$d$-electron induced icosahedral growth in strontium clusters

Tabish Qureshi and Vijay Kumar

Material Science Division, Indira Gandhi Center for Atomic Research, Kalpakkam-603102, India.

Strontium clusters of size 2 to 20 atoms have been studied within the local density approximation using the \textit{ab-initio} molecular dynamics method with a plane wave basis in which the $s$ and $p$ electron wavefunctions are well represented. The resulting low lying isomers are optimized using a full-potential linear muffin tin orbital method which treats the $d$-electrons also on an equal footing. We find that the $d$ electrons contribute significantly to the binding energy as the cluster size grows, expedite the onset of metallicity and induce icosahedral growth. These results are in complete agreement with the experimental finding of rare-gas like magic clusters of group IIA elements and suggest that the observation of icosahedral growth in some transition metal clusters may have a similar origin.

PACS numbers: 36.40.Cq; 36.40.-c; 71.15.Pd

An interesting question which has intrigued researchers for a long time is how atoms behave collectively as one goes from molecular state to the bulk. Small clusters of a variety of materials exhibit quite different properties as compared to the bulk and are, therefore, attracting much attention. It is indeed a challenge of cluster science to understand the evolution of the atomic structure and the growth of the physical and chemical properties of matter, from embrionic state to the bulk. Clusters of group IIA elements exhibit a non-metal - metal transition from a embryonic state to the bulk. Small clusters of group IIA elements exhibit a non-metal - metal transition from a weakly bonded dimer to a strongly bonded bulk as the size grows. Theoretical studies on Be clusters as well as Mg clusters showed their magic numbers to be different from those of rare gases. These could be qualitatively understood in terms of the filling of the electronic shells in a spherical jellium model, where one assumes that the valence electrons of the atoms move in a jellium of positively charged ions. Magic clusters of rare gases with 13, 19, 23, 26, 29, 32, 34, ... atoms, however, correspond to icosahedral growth which has been understood to arise due to a spherically symmetric pairwise interaction and corresponds to a close packing of hard spheres. But as one goes further down the group IIA, one encounters elements Ca, Sr and Ba where the unoccupied $d$-states could play an important role in the growth of the atomic and electronic properties of their clusters.

Currently there is little understanding of the growth and other properties of metal clusters involving $d$ electrons, in spite of their importance in several technological applications. Experiments on clusters of Ni have provided indirect evidence of icosahedral growth akin to rare gas clusters, even though bonding in the latter case is very different. Also the abundance spectra of Eu clusters is similar but not magic. The abundance spectrum of small Sr clusters is similar to the one of rare gases but it shows $\text{Sr}_{11}$ to be magic which can not be understood from either the jellium model or the rare gas like picture. Further, $\text{Sr}_{13}$ is surprisingly not magic. The abundance spectrum of Ba clusters is similar but $\text{Ba}_{13}$ is also magic. To understand these, we have carried out detailed investigation on Sr clusters.

We have used the Car-Parrinello (CP) method and simulated annealing technique to obtain the low lying isomers within the local density approximation. As a first approximation to the electronic structure of Sr clusters, we ignored the $d$ states in order to save the computer time because we expected their occupancy to be small in clusters. The ionic potential was represented by the norm-conserving pseudopotential of Bachelet et al in separable form and the wave functions were expanded in a plane wave basis with a cut-off of 8 Ry. The simulations were carried out using the $s$-nonlocality, which treats only the $s$- and $p$- ionic pseudopotentials accurately. The cluster was placed in an fcc cell of 64 a.u. with periodic boundary conditions. This size of the cell was large enough so that interaction between the cluster and its periodic images was negligible. The Brillouin zone was sampled by the $\Gamma$ point and all calculations were performed for the singlet state. For clusters with N
≤ 7, we, however, relaxed a few selected geometries with steepest descent method. Structures of the low lying isomers were subsequently optimized using the full potential linear muffin-tin orbital (FPLMTO) method [14] which treats the $s$, $p$- and $d$-states on an equal footing. This procedure thus allowed us to study the role of $d$-orbitals in the bonding of Sr clusters.

For $Sr_{12}$ simulated annealing yields a tetrahedrally packed structure to be of lower energy than an icosahedron with one vertex atom missing. However, for $Sr_{13}$ a regular icosahedron is of lowest energy, though neither $Be_{13}$, nor $Mg_{13}$ has an icosahedral structure. This is due to the fact that the $1f$ state (of the jellium model) splits into a 3-fold and a 4-fold state. The 3-fold state is completely occupied and it is separated from the unoccupied 4-fold state by a gap of about 0.5 eV. The lowest energy structure for $Sr_{14}$ is a capped icosahedron. $Sr_{15}$ is an incomplete icosahedron with 3 caps while $Sr_{16}$ is a distorted icosahedron with 3 capping atoms. $Sr_{17}$ is a highly symmetric Frank-Kasper polyhedron with 16 atoms forming a cage and one atom at the center. For $Sr_{18}$, the structure has similarity with $Sr_{17}$ and for $Sr_{19}$ an hcp-like structure (see Fig. 1) has lower energy than a double-icosahedron. $Sr_{20}$ is a double icosahedron with a cap in the middle. These results clearly show that there is no systematic icosahedral growth if the system is $s-p$ bonded.

![Minimum energy structures of Sr clusters calculated using the CP method.](image)

Figure 1. Minimum energy structures of Sr clusters calculated using the CP method.

The lowest energy structures obtained from the CP method are shown in Fig. 1. For $N ≤ 11$, these are similar to the results obtained earlier for magnesium clusters [3] except for $Sr_6$, which is an octahedron. $Sr_8$ is a capped pentagonal bipyramid and it is lower in energy than a bicapped prism as well as a hexagonal bipyramid. For $Sr_9$, a tricapped prism is lower in energy than a double-capped pentagonal bipyramid. $Sr_{10}$ is a tetra-capped prism whereas in the case of $Sr_{11}$ all the five faces of a prism get capped and this is lower in energy than an icosahedron with two atoms missing.

![Binding energy per atom and (b) second derivative of energy for Sr clusters as a function of cluster size.](image)

Figure 2. (a) Binding energy per atom and (b) second derivative of energy for Sr clusters as a function of cluster size. Solid (broken) lines denote the results from FPLMTO (CP) calculation.
The binding energy per atom is shown in Fig. 2. It is noted that the approach to the bulk value ($\approx 2.0$ eV/atom) is fairly weak. The second derivative of energy, $\Delta E_N = E_{N+1} + E_{N-1} - 2E_N$, $E_N$ being the energy of a $N$ atom cluster, is significantly positive for $N = 4, 7, 10, 15$ and 18 favoring a magic behavior for these clusters (see Fig. 2). An interesting result to note here is that although the lowest energy structure for $Sr_{13}$ is an icosahedron, it is not magic. On the other hand, clusters with 10 and 18 atoms are not magic experimentally. Thus these results do not agree with experiments on $Sr$ clusters.

In order to investigate the role of $d$-electrons, the low-lying isomers of all the clusters were optimized using the FPLMTO method, with $s$, $p$ and $d$ basis orbitals. The resulting lowest energy structures are shown in Fig. 3 for cases in which the structures are different from those obtained from the CP method. It is found that the $d$-electrons lead to a reduction in the bond lengths in all the structures investigated. Most of the larger clusters which did not have an icosahedral structure to be of lowest energy in the CP method, now turned out to have very well-defined icosahedral geometries. Other structures retained the geometry but there is relaxation in the bond lengths which have a spread in their values. $Sr_9$ now turned out to be a pentagonal bipyramid with two caps. Similarly, $Sr_{10}$, $Sr_{11}$ and $Sr_{12}$ now yielded pentagonal bipyramid with three, four and five caps respectively. These can also be visualized as icosahedra with three, two and one atom missing. From $Sr_{13}$ onwards all clusters are capped icosahedra until one obtains a double-icosahedron for $Sr_{19}$ with the exception of $Sr_{15}$ which is a bicapped hexagonal antiprism (see Fig. 3). However, the bicapped icosahedron, at the binding energy of 1.591 eV/atom, is nearly degenerate with the minimum energy structure at 1.595 eV/atom. It is clear that now the icosahedral growth becomes more favorable. Similar structures have been observed in the experimental studies on $Ni$ clusters and also in theoretical studies using empirical many-body potential for $Ni$ atoms.

The binding energy is substantially larger when the $d$ electrons are also included (Fig. 2). For $Sr_2$ it is 0.29 eV/atom in fair agreement with the value of 0.27 eV/atom obtained by Ortiz and Ballone. However, for $Sr_{19}$ the binding energy is 1.75 eV/atom. Therefore, we find a transition from a weak bonding to a strong metallic bonding as a function of the cluster size. It is also interesting to note that the contribution due to the inclusion of the $d$-states to the binding energy per atom is very small (about 0.18 eV) for a dimer, but it grows to approximately 1.1 eV for the 19-atom cluster. Thus, the $d$-states become increasingly important as the $sp-d$ hybridization increases with size. The presence of $d$-states expedites the approach to the bulk properties as also evidenced from Fig. 4 by a small highest occupied (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap (\approx 0.1 eV for $N > 10$).

We consider our results as compelling evidence that the presence of unoccupied $d$-states make icosahedral packing more favorable in $Sr$ clusters. This is the closest packing of atoms in clusters. Thus the reason for the occurrence of rare-gas like magic numbers in the abundance spectrum of $Sr$ clusters is the presence of unoccupied $d$-states close to the $s$ level which participate very significantly in the bonding.

The second derivative of energy now shows that $Sr_{10}$ is no longer a magic cluster. On the other hand, $Sr_{11}$ as well as $Sr_{19}$ now become magic in agreement with the experiment. This substantiates the generally observed feature that the $s$-$p$ bonded metals fall into the jellium picture. It shows in addition that the presence of $d$-states renders the jellium picture inappropriate. Our results with $d$-electrons also show $Sr_{13}$ not to be magic which is also in agreement with the experimental data. We find that for $Sr_{11}$ there is a significant contraction in the bond length which leads to a stronger bonding contribution from $d$ states. Whereas, for $Sr_{13}$, the bond lengths are slightly longer as compared to the one in $Sr_{11}$.

Thus our results agree with the experimental finding for $Sr$ and suggest that the observation of rare gas like magic behavior for $Ba$, $Yb$ and $Eu$ are also due to the significant contribution of $d$-states to the bonding in these clusters. Since 5$d$ states get more populated in $Ba$, $Yb$ and $Eu$, we would expect these to make a larger contribution which may give rise to a magic behavior for 13-atom cluster also as is found in the case for $Ni$ clus-
ters. Our results also suggest that the observation of temperature dependent abundance spectra could also be due to a change in the $sp-d$ hybridization resulting from thermal expansion in clusters. Note that for weak contribution from $d$-electrons we find 10- and 18-atom clusters to be magic which agrees with the experiments on Eu. Indeed, in our CP simulations on Sr clusters we observed large increase in the interatomic distance at finite temperatures which should make such clusters susceptible to structural changes. We feel that the icosahedral type of growth observed in coinage metal clusters [10,11] beyond a size of 40 atoms may be due to a growing $sp-d$ hybridization. It is also appropriate to recall here the structural changes in gold clusters due to electron irradiation [14], which may be a heating effect of radiation. It is known that the $s-d$ hybridization plays a crucial role in the stability of the fcc phase of gold. Therefore, there is a critical balance arising from $d$ electrons which transform the clusters to a closed packed structure.

To summarize, we have calculated the structure and electronic properties of Sr clusters in the range of 2-20 atoms, using the CP and the FPLMTO methods. We find that the $d$-electrons contribute substantially to the binding energy and induce icosahedral growth in these clusters. The contribution increases from a very small value for the dimer to a large one for a 20-atom cluster. The calculated magic numbers are in agreement with the experimental results. These are the first results where the effect of $d$ electrons has been studied on the growth of clusters and we hope that our studies would stimulate further work in the understanding of the properties of transition metals clusters.

This work was initiated when VK was a visiting Professor at the Laboratoire Aime Cotton, CNRS, Universite Paris-Sud, France and he would like to thank Professors C. Brechignac and P. Cahuzac for providing the experimental results on Strontium clusters, stimulating discussions and kind hospitality. He would also like to thank Professor C. Colliex and other members of the laboratory for providing all the help needed to carry out the work there. We are also thankful to Dr. G. Pari for his assistance in getting the FPLMTO code working.