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ZnS bubble clusters with onion-like structures

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Following recent studies which showed that the most stable structures for $(ZnS)_n$ clusters (n = 10–47) are the so-called "bubble clusters", in which all the atoms are three-coordinated, we have used simulated annealing techniques to find the most stable structure for a larger cluster, $(ZnS)_{60}$. We find an onion-like structure, with one small cluster enclosed inside a bigger one. The inner cluster has the structure of a sodalite cage. Bonding between the inner and the outer clusters creates a network of four-coordinated atoms.

Investigation of ZnS clusters is in part motivated by the applications in nanotechnology of II–VI and III–V semiconductor clusters;[1] indeed, nanoparticles of these compounds have been widely studied. However, there is still controversy as to the structure of the smaller clusters. CdS nanoclusters with the zincblende structure (tetracoordinated atoms) were synthesised using organic ligands to cap the surface atoms;[2] but when no ligands are present, more open structures are found. In the last decade, theoretical studies have suggested the possibility of forming II–VI and III–V nanoclusters with fullerene-like structures.[3,4] Application of minimisation techniques indicated that fullerene-like clusters might be local minima which were less stable than bulk-like clusters. BN fullerenes have been observed experimentally:[5,6] they are stoichiometric with an octahedral shape. Similar results were found for MoS_2 fullerenes.[7]

Our recent simulated annealing studies of small ZnS clusters found that the most stable structures are "bubble clusters"[8] (fullerene-like structures made of 4-, 6- and 8-membered rings) and not bulk-like clusters. We now apply the same technique to calculate the most stable structure of a bigger ZnS cluster, $(ZnS)_{60}$. The first step in a simulated annealing calculation is to run a 50 ps molecular dynamics simulation at 3000 K of a $(ZnS)_{60}$ cluster with a randomly chosen initial structure. Any order present in the cluster is removed by this high temperature simulation. In order to generate the most stable structure, we then cool the system by performing a succession of 50 ps simulations with the temperature of each being 10 K less than the previous one. This slow decrease in energy allows the system to reach the equilibrium structure at each temperature, so that the final structure at 300 K is likely to be the global minimum. However, since it is always possible that the system is trapped in a local minimum close to the global one, we performed three different simulated annealing calculations. The molecular dynamics simulations were performed with the DL_POLY code[9] and the interatomic potential used to model the system is described in ref. 10. Once the most stable structure of the cluster had been found, we then optimised it again, but this time using density functional theory. We utilised the Dmol^3 code[11,12] with the PW91 exchange-correlation functional,[13,14] effective core potentials and a double numerical plus polarisation basis set.

Previous work[8] established that the most stable structures of $(ZnS)_n$ clusters, with n = 10–47, are hollow polyhedral structures formed by hexagons and squares. There are 6 of the latter, unless octagons are present, in which case for each octagon there is an additional square. In all clusters, both types of atom are three-coordinated. It is interesting to note that a wide range of systems show the same tendency to form open polyhedral clusters when the cluster size is small, although, as yet, there is no simple explanation for this observation.

The structure of the $(ZnS)_{60}$ cluster obtained with the simulated annealing procedure is shown at the top of Fig. 1. To make it clearly visible, there is a circle surrounding the inner core of the cluster, which is a $(ZnS)_{12}$ bubble that is shown separately at the bottom right of the figure. The outer cluster, a $(ZnS)_{48}$ bubble, is shown at the bottom left of Fig. 1. Neither of these two bubble clusters contain octagons: $(ZnS)_{12}$ is formed of 6 squares and 8 hexagons and $(ZnS)_{48}$ is formed of 6 squares and 44 hexagons. The squares of both clusters are placed in the vertices of two octahedra and are very well aligned, so that both octahedra share the same axis. This can be clearly seen in Fig. 2, where the squares have been highlighted. The diameter of the whole particle is 1.65 nm and that of the innermost bubble is 0.75 nm. This innermost bubble has the same configuration as the sodalite cage, which is a very common structural unit that is present in several zeolites.

All these findings agree with the observed behaviour of the analogous BN system. High resolution transmission electron microscope (HRTEM) studies[5,6] have shown that BN forms fullerene-like structures, with a small number of layers (typically $\leq$3). Their B/N stoichiometry is $\sim$1. They also form concentrically arranged octahedral cages, with the smallest inner cage very often being a $(BN)_{12}$ cluster.

In single-shell bubbles, like any of the $(ZnS)_n$ bubbles with n = 10–47, all atoms have a coordination number of only three. In the $(ZnS)_{60}$ double bubble, there are many four-coordinated atoms. Fig. 3 shows another view of the particle, highlighting the four-coordinated atoms as well as the atoms bonded to them. Most of the

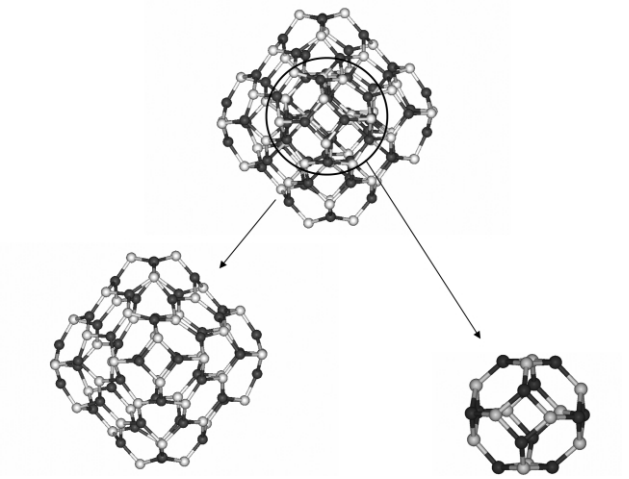

Fig. 1 Structure of the $(ZnS)_{60}$ cluster. The central cluster is the double bubble. The innermost encircled shell is shown separately in the right-hand corner and is a $(ZnS)_{12}$ bubble with the structure of a sodalite cage, a highly stable structure. The outermost shell, which is a $(ZnS)_{48}$ bubble, is shown on the left-hand side. White balls represent S atoms and black balls represent Zn atoms (this colour scheme applies to all the figures).

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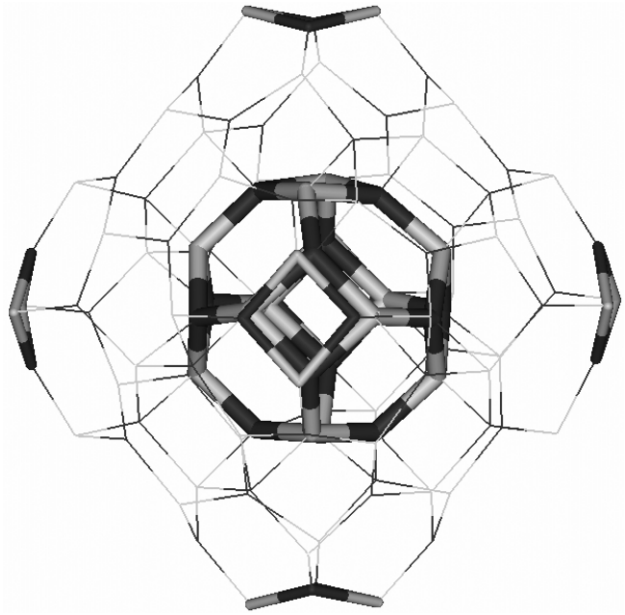

Fig. 2 View of the $(ZnS)_{60}$ cluster, where the atoms forming squares in the innermost bubble are drawn as thick sticks, the atoms forming squares in the outermost bubble as thin sticks and the rest as lines. The whole structure of the $(ZnS)_{12}$ bubble is drawn with thick sticks since all its atoms form part of a square.

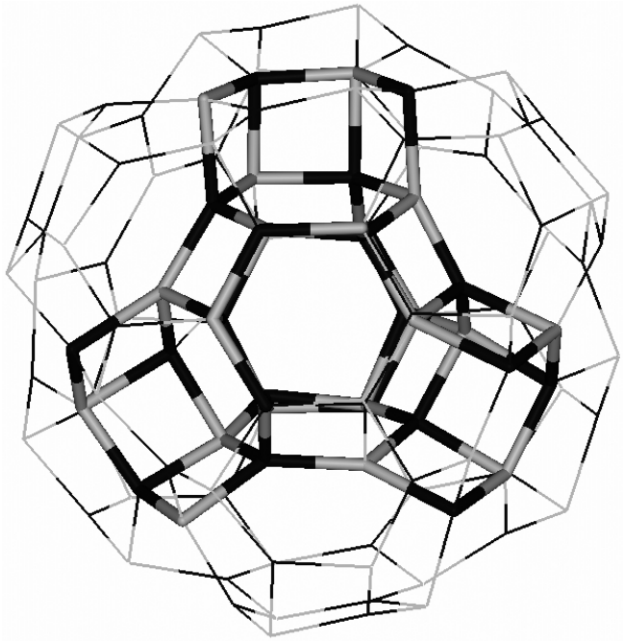

Fig. 3 View of the $(ZnS)_{60}$ cluster, where the tetracoordinated atoms and those bonded to them are shown as sticks and the rest as lines. Note the five channels formed between the innermost and outermost shell: three of these can be clearly seen and the other two are aligned in a direction perpendicular to the plane of the paper.

atoms in the innermost bubble belong to a network of tetracoordinated atoms; the average bond distance of the innermost bubble is ~2.36 Å. For the outermost bubble, the average bond distance is ~2.31 Å. The average distance between the atoms bonding the two shells is ~2.46 Å. This larger distance implies that the bonds between the two shells are weaker than the bonds within either shell.

The $(ZnS)_{60}$ cluster is very stable compared with the single-layer bubble clusters studied previously. For example, $(ZnS)_{60}$ is more stable than $(ZnS)_{12}$ by 13.05 kJ mol^{-1} per ZnS unit. There are still some three-coordinated atoms in the $(ZnS)_{60}$ structure, making the zincblende bulk structure more stable by 42.77 kJ mol^{-1} per ZnS unit. Moreover, these structures could be expected to have unusual physical and chemical properties; accurate *ab initio* calculations of their electronic structure are currently ongoing.

The presence of the network of tetracoordinated atoms and recent experimental and theoretical studies[15] suggest a possible path whereby bubble clusters can grow and form bulk-like clusters, which are more stable for larger cluster sizes. It might be possible for some of the atoms in this network to undergo relatively small displacements to form a region of bulk-like structure inside the cluster. This region could nucleate the process of structural transformation of the whole cluster.

Our calculations therefore strongly suggest onion-like structures for $(ZnS)_{60}$ clusters. Further calculations, currently in progress, aim to investigate the transformation from "bubble" to bulk-like structures for larger clusters.

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