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STRUCTURE AND BONDING IN CLUSTERS *

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ABSTRACT

We review here the recent progress made in the understanding of the electronic and atomic structure of small clusters of $s-p$ bonded materials using the density functional molecular dynamics technique within the local density approximation. Starting with a brief description of the method, results are presented for alkali metal clusters, clusters of divalent metals such Mg and Be which show a transition from van der Waals or weak chemical bonding to metallic behaviour as the cluster size grows and clusters of Al, Sn and Sb. In the case of semiconductors, we discuss results for Si, Ge and GaAs clusters. Clusters of other materials such as P, C, S, and Se are also briefly discussed. From these and other available results we suggest the possibility of unique structures for the magic clusters.

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1. INTRODUCTION

During the past few years much efforts[1-5] have been devoted to the study of clusters of several elements, alloys and compounds in order to understand their physical and chemical properties and evolution to bulk behaviour. Very recently it has also become possible[6] to prepare a new solid form of carbon from large carbon clusters which are now referred to as fullerenes or bucky balls. The discovery of superconductivity at relatively high temperatures in K[7](18 K) ,Rb[8](28 K) and Cs and Rb[9](33 K) doped fullerenes has created tremendous excitement and has led to feverish activities in the study of fullerene aggregates.

An important question in the study of clusters of different materials is their structure which is in general very different from the one, materials have in bulk. This is due to the fact that in a small cluster most of the atoms are on the surface and therefore have reduced coordination. As the cluster size grows there occur important changes in the structure and in some cases also in the bonding nature. In general this is due to interesting variations in the electronic structure of clusters which effects their physical and chemical properties as the cluster size grows. Just to mention a few examples, small clusters of Si have closed packed structures[10] as compared to strongly directional bonding in the bulk. On the other hand dimers of divalent metals such as mercury and magnesium are very weakly bonded due to ns^2 closed shell atomic electronic structure and large promotional energy to the p state. Therefore for such elements a transition to bulk chemical bonding should occur as the cluster size grows. However it is still unclear for which size this transition whould occur. This may range from a few tens to a few hundred atoms depending upon the species involved. For mercury, experiments[11] indicate this transition to occur for a moderate size of the clusters ($70 \geq n \geq 13$).

Regarding the physical properties, there have been several studies on the reactivity of clusters. For example Fe clusters show[12] several orders of magnitude change in the reactivity of deuterium as the cluster size changes from a few to few tens of atoms. This correlates well with the variation in the ionization potential of the clusters, thus clearly demonstrating the need for understanding the size dependence of the atomic and the electronic structure of clusters. Similarly Al clusters show marked variation in the reactivity with oxygen as a function of size[13]. It is found that Al_{13}^- is unreactive with oxygen whereas other clusters do. The magnetic properties of small clusters may be very different from the bulk due to the discrete nature of the electronic energy spectrum. In principle clusters form a much broader class of materials because different clusters of the *same* material may behave differently and in the case of more than one component, the atomic size of the constituents is not the limiting factor. Such studies can therefore help to prepare better catalysts, photographic films, magnetic materials, energy storage devices, etc. and can open doors for making new classes of materials such as fullerides, the crystals obtained from fullerenes.

While the experimental progress in this area has been very rapid, theoretical studies are much more difficult due to the very many atomic and electronic configurations that are possible for a given size of the cluster. Calculations based on a jellium model[14] have been very successful in providing a qualitative understanding of the variations in the stability , the ionization potentials, optical properties etc. of clusters of metals as a function of their size. However, for a quantitative understanding it is necessary to know the atomic structure and the sensitivity of the electronic structure on the geometries some of which may lie very close in energy. This is also likely to enhance our understanding of the phase transitions, dynamical behaviour, melting etc. of clusters and will be helpful in understanding the chemical reactions on clusters. Also in other cases like clusters of semiconductors and alloys the jellium model may not be suitable.

Though there have been several studies (see e.g. Refs. 1-5) of the lowest energy structures of clusters, these have largely been confined to clusters with a few atoms as it becomes computationally very demanding to search among the various atomic and electronic configurations, the lowest possible one. Very recently it has become possible to do calculations for clusters with a few tens of atoms using the density functional molecular dynamics technique[15] which allows one to explore the equilibrium structures within the framework of the simulated annealing and the local density approximation (LDA). This method has been successfully applied in recent years to the studies of equilibrium geometries of a variety of clusters[16] such as Si[10,16], Se[17], S[18], Na[19], P[20], Be[21], Mg[22], Sb[23], Sn[23], Al[24] , C[25], and mixed clusters of GaAs[16] and NaK[19]. Results of such calculations agreed with experimental data wherever available. Here we review the main results of these studies and discuss in particular our own results on Mg, Be, Sb, and Sn clusters. A comparison of the structures obtained for different clusters make us to believe that there may be unique structures for magic clusters of materials in which directional bonding is not important. This point of view is discussed and suggestions are made for some clusters which may prove interesting to provide further support for this.

In the following section we present the calculational procedure. Section III contains a review of most of the results on clusters obtained so far using the density functional molecular dynamics procedure. In section IV we discuss structures that may be unique for the ground state geometries of magic clusters. Section V contains an outlook for future work.

II. DENSITY FUNCTIONAL MOLECULAR DYNAMICS METHOD

The principal task of an *ab initio* total energy calculation is to solve the Kohn-Sham equations

$$[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_{coul}(\mathbf{r}) + V_{xc}(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i\psi_i, \qquad (1)$$

where V_{ext}, V_{coul} and V_{xc} are the electron-ion, electron-electron and exchange-correlation potentials respectively and atomic units $e = \hbar = m_e = 1$ are used . The total energy E for a given configuration of the ions $\{\mathbf{R_I}\}$ is a functional of the density n which is given by,

$$n(\mathbf{r}) = \sum_i^{occ} f(i)|\psi_i(\mathbf{r})|^2, \qquad (2)$$

where $f(i)$ is the occupation number for the state i. Therefore starting with a configuration of the ions, one has to iteratively solve (1) untill self-consistency is achieved and then take a new configuration and repeat this procedure untill a configuration is obtained which has the lowest energy. This challenging task is made simple if one uses the density functional molecular dynamics(DF-MD) method[15] which provides an efficient way for the optimization of energy with respect to the electronic and ionic degrees of freedom *simultaneouly*. In this method the electronic degrees of freedom ψ_i and the ionic degrees of freedom $\mathbf{R}_I$ in the energy functional $E[\{\psi_i\},\{\mathbf{R}_I\}]$ are taken to be time dependent and a Lagrangian is introduced :

$$L = \sum_i^{occ} \int d\mathbf{r} \mu_i |\dot{\psi}_i(\mathbf{r})|^2 + (1/2) \sum_I M_I \dot{\mathbf{R}}_I^2 - E[\{\psi_i\}, \mathbf{R}_I]$$

$$+ \sum_{ij} \Lambda_{ij} \left(\int d\mathbf{r} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) - \delta_{ij} \right), \tag{3}$$

which generates a dynamics for the parameters ψ_i and $\mathbf{R}_I$ through the equations of motion:

$$\mu_i \ddot{\psi}_i(\mathbf{r},t) = -\frac{\delta E}{\delta \psi_i^*(\mathbf{r},t)} + \sum_j \Lambda_{ij} \psi_j(\mathbf{r},t) \tag{4a}$$

and

$$M_I \ddot{\mathbf{R}}_I = -\frac{\delta E}{\delta \mathbf{R}_I(t)}, \tag{4b}$$

where M_I are the ionic masses and μ_i are the fictitious masses for the electronic degrees of freedom which are generally taken to be independent of the state i. Λ_{ij} are the Lagrangian multipliers for the orthonormalization of the single particle orbitals ψ_i. Here the ion dynamics is real whereas the dynamics of the electronic degrees of freedom is fictitious. The energy functional E is given by

$$E[\{\psi_i\},\{\mathbf{R}_I\}] = \sum_i^{occ} f(i) \int d\mathbf{r} \psi_i^*(\mathbf{r}) (-\frac{1}{2}\nabla^2) \psi_i(\mathbf{r}) + \int d\mathbf{r} V^{ext}(\mathbf{r}) n(\mathbf{r})$$

$$+ \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{xc}[n] + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \tag{5}$$

$E^{xc}[n]$ is the exchange correlation energy which has been calculated within the LDA,

$$E^{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})], \tag{6}$$

where $\epsilon_{xc}[n(\mathbf{r})]$ is the exchange and correlation energy per particle of a homogeneous electron gas with density $n(\mathbf{r})$. This approximation yields reliable binding energy trends and equilibrium structures for a variety of molecules and solids[26]. For the electron-ion interaction, a pseudopotential representation is used so that,

$$V_{ext}(\mathbf{r}) = \sum_I v_{ps}(\mathbf{r} - \mathbf{R}_I),$$

where

$$v_{ps}(\mathbf{r}) = \sum_{l=0}^{\infty} v_l(\mathbf{r}) \hat{P}_l. \tag{7}$$

$\hat{P}_l$ is the angular momentum projection operator and for $v_l(\mathbf{r})$, *ab initio* norm-conserving pseudopotentials of Bachelet et al[27] are generally used. Therefore Z_I in (5) represents the ionic pseudo-charges. If one assumes $v_l = v_{l_{max}}$ for $l \geq l_{max}$ then the infinite sum in (7) can be written as

$$v_{ps}(\mathbf{r}) = v_{l_{max}}(\mathbf{r}) + \sum_{l=0}^{l_{max}-1} \Delta v_l(\mathbf{r}) \hat{P}_l,$$

where

$$\Delta v_l(\mathbf{r}) = v_l(\mathbf{r}) - v_{l_{max}}(\mathbf{r}). \tag{8}$$

Depending upon the system, l_{max} is either taken to be 1 (s non-local) or 2 (s and p non-local).

The eigenfunctions in (1) are expanded in a plane wave basis,

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}}^i exp[i\mathbf{G}.\mathbf{r}]. \tag{9}$$

The sum over $\mathbf{G}$ is usually truncated to include plane waves upto a cutoff G_{max} which determines the accuracy of the calculation. The use of plane waves assumes periodic boundary conditions which are customarily used in MD simulations in bulk systems. For the problem under consideration, the MD cell is taken to be sufficiently large so that the interaction between the cluster and its periodic images is negligible. This allows also the use of just a single **k** point , the Γ point, in (9) to sample the Brillouin zone of the MD supercell and neglect the band dispersion.

Eqs.(4) are then numerically integrated using the standard MD procedures. For technical details interested reader may consult articles by Car and Parrinello[28] and Remler and Madden[29]. Here we would like to mention that in the simulated annealing technique which is used to obtain the lowest energy structures, the cluster is heated to a temperature T which is in general different for different materials and may also differ for different clusters of a material so that the ions start diffusing. The cluster is then allowed to evolve at this temperature for a few pico-seconds which is a rather short time as compared to standard classical-molecular dynamics calculations. Experience with different systems has, however, shown that this period is sufficient to make the cluster loose completely the memory of its starting configuration. Subsequently it is then cooled slowly so that the system remains on the Born-Oppenheimer surface. The time step for integration of the equations of motion is taken to be sufficiently small so that there is negligible transfer of energy from the ions to the electronic degrees of freedom. Occasionally (in particular for clusters of metals) the energy levels may be closely spaced and there is a non-negligible energy transfer. In such cases electron minimization is done to the instantaneous ionic configuration during the MD runs after a few hundred iterations. This simulated annealing procedure has proved very successful in finding new structures which had lower energy than the lowest energy structures obtained by other methods in some cases. Also it provides a natural way to study the dynamical properties of clusters and the changes in the atomic and electronic structure at finite temperatures. In the next section we discusss some of the systems to which this technique has been successfully applied.

III. A. CLUSTERS OF METALS

Clusters of metals such as Na, Be, Mg, Al, Sn and Na-K have been studied. Calculations have also been performed on dimers of group IB and IIB elements[30]

and a few clusters of Sb[23], a semimetal. Since the spherical jellium model has played a central role in the study of metal clusters, we first discuss briefly this model.

a. The Jellium Model

An important observation for simple metal clusters by Knight and coworkers[31] has been the particular stability of clusters with 8, 20, 40, 58, and 92 electrons. As shown in Fig.1, for Na there is one electron per atom and therefore clusters with 8, 20, 40, 58 and 92 atoms are particularly abundant. Such clusters are referred to as *magic* clusters. Similar results have been obtained for clusters of other alkali metals[32] and their mixed clusters[33] and divalent[34] and noble[35] metals. Stability of these clusters has also been inferred from studies of the ionization potentials[36] and the fragmentation[37] and polarizabilities[38] of clusters.

Alkali metals are quite well described by a free or nearly free electron model. The effective ionic potential seen by the electrons is nearly constant throughout the metal. This is because the orthogonality criterion between the wave functions of the core electrons and those of the valence electrons causes the effective ionic (pseudo) potential to be weak and because the crystal structure is relatively closed packed. The effect of the weak pseudopotential can be taken into account as a perturbation on the free electron behaviour of metals with $s-p$ conduction electrons. The same features can generally be expected to hold for clusters. Therefore Knight and coworkers[31] used a spherical potential well to interpret these results in terms of the electronic shells very similar to the shell structure in atomic[39] and nuclear[40] physics. Their results are also shown in Fig.1(b) and the agreement with the main features in the experimental data is very good. Later, Cohen and collaborators[41] used a spherical jellium model in which the ionic charges are smeared out in a uniform positive spherical background such that

$$n_+(\mathbf{r}) = \begin{cases} n_0 & \text{if } r < R \\ 0 & \text{otherwise} \end{cases} \tag{10}$$

Here R is the radius of the cluster and is related to the number of atoms N,

$$\frac{4}{3}\pi R^3 = N\Omega, \tag{11}$$

where Ω is the volume per atom in the macroscopic metal. The constant positive density n_0 is related to Ω and the valence Z by $Z = n_0\Omega$. The Kohn-Sham equations (1) are then solved to obtain the eigenvalues and the total energies. The energy levels of the electrons are characterized by the radial and angular quantum numbers. The successive energy levels (and their degeneracies) are 1s(2), 1p(6), 1d(10), 2s(2), 1f(14), 2p(6), 1g(18), 2d(10), 1h(22), ... Hence as electrons fill the shells, closing occurs for total electron numbers, 2, 8, 18, 20, 34, 40, 58, 68, 90, and so on. Since the closed shell configurations are stable due to energy gaps between electronic shells, this model provides a simple and elegant explanation of the marked stability observed in alkali metal clusters for 8, 20, 40, 58 and 92 atoms. The fine structure in the abundance spectrum can be understood in terms of the completion of subshells that arise due to deformation of the spherical positive background[42]. For shell closing numbers not observed in the experiment the reason may be that (1) only a large gap to the next shell enhances the stability of a closed shell and (2) the spherical jellium model is not a good representation of the actual potential seen by the electrons in a cluster. The absence of fine structure in the abundance spectrum for large clusters is due to smaller gaps for higher shells[14] while the variation in the intensities for clusters of different elements is due to different potential depths which lead to different gaps between shells. While all these general trends in several properties of metal clusters are well described by the jellium model and it is possible to apply this model to large clusters, it is of interest to also study these aspects from a more realistic model. In the following we review results obtained by using the Car-Parrinello method.

b. Monovalent Metals

Ballone *et al*[19] have studied Na_8, and $Na_{10}K_{10}$ clusters. Several interesting observations have been made. First of all when the results of these calculations are analysed in terms of the angular character around the center of mass of the cluster, then the electronic configuration agrees with the predictions of the shell model. The lowest energy structure of Na_8 is found to have the D_{2d} symmetry. This differs from the T_d symmetry obtained from the configuration interaction calculations[43]. However, the energy difference between the two structures is only 0.008eV/atom when

planewaves with energy upto 5 Ry are included in (9). The structure of Na_{20} cluster has layer structure and is shown in Fig.2. Again in this case the electronic states can be classified with good accuracy by their angular momentum in consistency with the shell model. However, in contrast to the Na_8 cluster, Na_{20} loses this shell model character even at as low temperatures as 200 K. Accordingly 8-atom clusters are predicted to be more stable with respect to increasing temperature.

For mixed clusters of Na and K , a tendency for K segregation on the surface has been found. This is expected also on the basis of simple models based on broken bonds on a surface and the size mismatch according to which the element having the lower surface energy tend to segregate at the surface[44]. The segregation might lead to preferential evaporation of the larger species and favour small sized atom rich clusters. The lowest energy state has a structure similar to that of Na_{20} and the one - electron orbitals are delocalized over the entire cluster. In agreement with the experimental observations[33], the shell model behaviour is applicable to the alloy in spite of the ionic segregation. Though calculations have not been done for other alkali metals with this technique, one can expect similar behaviour from them.

c. Divalent Metals

For divalent metals, extensive studies have been made recently for Mg[16,22,45] and Be[21] clusters. The equilibrium structures of Mg clusters with upto 13 atoms have been studied by Kumar and Car[22] and the lowest energy structures with singlet states are shown in Fig.3 and their atomization energies are given in table I. Mg_2 is very weakly bonded with a bond length 6.33 a.u.. Experimentally Mg_2 is found[46] to have a singlet ground state with a bond length 7.35 a.u. and cohesive energy 0.027 eV/atom. The larger value of the calculated cohesive energy is due to the use of the LDA which overestimates the binding energy. However, these results agree very well with a local spin density(LSD) calculation[47] which gives 0.11 eV and 6.37 a.u. respectively for the energy and the bond length. The lowest energy state for Mg_3 is equilateral triangle with bond length 5.93 a.u.. Mg_3 chain is 0.111 eV/atom higher in energy than the equilateral triangle. Thus Mg clusters favour to maximize the coordination number. This trend is continued for bigger clusters as well. The lowest energy structure for Mg_4 is a regular tetrahedron with its side equal to 5.63 a.u.. This is a particularly stable cluster with considerably smaller bond length. Mg_5 is a slightly elongated trigonal bipyramid with base atoms 5.47 a.u. apart and the other bond lengths equal 6.03 a.u.. These results are in good agreement with a local spin density (LSD) calculation[47] which also finds a singlet state for all these clusters to be of lowest energy. These results were obtained by performing steepest descent calculations for a few selected geometries of clusters. For larger clusters, however, simulated annealing technique was used. For Mg_6 it leads to a structure which is shown in Fig.3. This is obtained by capping a face (3-4-5) of Mg_5. Independently Reuse *et al*[47] obtained an octahedron with a rectangular base to be of lowest energy for this cluster. A steepest descent calculation for this structure gives it only 0.004 eV/atom higher in energy than the simulated annealing structure thus making them nearly degenerate.

For Mg_7 the lowest energy structure is a pentagonal bipyramid. Its two apex atoms with coordination 6 have the shortest distance (5.3 a.u.) whereas the base atoms with coordination four have a bond length 6.04 a.u. This structure can be obtained from Mg_5 by capping the two faces. Reuse et al[47] and Pacchioni et al[48] also obtained a pentagonal bipyramid for this cluster using the LSD and cofiguration interaction calculations respectively.

The lowest energy structure of Mg_8 can be simply obtained by capping a face (1-3-7 in figure 3) of the pentagonal bipyramid. For larger clusters a new structure starts. Mg_9 is a tricapped trigonal prism as shown in Fig.3. This structure has some similarity with a fragment of the hcp lattice except that the bond lengths 1-4, 2-5 and 3-6 are shorter whereas for bulk Mg they correspond to the c-axis.

Adding an atom to one of the triangular faces of the trigonal prism leads to the structure of Mg_{10} as shown in Fig.3. This is another most stable structure among the Mg clusters. This is apparent from the second order finite difference of the energy which is plotted in Fig. 4. The peaks in this plot can be correlated with the abundance in the mass spectrum. While the angular character of the charge densities have not been studied around the centre of mass of the cluster, the marked stability of 4 and 10 atom clusters agree with the jellium model. Also a small peak and a shoulder appear for the 7- and 9-atom clusters respectively which again agrees with the fine structure in the calculated spectrum in the jellium model.

Mg_{11} is obtained by capping the remaining triangular face of the trigonal prism. Mg_{12} is also a capped trigonal prism. However, in this case an atom caps an edge of the trigonal prism. Mg_{13} is neither an icosahedron nor a cuboctahedron. It can be considered to arise from the fusion of a Mg_9 and a Mg_4 cluster (atoms 10 to 13). The tetrahedron of Mg_4 opens up to form a bent distorted rhombus. Calculations[22] have shown that this is possible as there is no barrier for this distortion. It is interesting to note that a relaxed fcc and an icosahedron structure are respectively 0.032 and 0.043 eV/atom higher in energy. However, relaxing a hcp cluster leads to a structure which is nearly degenerate with the one obtained from the simulated annealing. From table I it can be seen that the cohesive energy (see Fig.4) is still about 54% of the bulk value (1.687 eV/atom) calculated by Moruzzi *et al*[49] and much larger clusters may be needed for getting the bulk like behaviour. An independent study of Mg clusters by de Coulon *et al*[45] also finds a tetracapped trigonal prism for 10-atom cluster using the Car-Parrinello method. However, their results for 6-, 8-, 12- and 13- atom clusters are different from those obtained by Kumar and Car[22] and their structures lie higher in energy. It may be noted that for these calculations simulated annealing was not used.

Regarding the nature of bonding in these clusters, the *p* character of charge around various ions was studied[22] and Fig.5 shows the same averaged over the cluster. It shows an oscillatory behaviour and the convergence to the bulk value is slow. Also plotted in this figure are the change in the mean bond length and the average coordination of an atom in the cluster. While the average coordination increases monotonically, the bond length shows an oscillatory behaviour which is suggested to be a feature of clusters showing a transition from van der Waals or weak chemical to metallic bonding. A simple reason for this is the fact that for van der Waals bonding the bond length is large and it should decrease till metallization occurs in the cluster. Beyond this there should be a tendency for the bond length to increase towards its bulk value. The sharp decrease in the bond length for 4- and 10-atom cluster may be due to shell closing. This behaviour is different from clusters of metals like Cu for which the bond length increases towards its bulk value monotonically[50]. Also different atoms in a cluster have different p character. There are some short bonds in the cluster which develop metalicity first. This may be important for the study of reactivity on clusters. The charge density in these clusters indicate that bonding changes slowly from weak chemical to covalent to metallic behaviour. Therefore the general agreement with the jellium model should be considered with caution.

Kawai and Weare[21] have done a similar study for Be clusters having 2 to 20 atoms. Small clusters of Be have the same structure as for Mg. However, Be clusters tend to attain some of the features (p character) of the bulk bonding even for a 6-atom cluster whereas this is quite slow for Mg. Also Be_8 is a bicapped trigonal prism as compared to the capped pentagonal bipyramid for Mg. While Be_9 has the same structure as for Mg_9, larger clusters of Be have somewhat different structures as compared to Mg and these have some similarity with the bulk hcp structure. While the trigonal prism structure is retained, the capping patterns are different for the two systems. Since Be_{10} corresponds to a shell closing in the spherical jellium model, we[51] performed a calculation for Be_{10} with the Mg_{10} structure. This lies 0.028 eV/atom higher in energy than the structure obtained by Kawai and Weare. Therefore in this size range, Be and Mg clusters have different behaviour. Interestingly for Be_{13} also, a relaxed icosahedron structure lies 0.7 eV higher in energy than the one obtained from the simulated annealing procedure. For Be clusters with more than 11 atoms two or more trigonal prisms can be identified and for 19 and 20 atoms even a hexagonal face appears. Unlike Mg clusters, there is a remarkable tendency for a two dimensional growth pattern related to hcp packing which suggests directional bonding to be very important for Be clusters and crystals. However, the orbital energies and the angular character of the orbital wave functions for Be clusters correlate well with the predictions of the shell model described above. Also the second-order finite difference of the calculated total energy shows large maxima at N = 4, 10, and 17 which again agrees with the shell model.

d. Trivalent Metals

In this group only the clusters of Al have been studied in detail. Jones[24] has studied Al clusters having upto 10 atoms. These calculations have been done within the LSD approximation. Small Al clusters favour planar geometries. Al_3 is an equilateral triangle (r_e = 4.65 a.u.) and has ${}^2A_1$ symmetry. Al_4 is a rhombus (r_e = 4.75 a.u.) with D_{2h} symmetry and is a triplet. For larger clusters three dimensional structures are favoured. The binding energy increases monotonically towards its bulk value as the cluster size increases. For Al_5 a planar C_{2v} structure is almost degenerate with a C_s structure with similar bond lengths (both doublets). For n $\geq$ 6 states with minimum spin degeneracies are favored. For Al_6, the lowest lying state is (D_{3d}) and is a singlet. This is nearly degenerate with triplet D_{2d} state. Al_7 is a nearly symmetric capping of Al_6 (D_{3d}). Al_7^+ is one of the most prominent in the mass spectrum. As it has 20 electrons, its stability has been correlated with the completion of the 1d shell in the spherical jellium model. For such clusters there is a large gap between the highest occupied and the lowest unoccupied orbitals. Similar behaviour was obtained by Kumar and Car for Mg_4 and Mg_{10} clusters which have 8 and 20 electrons respectively and are magic. Also the ionization potential of Al_7 and the dissociation energy of Al_8 are low. In addition to these lowest energy structures, a variety of planar and buckled structures (similar to one in α - Ga) are also found to be locally stable. This is consistent with the metallic nature of Al and the fact that there are usually unoccupied orbitals near the highest occupied orbitals and it is easy to transfer electrons between π orbitals (which dominate in the bonding in planar structures) and σ orbitals. The finding of several planar and buckled structures with arrays of triangles and nearly the same energies can be helpful in understanding layer arrangements with triangular nets in many Al - transition metal alloys[52].

Al_{13} cluster is a classic example for studying the relative stability of icosahedral and coboctahedral structures. Bernholc and coworkers[53] have studied 13- atom and a few other large clusters of Al. The energy differences between these two structures for 13-, 19-, and 55- atom clusters are found to be small. For 13- atom cluster a slightly distorted icosahedron is found to have the lowest energy, whereas for 55- atom cluster the structure has large distortions though its origin from an icosahedron can be discerned. While no efforts were made to make a systematic study as a function of the size, several structures were found to be close in energy for a 55- atom cluster. In the shell model of clusters, Al_{13} is nearly magic with 39 electrons and therefore a nearly perfect icosahedron has the lowest energy and a single well defined energy minimum. On the other hand a 55- atom cluster is not magic in the shell model. The fact that several nearly degenerate structures exist for this cluster agrees also with the results of Kumar and Car[22] for Mg_{13} cluster (non-magic) in which case the structure obtained from the simulated annealing is nearly degenerate with the one obtained from the relaxation of the hcp structure. However, for Al clusters the deviation from the bulk cohesive energy is not large and it was suggested that a transition from icosahedral to bulk structures may occur very early. Some studies[54] have also been made on mixed clusters of Al-Mg using the steepest descent approach. These are $Al_{12}Mg_3$ and $Al_{12}Mg_5$ clusters which are abundant in β-Al_3Mg_2 structure and other Frank-Kasper phases[55]. 14 and 16 coordinated clusters were predicted by Frank and Kasper on the basis of geometrical arguments. Their study is interesting to understand the role of electronic structure and the atomic sizes in the complicated crystalline and quasicrystalline structures. For $Al_{12}Mg_3$ cluster which has 42 valence electrons, there is only a little distortion from the capped hexagonal antiprism structure found in the crystal whereas for $Al_{12}Mg_5$ cluster which has 46 valence electrons, there are considerable John-Teller distortions from the bulk atomic packing. This suggests that the 17- atom cluster is not particularly stable and there are other considerations that play a more important role in the crystal packing.

e. Sn and Sb

Elements of Group IV and V are very interesting as they exihibit a variety of crystal structures and have differing bonding character in the bulk. Tin has both a metallic (white tin) and a semiconducting (grey tin) phase. Grey tin has the diamond structure, while white tin is body-centered tetragonal with a two atom basis. We[23] have done a calculation for Sn_5 cluster as it has 20 electrons and could be expected to be a magic cluster from the point of view of the jellium model. The calculations were done for a few selected geometries and the lowest energy structure is a trigonal bipyramid. The bond length between the base atoms is large and equals 6.50 a.u. whereas the bond length between the apex and base atoms is 4.94 a.u. . This structure is similar to a 5- atom cluster of Ge or Si[10] (see below) and therefore its behaviour is more like the clusters of semiconductors. It would be of interest to calculate the structure of Sn_{10} and see if it is the same as for Si_{10} cluster. Also studies on other Sn clusters would be interesting to explore the development of bonding in these clusters.

Clusters of pentavalent elements such as Sb and Bi (all of which are semimetals) have been experimentally studied[56]. For Sb clusters a very important feature in the mass spectrum is the abundance of Sb_{4n} clusters. Also as compared to monomer dissociation in alkali or divalent metal clusters, studies of the fragmentation of antimony clusters produce evidence of evaporation of tetramers[57]. The abundance spectrum of Bi is very different as compared to Sb. There is no particular preference to Bi_{4n} clusters. We[23] have studied Sb_4 cluster and the lowest energy structure is a regular tetrahedron with each side equal to 5.03 a.u.. A bent rhombus structure lies about 0.5 eV/atom higher in energy. Sb_4 has 20 electrons and can be expected to be a magic cluster as also observed. From this it will appear that the results of the jellium model may be applicable to Sb clusters as Sb_8 has 40 and Sb_{12} has 60 electrons which are close to the magic clusters with 40 and 58 electrons. However, recent studies[58] of the photoionization spectra of Sb clusters indicate striking differences in the behaviour of Sb_{4p} , $p > 1$ and other clusters which are not understood. Also the persistence of 4p type clusters for larger values of p (upto about 25) indicate a different bonding character in these clusters. Our preliminary results on Sb_8 show that a cube is not of lowest energy. More work on the atomic and electronic structure of Sb clusters is in progress.

B. CLUSTERS OF SEMICONDUCTORS AND OTHER MATERIALS

a. Si, Ge and GaAs

Andreoni and coworkers[16] have studied these clusters from the Car-Parrinello method. While Si and Ge clusters have similar structures, an important aspect of the structure of these clusters is that these are closedpacked as compared to more open diamond structure in the bulk. It is of considerable interest to know when directional bonding starts playing an important role in these clusters. Several efforts have been devoted to answer this question. Extensive calculations[10,16,59] for clusters with upto 45 atoms show no sign of bulklike features in the structure. Si was the first example where the advantage of simulated annealing became evident when an entirely new structure (tetracapped trigonal prism, same as for Mg_{10}) was found to be of lowest energy. The growth pattern of Si clusters is rather complex and no common seed can be identified. Si_5 and Ge_5 have the same structure as for Sn_5. Si_7 is a pentagonal bipyramid as Mg_7. Si_8 is a bicapped octahedron (two opposite faces capped) and Si_9 is a strongly reconstructed structure and is shown in Fig. 6. Si_{10} and Ge_{10} are tetracapped trigonal prisms similar to Mg_{10} whereas Si_{13} is neither an fcc nor an icosahedron. Its lowest energy structure is also shown in Fig. 6. An important message of these calculations is that the semiempirical potentials available so far for Si are not suitable for the representation of the potential energy surface of microclusters[60].

A few calculations have also been done for GaAs and GaP clusters[16]. Their structures appear to be similar to those of Si and Ge. We consider here Ga_5As_5 cluster. While the lowest energy structure is a distorted bicapped dodecahedron, a tetracapped trigonal prism is nearly degenerate. This is an interesting result because this as well as Si_{10} and Ge_{10} clusters have 40 electrons each. This is a magic number in the shell model. The occurrence of the same structure for Mg_{10} cluster makes us to believe that *there may be some unique structures which are either lowest or lie very close in energy with the lowest energy structures for some magic clusters for which directional bonding plays a less important role. The deviation from unique structures may also be indicative of the development of bulklike characteristics.*

b. S, Se, P, C

Hohl et al have made extensive calculations for S[18], Se[17] and P[20] clusters. In some of these cases it is possible to compare the results with the spectroscopic data available for the structure. These results give confidence in the simulated annealing procedure as the calculated bond lengths and angles agree remarkably with the experimental values. The atomization energies are ,however, overestimated which is due to the use of the LDA. As there is a large amount of information regarding the structure of these molecules, the reader is advised to consult the original papers for details. It would be worth while here to mention that similar to Sb_4, P_4 also has a regular tetrahedron structure which is lowest in energy. Whereas contrary to widespread belief, the most stable structure of P_8 is not cubic. This is a structure with C_{2v} symmetry and its energy lies 0.47 eV below that of two isolated P_4 tetrahedra. A roof-shaped tetramer is a prominent structural unit in low-lying states of P_5, P_6, P_7, P_8 clusters.

Some calculations have also been done[18] for C_4 and C_{10} clusters for which the structures are respectively a linear chain and a ring. Due to more localized orbitals these calculations require use of very large energy cutoff (about 35 Ry) in the plane wave expansion and therefore are very expensive to do. However, due to recent excitement in fullerenes, several efforts are going on to study large clusters of carbon with 60 or more atoms. C_{60} cluster (Fig. 7) has a football structure with 12 pentagons and 20 hexagons. There are two bond lengths (1.40 and 1.45 Å) as obtained from NMR data[61]. The bonds sharing two hexagons form double bonds and are short whereas the bonds sharing a pentagon and a hexagon are single bonds and are longer. All atoms have identical environment. Calculations by Feuston *et al*[62] produce these bond lengths to be 1.39 and 1.45 Å in very good agreement with the NMR experiments. As it is possible to do calculations at finite temperatures, they studied the structural changes and vibrational and average electronic density of states at 450 K. The fullerene structure of C_{60} is found to be very stable and the average structural parameters change by at most 0.01 Å. The calculated vibrational frequencies 530, 555, 1105 and 1345 cm^{-1} are in close agreement with 527.1, 570.3, 1169.1, 1406.9 cm^{-1} obtained from IR experiments[63].

Efforts are also being made to understand the properties of solids made from such large clusters. Zhang *et al*[64] have studied the structural properties of solid C_{60} with a fcc structure and found the bond lengths to be 1.40 and 1.45 Å i.e. very little change from the values in the cluster. We[65] have also done a similar calculation with 29 Ry. cutoff and find some anisotropy in the bond lengths due to different environments of the sites in the solid phase as compared to one in the isolated cluster. In particular there are three different environments of carbon atoms in the fcc structure. The double bonds have one bond length which is equal to 1.404 Å, whereas the single bonds have three slightly different values. These are 1.449, 1.454 and 1.462 Å. 24 atoms have their nearest neighbour bond lengths to be 1.404, 1.449 and 1.454 Å. The other 24 have 1.404, 1.449 and 1.462 Å and the remaining 12 have 1.404, 1.454 and 1.454 Å. Experimentally[66,67] at temperatures below 249 K an orientational ordering of the C_{60} balls has been found. This leads to a $Pa\bar{3}$ structure. Further work on this and the doped fullerenes is under progress.

IV. STRUCTURE OF MAGIC CLUSTERS

While the structure of clusters of different elements and compounds/alloys will in general depend upon the number of electrons, the orbitals and the relative sizes and therefore the potential involved, the success of the jellium model in predicting the relative stability of clusters and the agreement of the angular character of the states obtained from detailed atomic calculations with those predicted by the shell model are notworthy. From the fact that clusters (neutral and charged) with different number of atoms and having structures far from spherical, can correspond to the same shell closing, it seems to us that the gaps in the energy spectrum for electron count corresponding to shell closing are more general and less sensitive to a particular structure. However, since the gaps and degeneracy of levels will, in general, depend upon the symmetry, it may be that certain structures are more likely. In particular for materials where directional bonding is not important, one can ask the question whether, there will be unique structures for neutral magic clusters i.e. clusters with 8, 18, 20, 34, 40, 58, 68,.. electrons. Considering here only the elemental clusters in small and medium size range, some of the interesting cases are tetramers of divalent metals and pentavalent semimetals which have a regular tetrahedron to be of lowest energy (as far as results are available), the 5 atom clusters of Ge, Si, Sn (for Pb results are not available) which have the same structure (trigonal bipyramid), Al_6 (trigonal antiprism), 8-atom clusters of alkali metals and Sb_8, 10- and 17-atom clusters of divalent metals and Ge, Si, Sn and Pb, and 20-atom clusters of monovalent and divalent metals. In some of these cases a change in the bonding character is also involved as the cluster size increases. These are the divalent elements Be, Mg, Hg etc. which show a change from van der Waals or weak chemical to metallic bonding, clusters of Si, Ge and Sn and pentavalent elements for which the bonding character is still to be well understood. Also 5-atom clusters of Si, Ge are not magic. However, it is striking to note that Si_{10}, Ge_{10}, Mg_{10} and even Ga_5As_5 have the same structure. Be_{10} has a slightly different structure, but it may be due to the fact that directional bonding starts playing an important role. For 8-atom cluster of alkali metals configuration interaction calculations[43,48] predict a T_d symmetry structure, whereas calculations based on LDA predict a D_{2d} structure for Na. It would be interesting to study other alkali metal clusters if the same is true. For 17 atom cluster results are available for Be which has a highly symmetric D_{4d} structure with pentagonal faces. The 17-atom Friauf polyhedron which is a building block for the Frank-Kaspar phases and has hexagonal faces may be another interesting structure. More calculations on other divalent metals and tetravalent elements would be desirable. For 20-atom cluster results are available on Be and Na. In Be directional bonding plays an important role and hexagonal faces appear whereas for Na, pentagons play an important role and it is a layered structure[16]. In these cases the studies are too few and more results would be needed to identify if there are common structures. In general it would be fair to say that for magic clusters there are some interesting common structures such as a regular tetrahedron, trigonal and pentagonal bipyramids, tri- and tetracapped trigonal prisms, an icosahedron etc. which could be called *magic structures.* Some of these structures are the same as one would obtain for materials which can be described by a Lennard-Jones potential[68] but this could be accidental. The cases where a deviation from such structures will occur, it may signify the development of bulk bonding characteristics or the lowest energy structure may be nearly degenerate with that of the magic structure.

V. OUTLOOK

Fairly good amount of work has been carried out in recent years using the Car-Parrinello method for clusters of metals, semiconductors and other elements like S, Se, P etc. The simulated annealing technique has given a new thrust in the search for the ground state structures of clusters. The structures and the vibrational frequencies calculated with this technique are in general good agreement with experiments wherever results are available. There are some very interesting aspects to be studied regarding the change in the bonding character and the growth mode particularly for clusters of the elements (in a column in the periodic table) having different bulk structures. As better computational facilities become available, it would be desirable to study larger clusters in order to study the transition to bulk behaviour. Also it would be most interesting to apply this technique to problems related to reactions on clusters and to other mixed clusters. Of course from the point of view of applications, clusters of transition metals are very important and recent developments in pseudopotentials[69] and their implementation in the Car-Parrinello method is a step forward in this direction. Similar attempts to incorporate molecular dynamics aspects in localised basis such as gaussian or other efficient techniques would be very useful. In the next few years we hope to see important developments in these directions.

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Table 1: Atomization energies of Mg_n clusters in the singlet state.

n	Structure	Energy eV/atom
2	Dimer	0.115
3	Equilateral triangle	0.284
4	Regular tetrahedron	0.530
5	Trigonal bipyramid	0.540
6	Capped trigonal bipyramid	0.566
7	Pentagonal bipyramid	0.649
8	Capped pentagonal bipyramid	0.694
9	Tricapped trigonal prism	0.809
10	Tetracapped trigonal prism	0.886
11	Pentacapped tribonal prism	0.870
12	Capped trigonal prism (Fig.7a)	0.874
13	From simulated annealing	0.902
	Relaxed hcp	0.898
	Relaxed fcc	0.871
	Relaxed icosahedron	0.859
	Bulk#	1.687

#Ref.(49)

Figure Captions

Fig.1. Abundance spectrum of Na clusters: (a) experimental, and (b) theoretical. Important features can be noted at 8, 20, 40, 58 and 92 atoms. $\Delta(N)$ refers to the energy of a cluster with N atoms. [After Knight *et al*[31]].

Fig.2. The lowest energy structure of Na_{20}. [After Andreoni[16]].

Fig.3. Lowest energy structures of Mg clusters with 2 to 13 atoms.

Fig.4. Plot of the cohesive energy and its second derivative as a function of the cluster size.

Fig.5. a) Mean nearest neighbour bond lengths(left) and the number of nearest neighbour bonds(right) as a function of the cluster size. b) The ratio of the p- and s-characters of the electronic charge densities of the clusters for two values of the radius of spheres around atoms over which the integration was performed to calculate the total charge.

Fig.6. Lowest energy structures of 8-, 9-, 10-, and 13- atom Si clusters [After Andreoni[16]].

Fig.7. The truncated icosahedron structure of C_{60} cluster. It has 12 pentagons and 20 hexagons. The bonds joining two hexagons and a hexagon and a pentagon are respectively 1.40 and 1.45 Å long.

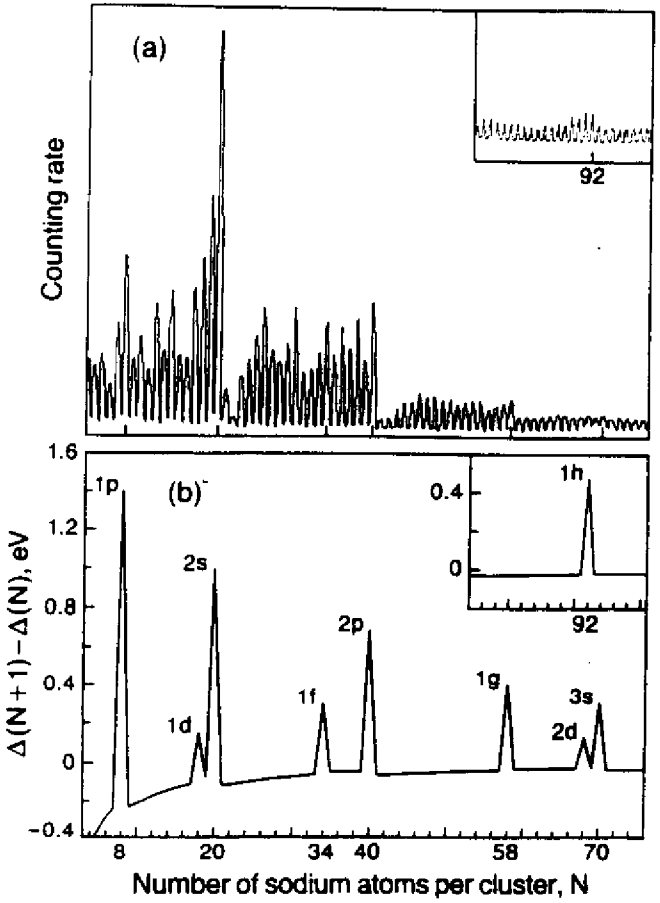
(a)
Counting rate
92
(b)
Δ(N+1)−Δ(N), eV
1.6
1.2
0.8
0.4
0
−0.4
1p
2s
1d
1f
2p
1g
2d
3s
1h
0.4
0
92
8
20
34
40
58
70
Number of sodium atoms per cluster, N

Fig.1

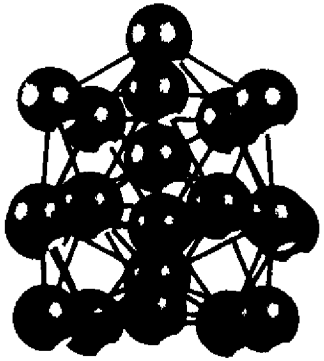

Fig.2

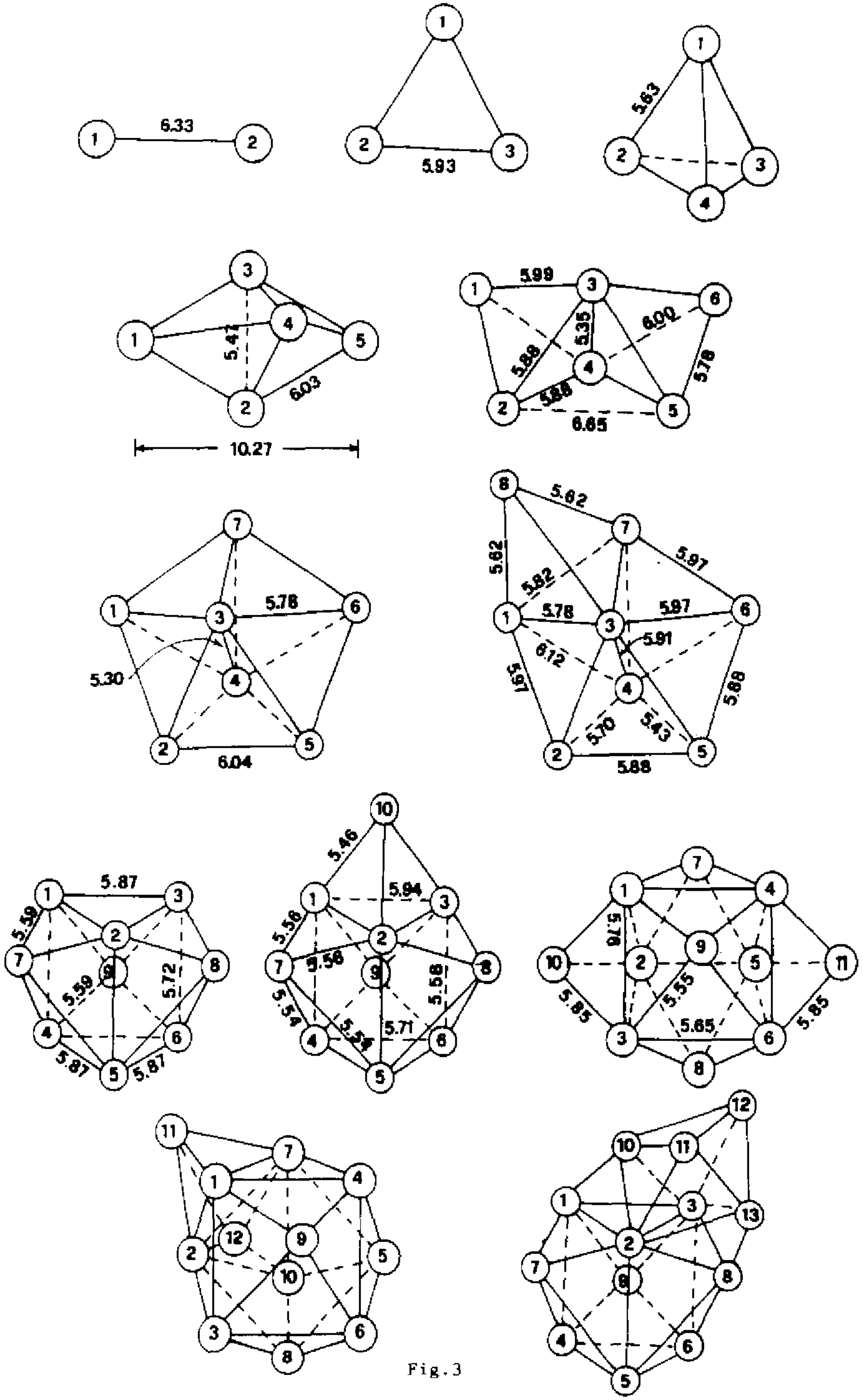
6.33
5.93
5.63
5.47
6.03
10.27
5.99
5.35
6.00
5.88
5.88
5.78
6.65
5.78
5.30
6.04
5.62
5.97
5.62
5.82
5.78
5.97
5.91
6.12
5.91
5.88
5.70
5.43
5.88
5.87
5.59
5.59
5.72
5.87
5.87
5.46
5.94
5.56
5.56
5.58
5.54
5.54
5.71
5.78
5.85
5.55
5.65
5.85

Fig.3

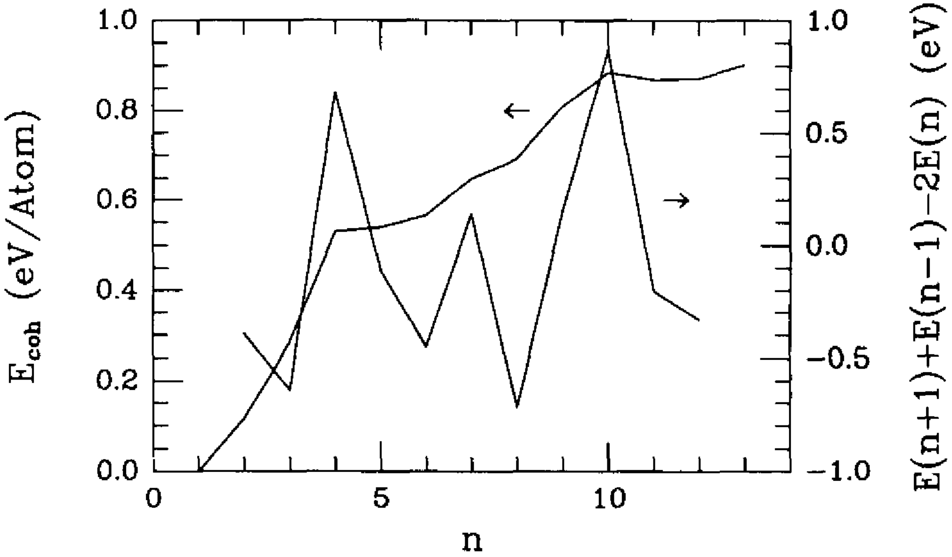
E_coh (eV/Atom)
E(n+1)+E(n−1)−2E(n) (eV)
n
1.0
0.8
0.6
0.4
0.2
0.0
1.0
0.5
0.0
−0.5
−1.0
0
5
10
←
→

Fig.4

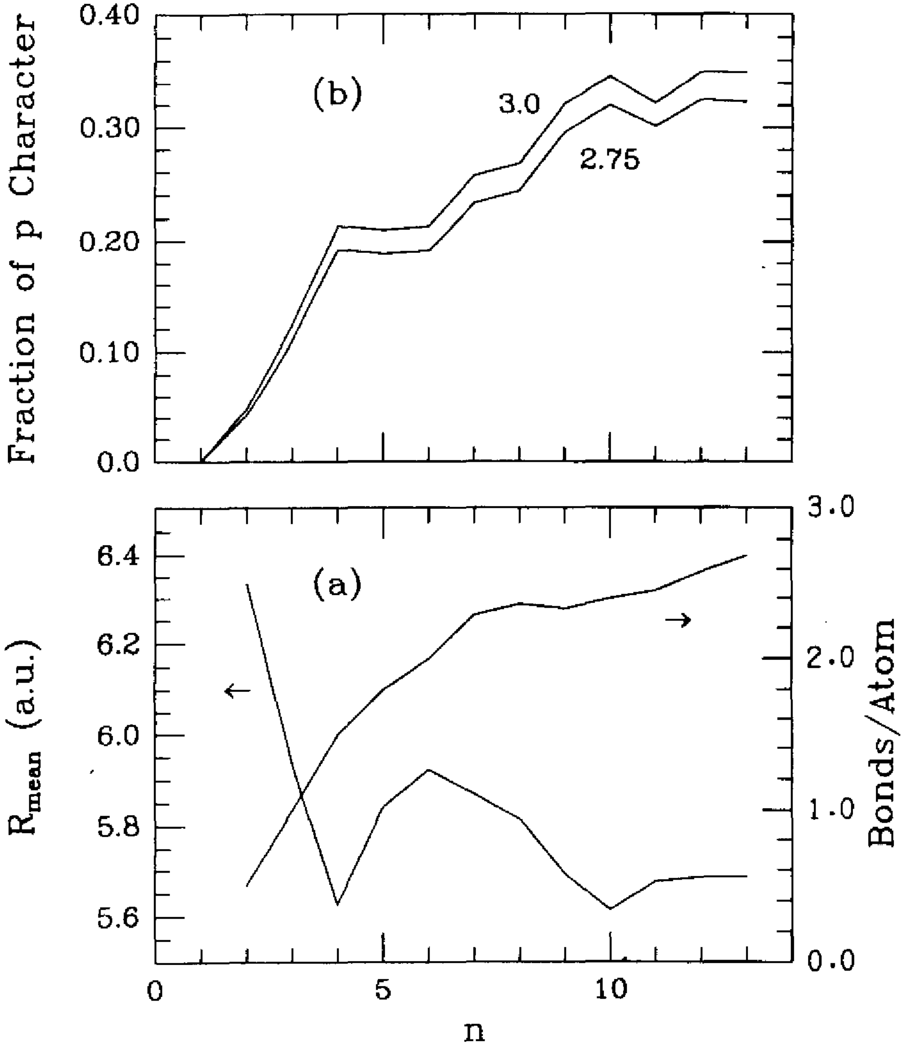
Fraction of p Character
0.40
0.30
0.20
0.10
0.0
(b)
3.0
2.75
R_mean (a.u.)
6.4
6.2
6.0
5.8
5.6
(a)
←
→
3.0
2.0
1.0
0.0
Bonds/Atom
0
5
10
n

Fig.5

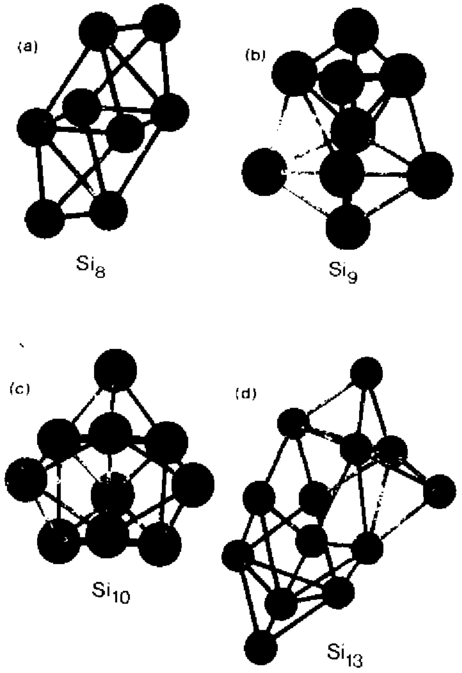
(a)
Si8
(b)
Si9
(c)
Si10
(d)
Si13

Fig.6

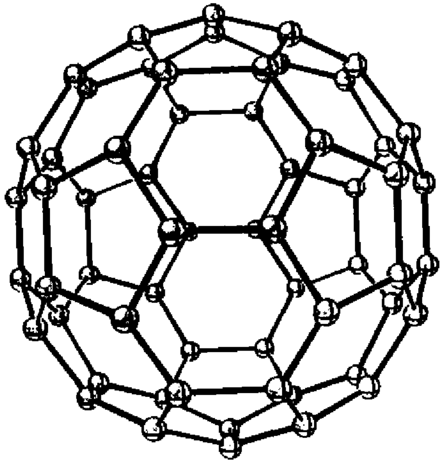

Fig.7