

Quantum-Chemical Study of Mechanism of Growth of Nanometer-Tin-Particles

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Abstract

Big clusters of Tin Sn_N (so called mesoscopic particles) containing hundreds of atoms with diameter up to 15 nm show that cohesion of mesoscopic particles results from local interactions between nearest neighbor atoms. Many body interactions play only a minor role. Using Semi-empirical calculation, we were able to build a growth models for Tin particles. The criteria for the best model is determined by structure of particles, localization of interactions and mainly the values of the binding energies and internuclear distances and their convergence to cluster particles of the bulk.

Keywords: Quantum-Chemistry; Tin; Growth; Cluster; Mechanism; Nanometer

Introduction:

In a previous study we tried to explain properties of small free clusters Sn_N ($N = 2, 3, \dots, 17$). It has been shown ^[1] that highly intensive peaks in mass spectra at $N=3, 7, 10, 13$ and 15 are related to high stabilities of clusters. The structures of such small clusters differ remarkably from that of the bulk.

In the present study we are focusing attention to bigger clusters of Tin (so-called mesoscopic particles) containing a few hundreds of atoms with diameters up to 15 nm. Their importance lies in their potential use in modern semiconductor electronics.

Our goal is to determine their favorable structure, obtain how they differed from bulk, optimize the properties of particles convergence continuously to corresponding value of the bulk and obtain their electronic interactions.

Method:

In order to attain above goals, three models of growth of shell-like clusters of Tin is discussed (see sec. 3). In each model we optimize the shortest distance (R_1) by minimization of energy of interactions i.e. binding energy (BE) according to semi-empirical, Extended Hückel Molecular Orbital method (EHMO) ^[2]. By doing so, we were able attain the goals presented in the introduction.

In the frame of EHMO-method the molecular orbitals ψ_μ are considered as linear combinations of atomic orbitals ϕ_j :

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$$\psi_{\mu} = \sum_{j=1} C_{\mu j} \varphi_j \quad (1)$$

The linear combination coefficients $C_{\mu j}$ and the molecular orbital energies ε_{μ} are given as solutions of linear eigenvalue-problem:

$$\det \left(H_{ij} - \varepsilon_{\mu} S_{ij} \right) = 0 \quad (2)$$

The matrix-elements H_{ij} are parameterized:

$$H_{ii} = (\varphi_i, \hat{H}_i \varphi_i) = -\alpha \quad (3)$$

(α_i : orbital ionization potential of atom of state i).

$$H_{ij} = 0,5 \cdot K \cdot (H_{ii} + H_{jj}) \cdot S_{ij} \quad ; \quad (K = 1,75) \quad (4)$$

($S_{ij} = (\varphi_i, \varphi_j)$): overlap-integral of the atomic orbitals φ_i and φ_j).

The total electronic energy of interaction (E) is a sum of molecular orbital energies ε_{μ} for all occupied molecular states μ :

$$E = \sum_{\mu=1} n_{\mu} \varepsilon_{\mu} \quad (5)$$

(n_{μ} : occupation-number of molecular orbital ψ_{μ}).

Per Tin-atom we use a basic set of one 5s-function and three 5p-functions. In TABLE (1) the values of parameters are given (α -values and ζ -values according to reference [3]).

Table (1): EHMO-Parameters for Tin.

Atom	Orbital	ζ (a.u. ⁻¹)	α (eV)
Sn	5s	2.12506	10.18371
	5p	1.81924	5.75721

Results and Discussion:

Investigations of structures of clusters made of few 100's particles of Tin are remarkable different from those of small ones ^[1]. A comparison between three models of growth of particles is reported. For the case of Model I and Model II, FIGURE (1), the mesoscopic particles Sn_N have shell-like tetrahedral structures where the atoms of Tin inside have the same local environment as it is in the crystal lattice. In the surface however the atoms has less coordination as compared to the ones inside. For the case of the model III, the mesoscopic particles Sn_N have shell-like quadruple-pyramidal structures, (n: number of shells, N: number of atoms). The ratio of surface atoms to volume atoms decreases with cluster growth. Therefore, the properties of big clusters come close to the corresponding properties of bulk.

In order to be able to study the convergence through a wide range of clusters, we have taken into consideration even extremely small clusters like Sn_5 . It must be noted however that the tetrahedron Sn_5 is not the structure at equilibrium ^[1].

Model I (Anagnostatos ^[4]):

In this model the surface of tetrahedron of n shells of atoms is covered with a network of atoms (i.e. n+1 atoms at an edge of the tetrahedron). In the inside there are n-1 smaller tetrahedrons of similar structure of atoms. Therefore an overlap up to 40% between atomic spheres is expected to occurs. In other works, as if we start with the smallest tetrahedron with $N(n=1)=0+4=4$ atoms (all atoms at the surface), followed by clusters of two shells (n=2), one consists 4 inner atoms and the other 10 surface atoms: $N(n=2)=4+10=14$. This is best expressed by

$$N(n)=N(n=1) + N(n=2) + \dots + N(n=n-1) + N'$$

(with N' = number of surface atoms).

Model II:

In this model the atomic structure of a tetrahedral particle of n shells is considered as a cutout of an undeformed diamond-lattice of Tin, where nearest-neighboring atomic spheres touch each other. According to this building-model the stable clusters are:



Model III:

In this model the surface of a quadruple-pyramid of n shells of atoms is covered by network of atoms (with $n+1$ atoms at an edge of the pyramid). Inside are $n-1$ smaller pyramids of similar structure of atoms. That means: we start with the smallest pyramid with $N(n=1)=0+5=5$ atoms (all atoms at the surface). Then, the cluster of two shells ($n=2$) consists of 4 inner atoms and 10 surface atoms: $N(n=2)=4+10=14$. This is best expressed by

$$N(n) = N(n-1) + N'$$

(With N' = number of surface atoms).

Figure (1) shows a comparison between the clusters according to the three models.

Model I

Model II

Model III

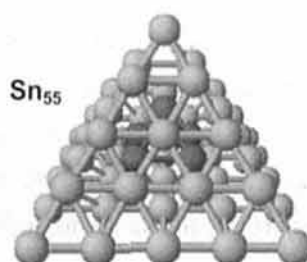
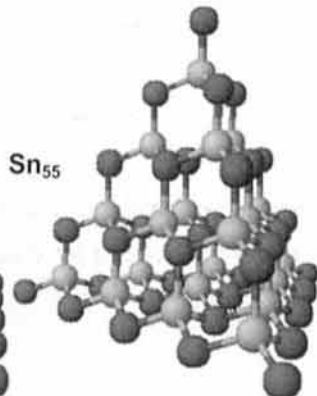
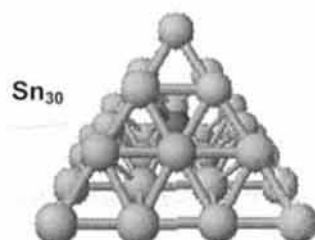
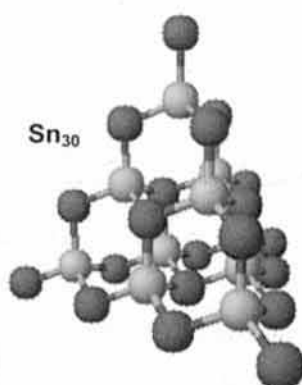
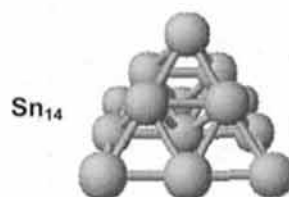
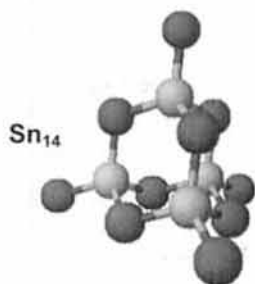
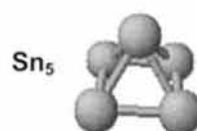
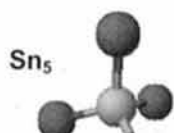
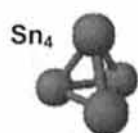


Figure (1): Growth models for tin particles

Figure (2) shows the mean binding energy per atom (BE/N) for the three models.

$$\frac{BE}{N} = \frac{E(Sn_N) - N \cdot E(Sn_1)}{N} \quad (6)$$

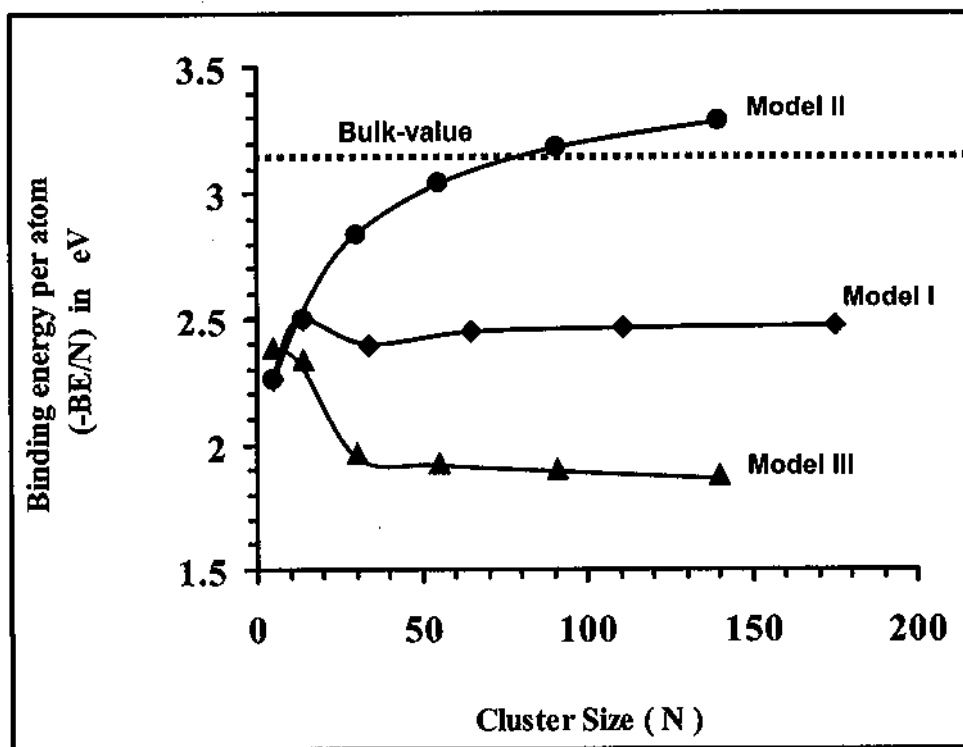


Figure (2): Binding energy per Tin-atom (-BE/N) in clusters Sn_N in dependence on cluster-size (N):

- (a) = Model I (Anagnostatos-model ^[4]).
- (b) = Model II (Tetrahedral-model).
- (c) = Model III (quadruple-pyramid model).

In each case the shortest pair distance (R_1) in the cluster was optimized by minimization of (BE/N).

It is obvious; that clusters built by model II are more stable. Therefore we shall discuss below only results of model II (shell-like tetrahedrons with diamond-structure). Figure (3) shows some of these clusters.

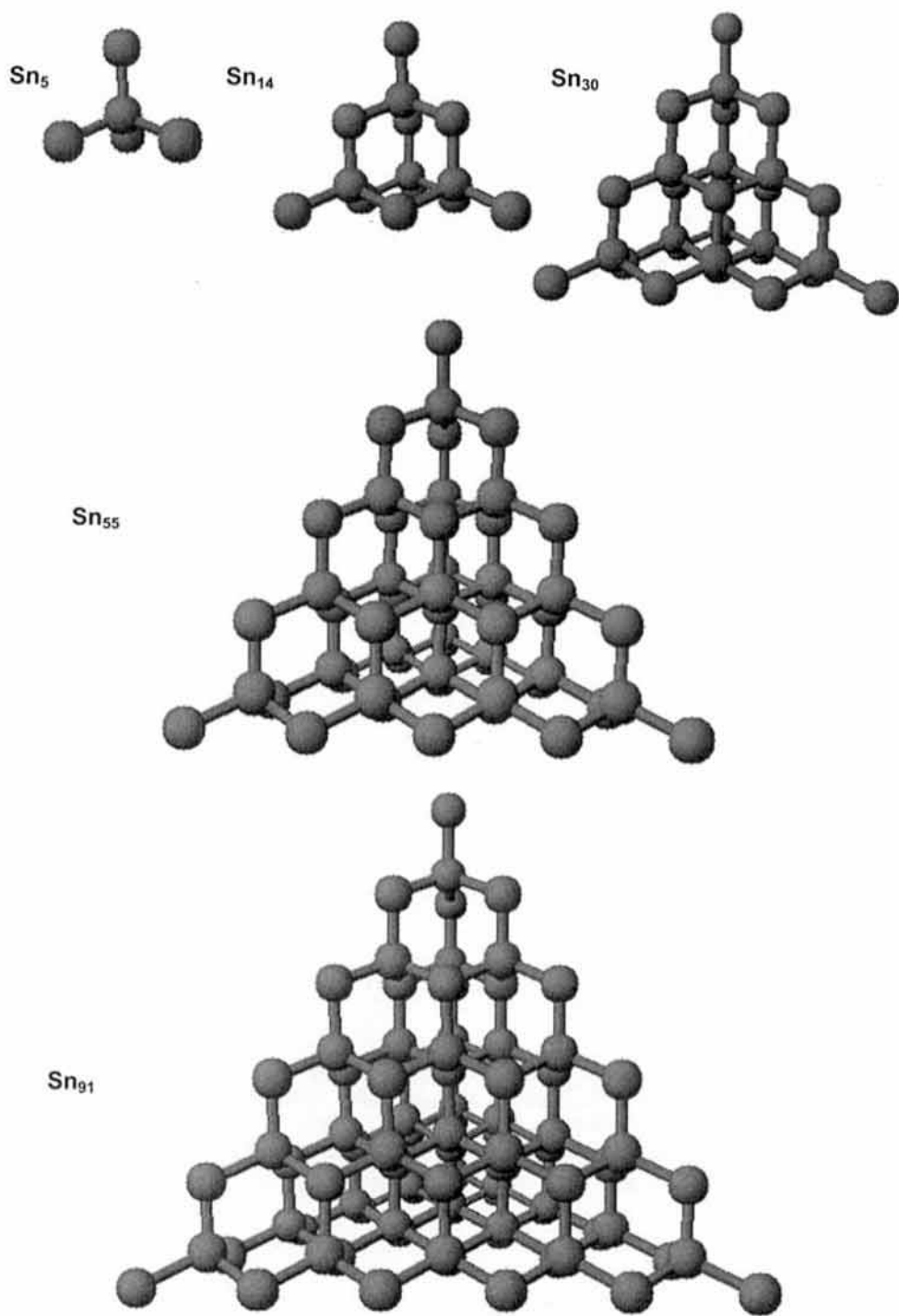


Figure (3a): Structures of clusters Sn_N according to the model II

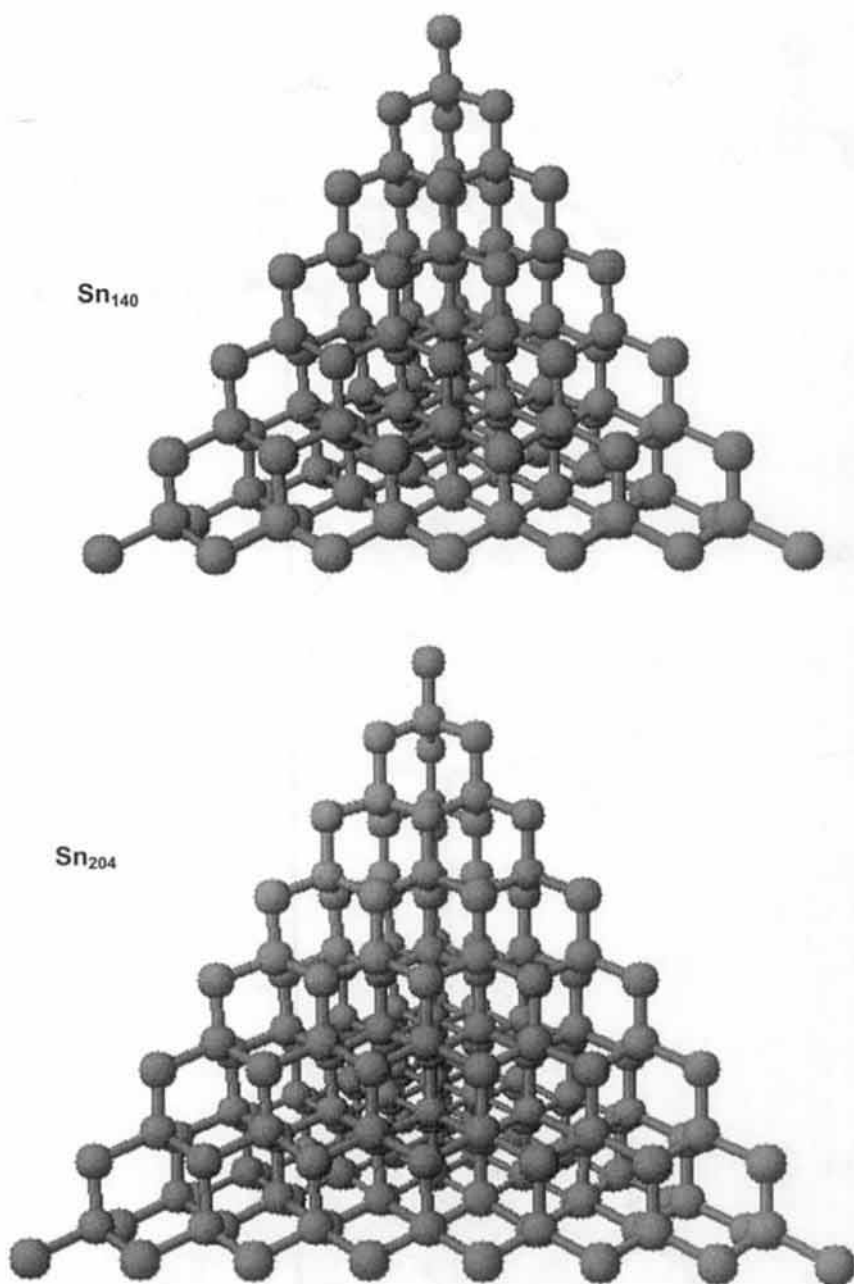


Figure (3b): Structures of clusters Sn_N according to the model II

Particles built by model II during their growth come close to macroscopic Tin crystal of definite size (i.e. with surface), where dangling-bonds (DB) of clusters are kept as surface states (DB/2) of bulk. Such states build discrete unoccupied energy levels between the HOMO (highest occupied energy level = the upper edge of the valence band) and the COND (the bottom edge of the conduction band). Table (2) and Figure (4) show that the energy gap (GAP) between the occupied valence band and the unoccupied conduction band decreases during the growth of particles.

Table (2): Size-effects of shortest pair distance (R_1), binding energy per atom (BE/N), coordination number (CN_1), energy-gap (GAP), dangling-bond states ($DB/2$), and dangling-bonds per atom (DB/N) of tetrahedral Tin-particles of n shells, which have an atomic structure similar to diamond lattice.

Cluster Sn_N	R_1 (Å)	BE/N (eV)	CN_1	$DB/2$	DB/N	ϵ_{HOMO} (eV)	ϵ_{COND} (eV)	GAP (eV)
Sn_5	2.22	-2.2570	1.600	6	1.2	-6.144	+33.94	38.57
Sn_{14}	2.60	-2.4986	2.286	12	0.86	-5.659	+6.03	11.68
Sn_{30}	2.63	-2.8392	2.667	20	0.67	-5.641	+3.29	8.91
Sn_{55}	2.66	-3.0425	2.903	30	0.55	-5.651	+1.64	7.29
Sn_{91}	2.68	-3.1844	3.077	42	0.46	-5.653	+0.67	6.32
Sn_{140}	2.68	-3.2892	3.200	56	0.4	-5.649	+0.17	5.80
Sn_{204}	2.69	-3.3737	3.294	72	0.35	-5.633	-0.25	5.38
Sn_{285}	2.69	-3.4410	3.368	90	0.32	-5.619	-0.52	5.10
Sn_{385}	2.69	-3.4954	3.429	110	0.29	-5.622	-0.73	4.89
Sn_{506}	2.70	-3.5414	3.490	132	0.26	-5.628	-0.92	4.52
$Sn_{\infty}^{[6]}$	2.81	-3.14	4.00	-	0.00	-	-	0.00

When mesoscopic particles grow without changing their structure one can approximately describe the size-dependence of a continuously changing property G by means of the following equation ^[5]:

$$G(N) \cong A + B \cdot N^{-\frac{1}{3}} \quad (7)$$

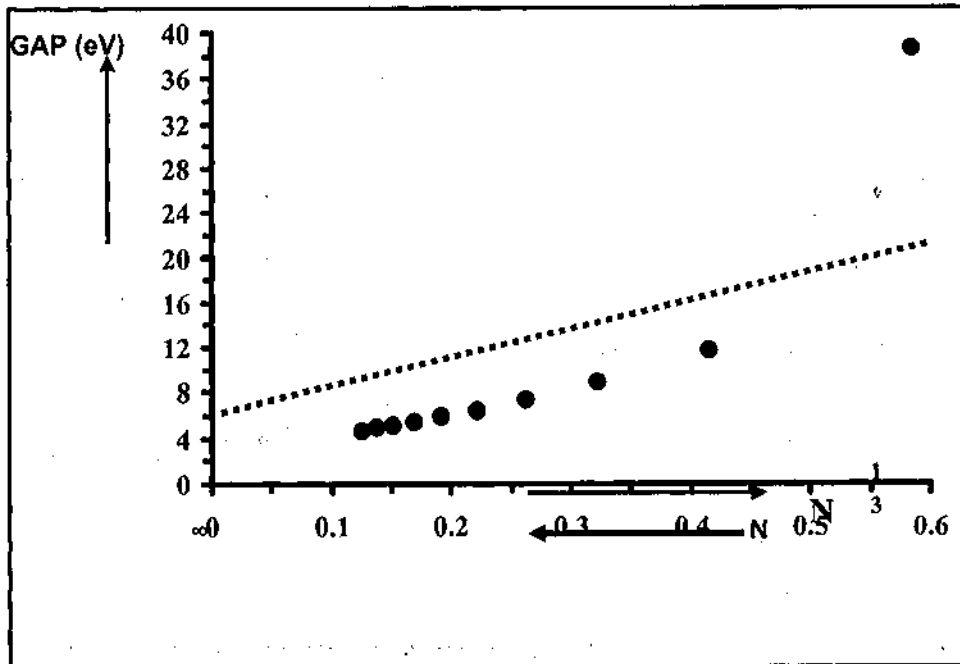


Figure (4): Size-effect of Gap energy (GAP) of tetrahedral Tin particles of n shells which have an atomic structure similar to diamond lattice.

The constant A is here the bulk-value of the property $G(\infty)$. The second term in equation (7) is proportional to the surface-to-volume ratio of particles.

We now examine equ. (7) for the tetrahedral shell-like particles of Tin with diamond-like atomic structure suggested by us.

Doing this we additionally obtain a hint about the accuracy of the results of our semi-empirical quantum-chemical calculations.

We represent the calculated values of the shortest pair distance (R_1) and the mean binding energy per cluster atom (BE/N) through the amount $N^{-1/3}$ (figures. (5) and (6)).

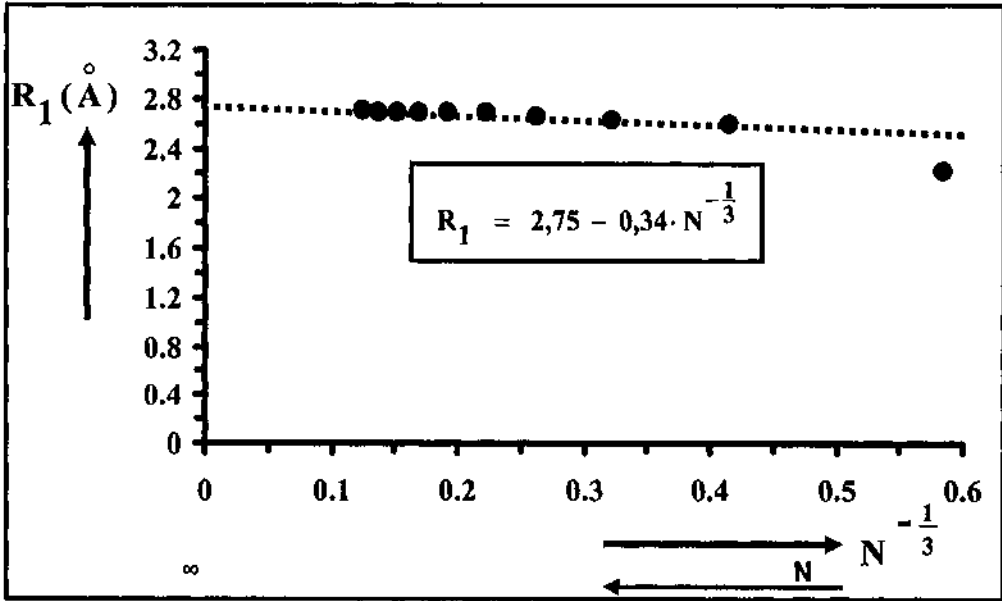


Figure (5): Size-effect of shortest atom-pair distance (R_1) of tetrahedral Tin-particles of n shells, which have an atomic structure similar to diamond lattice.

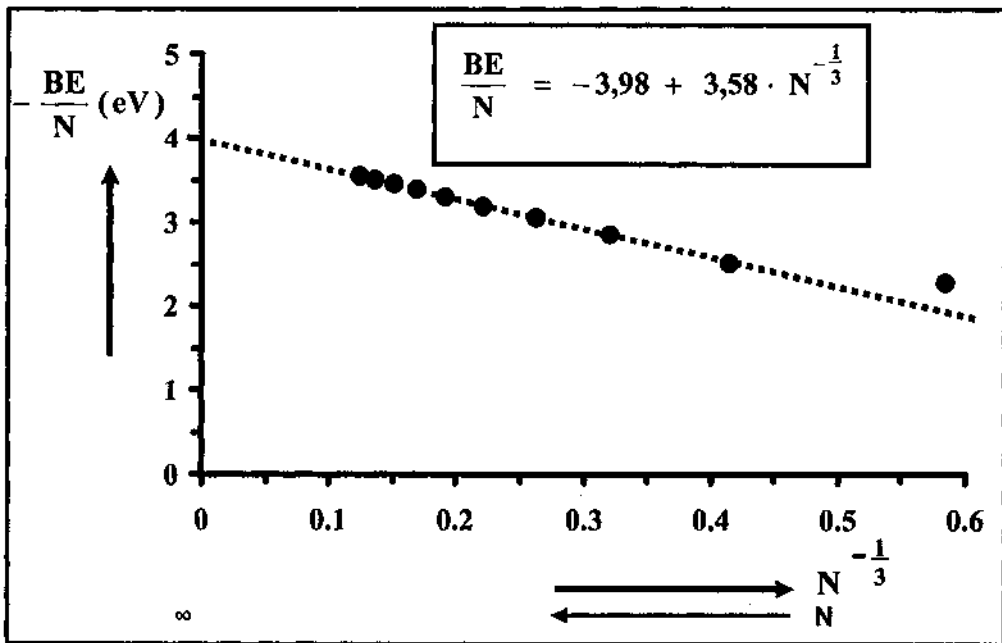


Figure (6): Size-effect of mean binding energy per cluster-atom (BE/N) of tetrahedral Tin-particles of n shells which have an atomic structure similar to diamond lattice.

Obviously, the relation (7) for $n \geq 2$ or $N \geq 14$ is a very good approximation. Only at extremely small particles ($n=1$, $N=5$), which have other structure of equilibrium, additional terms in the expansion (7) must be taken into consideration.

From a linear extrapolation to $N^{-1/3} = 0$ or $N = \infty$ are obtained the following bulk values:

$$R_{1(bulk)}^{EHMO} = A = 2,75 \text{ \AA}$$

$$\left(\frac{BE}{N}\right)_{(bulk)}^{EHMO} = A = -3,98 \text{ eV}$$

The experimentally determined values of bulk are ^[6]:

$$R_{1(bulk)}^{exp} = A = 2,81 \text{ \AA}$$

$$\left(\frac{BE}{N}\right)_{(bulk)}^{exp} = A = -3,14 \text{ eV}$$

In order to draw conclusions about the localization of interactions in mesoscopic Tin-particles, we focus on mean coordination number per Tin-atom (CN_1) regarding nearest-neighbor distances (R_1). At unlimited growth of particles CN_1 amounts to the value 4.0 (diamond-lattice).

$$CN_1 = \frac{4N - DB}{N} \quad (8)$$

Figure (7) shows the mean binding energy per cluster atom (BE/N) calculated by us as function of (CN_1).

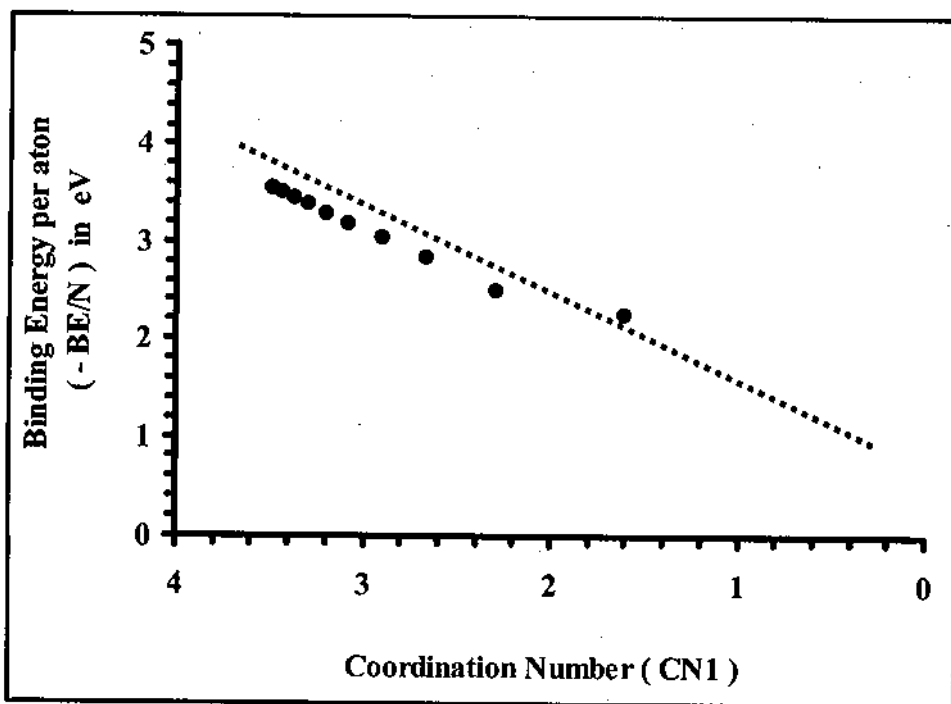


Figure (7): Binding energy per atom (-BE/N) as function of coordination number (CN₁).

Apparently, an atom in the cluster is not bound more firmly when the number of neighboring atoms increases. The amount BE/N grows strongly in proportion with the increase of CN₁. This is true for particles having more than one shell of atoms

Conclusions:

As compared to results obtained previously^[7,8] the proved relation for mesoscopic Tin-particles:

$$\frac{BE}{N} \approx CN_1(N) \quad (9)$$

takes into consideration the interaction between nearest- neighboring pair atoms to be important for cohesion of particles.

This mean:

1- In the description of binding energy BE according to many-body interactions:

$$BE = \sum_{i<j} U_{ij}(R_{ij}) + \sum_{i<j<k} U_{ijk}(R_{ijk}) + \dots \quad (10)$$

The interactions U_j between the two atoms separated by the distance R_j dominate. After entering mean coordination numbers CN_k related to the noticed pair distances R_k , the double sum can be described identically by:

$$BE \cong \sum_{i<j} U_{ij}(R_{ij}) = 0,5 \cdot N \cdot \sum_k CN_k \cdot U_k(R_k) \quad (11)$$

2- From the seen sum in the equation (11) is the first term the most essential:

$$BE \cong 0,5 \cdot N \cdot CN_1 \cdot U_1(R_1) \quad (12)$$

That means: for pair interaction potentials $U_k(R_k)$ at mesoscopic particles of Tin, the topological approximation is allowed:

$$U_k(R_k) \cong \begin{cases} U_1(R_1) & ; k=1 \\ 0 & ; k \neq 1 \end{cases} \quad (13)$$

Within this approximation the interaction energy is restricted only to interactions between nearest-neighboring atoms.

We summarize:

- 1- In mesoscopic Tin particles, the local interactions dominate, whereas the pair interactions between the atoms separated by wide distances and also the many-body interactions play only a minor role.
- 2- These conclusions are applicable to bulk with an energetic accuracy of 26.7% and with an accuracy of distance of 2.1%.
- 3- Looking for any atom in the cluster, the number of non-nearest neighboring atoms is always less than those in bulk. Also, the number of terms of many-body interactions ($U_{ijk} \dots$) in clusters is less than those in bulk. Therefore, we can expect the errors found by us for bulk (26.7% for BE/N and 2.1% for R_1) to be upper limits for errors in clusters.
- 4- The usefulness of the topological approximation of pair potentials encourage us to suggest:

Looking for the possibility of a presentation of the interaction energy BE for particles of Tin as a sum of simple analytical pair potentials, whereby it might be possible to overcome the numerical problems known in literature of many-body representations in the case of Tin (see for example [9] and [11]). This would be an important step towards a simplification of dynamic investigations of so-called nano-structured semiconductors.

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