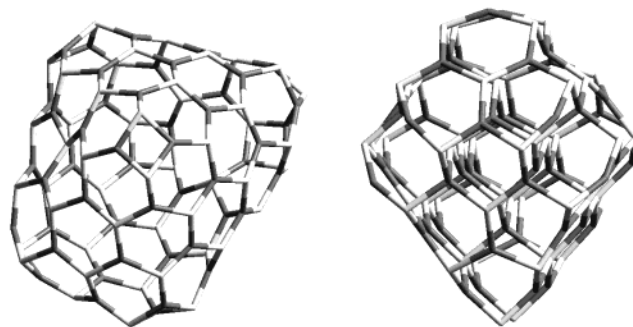


Figure 4. Structures of two (ZnS)₄₇ clusters. The bubble cluster is on the left and the bulklike cluster on the right. Light grey sticks refer to sulfide atoms and dark grey sticks to zinc atoms.

six 4-rings and eight 6-rings forming a spheroidal structure with the shape of the beta cage (building units of Sodalite). This cluster is highly symmetric, belonging to the D_{4h} symmetry point group, and is the smaller cluster in which there are no 4-rings sharing edges; 6-rings separate the 4-rings, reducing considerably the structural strain. (ZnS)₁₈ is characterized by a tubular structure and belongs to symmetry point group S_{2v} and (ZnS)₂₆ is an ellipsoid and belongs to symmetry point group D_{2h} .

The (ZnS)₄₇ bubble cluster includes an 8-ring, suggesting that it might be possible to find a cluster that is even more stable. The structure consists of seven 4-rings, forty-two 6-rings, and one 8-ring. This bubble is not symmetric, but there is an interesting arrangement of the rings: the structure is polyhedral-like and the 4-rings make the seven corners. The volume of the cage is 1375 Å³, the total surface area is 1666 Å², and the radius is approximately 15 Å. Gavartin and Stoneham¹⁹ studied the properties of a (ZnS)₄₇ cluster with zinc blende structure, which is shown in the right side of Figure 4. Ab initio PW91/ecp-dnp calculations show that the bubble structure of this (ZnS)₄₇ cluster is 283 kJ/mol more stable than the zinc blende cluster, as can be observed in Figure 2.

4. Summary

We have applied global minimization techniques to show that bubble clusters are more stable than bulklike stoichiometric clusters. Both, interatomic potentials methods and ab initio calculations, predict this feature; and the bubble clusters obtained with simulated annealing methods are around 200 kJ/mol more stable than bulklike clusters.

Bubble clusters are assembled from 4- and 6-rings, although in some cases octagons also appear, which decrease the stability. Many questions are now open. What are the physical and chemical properties of these clusters? Is it possible to form ZnS nanotubes? Further investigations are in progress, to answer these questions. We also note that in our study, only stoichiometric clusters were investigated, as in experimental studies on onion fullerene-like clusters of BN.²⁰ It may be that under certain conditions, the growth of ZnS clusters, occurs via structures whose composition is nonstoichiometric, which may favor more bulklike structures. The present study, however, clearly shows that large spheroidal stoichiometric clusters of ZnS may be stable. It would be of interest to address experimental studies on the synthesis of these small clusters, possibly using appropriate templates.

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