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Citation: The Journal of Chemical Physics **102**, 9631 (1995); doi: 10.1063/1.468781
View online: http://dx.doi.org/10.1063/1.468781
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/102/24?ver=pdfcov
Published by the AIP Publishing

Ab initio molecular dynamics study of antimony clusters

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(Received 9 February 1995; accepted 23 March 1995)

We present an *ab initio* molecular dynamics study of the atomic and electronic structure of Sb_N ($N=2-8$ and 12) clusters within the local density approximation and pseudopotential representation of the electron–ion interaction. Simulated annealing calculations have been done for 6-, 7-, 8-, and 12-atom clusters. While for Sb_4 a bent rhombus is about 2 eV higher in energy than a regular tetrahedron, we find that it plays an important role in the structure of larger clusters. For Sb_8 we obtain two weakly interacting tetrahedra to be of lowest energy. However, this is nearly degenerate with a bent rhombus interacting with a distorted tetrahedron. Further, our calculations suggest a bent rhombus based structure for Sb_{12} cluster indicating the observation of Sb_{4n} clusters in Sb vapor condensation cell to be due to abundance of Sb_4 clusters. A large gap is found to exist between the highest and the next occupied Kohn–Sham eigenvalues of the lowest energy isomers of 3-, 5-, and 7-atom clusters. This is in agreement with the abundance of cations of these clusters in the laser ablation experiments. © *1995 American Institute of Physics.*

I. INTRODUCTION

Much effort is currently being devoted to the study of the physical and chemical properties of clusters as these play an important role in several technological applications and there is academic interest to understand the evolution of material properties from atoms to solids. One of the first experiments on unsupported metal clusters were done[1] on antimony and bismuth by thermal evaporation followed by condensation in an inert gas atmosphere. However, the structure of these clusters is still not well understood. The mass spectrum of Sb clusters was unique as clusters with multiples of four atoms were prominently observed. This is in contrast to bismuth which has the same structure in bulk but shows a completely different abundance spectrum having clusters of various number of atoms which is typical for a metal. For antimony, 8-, 36-, 52-, and 84-atom clusters are magic. It is known[2] that direct heating of antimony at around 800 K leads to metal evaporation in the form of Sb_4 clusters. Therefore, the abundance of antimony clusters in multiples of four at low temperatures has been interpreted to be due to weak interaction between the tetramer units.

Geusic *et al.*[3] studied the neutral and ionic clusters of Sb and Bi from laser vaporization experiments in which condensation is believed to occur atom by atom. They obtained similar abundance spectra for both Sb and Bi in contrast to the gas condensation studies of Sattler *et al.*[1] In particular their aggregation and fragmentation experiments suggested Sb_3^+, Sb_5^+, and Sb_7^+ to be the most stable clusters in the small size range. In their experiments they could obtain clusters having only upto 15 atoms. They suggested the importance of p bonding in these clusters and interpreted the stability of different clusters following Wade's rule[4] of electron counting according to which a cluster of N atoms involving p orbitals for bonding should be stable if it has $2N+2$, $2N+4$, or $2N+6$ skeletal electrons. According to these rules Sb_6 should also be stable but studies[5] of neutral clusters showed truncation of the mass spectrum at five. This was attributed to the possible reorganization of the cluster geometry, necessary in the transition to six-atom cluster which hinders its formation.

Rayane *et al.*[5] found abundance of Sb_{4n} (n, an integer) clusters in inert gas condensation experiments and measured the binding energy of Sb_4 units. An interesting feature of their study was the observation of mainly Sb_{2n+1} clusters under different nucleation conditions. A strong dependence of the photoionization resonance intensity of antimony clusters on nucleation conditions was also observed by Bréchignac *et al.*[6] These studies strongly suggest that the growth and structure of antimony clusters depend on the nucleation and growth conditions.

In bulk, group V–A elements exist in more than one phase. Arsenic, antimony, and bismuth are semimetals and have the same rhombohedral structure. However, As and Sb also have allotropic forms which are nonmetallic and therefore their clusters could exhibit a variety of structures and changes in bonding characteristics. Phosphorus, arsenic, and antimony are also used in the development of electronic devices and therefore study of their clusters could help in understanding the growth of layers in vapor deposition. While tetramers of all these elements are known[7] to be very stable and to exist in the form of a tetrahedron, the abundance spectra of various group V–A elements are different[1,8] indicating the changes in the electronic structure of these clusters in going from P to Bi. Very few theoretical studies have been done on clusters of these elements. Jones and Hohl[9] have studied clusters of phosphorus. Balasubramanian and coworkers[10] have done calculations for dimer, trimer and tetramer of group V–A metals. Recently, Kumar[11] has reported the electronic structure of Sb_2, Sb_4, and Sb_8 clusters using the *ab initio* molecular dynamics method.[12] For Sb_4, a regular tetrahedron was found to be about 2 eV lower

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in energy than a roof or bent-rhombus structure. For Sb_8, however, two very different structures, (i) two weakly interacting tetrahedra and (ii) a bent rhombus interacting with a stretched tetrahedron were found to lie within about 0.1 eV of each other. This is in agreement with the above experiments which indicated strong dependence of formation of Sb clusters on nucleation conditions. In order to make a systematic study of the growth of Sb clusters, we have performed *ab initio* molecular dynamics calculations for the intermediate range of clusters viz. Sb_3, Sb_5, Sb_6, and Sb_7 and also for Sb_{12}. Our results are in agreement with both the thermal and the laser evaporation experiments and show the importance of bent rhombus structure for larger clusters.

The paper is organized as follows. The next section gives the computational details. In Sec. III we present results on Sb_2 to Sb_8 and Sb_{12} clusters. These results are discussed in the light of the above-mentioned experiments and a comparison is made with the results obtained for phosphorus clusters. In the last section we present our conclusions.

II. COMPUTATIONAL DETAILS

The calculations have been performed using the *ab initio* molecular dynamics method[12] within the local density approximation (LDA). The details of the method can be found in Ref. 13 and in other review articles.[14] Here, we present only the relevant computational details. The cluster was placed in a supercell with periodic boundary conditions. An fcc supercell with sides equal to 46 a.u. was found to be 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 sampling of the Brillouin zone. Norm-conserving pseudopotential of Bachelet *et al.*[15] with *s* nonlocality was adopted in the Kleinman and Bylander[16] separable form to speed up the calculations. Exchange and correlation data of Ceperley and Alder[17] as parametrized by Perdew and Zunger[18] was used. All the calculations were done by neglecting the effect of spin-orbit coupling. Initial tests of convergence were performed on a dimer and a cutoff of 11.5 Ry was found to be satisfactory for the plane wave expansion. Calculations for Sb_N ($N<6$) have been done using the steepest descent technique while for larger clusters simulated annealing (SA) calculations have been performed. In these calculations the clusters were heated upto about 3500 K and cooled at the rate of about 2.75×10^{14} K/s.

III. RESULTS

In this section, we discuss the low lying structures found for different clusters of antimony. The corresponding binding energies, bond lengths and angles are given in Table I. Results of experimental measurements are also cited where available.

A. Sb_2–Sb_5

The low energy isomers obtained from our calculations are shown in Fig. 1. The dissociation energy for the dimer was found to be 7.19 eV and the bond length was 4.48 a.u. While the dissociation energy is overestimated as compared to the experimental value,[19] the bond length is in good agreement with the experimental result of 4.425 a.u. It is well known that the LDA overestimates the binding energy whereas the bond length is usually underestimated. The slight overestimation of the bond length in our calculations indicates that the core *d* orbitals may be needed as part of the valence states to get a better agreement. However, it should be noted that Wang *et al.*,[20] who included *d* orbitals as part of the basis set in their configuration interaction calculations, obtained a smaller dissociation energy (2.17 eV) and a larger bond length as compared to the experimental value. As the difference is small, we have neglected it in the present cal-

TABLE I. Cohesive energies, E_{coh}, bond lengths and angles in antimony clusters. Experimental values of binding energy and bond lengths are also given in square brackets wherever available. For the tetrahedron–rhombus structure of Sb_8 and for Sb_{12}, bond lengths and angles have a spread and therefore only representative values have been given.

Cluster	E_{coh} (eV/atom)	Bond length (a.u.)	Bond angles (°)
Dimer	3.595 [1.55][a]	4.485 [4.425][a]	
Trimer	3.9	4.85, 5.16	57.84, 64.32
Bent rhombus	4.15	4.97, 5.34	57.55, 64.9, 104.19
Tetrahedron	4.67	5.03	60.0
Pentagon	4.19	4.85, 4.92	95.77, 96.81, 111.03 112.94, 123.45
Capped square	4.41	5.17, 5.24	59.14, 60.43, 90.0
Prism	4.58	5.16, 5.25	60, 90
Sb_7	4.63	5.06, 5.17 5.28, 5.65	57.85, 60, 62.2 83.4, 86.7, 97.2 97.8, 100, 104.3 105
Fused tetrahedra	4.73	5.06, 5.13, 7.09	59.1, 60, 60.45
Tetrahedron rhombus		5.01, 5.03, 5.06, 5.13, 5.17, 5.38, 5.69	55.5–62, 69–73, 80, 92–97, 103.8, 139, 145.5
Sb_{12}	4.76	5.0, 5.1, 5.3 5.4, 5.7, 5.8	55.5, 61.2, 62.3, 72.7, 93, 97, 99, 118, 126, 142

[a]Reference 19.

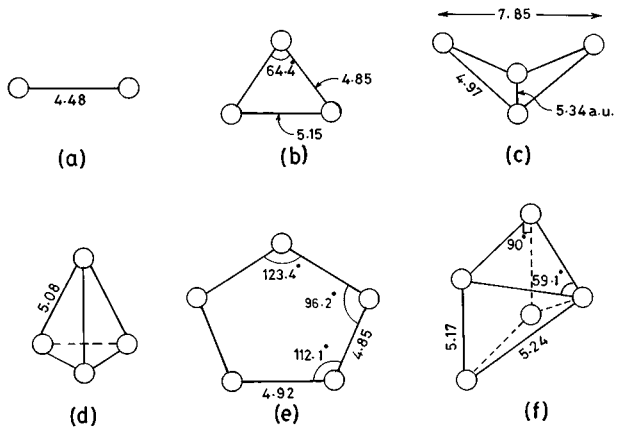

FIG. 1. Structures of (a) Sb_2, (b) Sb_3, (c) Sb_4 (bent rhombus), (d) Sb_4 (Tetrahedron), (e) Sb_5 (pentagon) and (f) Sb_5 (capped square) clusters. Bond lengths are in a.u.

culations. Inclusion of the p nonlocality was found to result in only a slightly longer bond length and a smaller binding energy and therefore it has been ignored.

Antimony trimer is an isosceles triangle [Fig. 1(b)] with a cohesive energy of 3.9 eV/atom. The Jahn–Teller distortion from an equilateral triangle is small and is about 4.4° as against a value of 5.8° obtained by multireference configuration interactions calculations.[20] The situation is similar to the case[9] of P_3 where the distortion is about 5.6°. We find that the triangular structure with about 60° angles is a common feature of the antimony clusters (see Table I).

For Sb_4, steepest descent calculations have been performed for a tetrahedron and a planar structure. On convergence the planar structure becomes a bent rhombus with dihedral angle equal to 138.9° as shown in Fig. 1(c). Angle between the bonds is either around 60° or 104°. This structure is found to be 2.05 eV higher in energy than a regular tetrahedron [Fig. 1(d)]. Our results therefore agree with those obtained from other calculations which also find a tetrahedron to be of lowest energy for a tetramer. However, later we shall show that the bent rhombus structure plays an important role in the structure of larger clusters.

Sb_5^+ has been found to be abundant by Geusic *et al.*[3] in their laser ablation experiments. We did two combined steepest descent calculations, one with capped rhombus and the other with a pentagonal structure. The capped rhombus structure converges to a capped square structure [Fig. 1(f)] and is 1.1 eV lower in energy than the pentagonal structure [Fig. 1(e)]. In the case of P_5, Jones and Hohl[9] have found a capped bent rhombus (roof) structure to be of lowest energy. This difference could also be due to the fact that in our calculations we have not included spin polarization. However, our result agrees with the prediction based on the electron counting model.[3,21]

B. Sb_6

For larger clusters the number of possible configurations increases and therefore we performed simulated annealing calculations to obtain the lowest energy structure. For Sb_6, the initial configuration was taken to be a prism with random displacement of ions [Fig. 2(a)] and the cluster was heated upto 1500 K. Figure 2 shows snapshots of some of the structures observed during the annealing of the cluster at different temperatures. The salient features of the dynamics of this cluster can be described in terms of triangles and rhombi. When the cluster is heated to 1500 K and allowed to evolve, the square like faces start becoming rhombi [Fig. 2(b)]. Besides ionic vibrations, the triangles 134 and 256 remain nearly intact. Bonds having 90° angle between them are deformed and these have the tendency to form 60° bonds. As we shall see from the final converged structure which is a prism, the bonds between the two triangles in a prism are slightly longer than the bonds within a triangle. This also suggests that the bonds between the triangles are weaker and that structures based on rhombi have a large basin of attraction at finite temperatures. Figure 2(c) can be described in terms of fused bent rhombi, namely, 1345, 1346, 1456, 2346, 2356, 2645, and 3456. Further evolution of the cluster at 1500 K makes it visit the initial structure [Fig. 2(d)]. When

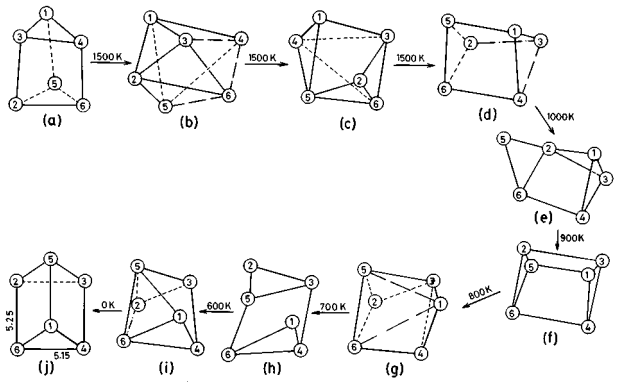

FIG. 2. A few snap shots of structures of Sb_6 during the simulated annealing at various stages: (a) starting structure (distorted prism), (b), (c), and (d) at 1500 K, (e) at 1000 K, (f) at 900 K, (g) at 800 K, (h) at 700 K, (i) at 600 K and (j) the equilibrium structure (prism). The continuous line is for the bonds in the foreground, dashed line for bonds in the background, long-dashed line for weak bonds in the foreground and long-dotted–dashed line for weak bonds in the background. The same convention is used in other figures.

the cluster is annealed at lower temperatures (1000, 900, and 800 K) similar tendency is continued [Figs. 2(e), 2(f), and 2(g)]. However, at 700 K in the two triangles which were nearly intact some bonds are broken and two other triangles 235 and 146 are formed. These form a chair type structure [Fig. 2(h)] which was also found to be a local minimum by Jones and Hohl for P_6. Further cooling leads to a fused rhombi structure [Fig. 2(i)] which ultimately becomes a prism [Fig. 2(j)] at $T=0$ with D_{3h} symmetry. However, the ions get rearranged as compared to the starting configuration. While a prism is also a local minimum for P_6, Jones and Hohl obtained a C_{2v} structure to be of lowest energy. Though we did not study all the structures that the cluster might have had during the SA, the few low lying structures that we have shown in Fig. 2 suggest that the minimum energy structure of P_6 is not quite favorable for Sb_6 and that a prism and fused rhombi structures are the most preferred. From the fact that the abundance spectrum for phosphorus and antimony are different, our results can be considered to be in agreement with this finding which indicates that the bonding in the two systems is somewhat different.

C. Sb_7

While Sb clusters other than those having $4n$ atoms are less abundant and are nonmagic, Rayane *et al.*[5] have found that under different nucleation conditions the intensity of $2n+1$ clusters can be increased. In particular they observed an increase in the intensity of Sb_7^+ cluster as the temperature of the helium gas in the condensation cell is increased. They also observed that evaporation in $2n+1$ clusters was less efficient than in the case of Sb_{4n} clusters. Sb_7^+ cluster was also found in abundance in the laser ablation experiments.

We performed simulated annealing calculations by heating the cluster to 2800 K. A higher temperature was required for this cluster to make ions diffuse. Figure 3 shows the evolution of structures as the cluster is cooled. The simulation was started with a configuration of a prism with an atom capping one of the rectangular faces [Fig. 3(a)]. An interest-

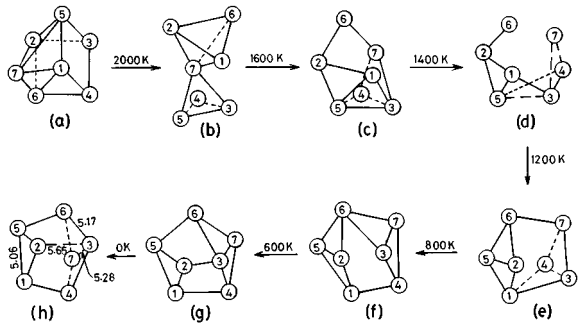

FIG. 3. A few snap shots of the structures of Sb_7 during the simulated annealing at various temperatures: (a) starting structure (capped prism), (b) at 2000 K, (c) at 1600 K, (d) at 1400 K, (e) at 1200 K, (f) at 800 K, (g) at 600 K and (h) converged structure (coupled triangle and bent rhombus structure). Explanation of the various types of lines is the same as in Fig. 2.

ing structural feature of the cluster encountered during the process of annealing at 2000 K was a tetrahedron capping a triangle as shown in Fig. 3(b). Both triangle and tetrahedron are stable clusters of antimony. At around 1600 K, this becomes a fused bent rhombi structure as shown in Fig. 3(c). This structure has a large basin of attraction and shows interesting dynamical behavior during the SA. In a very short time a bond is broken and another bond is formed so that, there is a transformation to an equivalent structure [Figs. 3(e) and 3(f)]. One can say that at temperatures above 600 K which we have studied, this cluster prefers a fused bent rhombi structure. The final structure that we have obtained is shown in Fig. 3(h) and can be better described as a bent rhombus fused with a triangle. In this structure all the vertices are three fold coordinated except vertex 3 which is four-fold coordinated. Bond 2–3 is longer than other bonds in this cluster. It is noted that most ions in different Sb clusters are tricoordinated. In a few cases where coordination is more than three, at least one of the bonds is elongated and therefore it is weak. Interestingly Jones and Hohl also obtained the same structure for P_7.

D. Sb_8

Sb_8 is the smallest cluster in which we can have two weakly interacting tetrahedra as originally speculated by Sattler *et al.*[22] Also since bonding in these clusters involves mainly p orbitals, one could ask if a cube would be of lower energy. We performed several steepest descent and two simulated annealing calculations[11] for Sb_8. Results of the steepest descent calculations are shown in Figs. 4(a)–4(c). Though a cube, two fused rhombi [Fig. 4(b)] and a bicapped octahedron [Fig. 4(c)] are a local minimum, these lie higher in energy as compared to two noninteracting tetrahedra. One of the simulated annealing calculations was done starting with a cubic structure with random displacement of ions. The cluster was heated upto 3500 K and then cooled. The resulting structure is shown in Fig. 4(e). This is the lowest energy structure among all the calculations that we have done for Sb_8. It can be viewed as two tetrahedra interacting weakly through their faces such that they are rotated with respect to each other by 60°. In this way the atoms maximize the number of neighbors as one can expect in the case of van der

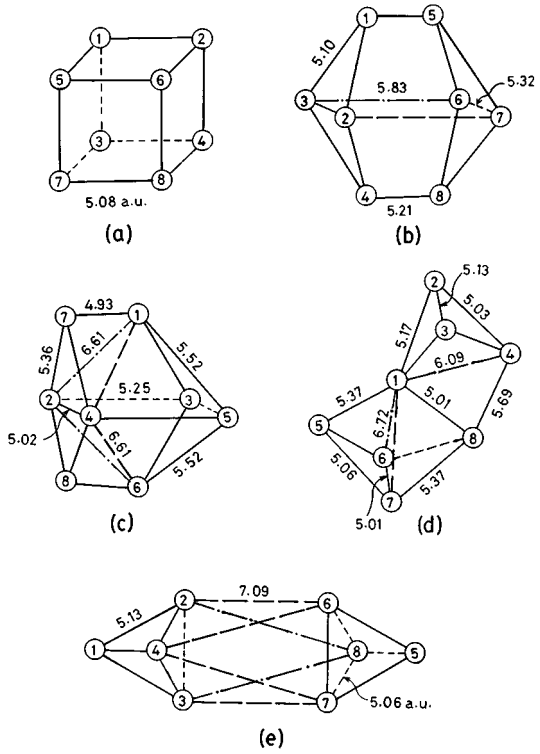

FIG. 4. Low lying structures of Sb_8: (a) cube, (b) two fused bent rhombi, (c) bicapped octahedron, (d) and (e) structures obtained from simulated annealing. The two tetrahedra in (e) are bonded by van der Waals type weak interactions.

Waals bonded systems which is manifested from a large intertetrahedron separation. 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.*[5] in the range of Sb_8 to Sb_{20} clusters. Our results thus support the prediction of Sattler *et al.*[22] However, Sb_{4n} clusters have been observed only at low temperatures. At high temperatures Sb_4 is the most abundant. In order to check if the structure of Fig. 4(e) was not an artifact of SA at a high temperature, we performed another SA calculation in which the bicapped octahedron structure was heated upto 2000 K such that the ions started diffusing within the time scale we used. However, the displacement of the ions from their initial positions was not as large as in the first SA calculation. The cluster was cooled again with a similar rate and the final structure is shown in Fig. 4(d). It is quite different from the one shown in Fig. 4(e) and is only 0.12 eV higher in energy than the tetrahedron based structure. This structure can be viewed as a stretched tetrahedron interacting with a bent rhombus via three bonds which are of nearly the same length as the bonds in the bent rhombus. Therefore, the interaction between the two tetramers is not of van der Waals type as in the case of two tetrahedra. Atoms 1 and 8 are more than threefold coordinated and as we discussed earlier some of the bonds joining at these sites are elongated.

Generally the magic clusters have a structure with high symmetry. In order to check if we were not trapped in a local minimum, we did another steepest descent calculation in which the bonds 5–8 and 1–4 [Fig. 4(d)] were made nearly

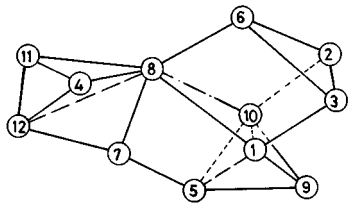

FIG. 5. Structure of Sb_{12} obtained from simulated annealing.

equal (both long and short distances were used). However, the structure relaxed back to the same configuration as shown in Fig. 4(d). The energy difference between the two structures obtained from simulated annealing is small. It is well known that LDA does not describe the van der Waals interaction properly. Therefore within the accuracy of our calculations we consider the two structures to be degenerate. It should be noted here that the two fused tetrahedron structure would have a soft mode of vibration while we do not expect the same for the other structure. Bréchignac *et al.*[23] in recent experiments find no soft mode which supports the structure based on bent rhombi and reaffirms that the growth and structure of antimony clusters depend on the nucleation conditions. Both these structures are different from the lowest energy structures obtained by Jones and Hohl[9] for P_8 and suggest that the bonding in phosphorus and antimony clusters is different. Our results are thus in agreement with the experiments which suggest that the structure of antimony clusters may depend upon nucleation conditions and explain the observation of predominantly tetramers in the mass spectrum above room temperature to be due to very weak interaction between the tetramers.

E. Sb_{12}

In order to check the growth mode for larger clusters, we did a simulated annealing calculation for Sb_{12}. The resulting structure is shown in Fig. 5. This structure has two elongated tetrahedra fused together with atom 7 in the figure. This is capped by triangle 236 which forms a prism like structure. This structure has similarity with the second isomer obtained for Sb_8. This together with the results of other clusters indicate that for larger clusters a bent rhombus may be the dominant constituent and the observation of Sb_{4n} clusters is likely due to the nucleation conditions which give rise to an abundance of Sb_4.

IV. ABUNDANCE, GROWTH AND FRAGMENTATION

As stated in the beginning, Sb clusters have been found to show abundance of Sb_{4n} ($n \geq 1$). This has led to a model based on the tetrahedral packing to explain the magic numbers 8, 36, 52, and 84. Later observations by Geusic *et al.*[3] and Rayane *et al.*[5] indicated the formation of other clusters with odd number of atoms as well. It was pointed out[5,6] that Sb_{4n}, $n>1$ clusters behave differently from the bulk and different nucleation conditions could lead to the formation of Sb_{2n+1} clusters. Rayane *et al.*[5] found the intensity of 3-, 4-, 5-, 7-, and 9- atom clusters to increase with an increase in the He gas temperature while at the same time the intensity of

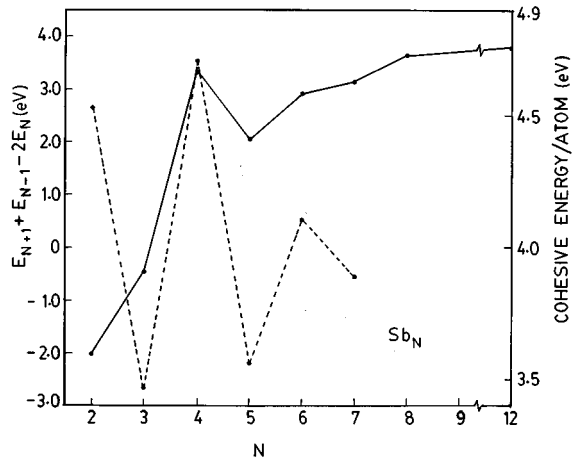

FIG. 6. Cohesive energy of the lowest energy isomers of Sb clusters (continuous line) and the second order difference spectrum of total energy (dashed line).

Sb_{4n}, ($n>1$) clusters decreases. They suggested that the fragmentation of Sb_8 into Sb_3 and Sb_5 could help in the formation of odd numbered clusters. Mühlbach *et al.*[2] observed that the Langmuir evaporation below the melting point was dominated by the emission of Sb_4 clusters but around 1050 K there was a sudden fall in the relative intensity of tetramers and an increase in the dimer intensity. In the following we discuss these aspects in the light of our results.

Figure 6 shows the cohesive energy and the second order difference of energy of clusters, $\Delta_2(E_N)=E_{N+1}+E_{N-1}-2E_N$ for Sb clusters of size 2 to 8 and 12. Here, E_N is the total energy of a cluster with N atoms. As one can see from this figure and Table I, the cohesive energy increases upto Sb_4 and then there is a small decrease at Sb_5. After this the cohesive energy increases slowly. The second order difference spectrum shows dimers and tetramers to be abundant whereas Sb_6 is marginally favorable. On the other hand, clusters with odd number of atoms are not expected to be adundant from these results. It is evident that the tetramer should be the most abundant out of all the clusters we have studied. Further, from the structure of these clusters the following growth pattern can be inferred. Up to 5- atom clusters the growth could be atom by atom while Sb_6 can not be considered to arise from Sb_4 or Sb_5 due to strongly directional nature of the bonding. From Table I it can be noted that the bond angles in a cluster are either around 60° or 90° or 105° or 130°. One can think that two Sb_3 clusters can combine to form Sb_6 but Sb_3 itself is not likely to be abundant. This is perhaps the reason why Sb_6 has not been observed in the mass spectrum. These results are in agreement with the observation[5] of neutral antimony clusters with only up to five atoms. For larger clusters, bent rhombus or distorted tetrahedron play an important role but a bent rhombus lies very high in energy as compared to the tetrahedron and this could be the reason for little abundance of Sb_7. For Sb_8 we have obtained two nearly degenerate isomers which differ from each other very significantly. This agrees with the observation[5,6] that the structure of these clusters could depend upon nucleation conditions. Under conditions of abundance of Sb_4,

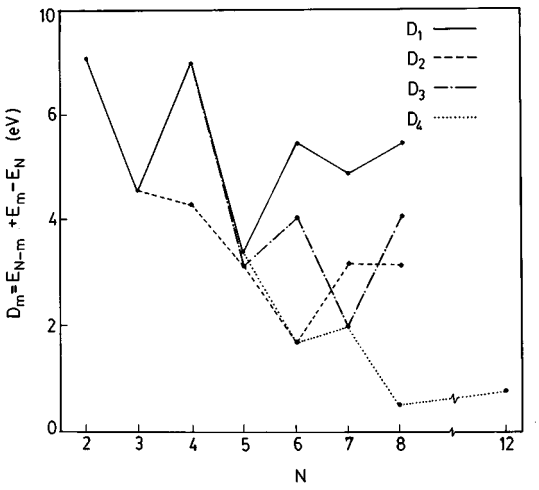

FIG. 7. Dissociation energy spectra of the lowest energy antimony clusters for different channels.

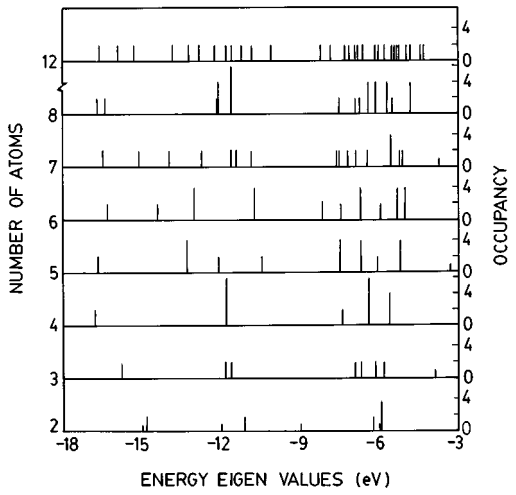

FIG. 8. Kohn–Sham eigenvalues of the lowest energy Sb_2 to Sb_8 and Sb_{12} clusters. The height of the lines corresponds to the number of electrons in that state.

there is an aggregation of tetrahedra whereas in situations where clusters with odd number of atoms may be abundant, one can get the other isomer, e.g., from fusion of Sb_3 and Sb_5 or addition of an atom to Sb_7. For Sb_{4n} clusters with tetrahedra, we find that the intertetrahedron distance is much larger than the interatomic distance in a tetrahedron. If all the four faces of a tetrahedron are capped with tetrahedra, 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 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 Rayane *et al.*[5]

The fragmentation energies $D_m = E_{N-m} + E_m - E_N$ for the lowest energy isomers of antimony clusters having 2 to 8 atoms are shown in Fig. 7. It can be noted that among all the clusters we have studied, fragmentation of Sb_8 into tetramers is the most favorable one and Sb_{12} shows a similar behavior. We, therefore, expect the same for other $4n$ clusters also. It may be noted that a recent study[24] of the fragmentation of Sb_{4n}^+, $2 \leqslant n < 20$, clusters also finds the loss of a neutral Sb_4 to be the predominant dissociation channel. Next possible type of fragmentation for Sb_8 could be into dimer and hexamer for which the dissociation energy is nearly 3 eV while fragmentation into Sb_3 and Sb_5 or Sb and Sb_7 is least favorable. Therefore, the possibility of producing odd atom clusters from fragmentation of neutral larger clusters is very little. Further, the fragmentation energies of the odd atom clusters are larger than the ones for Sb_{4n}. These results are in agreement with the observation of odd atom clusters under different nucleation conditions and their stability against fragmentation as compared to $4n$ clusters. It can be noted that in our calculations the cohesive energy of the odd atom clusters relative to their lowest energy fragmentation channel is more than 2.0 eV. This again agrees with the experimental observation that this energy should be more than 1.3 eV.

Considering the Sb_7 cluster, dissociation into a tetramer and a trimer is the most favored while for other clusters fragmentation into Sb_2 and Sb_{N-2} is the most likely one. These results are in contrast to other metal clusters[25] where generally monomer is the most preferred fragmentation channel. For Sb_5, fragmentation into tetramer and a monomer is only slightly less favorable as compared to fragmentation into dimer and a trimer. Similar result has been obtained recently by Bréchignac *et al.*[24] for Sb_5^+. These results therefore suggest that at higher temperatures one should expect abundance of Sb_4 clusters which should ultimately fragment into dimers as observed[2] because the fragmentation energy of Sb_4 into dimers is 2.665 eV less than that for $Sb + Sb_3$. Also Sb_5 and Sb_7 are more stable against fragmentation than Sb_6 and Sb_8 and similarly a trimer is more stable than a tetramer. Therefore, formation of $2n+1$ atom clusters is possible at higher temperatures or under different nucleation conditions (such as due to presence of charged clusters) as found by Rayane *et al.*[5] and Bréchignac *et al.*[6]

The Kohn–Sham energy spectrum for the lowest energy structures is shown in Fig. 8. The spectra of clusters with low symmetry structures have more spread though the overall bandwidth of the occupied states for most of the clusters is about 12 eV. For Sb_2, Sb_4, and Sb_8 clusters all the states are doubly occupied. However, for Sb_3, Sb_5, and Sb_7 clusters the highest level is singly occupied and this level is separated from the next occupied level by a gap of 1.93, 1.88, and 1.4 eV, respectively. Therefore positively charged Sb_3, Sb_5, and Sb_7 clusters should be expected to be stable as also found in laser ablation experiments.[3] As stated earlier, Sb_3^+, Sb_5^+, and Sb_7^+ have 8, 14, and 20 valence p electrons which are equal to $2N+2$, $2N+4$, and $2N+6$, respectively, as required by Wade's rule according to which these are also expected to be stable. Abundance of such cations could lead to a different mass spectrum for Sb clusters. Conversely 3-, 5-, and 7-atom cations could become preferred fragments as observed in photofragmentation studies.[5,24] The gap between the highest and the next occupied states for odd clusters would decrease with the increase in the cluster size and therefore positively charged large odd clusters may not show any particular

abundance. In fact, in an independent study of fragmentation of Sb_N^{++} clusters, very recently Bréchignac *et al.*[24] have found Sb_5^+ as the dominant small fragment for clusters with $N \leqslant 30$. For $30 < N < 40$, Sb_5^+ and Sb_7^+ are dominant whereas for larger ($N \geqslant 44$) clusters, there is a transition from asymmetric fission to a more symmetric behavior as the number of observable fission channels increases and the fission is realized as a fragmentation into two singly charged clusters of comparable sizes. Our calculations support these findings because the binding energy of clusters increases slowly with cluster size and therefore fragmentation of parent clusters into larger fragments should be expected with increasing N. On the other hand as stated earlier, for larger odd clusters the gap between the highest and the next occupied states would become small and this could therefore eliminate the preference for certain channels.

V. SUMMARY AND DISCUSSION

In summary we have presented results of a detailed study of the atomic and electronic structure of Sb clusters obtained from *ab initio* molecular dynamics calculations. Our results of the cohesive energy and the second order difference spectrum of energy show that Sb_4 should be the most abundant as also observed experimentally. Further, in agreement with the experimental observations we find that the structure of these clusters depend upon the nucleation conditions. The lowest energy structure that we obtained for Sb_8 is two weakly interacting tetrahedra that agrees with the observation of Sb_{4n} ($n > 1$) clusters and their nonmetallic weak bonding nature. However, there is another very different structure which is nearly degenerate. It is a bent rhombus interacting with a distorted tetrahedron. The vibrational frequencies for the two structures are expected to be quite different as the structure with two weakly interacting tetrahedra would have a soft mode while no such mode is expected for the other structure. Therefore study of the vibrational spectrum and properties related to it could give useful information about the isomers of these clusters. Our results also suggest importance of bent-rhombus structure for larger clusters and further study would be required to confirm this. The structure of Sb_8 is different from the one obtained by Jones and Hohl[9] for P_8. Therefore, though tetramers and a few other clusters of these elements have the same structure, the larger clusters behave differently.

The most favored dissociation channel for Sb_{4n} clusters is through evaporation of tetramers whereas for Sb_4, dissociation into dimers is the most preferred as also observed. Our calculations also suggest the stability of Sb_3^+, Sb_5^+, and Sb_7^+ clusters as seen in the laser ablation experiments. These clusters are more stable against fragmentation as compared to Sb_{4n} clusters. The growth of Sb clusters can be considered to be atom by atom upto Sb_5 but for larger clusters very different structure arise. This is likely to be the reason that neutral clusters upto Sb_5 have been observed in the experiments. All these results are in excellent agreement with both the thermal evaporation and laser ablation experiments. To further understand the growth of Sb clusters, it would be useful to study larger clusters and to do calculations with larger basis set including d orbitals and nonlocal treatment of exchange and correlations as the LDA does not describe the weak interactions well. We plan to do such studies in the future.

ACKNOWLEDGMENTS

One of us (V.K.) would like to thank C. Bréchignac for interesting discussions and for providing a preprint of her work on doubly charged clusters. Much of this work was carried out when the authors were at the International Centre for Theoretical Physics (ICTP), Trieste, Italy and V.S. is thankful to Professor Abdus Salam, the International Atomic Energy Agency and the UNESCO for the hospitality at the ICTP.

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