IC/93/52

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ARE Sb_{4n} $(n > 1)$ CLUSTERS WEAKLY INTERACTING TETRAHEDRA?

Vijay Kumar

INTERNATIONAL ATOMIC ENERGY AGENCY

UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

MIRAMARE-TRIESTE

International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ARE Sb_{4n} ($n > 1$) CLUSTERS WEAKLY INTERACTING TETRAHEDRA?

Vijay Kumar *
International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

The electronic and atomic structure of Sb_4 and Sb_8 clusters is studied using the ab-initio molecular dynamics method in the local density approximation. While for Sb_4 we obtain a regular tetrahedron to be about 2.0 eV lower in energy than a bent rhombus, for Sb_8 two structures, (1) two weakly interaction tetrahedra and (2) a bent rhombus interacting with a stratched tetrahedron, obtained from the simulated annealing lie only within about 0.1 eV indicating the importance of the bent rhombus structure for larger clusters. As compared to two isolated tetrahedra, the binding energy of Sb_8 is about 0.5 eV. Our results are thus in excellent agreement with the experimental data which show predominantly the abundance of tetramers above room temperature.

MIRAMARE - TRIESTE
March 1993

* Permanent address: Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India.

About a decade ago Sattler et al[1] reported mass spectrum of antimony clusters formed by condensation of metal vapor in a liquid nitrogen cooled He-gas condensation cell. The most striking feature of this spectrum was the abundance of Sb_{4n}, ($n \geq 1$) clusters. Experiments[1,2] on bulk antimony ,however, show evaporation of predominantly Sb_4 clusters at 800 K and higher masses are not observed. Similar results have been obtained for neutral clusters of antimony from laser evaporation[3]. Therefore Sb_{4n} clusters have been considered to be formed of weakly interacting antimony tetramers. On the other hand bismuth which has the same rhombohedral structure and is also a semimetal in bulk, shows a completely different mass spectrum[1]. It is not well understood if this happens due to the nucleation conditions that antimony has predominantly Sb_4 species in the vapor while for bismuth monomers and dimers are the main species[2,3]. In fact similar mass spectrum has been obtained[3] for cation and anion clusters of Bi and Sb with less than 15 atoms in laser vaporization experiments. Also recent experiments of Bréchignac et al[4] on photoionization of antimony clusters show a dramatic collapse of the shape resonance for Sb_{4n} with $n > 1$. This resonance is found to depend upon the nucleation conditions. These experiments, therefore, indicate that not only the abundance of different clusters but also the molecular architecture could itself depend upon nucleation conditions.

Sb and As have bulk allotropic structures, the non-metallic yellow forms, which are metastable and probably consist of tetrameric molecules. It is of interest to know the isomeric structures for their clusters and how the growth occurs towards bulk behaviour. While tetramers of these pentavalent elements are known to be regular tetrahedra[5] , little is known about the atomic and electronic structure of larger clusters. Here we report[6] for the first time the results of a study of the atomic and electronic structure of Sb_8 clusters together with the results for a dimer and a tetramer. In agreement with the above experiments, our calculations predict two quite different isomers for Sb_8 clusters with a small binding energy of approximately 0.5 eV as compared to two isolated regular tetrahedra.

The calculations have been performed using the ab-initio molecular dynamics method[7] together with the simulated annealing technique within the local density approximation (LDA). This method has been successfully applied[8] to clusters of

several metals, semiconductors and other elements such as B, C, P, S, Se etc. and the results have been in good agreement with experiments wherever available. In these calculations the cluster is placed in a supercell with periodic boundary conditions. We chose a fcc supercell with sides equal to 46 a.u. This was large enough so that the interaction between the periodic images of the cluster was negligible. A plane wave expansion was used with the Γ point to sample the Brillouin zone of the molecular dynamics supercell. Further we used the norm-conserving pseudopotential of Bachelet et al[9] with s non-locality and adopted the Kleinman and Bylander[10] separable form of the pseudopotential to speed up the calculations. For the exchange and correlation we used the Perdew and Zunger[11] parametrization of the Ceperley-Alder exchange correlation data[12]. All the calculations have been done for a singlet state and effects due to spin-orbit coupling have been neglected. Initial tests of convergence were performed on a dimer and a cut-off of 11.5 Ry was found to be satisfactory for the plane wave expansion. This gave the dissociation energy for the dimer to be 7.19 eV and a bond length of 4.48 a.u.. While the binding energy is overestimated[13], the latter is in very good agreement with the experimental value[14] of 4.425 a.u.. Inclusion of p non-locality resulted in a slightly longer bond length and smaller binding energy.

For Sb_4 steepest descent calculations have been done for a tetrahedron and a planar structure. On convergence the planar structure becomes a bent rhombus with dihedral angle 138.9° as shown in Fig. 1. While a regular tetrahedron is found to be 2.052 eV lower in energy than a bent rhombus, we shall show in the following that the bent rhombus structure may be important for larger clusters. Our results indicate a barrier in going from a bent rhombus structure to a tetrahedron and are in agreement with the earlier work[5] according to which tetramers of group V elements are regular tetrahedra. However, as expected in LDA, our calculations overestimate the binding energy (4.666 eV/atom) as compared to the experimental value[15] of 2.9 eV/atom. The nearest neighbour bond length (5.08 a.u.) in Sb_4 is much shorter than its experimental value in the bulk (5.50 a.u.).

For Sb_8 we performed two simulated annealing and several steepest descent calculations. These results are summarized in table I and the resulting structures are

shown in Fig. 2. A cube (Fig. 2a), two bent rhombuses interacting through the end atoms (Fig. 2b) and a bicapped octahedron (Fig. 2c) are not even stable against two isolated tetrahedra. One of the simulated annealing calculations was performed by starting with a cubic structure with random displacement of the ions. The cluster was heated upto 3500 K so that the ions started diffusing. It was then cooled at the rate of 2.75 X 10^{14} K/sec and the resulting structure is shown in Fig. 2e. This is the lowest energy structure among all the calculations that we have done. It can be viewed as two tetrahedra interacting weakly through their faces such that they are rotated with respect to each other by 60°. The intercluster separation is quite large and the interaction is of van der Waals type[16]. This is understandable because Sb has s^2p^3 electronic configuration and therefore in the tetrahedron structure 3 electrons from each atom form strong bonds with three nearest neighbours leaving a lone pair and therefore the interaction between tetrahedra is weak. This is also reflected from the small changes in the Kohn-Sham eigenvalues of this cluster as compared to the tetrahedron (Fig. 3a and g). In this way, as expected for van der Waals bonded systems, the atoms maximize the number of neighbours. As compared to two isolated tetrahedra, its binding energy is 0.5 eV. This is comparable to the value of 1.3 ± 0.25 eV reported by Rayane et al[2] in the range of Sb_8 to Sb_{20} clusters. This structure is the same as speculated by Sattler et al[17]. However, in order to check whether it was an artifact of heating at such a high temperature because of the evidence that Sb_4 is the most abundant, we performed another simulated annealing calculation in which the bicapped octahedron structure was heated upto 2000 K such that the ions started again diffusing though within the time scale we used, the displacement of the ions from their initial positions was not as large as in the other calculation. The cluster was cooled again with a similar rate and the final structure is shown in Fig. 2d. It is quite different from the one in Fig. 2e and is only 0.117 eV higher in energy than the tetrahedron based structure. This structure can be viewed as a stratched tetrahedron interacting with a bent rhombus. Three short bonds are created and therefore the interaction between the two tetramers is not van der Waals type as in the case of two tetrahedra. This is also reflected in the distribution of electronic states which is broader (Fig. 3f) as compared to Fig.

3g. Since we would have expected a more symmetric structure for magic clusters, we made this cluster more symmetric by making the distances 5-8 and 1-4 (Fig. 2d) nearly equal (both long and short distances were used) in order to further check if we were not trapped in a local minimum, but the structure relaxed back to this configuration. Therefore even though a bent rhombus lies much higher in energy than a regular tetrahedron, our calculations indicate that they could play an important role in the structure of larger clusters. Our results are in agreement with the experimental observations that 1) the structure of these clusters may depend upon the nucleation conditions and 2) predominantly tetramers are observed in the mass spectrum above room temperature due to very weak interactions. However, it is well known that the LDA does not describe the van der Waals interactions properly and since the difference in the binding energies of the two lowest energy structures is small, it is difficult to conclude which one may be more favourable. It would require calculations beyond LDA. Also as the structure in Fig. 2d is of lower symmetry, a calculation using local spin density approximation will help to clearify whether it is so or a more symmetric structure is favored. Therefore within the accuracy of the present calculations we shall consider these two low lying structures as degenerate.

The Kohn-Sham eigenvalue spectrum for various clusters is shown in Fig. 3. Besides the comparison between the spectra of tetramers and the two lowest energy structures of Sb_8 mentioned above, the spectra of the low symmetry structures has more spread though the overall bandwith of the occupied states for all clusters is about 12 eV.

From photoionization experiments[4] since Sb_4 behaves differently than the other Sb_{4n} clusters, it may also be quite likely that the structure in Fig. 2d has the lower energy. However, experience with other clusters suggest that the magic clusters tend to have a high symmetry and low spin configuration structure. In order to get further insight, we show in Fig. 4 a snapshot of the tetrahedron structure (Fig. 2e) at 800K. It is clear that the structure of the individual tetrahedron units remains intact. However, except for two bonds the other bonds between the two tetrahedra are broken. The length of these two bonds is quite large but interestingly one bond is quite small (5.88 a.u.) as compared to the nearest neighbour inter-tetrahedron

distance (7.09 a.u.) in equilibrium. In order to check the nature of this bond we calculated the pseudo-electronic charge density in a plane containing these two bonds (Fig. 5). It is clear that there is an accumulation of charge in the bond belonging to a tetrahedron, but there is no such accumulation for inter-tetrahedra bonds except for small polarization. Therefore this short bond is weak. On the other hand at 800 K, most of the bonds for the other geometry have nearly the same length as in the case of the equilibrium geometry. Also as compared to an isolated tetrahedron and a bent rhombus the binding energy of the rhombus-tetrahedron structure is 1.013 eV. This would suggest that most likely the tetrahedron based structure would be the preferred one as we also find from our calculations. More tetrahedra can then be added to obtain larger clusters whereas for tetrahedron -rhombus structure it is not obvious how further growth would occur. Sattler et al[17] suggested the tetrahedron growth model. According to our calculations the distances between the tetrahedra will be longer than the one which can be inferred from their model. Thus by capping all the four faces of a tetrahedron one can get a quite symmetric cluster of 20 atoms. But as this will have a very open structure, further capping of the four vertices of the central tetrahedron by four tetrahedra (similar to Fig. 3) will lead to a 36 atom more compact cluster which has been observed to be magic in the experiments of Sattler et al[1] and as well as of Geusic et al[2].

In summary we have presented results for the atomic and electronic structure of Sb_4 and Sb_8 clusters. Our results are in agreement with the experimental observations that the structure of the larger clusters may depend upon the nucleation conditions and that Sb_{4n} ($n > 1$) clusters are weakly interacting. The structure of Sb_8 is different from the one obtained by Jones and Hohl[18] for P_8. Therefore though their tetramer have the same structure, the larger clusters behave differently. For Sb_8 we find two structures lying close in energy. Though the structure of Sb_{4n} clusters is likely to be a packing of tetrahedra, our results also show importance of the bent rhombus structure for larger clusters and perhaps the low temperature metastable phase of antimony may be amorphous. However, more calculations using the local spin density approximation and going beyond the LDA on Sb_8 and larger clusters will be helpful to understand properly the growth model of antimony

clusters. A systematic study for other clusters is under progress.

ACKNOWLEDGMENTS

I am thankful to A. Nobile for his help in the implementation of the Car-Parrinello code on ICTP Convex machine and to V. Sundararajan and A. Shiekh for their help on computer graphics.

REFERENCES

1. K. Sattler, J. Mühlbach and E. Recknagel, Phys. Rev. Lett. **45**, 821 (1980); J. Múhlbach, P. Pfau, E. Recknagel and K. Sattler, Surf. Sci. **106**,18 (1981).

2. D. Rayane et al, J. Chem. Phys. **91**, 3100 (1989).

3. M. E. Geusic, R. R. Freeman and M. A. Duncan, J. Chem. Phys. **89**, 223 (1988).

4. C. Bréchignac et al, Phys. Rev. Lett. **67**, 1222 (1991).

5. See L.-S. Wang et al, J. Chem. Phys. **93**, 6318 (1990) and references therein.

6. A preliminary report of these results was presented in Proceedings of Adriatico Research Conference on *Clusters and Fullerenes*, Eds. V. Kumar, T. P. Martin and E. Tosatti, World Scientific, Singapore (1993), pp. 97.

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

8. V. Kumar, in Proc. of 8^{th} National Workshop on Atomic and Molecular Physics, Hyderabad, 1990, Ed. A. P. Pathak, Narosa Publications (1992); V. Kumar, to be published.

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

10. L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

11. J. P. Perdew and A. Zunger, Phys. Rev. **B23**, 5048 (1981).

12. D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

13. The larger binding energy is also due to the fact that we have not included spin polarization effects for the atom.

14. K.P.Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules (Van Norstrand Reinhold, New York, 1974)

15. B. Cabaud, A. Hoareau, P. Nounou and R. Uzan, Int. J. Mass Spectrom. Ion Phys. **11**, 157 (1973).

16. We must say that because of these weak interactions, the forces on the ions were very small and it required a very long computer time to get this structure converged. The inter cluster nearest neighbour distances still varied in between 7.0 and 7.17 a.u. . We have given the mean value in the figure.

17. K. Sattler, J. Mühlbach, P. Pfau and E. Recknagel, Phys. Lett. **87A**, 418 (1982).

18. R. O. Jones and D. Hohl, J. Chem. Phys. **92**, 6710 (1990).

Figure Captions

Fig. 1. Structure of Sb_4 cluster. a) bent rhombus and b) regular tetrahedron.

Fig. 2. Various structures of Sb_8 cluster. a) - c) steepest descent calculations, d) and e) simulated annealing. e) has the lowest energy.

Fig. 3. Kohn-Sham eigenvalues for a) tetrahedron, b) rhombus, and c) - g) corresponding to structures in Fig. 2a - e.

Fig. 4. A snapshot of the structure (Fig. 2e) at 800 K. The two tetrahedra are perturbed slightly but all except two intercluster bonds are broken.

Fig. 5. Pseudo-electronic charge density for the structure in Fig. 4 in a plane containing the three interacting atoms between the two tetrahedra. The brighter the spot, the higher is the charge density. The two strongly interacting atoms belong to a tetrahedron while the third one to the other tetrahedron. Obviously the interaction between the two tetrahedra is weak.

Table 1: Comparison of the equilibrium binding energy (B.E.) of different antimony clusters

Cluster	B.E. (eV/atom)
Dimer	3.595
Bent rhombus	4.152
Tetrahedron	4.666
Sb_4 (Expt.)	2.900
Cube	4.578
Fused rhombii	4.578
Bicapped octahedron	4.620
Tetrahedron-rhombus	4.716
Fused tetrahedra	4.731

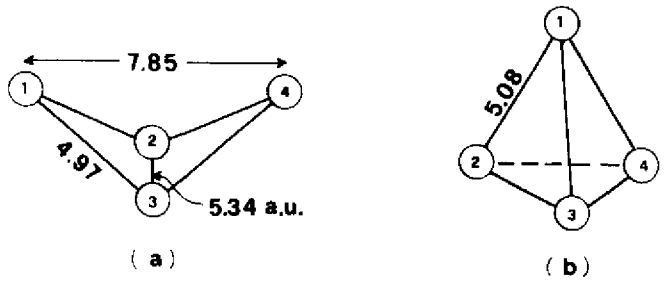

Fig.1

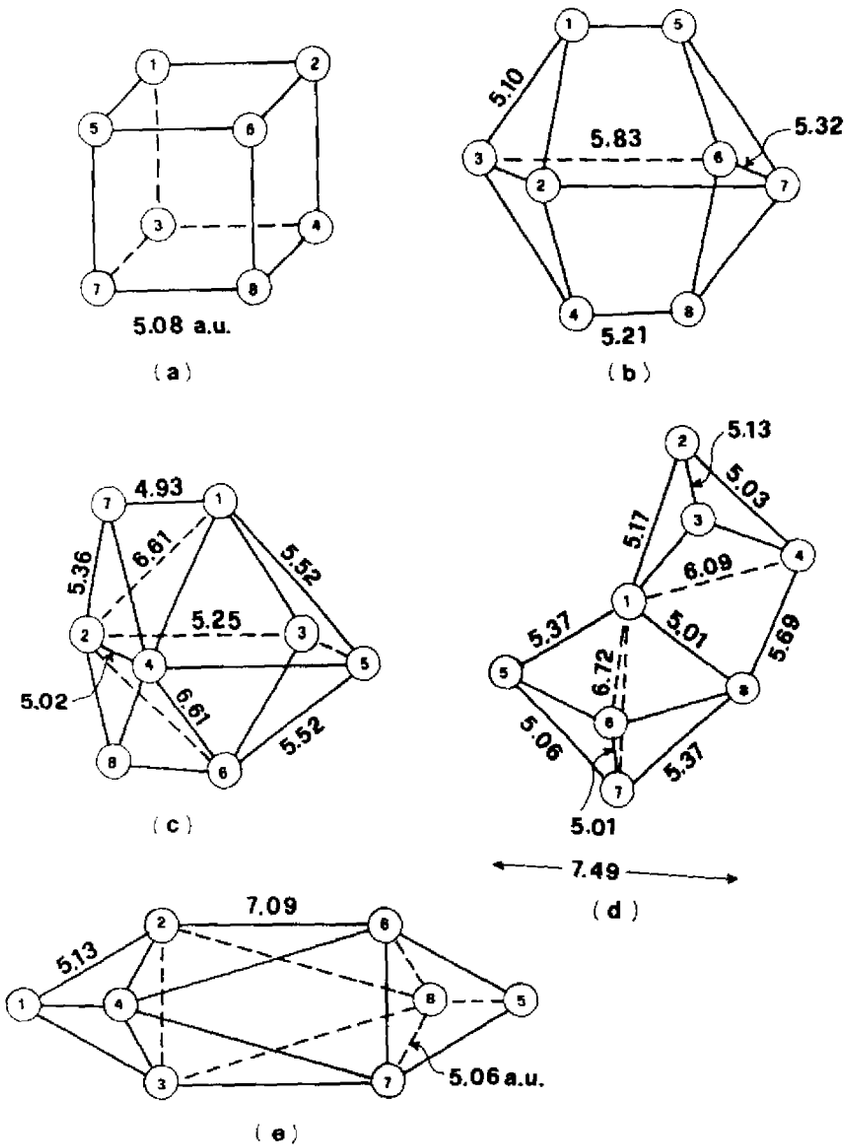
5.08 a.u.
(a)
5.10
5.83
5.32
5.21
(b)
4.93
5.36
6.61
5.52
5.25
5.02
6.61
5.52
(c)
5.13
5.03
5.17
6.09
5.37
5.01
5.69
6.72
5.06
5.37
5.01
7.49
(d)
7.09
5.13
5.06 a.u.
(e)

Fig.2

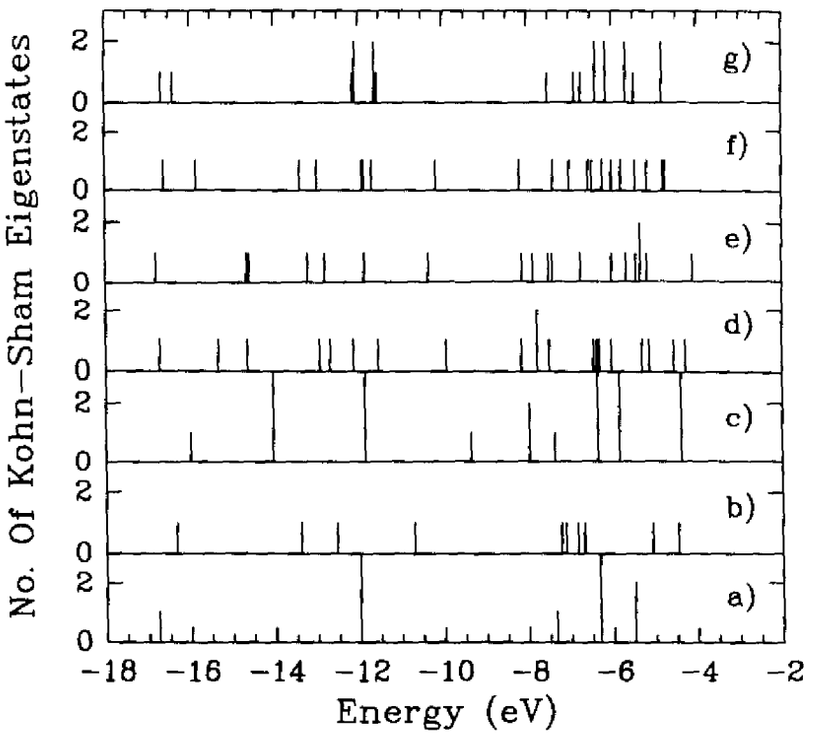
No. Of Kohn-Sham Eigenstates
Energy (eV)
−18
−16
−14
−12
−10
−8
−6
−4
−2
0
2
g)
f)
e)
d)
c)
b)
a)

Fig.3

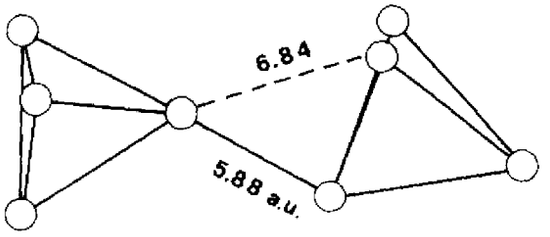

Fig.4

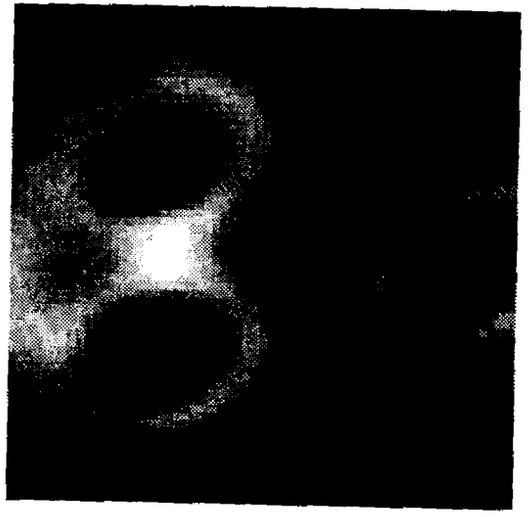

Fig.5