

Small clusters of tin: Atomic structures, energetics, and fragmentation behavior

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Ab initio electronic structure calculations on Sn_n ($n \leq 20$) clusters using ultrasoft pseudopotentials and generalized gradient approximation for the exchange-correlation energy show the binding energies of clusters with $n \geq 10$ to be only about 11% less than the calculated bulk value. This is likely to be responsible for the recently reported [Phys. Rev. Lett. **85**, 2530 (2000)] higher melting temperatures of these clusters than the bulk value. The growth behavior is found to differ from the one known for Si and Ge clusters at $n \geq 8$ but 10- and 18- to 20-atom clusters are similar. The calculated lowest energy fragmentation products are in excellent agreement with experiments and suggest that the lowest energy structures, obtained here, are close to the global minima.

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It has been a common belief as well as the finding of several experiments^{1,2} that melting temperatures of clusters are lower than the bulk value. However, recent experiments³ surprisingly suggest that tin clusters melt at least 50 K above the bulk value in the range of 16–30 atoms. This result has important implications for nanoscience and technology as the same may also be true for other clusters such as those of Si and Ge. On the other hand, large clusters of tin with 5–50 nm radii exhibit⁴ a depression of the melting temperatures as compared to the bulk value. Therefore, there appears to be a critical size below which tin clusters may acquire higher melting temperatures than bulk. Why is it so?

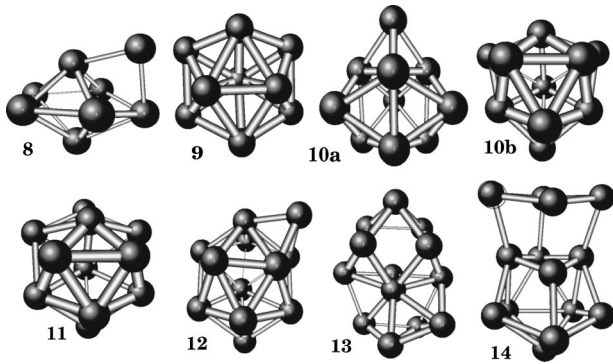
Properties of small clusters differ from bulk because most of the atoms lie on the surface. This often leads to structures that are very different from bulk. Therefore, the higher melting temperatures of small tin clusters have been speculated³ to be due to their different structures. Also, bulk tin is unique as it has two allotropes with distinct properties (1) semiconducting α -tin with diamond structure stable below 286 K and (2) metallic β -tin with body centered tetragonal structure that is stable under ambient conditions. It is unknown whether small tin clusters would prefer covalent or metallic bonding. It is possible that there are competing growth modes. Mass abundance spectra of tin clusters show both Pb and Si/Ge type behaviors^{5,6} depending upon the growth conditions. Ion mobility measurements⁷ suggest prolate structures of tin clusters similar to Si and Ge and a transition to compact structures in the range of $n = 35 - 65$. Isomers have also been observed for some clusters. The high melting temperatures of tin clusters make it interesting to understand the deviations and similarities with respect to properties of Si and Ge that have attracted much attention in recent years. In this letter, we study Sn_n isomers with $n \leq 20$ and report the finding of unusually high binding energies (BE's) that could be responsible for their higher melting temperatures.

Higher melting temperatures of Si, Ge, and Sn clusters with $n \leq 13$ were reported⁸ from a first principles study within the local density approximation (LDA). However, the calculated BE's are even more than the bulk value for some clusters. The higher melting temperatures could, therefore, be a consequence of this overbinding.

We use the generalized gradient approximation (GGA)⁹ for the exchange-correlation energy and obtain significantly

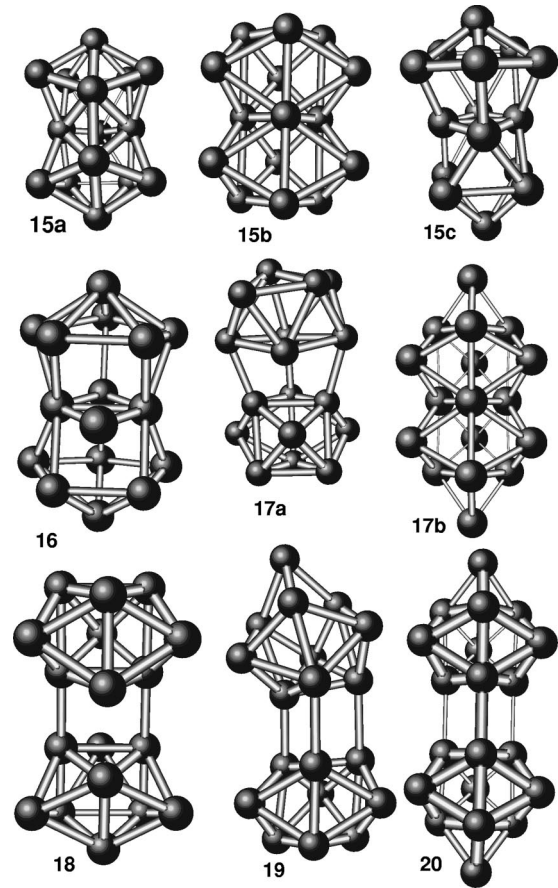
improved estimates of the BE from *ab initio* ultrasoft pseudopotential calculations^{10,11} with a plane wave basis. The cutoff energy of the plane waves is taken to be 19.1156 Ry. Test calculations on bulk tin in the diamond structure give the lattice constant and cohesive energy to be 6.62 Å and 3.08 eV/atom which are in excellent agreement with the experimental values¹² of 6.49 Å and 3.14 eV/atom, respectively. For clusters, we use a simple cubic supercell of side 20 Å and Γ point for the Brillouin zone integrations. The simulated annealing method, often best suited to obtain the lowest energy structures of clusters, is known to fail in systems such as Si.¹³ Therefore, we optimize a large number of structures, including those reported for Si (Ref. 13) and Ge (Ref. 14) clusters, using the conjugate-gradient method. For a dimer, the bond length and the BE are calculated to be 2.78 Å and 1.208 eV, respectively, taking four valence electrons for each tin atom. Inclusion of *4d* electrons also as valence gave very little change in the BE and the bond length. Therefore, all calculations have been done with four valence electrons in Sn. Sn_2 is found to have a magnetic moment of $2\mu_B$ but all other clusters are nonmagnetic.

Clusters with $n \leq 7$ have the same structures as those of Si and Ge, in agreement with experiments.¹⁵ For $n = 3$ to 7, these are C_{2v} triangle, D_{2h} rhombus, D_{3h} trigonal bipyramid, D_{4h} (two intersecting rhombi) and D_{5h} pentagonal bipyramid (PBP), respectively. As the size increases, there appear other isomers that are comparable or lower in energy than those obtained from the lowest energy structures of Si or Ge clusters. For Sn_8 , an edge capped PBP (Fig. 1) has lower energy than the distorted bicapped octahedron for Si_8 (Ref. 12) and Ge_8 .¹³ Sn_9 is a tetracapped trigonal bipyramid which is again different from the distorted tricapped trigonal prism (TTP) structure of Si_9 and Ge_9 . This agrees with the result reported in Ref. 8 but for Sn_8 their results differ from ours in the way an atom is added to the PBP structure. Wang *et al.*¹⁶ have also done an LDA study of tin clusters with $n \leq 10$ and their structure for Sn_8 is similar to ours. For Sn_{10} , a distorted tetracapped prism (10a) has the lowest energy as it is also for Si_{10} and Ge_{10} . However, we find another compact isomer (10b in Fig. 1) with near C_{3v} symmetry. It lies only 0.09 eV higher in energy and is important for the lowest energy structures of Sn_{11} and Sn_{12} which are cappings of this isomer (Fig. 1). These differ from the pentacapped trigonal

FIG. 1. Lowest energy isomers of Sn_n ($n=9-13$).

prism and a C_{2v} isomer reported in Ref. 8 and which we find to be, respectively, 0.42 and 0.23 eV higher in energy. Therefore, there is an onset of structural divergence of tin clusters at $n=8$ and then at $n=11$ as compared to Si and Ge clusters. It is interesting to note that measurements⁷ of ionization potentials (IPs) also indicate a different behavior of tin clusters as compared to Si_n at around $n=12$. For Sn_{13} , the lowest energy structure is obtained from the optimization of the isomer reported in Ref. 8. It differs from Si_{13} in the way the bottom rhombus (Fig. 1) caps the rest of the cluster. We also optimized an icosahedron as the metallic behavior of tin as well as the low intensity of Sn_{14} (Ref. 17) as compared to Ge_{14} raised speculation about it. However, we find it to lie 0.59 eV higher in energy. The lowest energy isomer (Fig. 1) of Sn_{14} is found to be different from Si_{14} . Other isomers obtained by removing one or two atoms from the structures of Sn_{15} and Sn_{16} lie significantly higher in energy.

Figure 2 shows the low lying isomers for $n=15-20$. We optimized several structures for $n=15$ and 16 to understand the growth mode in this size range. Here we show only those isomers which have lowest energies or are nearly degenerate with it. Our results show an intermediate growth behavior of tin clusters, in between the compact structures of metals and the elongated ones of Si.^{13,18} In particular, icosahedral compact structures are not among the low lying isomers. But, a 6-atom capped pentagon, a PBP and a tricapped or tetra-capped prism are among the units that are present in most of the clusters in this size range. The lowest energy isomers for $n=15$ and 16 are similar to those of Ge_{15} and Ge_{16} .¹⁴ Another isomer, 15b, with two fused tricapped prisms is nearly degenerate with 15a while 15c with fused 6- and 9-atom units is only 0.017 eV/atom higher in energy. Therefore, more than one isomers of Sn_{15} are likely to be present in experiments while for Sn_{16} other isomers lie more than 0.059 eV/atom higher in energy and may not be observed. This could be a reason for more abundance of Sn_{15} as the growth is possible in more than one ways. Sn_{17} is also different from Si_{17} in the way a TTP is capped. For Sn_{17} the capping 8-atom unit is a D_{2d} type cluster which is frequently found in metal clusters,¹ while for Si_{17} , it is a capped boat type structure¹³ that is typical in covalently bonded systems. Another isomer, 17b, resulting from the fusion of two 10-atom capped prism units on the base, is nearly degenerate. For Sn_{18} - Sn_{20} , a number of structures were optimized starting with those de-

FIG. 2. Lowest energy isomers of Sn_n ($n=14-20$).

rived from 15- and 16-atom isomers as well as the spherical and prolate isomers reported in Ref. 13. We find that the elongated structures based on TTP units are more favorable for Sn clusters as for Si_n but these differ in details. A double icosahedron, often found to be favored for a 19-atom metal cluster, reconstructs for Sn_{19} and lies 0.036 eV/atom higher in energy. Therefore, the growth behavior of Sn clusters flip flops between partial metal-like and silicon-type structures. The bond lengths also confirm this behavior. Some clusters have a few nearest neighbor bonds that are even longer than in bulk allotropes and at the expense of some strong short bonds. In some other clusters, however, the nearest neighbor bond lengths are nearly uniform and are shorter than in the bulk. This is typical for metal clusters.

The calculated $\text{BE}=[E(n)-nE(1)]/n$, $E(n)$ being the total energy of an n atom cluster, and the highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) gaps (Table I) show significant deviations from LDA results.⁸ A linear fit of the calculated values of the BE shows that the data can be fitted well with two slopes. The extrapolation to bulk incidently matches with the calculated bulk value (3.08 eV/atom) (Fig. 3). The good agreement of the latter with experiments (3.14 eV/atom) also gives confidence in the values for clusters.¹⁹ Considering a simple relation $E_c=E_B+\gamma n^{2/3}$ of the cluster BE (E_c) with the bulk BE (E_B), we find the calculated surface energy to be 0.79 eV/atom. This is in good agreement with the experimental value of 0.72 eV/

TABLE I. Calculated binding energies (BE) in eV/atom and HOMO-LUMO gaps (eV) of Sn_n ($n=2-20$). The LDA results are taken from Ref. 8.

n	BE		Gap		n	BE	
	GGA	LDA	GGA	LDA		GGA	GGA
2	1.208		0.32		14	2.772	1.34
3	1.771	2.227	0.84	1.10	15a	2.786	0.77
4	2.220	2.736	1.05	0.98	15b	2.783	1.32
5	2.402	2.965	1.58	1.25	15c	2.769	1.06
6	2.571	3.167	1.61	1.56	16	2.795	1.37
7	2.695	3.308	1.50	1.55	17a	2.761	0.63
8	2.628	3.236	1.01	0.88	17b	2.751	1.27
9	2.710	3.334	1.45	1.36	18	2.782	0.88
10a	2.772	3.432	1.54	1.54	19	2.772	0.60
10b	2.765		1.71		20	2.793	0.84
11	2.716		0.92				
12	2.709		0.98				
13	2.720	3.407	0.91	0.80			

atom assuming a (100) type surface. The low value of the slope indicates low surface energies as compared to other metals such as Al. An exceptional outcome of the present calculations is the high BE of clusters. Even a cluster of about 10 atoms with all the atoms on the surface already has its BE only about 11% less than the calculated bulk value. Thereafter, the BE decreases slightly and then increases but very slowly (Table I). This result is in sharp contrast to about 30% lower binding energies of aluminum clusters²⁰ in this

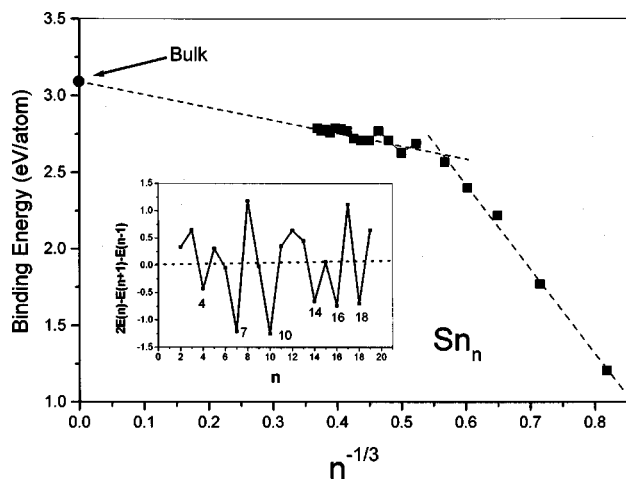


FIG. 3. Plot of binding energy as a function of $n^{-1/3}$. The broken line shows extrapolation to the bulk value. The inset shows second order difference in energy. Magic clusters are marked with numbers.

size range and suggests that the bonds in tin clusters are significantly stronger than in the bulk. This is important to understand the higher melting temperatures of Sn clusters. As melting starts on the surface of a material, our results indicate that for small tin clusters with most of the atoms on the surface, the melting temperatures could be higher than the bulk. In order to understand this unusual result, we further calculated energies of fragments (center atom and its nearest neighbors) in the bulk body centered tetragonal as well as the diamond structures. Atomic relaxations keeping the same symmetry lead to total energies that are, respectively, 3.06 and 4.28 eV higher than the values for the corresponding ground states of the 7- and 5-atom clusters. Therefore, structural rearrangements lead to large gains in the BE's of these clusters and they affect the bonding. If we could consider a solid with the same bonding nature as in these small clusters, naturally the melting temperature of such a hypothetical solid would be significantly higher than the bulk tin we know. The present results suggest that with an increase in the cluster size there is an effective decrease in the binding energy of the interior part of the cluster (as it tries to attain more bulk-like structure) but a gain in the surface contribution due to an effective reduction in the fraction of surface atoms, leading ultimately to a decrease in the melting temperature for large clusters.

The second order difference of total energies $2E(n) - E(n+1) - E(n-1)$, shows (inset in Fig. 3) 4-, 7-, 10-, 14-, 16-, and 18-atom clusters to be magic. Among these, 7, 10, and 18 are in agreement with the mass abundance spectra.^{15,17} However, experiments on cation clusters show 15 also to be magic (weak intensity only) instead of 14 and 16. It is at the boundary in our calculations. This slight difference could arise because experiments are on cation clusters and also from the existence of isomers as discussed above. Clusters with 6 and 9 atoms are at the boundary of becoming magic. Interestingly, 4-, 6-, 7-, 9-, and 10-atom clusters are among the lowest energy fragments for $n > 9$. This is another important measure of the stability of clusters. Assuming fragmentation to occur along the lowest energy pathways with no activation barrier, we calculate the fragmentation energy, $E_f(n) = E(p) + E(q) - E(n)$, of an n -atom cluster into p - and q -atom ($n = p + q$) fragments. It is found²¹ that neutral Sn_n clusters with $n \leq 8$ favor monomer evaporation (Fig. 4) similar to metal clusters. However, for $n > 8$, the fragmentation pattern changes and larger units become energetically more favorable products. For $n = 12$ and 13, the size of fragments increases further and the products are Sn_6 and Sn_7 . These results are in excellent agreement with recent experiments²² and support the results obtained here. Sn_{10} is found to be the largest fragmentation product and it is in good agreement with the available data on charged clusters^{15,17} that show 14-atom unit to be the largest fragment. This also supports the finding of magic behavior for Sn_{14} . Fragments with more than 10 atoms could arise from larger clusters. The fragmentation energy for Sn_{15} is higher than the values for Sn_{14} and Sn_{16} . This could also result in higher abundance of Sn_{15} . The low fragmentation energies for $n = 17, 19$, and 20 again corroborate the low intensities observed in the mass spectra.^{15,17} In particular, the energy to

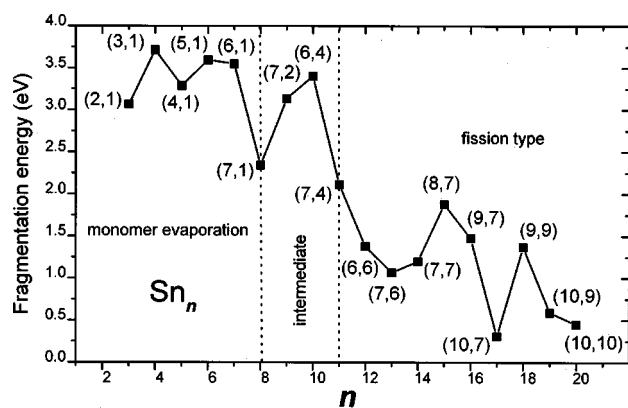


FIG. 4. Lowest energy fragmentation channels of tin clusters. The numbers in the brackets indicate the products. The three regions represent different fragmentation behaviors.

fragment Sn_{17} into 7- and 10-atom clusters, both of which are magic, is the lowest. Noteworthy, it has been difficult to detect Sn_{17} .¹⁵ This good agreement with experimental observations gives us confidence that our search for the lowest energy structures should be close to the global minima. The HOMO-LUMO gap shows discontinuity from $n=7$ to 8, 10 to 11, and 16 to 17. The gap is the largest for the isomer $10b$. Also isomers $15b$ and $17b$ have significantly (Table I) larger

HOMO-LUMO gaps and this could be used to identify the lowest energy isomers from photoemission experiments.

In summary we have carried out a systematic investigation of the lowest energy isomers of Sn_n clusters with $n \leq 20$. Our results show that tin clusters adopt different structures as compared to Si and Ge for $n=8, 9$, and ≥ 11 but some of the larger prolate clusters have similarities. The bonding nature in these clusters is different from that of the bulk fragments and surprisingly, beyond $n=10$ the BE's are within about 11% of the calculated bulk value. This seems to be the reason for the higher melting temperatures in these clusters as compared to the bulk. A comparison of BE's of Si_{10} and Ge_{10} with bulk gives, respectively, 18 and 15% lower BE's. Therefore, if the silicon clusters would melt at higher temperatures than the bulk, the relative difference is likely to be much smaller than tin clusters. This finding makes tin very special. The calculated fragmentation behavior of these clusters is in excellent agreement with the experimental observations that support the structures obtained here.

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¹V. Kumar, K. Esfarjani, and Y. Kawazoe, in *Clusters and Nanomaterials*, edited by Y. Kawazoe, T. Kondow, and K. Ohno, *Springer Series in Cluster Science* (Springer Verlag, Berlin, 2001), p. 9.

²D. A. Baffat and J. P. Borel, *Phys. Rev. A* **13**, 229 (1976); Y. Leereah, G. Deutscher, P. Cheyssac, and R. Kofman, *Europhys. Lett.* **12**, 709 (1990); M. Schmidt, R. Kusche, B. von Issendorff, and H. Haberland, *Nature (London)* **393**, 238 (1998).

³A. A. Shvartsburg and M. F. Jarrold, *Phys. Rev. Lett.* **85**, 2530 (2000).

⁴S. L. Lai *et al.*, *Phys. Rev. Lett.* **77**, 99 (1996).

⁵T. P. Martin and H. Schaber, *J. Chem. Phys.* **83**, 855 (1985).

⁶M. Watanabe, Y. Saito, S. Nishigaki, and T. Noda, *Jpn. J. Appl. Phys., Part I* **27**, 344 (1988); Y. Saito and T. Node, *Z. Phys. D: At., Mol. Clusters* **12**, 225 (1989).

⁷A. A. Shvartsburg and M. F. Jarrold, *Phys. Rev. A* **60**, 1235 (1999).

⁸Z.-Y. Lu, C.-Z. Wang, and K.-M. Ho, *Phys. Rev. B* **61**, 2329 (2000).

⁹J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).

¹⁰Vienna *ab initio* simulation package, Technische Universität Wien, 1999; G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11 169 (1996).

¹¹D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

¹²C. Kittel, *Introduction to Solid State Physics*, 7th ed. (Wiley & Sons, New York, 1996), p. 57.

¹³B. Liu *et al.*, *J. Chem. Phys.* **109**, 9401 (1998); K.-M. Ho *et al.*, *Nature (London)* **392**, 582 (1998).

¹⁴A. A. Shvartsburg *et al.*, *Phys. Rev. Lett.* **83**, 2167 (1999).

¹⁵S. Yoshida and K. Fuke, *J. Chem. Phys.* **111**, 3880 (1999).

¹⁶B. Wang *et al.*, *Ann. Phys. (Leipzig)* **7**, 107 (1998).

¹⁷K. LaiHing, R. G. Wheeler, W. L. Wilson, and M. A. Duncan, *J. Chem. Phys.* **87**, 3401 (1987).

¹⁸L. Mitás, J. C. Grossman, I. Stich, and J. Tobik, *Phys. Rev. Lett.* **84**, 1479 (2000).

¹⁹The BEs of small tin clusters with $n < 8$ have been measured [A. Desideri and D. L. Cocke, *J. Chem. Phys.* **62**, 731 (1975)]. These are about 15–20% lower than the calculated values. This higher discrepancy with experiments as compared to about 3% for the bulk could be due to some uncertainties in the experimental values or correlation may be playing a more important role as in Si clusters (Ref. 18). This would need to be further studied.

²⁰V. Kumar, S. Bhattacharjee, and Y. Kawazoe, *Phys. Rev. B* **61**, 8541 (2000).

²¹Besides the lowest energy channels shown in Fig. 4, other competing channels are (8,1) and (6,3) for Sn_9 with 0.021 and 0.119; (9,1) and (7,3) for Sn_{10} with 0.098 and 0.165; (10,1) and (6,5) for Sn_{11} with 0.144 and 0.262; (7,5) for Sn_{12} with 0.046; (9,6) and (10,5) for Sn_{15} with 0.031 and 0.123; (10,6) for Sn_{16} with 0.046; (10,8) and (11,7) for Sn_{18} with 0.015 and 0.103 eV higher in energy, respectively.

²²T. Yutaka (private communication).