Phase Transition in Silicon Clusters

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Abstract

In this paper, I give a review of the recent works on phase transition in slicon clusters, and a systematic analysis on the available data of silicon cluster phase transition. So far by now, most of the work in this area is on geometry searching, as well as some property calculation. Roughly, there are three groups contribute most on the problem: Kai-Ming Ho at Ames Lab; Chelikowsky group at Minnesota University;Parrinello at Zurich Lab of IBM Research Division. Both the experimental work and theoteticla work shows that, there is a phase transition at size of about 27. It can be under stood in that, for Si clusters, we have small cluser with metalliclike structure on this hand and bulk system with covalent open structure on the other hand. There should be one ore more phase transition in between. One of them is the transion found in previous experiment work [1]. The systematic analysis gives a defination of order parameter η as the single bond density ρ_b, which is the ratio of single bond number to the total bond number. Under this framework, the total hamiltanian can be written in the similar form as alloy system, which can be solved within Lattice Gas model. The work along this line is far beyond finished.

1   Introduction

The drive towards nanoscale technology has motivated intensive research [1, 2] on small Si_n clusters. Since their bonding properties are very different from those of the crystal, this new form of Si is expected to have with properties different from those of bulk phases. The structural properties of clusters with n $\leq$ 10 are relatively well understood through a combination of experiments [3] and theory [4]. The structure of the larger clusters is still a puzzle, but the following experimental facts are known[10]. (i) The abundance spectrum exhibits neither special features nor magic numbers; (ii) the shape changes from prolate to "more spherical" in the narrow range between n $\approx$ 24 and n $\approx$ 30 ; (iii) the dissociation energy, which is strongly size dependent in the smaller clusters, becomes a smooth function of n and exhibits no magic numbers for n $\geq$ 25 ; (iv) the reactivity to several molecules is lower by 2   3 orders of magnitude than that of the most stable Si surface; and (v) the reactivity has minima at n = 33, 39, 45 for well annealed clusters.

Though motivated by an experenetal work [2], most of the work was done theoretically. In addition to the geometry searching of Si cluster, there are also calculations on the properties. Corresponding to the experimental work, the properties studied include: i) ionic mobilities [1, 2, 6, 7], ii) ionization potentials [6], iii) dissociation energy [5], iv) polarizabilities [8, 9], and v) electron affinities [8]. The methods include empirical Tight-binding [14], ab initio K-space [5, 6, 10, 12] and the ab initio real space [9] calculations.

Both experimental and theoretical works reveal that, there is a phase transition as the cluster size goes from n $\approx$ 24 to n $\approx$ 30. For clusters with n $\leq$, the shape tends to be prolated, while for clusters with $\geq$ 10, the shape tends to be spherical. There is a critical cluster size with atom number n_c.

The reason for this transition, is that, as n $<$ n_c, the bond lenth determins that, almost all the atoms are on the surfaces. To stabilize the system, the cluster tend to form some 4-fold bonding. This prolong the cluster. For n $>$ n_c, the clusters tend to have the 4-fold bonding cental atom to stabilize the system.

2   Experiment

The experimental work that brought the intensive siliocn cluster transition is that by M.F. Jarrod and his co-worker [1, 2]. In their work, for the first time, they find the silicon cluster growth pattern goes from prolated shape below n_c to the spherical shape above n_c. Below n_c, the ratio for the prolated clusters can be as large as   3.

They got the result by measuring the mobilities of silicon clusters in helium. The shape of a particular selected size of cluster can affect the mobility. After passing through a drift tube in a short pulse of cluster, the clusters arrive at the detector with time distribution, which can be recorded to meassure the mobility.

The mobility K_0 can be obtained by [2]

$$K_0 = \frac{v_d}{E} \frac{P}{760} \frac{273}{T} \tag{1}$$

where v_d is the average drift velocity , E is the electric filed in the drift tube , P and T are pressure and tempretur in the tube respectively. The comparison between different size of cluster is done by the scaled mobility, which is measured mobility divided by the hard-sphere mobility, which is [2]

$$K_{HS} = \frac{(18\pi)^{\frac{1}{2}}}{16} (\frac{1}{m} + \frac{1}{M})^{\frac{1}{2}} \frac{e}{(k_B T)^{\frac{1}{2}} Q_{HS}} \frac{1}{N} \tag{2}$$

where Q_{HS} is the hard sphere collision cross section, m and M are the masses of the cluster ion and the buffer gas in the drift tube, and N is the buffer gas number density.

The result is shown in Fig.1. The figure clearly show that, the relative mobility has a trend to decrease as the increasing cluster size. More important is that, as the cluster size increases, the relative mobility of the prolate cluster decrease faster than that of the oblate cluster.

The trend is clearly shown in Figure 2, which is plot of the relative abundance of the prolate form as a function of cluster size. For cluster with size n $< n_c$, prolate cluster dominates. Whereas, for clusters with size n $> n_c$, oblate cluster dominates. There is a transion of the two different forms over a narrow range of cluster size.

It is this experiment work that promoted a new wave the theoretical study of silicon clusters. In theoretical study, most of the work is done on the optimal geometry search. In addition to getting the result geometry, one or more properties are calculated to justify that the geometry obtained is corresponding to the experimental results. Th properties include, (i) Dissociation Energy, (ii) ionic mobility, (iii) ionization potential and (iv) polarization etc.

3   Dissociation Energy

The calculation of dissociation energy of cluster was first promoted by K.M. Ho group of Iowa State University. In comparing the selected geometries, the cohensive energy is a favorite property. It is desirable to the cohensive energies calculated for different geometries with experimental results. These can be determined by measuring the dissociation energy of a selected size of cluster.

The dissociation energy of a si_n neutral cluster along channel leading to si_m and si_{n-m} is [5]

$$D_{(n,m)} = nE_n - mE_m - (n-m)E_{n-m} \tag{3}$$

where E_n id the cohesive energy per atom of the Si_n cluster. With the values of E_n calculated for the selected geometry, the dissociation energy can be found through various dissociation path.

In their calculation, they employed the ab initio plane wave calculation with generalized gradient correction.

Since their work involve the cluster size up to 21, the data is not much ralated to the this paper.

One feature of their work is very interesting, genetic algorithm geometry searching. In the genetic algorithm, the system keeps a geometry reservoir, a gene reservoir. At each step, the intial geometry of the system is a combination of the parents, two individuals in the gene reservoir. After the system get to a new energy minimal, the new geometry is queued into the reservoir. And a defite number of elements in the queue with the lowest energy are selected to survive. And a next generation of initial geometry will be generated from the new reservoir, a new set of elements. After enough generation, the element of the geometry set may be highly generated in structure or generaated in energy. These surviving elements are the most possible geometries in macroscopy. The success of the algorithm depends on the population in the reservoir.

4 Evaluation of Mobilities Using Trajectory Calculations

The mobility of each given geometry, can be considered as a creterion to assign optimal atomic positions. The mobility, K_0, is inversly proportional to the orientationallly averaged collision integral Ω^0,

$$K = K_{HS} \times \frac{z \times \Omega^{HS}}{\Omega^0} \tag{4}$$

where K_{HS} is the hard sphere scatter cross section described in the previous experiment section.

The collision integral is evaluated by numerically integrating the momentum transfer cross section over the Maxwellian distribution of relative velocities between the buffer gas and the ion. This cross section is calculated by averaging a function of the scattering angle over the impact parameter and collision geometry. The scattering angles are determined by propagating classical trajectories of He atoms in their intramolecular potential with the polyatomic ion. This potential is constructed as a sum of pairwise Lennard-Jones interactions plus a charge-induced dipole term.

According to their calculation, for small size of clusters, n < 9, the partial charge is equally distributed among atoms. After reach n ≥ 9, the charge becomes increasingly localized on just a few atoms. This causes a slight increase in the collision integrals for such size of clusters. Their result gives one exlanation on the origin of the mobility difference, i.e., the charge uneven distribution.

The transition is also reproduced in their anotther work [7]. In the work, the genetic algorithm and ab initio plane wave method is employed as usual. The computation results shows that, in the n < 19 size range, the geometry is constructed

as stacked Si_9 tricapped trigonalprisms. Starting with n = 19, the result global minima drastically change from the prolate assemblies of Si_9 subunits to more compact cage-like geometries. The calculated mobilities for this new family of isomers disagree with the measured valued measured until n $\geq$ 24, where they fit the second experimentally observed isomer ("spherical"). The discrapancy in the point of transition onset is due to the entropy effect.

Their calculation supports that there is a structure transition from the prolate geometry to oblate geometry at some critical point n_c. The calculated n_c is different to that obtained in experiment. The dicrepancy may be caused by some detail in the model.

5   Ionization Energy

Ionization potentials of silicon clusters have been measured by threshold photoionization. Ideally, if the internal temperature of the neutral is close to absolute zero and the true threshold is identified, the measurement would provide the adiabatic ionization potential (AIP). If the geometry changes significantly upon ionization, the true threshold would probably not be located, and the measured value would lie between the AIP and the vertical ionization potential (VIP).

The work in the ionization energy in K.M. Ho group [6] also shows that there is a structrural transition from the prolate to oblated structure. In the ab initio calculation, the result with LDA only, gives a smaller n_c. Whereas, GGA correction improves the n_c from 5 to 19 or 20, in contrast of the experimental result n_c 27. The result shows that the critical point n_c is model-depended.

6   Polarization

Polarization is another important property of siliocn clusters. It reflects how strong the electrons in clusters react with the external electric field. In band theoty, whether a material is metal or not is determined bytthe band structure. If there is gap between the upper occupied band and the lower unoccupied band, the material is non metal, *visa versa*.

But here for cluster, the band theory is not aapliable. In clusters, the energy levels are separated. There is always a gap between the upper occupied band and the lower unoccupied band. In this case, polarization is good parameter to indicate whether a cluster is matal-like or insulator like. As the size of silicon cluster grows from a few to thermal dynamics limit, we expect to have a drastic drop in polarization is there there is a transition from the matllic to insulating.

Polarization is defined by [9]

$$\alpha_{ij} = \frac{\partial \mu_i(F)}{\partial F_j} = -\frac{\partial^2 E(f)}{\partial F_i \partial F_j}; i, j = \{x, y, z\}. \tag{5}$$

where α_{ij} is the dipole moment component, F is the applied uniform electric field, and $E(F)$ is the total energy wit hthe electric field F. The normally measured polarization in experiment is the average polarization given by $<\alpha>=\frac{1}{3}tr(\alpha_{ij})=(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})/3$, where $\alpha_{xx},\alpha_{yy},\alpha_{zz}$ are the diagonal elements of the polarization tensor. Because of the rotation invariance of the trace of the polarization tensor, the value does not depend on the choice of the coordinate system.

The difficulty in doing *ab initio* plane wave calculation of the polarization is that, The periodic effect imposed by the supercell of the plane wave calculation override the privalege that the plane wave method has. For such a consideration, J.R. Chelikowskey group employed the real space higher-order finit-differenctial method. In this real space calculation, the boundary condition is set that the wavefunction is rtequired to vanish outside the domain of the cluster.

The clusters studied are siliocn, germanium and gallium arsenide clusters up to size of n =10. Figure 3. shows their result on the polarization calculation. Although the size has not reached the experimental observed transition regime, the result partial satisfies the expectation that, the polarization decreases as the size of the cluster increases.

7 Phase Transition

Untill now, the work on silicon cluster is done geometry and properties such as ionic mobility, dissociation energy, and polarization etc. both theoretically and experimentally. To the knowledge of the author, there is no work published on the systematic analysis of phase transition in silicon clusters. In this section of the paper, I am going to do an analysis on the phase transition phenomena in silicon cluser.

The results reviewed in previous sections clearly show that, there is a phase transition as the cluster size goes from a few to thermodynamics limit. The phase transition reflectes the bond state changing from double bond or triple bond dominant, refered to surface bonds, to single bond dominant, refered to bulk bond. Comparing to the thermodynamics phase transition, we can define the order paramer as the density of single bond,

$$\eta \equiv \rho_b = \frac{n_{single-bonds}}{n_{total-bonds}}, \tag{6}$$

whereas the scaled temperature as ratio of the critical cluster size to the cluster size considered

$$t = \frac{n_c - n}{n_c}. \tag{7}$$

where n_c is the critical cluster size, and n is the size of clusters in the system.

First, we need to justify that, 1) there is a order parameter in the system, 2) the defination of the order parameter and scaled temperature. For a single cluster, it is

6

no meaning to define an order parameter, which is a macroscopic varible that exists in the thermodynamics limit. We can also have another side of view.

In experiment, the clusters are made of bulk system, which is a macroscopic system. The process of producing cluasters is considered as the fragmentation process of the bulk system. In addition, when measuring properties of clusters, we use a massive of clusters, which is also a macroscopic system. Single cluster can not make the macroscopic measurement eminent. Therefore, there is an order parameter in the clusters system.

For a silicon crystal in thermodynamics limit, the bonding method is dominated by the 4-fold single bond. During the segmentation process, the ratio of the single bond to the total bond diminishes, as the fragments get smaller and smaller. It is similar to the heating process of the ferromagnetic system. As the size of each cluster decreases, which corresponds to the high temperature phase where the order parameter decreases to infinitysmal, the single bond density ρ_b goes to infinitismal. On the other hand, during the cluster growth process, as the cluster size increases, the single bond density ρ_b increases and is saturated to 1 at the thermodynamics limit. Therefore, the behavior that the system depends on the cluster size is slimiar to that the magnetic system depends on temperature. Hence in this silicon cluster system, the temperature analogue is defined as

$$T_n = \frac{1}{n} \tag{8}$$

From this defination, we can get the scaled temperatuer in the following way,

$$t \equiv \frac{T_n - T_C}{T_c} = \frac{\frac{1}{n} - \frac{1}{n_c}}{\frac{1}{n_c}} = \frac{n_c - n}{n_c}. \tag{9}$$

where n_c is the critical cluster size, at which there is a phase transition.

Under this framework, the Hamiltanian can be written as the summation of the energy of all bonds. this is similar to the alloy problem, which can be mapped to the 1-D Ising model. The solution to this problem will lead to the scale phenomena and data collapse[15, 16]. Further developement of the model falls off the scope of this paper.

8   Discussion

In this paper, I give a review on the experimental and theoretical study of silicon clusters. The first experiment work[1, 2] on the phase transition of silicon cluster, promoted a new wave of theoretical study of silicon cluster. Under the influence of powerful computer and adcvanced algorithm, there is more work done in this area. Most of the work is done on the geometry searching. The details of small clusters are studied thoroughly. The searching work finds that, there is a phase transion at n = 20   30. This confirms the experimental results that, there is a phase transition at n   27.

In addition to the review on the phase transition of silicon cluster, I analyze both the experimental work and the theoretical work. In the systematic study, I define the temperature analogue as the reversal of cluster size $T = 1/n$, and define the order paremeter as $\eta = n_{single\ bond}/n_{total\ bond}$.

Under this framework, we can work through the problem similar to alloy problem, which falls into the category of 1-D Ising model.

Though the model may predict data collapse and scaling phenomena, the available data is not enough to verify that.

In addition to this line of work on phase transition of silicon clusters, there is another experimental work on it[13]. In this work, the author published their work on the silicon cluster phase transition due to the temperature of clusters, which is related to the activation energy in producin clusters.

9   Acknowledgment

References

[1] M. F. Jarrold, Science 252, 1085 (1991).

[2] M. F. Jarrold and V. A. Constant, Phys. Rev. Lett. 67, 2994 (1991).

[3] O. Cheshnovsky **et al.** , Chem. Phys. Lett. 138, 119 (1987)

[4] U. Roumlthlisberger, W. Andreoni, and P. Giannozzi, J. Chem. Phys. 96, 1248 (1992)

[5] Shvartsburg AA. Jarrold MF. Bei Liu. Zhong-Yi Lu. Cai-Zhuang Wang. Kai-Ming Ho., Physical Review Letters, vol.81, no.21, 23 Nov. 1998, pp.4616-19.

[6] B. Liu, A. A. Shvartsburg, Z. Y. Lu, B. Pan, C. Z. Wang, K. M. Ho, and M. F. Jarrold, J. Chem. Phys. vol.109, no.21, 1 Dec. 1998, pp.9401-09

[7] K. M. Ho, A. A. Shvartsburg, B. Pan, Z. Y. Lu, C. Z. Wang, J. G. Wacker, J. L. Fye, and M. F. Jarrold, Nature (London) 392, 582 (1998).

[8] W. de Heer, Rev. Mod. Phys. vol.65, 611 (1993).

[9] Vasiliev I. Ogut S. Chelikowsky JR., Physical Review Letters, vol.78, no.25, 23 June 1997, pp.4805-8.

[10] Rothlisberger U. Andreoni W. Parrinello M., Physical Review Letters, vol.72, no.5, 31 Jan. 1994, pp.665-8.

[11] Kaxiras E. Jackson K. Physical Review Letters, vol.71, no.5, 2 Aug. 1993, pp.721-30.

[12] Ballone P. Andreoni W. Car R. Parrinello M., Physical Review Letters, vol.60, no.4, 25 Jan. 1988, pp.271-4.

[13] Beck SM. Andrews JM. Journal of Chemical Physics, vol.91, no.7, 1 Oct. 1989, pp.4420-1.

[14] Blaisten-Barojas E. Levesque D., Physical Review B-Condensed Matter, vol.34, no.6, 15 Sept. 1986, pp.3910-16.

[15] H. Eugene Stanley, Review of Mordern Physics, Vol.71, no.2, March 1999, pp.s358-66.

[16] N. Goldenfeld, A Lecture on Phase Transition and the Renormalization Group.
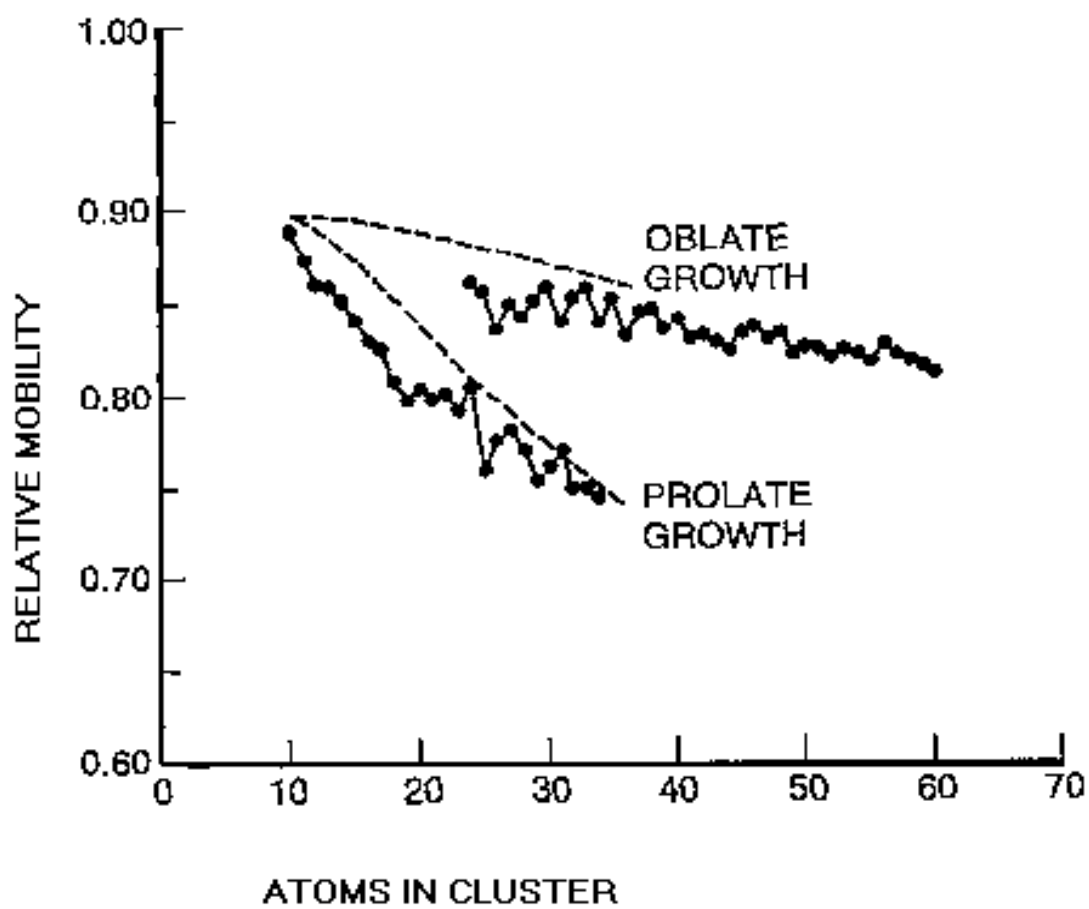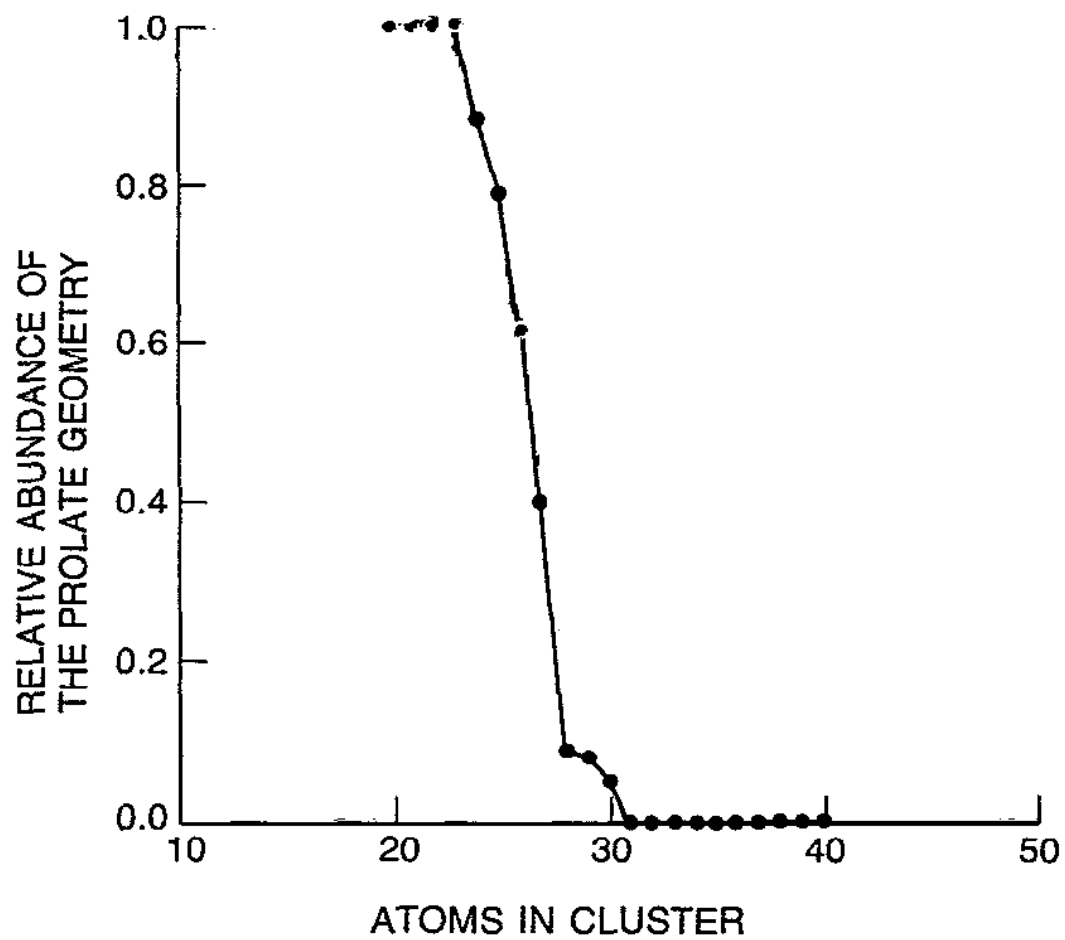
Figure 1: The relative mobility against cluster size.

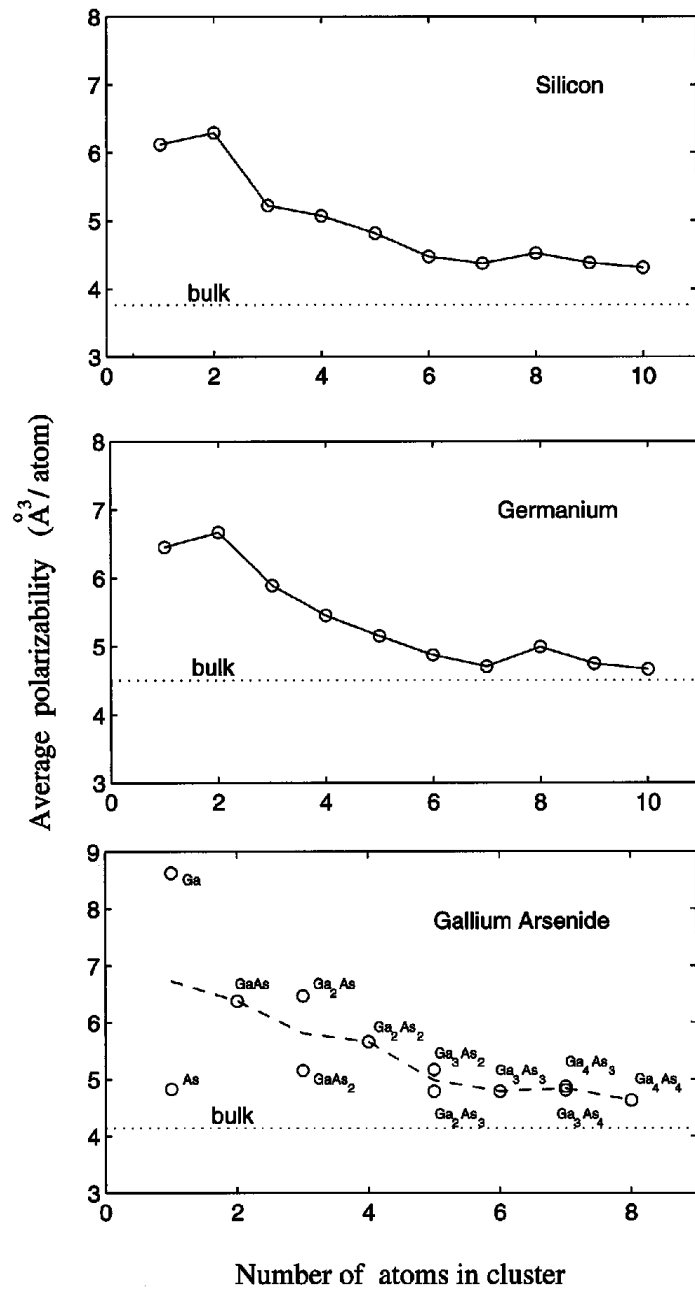Figure 2: The relative abundance of the prolate geometry against cluster size.

Figure 3: Average polarizabilities per atom of Si_m, Ge_n, and Ga_nAs_m clusters vs cluster size.