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# STRUCTURE OF $s-p$ BONDED METAL CLUSTERS WITH 8, 20 AND 40 VALENCE ELECTRONS *

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**Abstract**

From studies on some clusters of metals and semiconductors, there appear some similarities in the structure of clusters with a given number of atoms and having the number of valence electrons corresponding to a shell closing. Here we present results of the atomic and electronic structure of a few other clusters with 20 and 40 valence electrons, namely $Sb_4$, $Sn_5$ and $Sb_8$ using the density functional molecular dynamics method. We suggest that the similarities in the structure and deviation from them may help to understand bonding characteristics in clusters and its evolution to bulk behaviour. Our results on $Sb_8$ cluster are preliminary but indicate that above room temperature its structure is two weakly interacting tetrahedra which is in general agreement with the observation of predominently antimony tetramers at $T > 300K$.

## Introduction

Understanding the atomic and electronic structure of clusters and their progression towards bulk behaviour is one of the important goals in research on clusters and may lead to the development of some new materials as it is the case of solid $C_{60}$. In recent years much attention has been focussed on the study of clusters of metals and semiconductors because of their technological importance. These studies have revealed existance of the so called magic clusters which are much more abundant as compared to those having one more atom. For metals such magic clusters were discovered by Knight et al[1] who found Na and K clusters with 8, 20 and 40 atoms to be magic. Since in the bulk, these metals are described very well by a nearly free

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electron model. Cohen and coworkers[2] adopted a simple spherical jellium model to study the stability and other properties of such clusters. Similar to the nuclear shell model, they obtained electronic shells in the sequence 1s, 1p, 1d, 2s, 1f, 2p, 2d, ... which can accomodate 2, 6, 10... electrons and associated the stability of such clusters with 8, 20 and 40 valence electrons with the filling of the 1p, 2s and 2p shells. Since then the jellium model has proved to be very successful in understanding the general trends in the electronic structure and associated properties of metal clusters.

The study of the structure of clusters is, however, a much more demanding task and for each cluster a lot of efforts have to be devoted in order to be able to say something about the low lying structures. Here we ask the question whether for a given number of atoms, the electronic shell filling clusters can have a particular structure. We recall that about 60 years ago Hume-Rothery[3] pointed out certain alloy structures which occur at a definite electron/atom ratio. He proposed the rules that the $\beta$ -phase is associated with an electron/atom ratio 3/2, the $\gamma$ -phase with 21/13 and the $\epsilon$ -phase with 7/4. Later Jones[4] associated the stability of these structures with the Fermi surface touching the Brillouin zone boundary. While the specific value of the electron/atom ratio is not so important, these rules are found to be valid for a very large number of alloys. For clusters, due to the discrete nature of the spectrum, the equivalent of the Fermi surface touching the zone boundary is the filling of an electronic shell. While jellium and atomic calculations suggest this shell structure not to be sensitive to the structure of a cluster, the finding of the same structure[5] in some seemingly different systems e.g. $Mg_{10}$ and $Si_{10}$, raised an interesting question about the structure of shell filling clusters and if one can learn something about the bonding nature in small clusters from such a study.

In contrast to bulk alloys, in clusters an electronic shell can be completed in some cases even with one element. If $Z_v$ is the number of valence electrons per atom and $n$ is the number of atoms in a cluster, then the total number of valence electrons will be $N = n\ Z_v$. Considering here only neutral clusters with N = 8, 20 and 40, then some of the interesting cases are:

1a) $Z_v = 1$, $n = 8$, 20 and 40: These are clusters of alkali and noble metals. Here



it can also be noted that all alkali and noble metals have respectively the bcc and fcc structure in bulk. Though there is not much information about the structure of noble metal clusters, they have the same magic clusters[6] as alkali metals.

1b) $Z_v = 2$, $n = 4$, 10 and 20: These are clusters of divalent metals such as Be, Mg, Zn and Cd which are hcp or Ca and Sr which are fcc in bulk.

1c) $Z_v = 4$, $n = 2$, 5 and 10: These are clusters of Si, Ge and Sn which have diamond structure in bulk or Pb which is fcc in bulk. In these cases, metallic nature of elements increases in going from Si to Pb. Also unlike bulk, small clusters of Si and Ge tend to be closed packed and a change in the bonding nature should be expected as a function of the cluster size.

1d) $Z_v = 5$, $n = 4$ and 8: These are clusters of As, Sb and Bi. All the three have rhombohedral structure in bulk and are semimetals.

If two or more components or charged clusters are considered, then there would be a large variety and an interesting example of 40 valence electrons would be[7] $Al_{13}^-$ cluster or doped clusters of $Al_{12}$ with B, Ga, C, Si, Ge, As, Ti etc. which are believed to have an icosahedral structure. But we shall not consider these here as there is very little information available on the structure of such systems.

It is quite well known that the energy difference between two structures can be very small and that a material may exist in more than one stable structures. The same can be expected to happen for clusters as well. However, since there is no constraint such as periodicity in the bulk, clusters have more degrees of freedom. Therefore, as the number of atoms in a cluster increases, calculation of the lowest energy structure become increasingly difficult. During the past few years, significant progress has been made in understanding the structure of clusters of several metal and semiconductors using the density functional molecular dynamics method[8] (DF-MD)together with the simulated annealing technique which has been very successful in the search of the lowest energy structures of different clusters. Also the DF-MD has the advantage that temperature effects on structure can be studied. A brief review of these results can be found in Ref. 9. Of our present interest are the results on Na, K, Mg, Be , Al, Si and Ge clusters. In addition we report here

calculations on $Sb_4$ and $Sn_5$ clusters which have 20 valence electrons as well as some work on $Sb_8$ cluster (40 valence electrons) using the DF-MD method. Antimony clusters are interesting as at low temperatures (≈150K of the carrier gas), these occur abundantly[10] in multiples of four (4, 8, 12, 16, 20, ..). However, if the gas temperature is raised to 250 - 300 K, the intensity of $4n$ ($n > 1$) clusters decreases dramatically and $Sb_4$ is the most prominent cluster in the mass spectrum. The structure of $Sb_n$ ($n > 4$) is still unknown.

**Results: a. $Sb_4$ and $Sb_8$**

We have used the norm-conserving pseudo-potentials of Bachelet et al[11] with $s$ non-locality and a plane wave basis with the Γ point to sample the Brillouin zone of the MD supercell. For $Sb_4$ we have studied a planar and a three dimensional structure using the steepest descent technique. The relaxed structures are shown in Figure 1. We find a regular tetrahedron to be 0.505 eV/atom lower in energy than a bent rhombus.

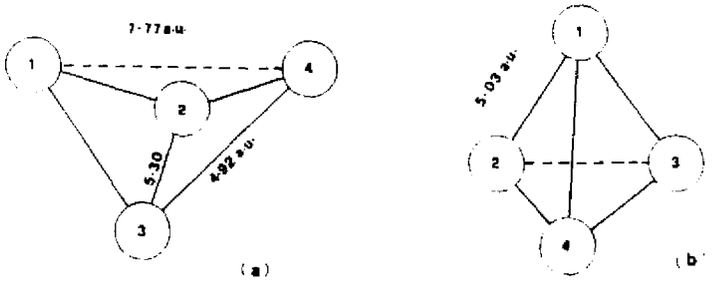


**Fig. 1.** (a) Bent rhombus and (b) tetrahedron structures of $Sb_4$. The former is about 0.5 eV/atom higher in energy than (b).

For $Sb_8$, we have done several calculations. These include steepest descent calculations for a cube, a bicapped octahedron and a $D_{2d}$ structure and also simulated annealing calculations. Cube, bicapped octahedron and $D_{2d}$ structures are not of lowest energy. Our simulated annealing results are preliminary but indicate that above room temperature the structure of $Sb_8$ is two tetrahedra interacting weakly



through vertices. Very careful annealings will be required to obtain the lowest energy structure at T=0 K. This result is, however, in agreement with the experiments[10] which indicate only the existance of $Sb_4$ clusters at higher temperatures. Details of these calculations will be published elsewhere[12].

**b. $Sn_5$**

Clusters of tin are interesting as it exists in both a metallic (white tin) and a semiconducting (grey tin) phase. Grey tin has the diamond structure while the white tin is body-centered tetragonal. We have done calculations for $Sn_5$ cluster as it has 20 valence electrons, for a few selected starting geometries such as a pentagon, a trigonal bipyramid and a square pyramid. All these structures relax significantly. The pentagon relaxes to become a part of a triangular net as shown in Fig.2a. The lowest energy structure we obtained is a trigonal bipyramid (Fig. 2b) which is very similar to $Si_5$ and $Ge_5$. The bond length between the base atoms is large (6.49 a.u.) while the distance between apex and base atoms is 4.94 a.u. Therefore $Sn_5$ cluster behaves as clusters of Si and Ge. This is in agreement with the experimental results[13]. The energy of the trigonal prism is 0.265 eV/atom lower as compared to the triangular net. All these calculations were done for a singlet state.

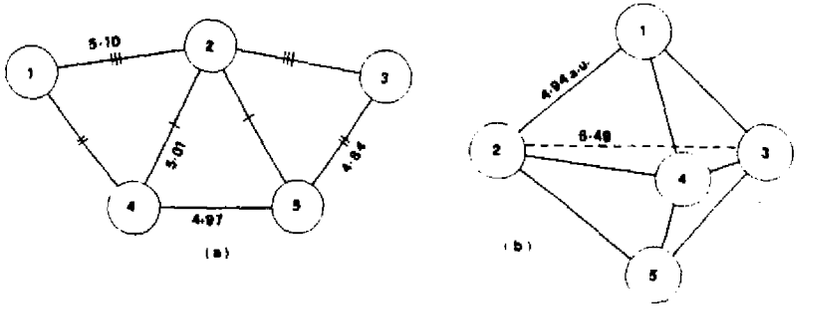


**Fig. 2.** Two low lying structures of $Sn_5$. The triangular bipyramid (b) is 0.265 eV/atom lower in energy than (a).

**Structure of magic clusters**

Now coming to the structure of clusters with 8, 20 and 40 valence electrons.

we notice that $Na_8$ and $K_8$ have the $D_{2d}$ structure[14] which is different from the one obtained for van der Waals bonded systems. As mentioned previously, 8 atom clusters of Cu, Ag and Au have also been found[6] to be magic and it would be of interest to study their structure if it is the same[15].

Tetramers of divalent metals and pentavalent semimetals have a regular tetrahedron to be of lowest energy. A tetrahedron is also the lowest energy structure for van der Waals clusters. It is to be noted that clusters of divalent metals such as Be, Mg and Hg show a transition from van der Waals to metallic bonding as the cluster size increases. While recent ab-initio calculations on $Mg_n^5$ and $Be_n^{16}$ suggest a gradual build up of chemical bonding for these clusters, results for $Sb_8$ cluster suggest that directional bonding is important in these molecular clusters.

5 atom clusters of Si, Ge and Sn have the same trigonal bipyramid structure. These have 20 valence electrons but are not magic. The trigonal bipyramid is also not closed packed as one can expect for magic clusters and therefore the bonding is not like in metals.

For 10 atom clusters, interesting known examples are clusters of Be, Mg, Si, and Ge. Except for $Be_{10}$ all others have the same structure[9,14], namely tetracapped trigonal prism. As mentioned above, clusters of Be, Mg and Hg exhibit non-metal - metal transition as the cluster size grows whereas bonding in small Si clusters is still an open problem. One can , however, say that similar to metals structure of small Si clusters tend to be closed packed in contrast to bulk. Thus the bonding in clusters of group 2 metals and some clusters of Si and Ge may have similarities. The behaviour of $Be_{10}$ is slightly different from Mg in the way of capping. $Be_9$ and $Mg_9$ clusters have the tricapped trigonal prism structure[9]. In the case of $Be_{10}$ the tenth atom caps an edge whereas for $Mg_{10}$, it caps one of the triangular faces of the prism. This difference is likely due to the fact that Be clusters tend to approach their bulk behaviour for smaller clusters[9,16] as compared to Mg. Therefore we can say that for a given number of atoms, clusters of different elements having similar bonding character and the number of valence electrons corresponding to a shell closing tend to have the same structure. However, further work on other clusters would be helpful



to find the rules for the stability of certain structures.

In summary we have presented results on $Sb_4$, $Sb_8$ and $Sn_5$ clusters obtained from the density functional molecular dynamics method. Our results are in agreement with experiments that above room temperature $Sb_{4n}$ ($n > 1$) tend to be unstable and also that Sn clusters behave like those of Si and Ge. It is likely that other $Sb_{4n}$ ($n > 2$) clusters may also be weakly bonded tetrahedra. We also pointed out some similarities which exist in the structure of clusters with 8, 20 and 40 valence electrons. As the bonding nature in small clusters of a variety of materials is still a largely open area, a knowledge of these similarities and deviations from them can be helpful to bridge this gap. Finally, the particular stability of clusters like $Sb_4$ and the possibility to produce them in abundance make it attractive to explore new cluster assembled materials from them.

## References


1. W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou and M. L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).

2. M. Y. Chou and M. L. Cohen, Phys. Lett. **A113**, 420 (1986); W. A. de Heer, W. D. Knight, M. Y. Chou and M. L. Cohen, Solid State Phys. Vol. **40**, Eds. H. Ehrenreich and D. Turnbull, Academic Press (1987).

3. W. Hume-Rothery, *The Metallic State*, p. 328, Oxford (1931).

4. H. Jones, Proc. Roy. Soc. A **144**, 225 (1934).

5. V. Kumar and R. Car, Phys. Rev. **B44**, 8243 (1991).

6. I. Katakuse, I. Ichihara, Y. Fujita, T. Matsuo, T. Sakurai and H. Matsuda , Int. J. Mass Spectrom. Ion. Proc. **67**,229 (1985).

7. X.-G. Gong and V. Kumar, to be published; for doped clusters see also P. Jena, S. N. Khanna and B. K. Rao, this proceedings.

8. R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

9. V. Kumar, ICTP preprint IC/91/358.

10. D. Rayane, P. Melinon, B. Tribollet, B. Cabaud, A. Hoareau and M. Broyer, J. Chem. Phys. **91**, 3100, (1989); K. Sattler, J. Muhlbach and E. Recknagel, Phys. Rev. Lett. **45**, 821 (1980).

11. G. B. Bachelet, D.R. Hamann and M. Schluter, Phys. Rev. **B26**, 4199 (1982).

12. V. Kumar, to be published.

13. Y. Saito and T. Noda, Z. Phys. **D12**,225 (1989); G. Gantefor, M. Gausa, K. H. Meiwes-Broer and H. O. Lutz, Z. Phys. **D12**, 405 (1989).

14. W. Andreoni, Z. Phys. **D 19**, 31 (1991) and private communication.

15. Calculations based on effective medium theory on $Cu_8$ and $Cu_{20}$ clusters predict the same structure as for $Na_8$ and $Na_{20}$ (K.W. Jacobsen, private communications).

16. R. Kawai and J. H. Weare, Phys. Rev. Lett. **65**, 80 (1990).