Eur. Phys. J. D **6**, 495–500 (1999)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

Ground-state geometries and stability of $\mathrm{Na_nMg}$ ($\mathrm{n = 1–12}$) clusters using ab initio molecular dynamics method

Ajeeta Dhavale[1,a], D.G. Kanhere[1,b], C. Majumder[2], and G.P. Das[3]

[1] Department of Physics, University of Pune, Pune 411 007, India
[2] Chemistry Division, Bhabha Atomic Research Center, Mumbai-400 085, India
[3] Solid State Physics Division, Bhabha Atomic Research Center, Mumbai-400 085, India

Received: 16 September 1998 / Received in final form: 15 February 1999

Abstract. The ground-state geometries, energetics and the stability of $\mathrm{Na}_n\mathrm{Mg}$ ($n = 1 - 12$) clusters are studied using *ab initio* molecular dynamics method. Our results indicate that the ground-state geometries of large clusters ($n \geq 6$) are different from those of $\mathrm{Na}_n\mathrm{Al}$ clusters where a trivalent impurity Al is added to the same monovalent host Na. Other features observed are an early appearance of 3-dimensional structure and a pentagonal growth path from $n = 6$ up to $n = 11$. As expected, the ground-state geometry of $\mathrm{Na_{12}Mg}$ is not an icosahedron but can be viewed as a distorted form of one of the low lying geometries of $\mathrm{Na_{13}}$ cluster. In the energetically favored structures impurity atom Mg is never located at the center of the cluster. The stability analysis based on the energetics shows $\mathrm{Na_6Mg}$ (8 valence electrons) to be the most stable. In addition there is a remarkable even-odd pattern observed in the dissociation energy and the second difference in energy which is absent in earlier studies of $\mathrm{Na}_n\mathrm{Al}$ and $\mathrm{Li}_n\mathrm{Al}$ clusters.

PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Mr Spectroscopy and geometrical structure of clusters – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials

1 Introduction

Atomic clusters form a special class of matter in which the finite size leads to unusual combinations of physical and chemical properties. The recent advances in experimental techniques like matrix-isolation method and the development of molecular beam technology have enabled researchers to produce small metal clusters consisting of a few tens of atoms. The areas of interest include cluster-cluster, cluster-surface interaction, fragmentation dynamics of clusters *etc.* In addition, clusters also serve as a prototype for gaining the understanding of nanoscaled materials and cluster assembled materials. The studies of their structural and electronic properties have revealed novel properties like magic clusters. The gross features in the stability of these magic clusters can be understood from a spherical jellium model [1,2] (SJM). However the sophisticated theoretical methods are required to understand the details of the geometry and other properties.

With the advent of *ab initio* molecular dynamics method [3], the study of electronic and geometric structure of small clusters has emerged as an exciting field of research. Such simulations are carried out using the Car-Parrinello molecular dynamics (CPMD) method which involves electron wave functions. This method turns out to be computationally expensive, especially if the long simulation runs are required to span the configuration space as in the case of heteroatomic clusters. Recently, we have used a combination of density based molecular dynamics (DBMD) method and CPMD which has proved [4] to be a cost effective way for calculating the ground-state geometries of clusters without a loss of accuracy. In the case of DBMD the total energy functional is expressed in terms of density only [5]. As a consequence, this method scales linearly with the system size since there is no computationally expensive orthonormality constraint due to the absence of wave functions. This method has been found to predict the correct ground-state geometries (symmetry) and reasonably accurate bond lengths for dimers and trimers of Na, Li, Mg, Al, *etc.* [6,7].

A significant number of *ab initio* studies have been reported on homoatomic clusters like Na [8], Mg [9], Al [10], Li [11], *etc.* to understand their ground-state geometries, growth and the nature of bonding. However, it is of considerable importance to investigate clusters containing impurities for a number of reasons. Firstly, studies on such heteroatomic clusters help to understand the effect of doping and alloying between the two different elements with varying concentrations. Secondly, it has also been observed that the structure and stability depends on chemical nature of constituent atoms. A few such investigations on simple metal atom clusters are available.

---

[a] e-mail: `ajd@physics.unipune.ernet.in`
[b] e-mail: `kanhere@unipune.ernet.in`

Mixed clusters like Li_nAl ($n = 1$–8) [6,12] and Na_nAl ($n = 1$–10) [4], where the trivalent impurity Al is added in different monovalent hosts have been studied theoretically. The results are also available for Al_nLi ($n = 1$–10) [13], where monovalent impurity is added to a trivalent host. Work has been reported for alkali-metal-atom-antimony clusters [14], Na_nF_n [15], and Na_nK_m [16]. Some interesting features like an early appearance of 3-dimensional structure and changes in geometries of pure clusters have been observed in all these studies. It is also seen that trapping of an impurity atom is system dependent, *e.g.*, for Na_nAl or Li_nAl clusters impurity atom Al gets trapped inside the cage of host atoms while for Al_nLi [13] clusters Li remains on the surface and for Na_nMg clusters the impurity atom Mg does not get trapped inside the cage of Na atoms till $n = 11$.

In the earlier work [4] we have reported a systematic investigation of a trivalent impurity Al in a monovalent host Na. Therefore it is of considerable interest to study the changes in the ground-state geometries and energetics for clusters where a divalent impurity like Mg is added to the same host Na and compare the results with that of a trivalent impurity. Though some theoretical results [17–20] are already available for Na_nMg clusters, a systematic study of the growth of Na_nMg clusters is unavailable. Here, we report such a study of the equilibrium ground-state geometries, bond lengths and energetics for Na_nMg ($n = 1$–12) clusters. We have used a combination of DBMD and CPMD methods. The ground-state geometries are first obtained by DBMD method, where full simulated annealing strategy is used. These geometries are then quenched further using CPMD method to get the final ground-state structures. This strategy saves considerable amount of computational time. Bonacic-Koutecky [20] have reported geometries of Na_nMg ($n = 5$–8) clusters obtained using SCF and in some cases the Moller-Plesset perturbation theory (MP2). They have computed stability of these clusters by means of large scale configuration interaction. The reported structures are identicle with those obtained by us except for Na_5Mg. Rothlisberger and Andreoni [17] have also studied these clusters for $n = 6$–9 and 18 using CPMD method. They have observed that pentagonal growth path is favored over tetrahedral growth path for $n = 6$–9 clusters and the Mg atom is never located at the center of the cluster in contrast to the SJM due to a weak bonding of Mg with Na. Our results are consistent with these.

In the next section, we describe in brief the method used and then present the results.

2 Computational details

In order to accelerate the process of obtaining the ground-state geometries we have used the DBMD method first, which is followed by the CPMD method in quenching mode. During the DBMD calculations, the ground-state configurations are obtained either by starting with different initial configurations and then quenching the structures or by dynamical simulated annealing where the cluster is heated up to 600 K–650 K and then cooled very slowly. In all the cases the stability of the final ground-state configuration has been tested by reheating the cluster and allowing it to span the configuration space for a few thousand iterations and then cooling it to get the lowest energy configuration. The ground-state geometry thus obtained is then quenched further using the CPMD method to get more accurate results. For $Na_{12}Mg$ cluster we have carried out full simulated annealing using CPMD method where the arbitrary geometry is heated up to 600 K and then cooled. It is observed that the ground-state geometry thus obtained is not an icosahedron which is the result of the DBMD calculation.

All the calculations are carried out using a periodic cell of length 30 a.u. with $54 \times 54 \times 54$ mesh. The energy cutoff of 12 rydbergs has been used for plane wave expansion. The electron-ion interaction is described by a norm-conserving nonlocal pseudopotential of Bachelet, Hamann and Schluter [21] with the p component taken as local and the s component as nonlocal. For the exchange-correlation potential we have used the Berth-Hedin approximation. The total energy E of the system is minimized for fixed ionic positions using the conjugate gradient method [22]. The trajectories of ions and the fictitious electron dynamics are simulated using Lagrange's equations of motion which are solved by Verlet algorithm [3]. More details about our calculational procedure are described elsewhere [7]. All the results reported in the next section are based on the final CPMD calculations.

3 Results and discussion

The ground-state geometries for Na_nMg ($n = 1$–12) clusters are shown in Figures 1(a) and 1(b). The black circle corresponds to a Mg atom and the open circles to Na atoms. We will first discuss the nature of the ground-state geometries and wherever appropriate compare them with the corresponding geometries of Na_n [8] and Na_nAl [4] clusters. The calculated bond length for NaMg cluster with a ($C_{\infty v}$) symmetry is 5.93 a.u. which is 8% more than Na dimer. This is expected because of a weaker bonding of Mg atom with Na atom. The ground-state geometry of Na_2Mg turns out to be Jahn-Teller distorted planer configuration which is a scalene triangle. It may be noted that the DBMD method yields an isosceles triangle as a ground-state geometry since it is not able to pick up Jahn-Teller distortion. The first 3-dimensional structure is seen for Na_3Mg which is a tetrahedron (C_{3v} symmetry). However in case of Na_n clusters the first 3-dimensional structure is seen for $n = 6$. The early appearance of 3-dimensional structures is related to the occupancy of p_z orbital. This can be understood by examining the highest occupied state for Na_3Mg which turns out to be of p_z type. The structure of Na_4 is a rhombus. The addition of Mg atom bends this rhombus and tries to form bonds with 4 Na atoms resulting in a distorted structure. In the case of Na_5Mg cluster 5 sodium atoms form a regular square pyramid and the Mg atom takes the other vertex of the square pyramid forming an octahedron. Thus apart from some

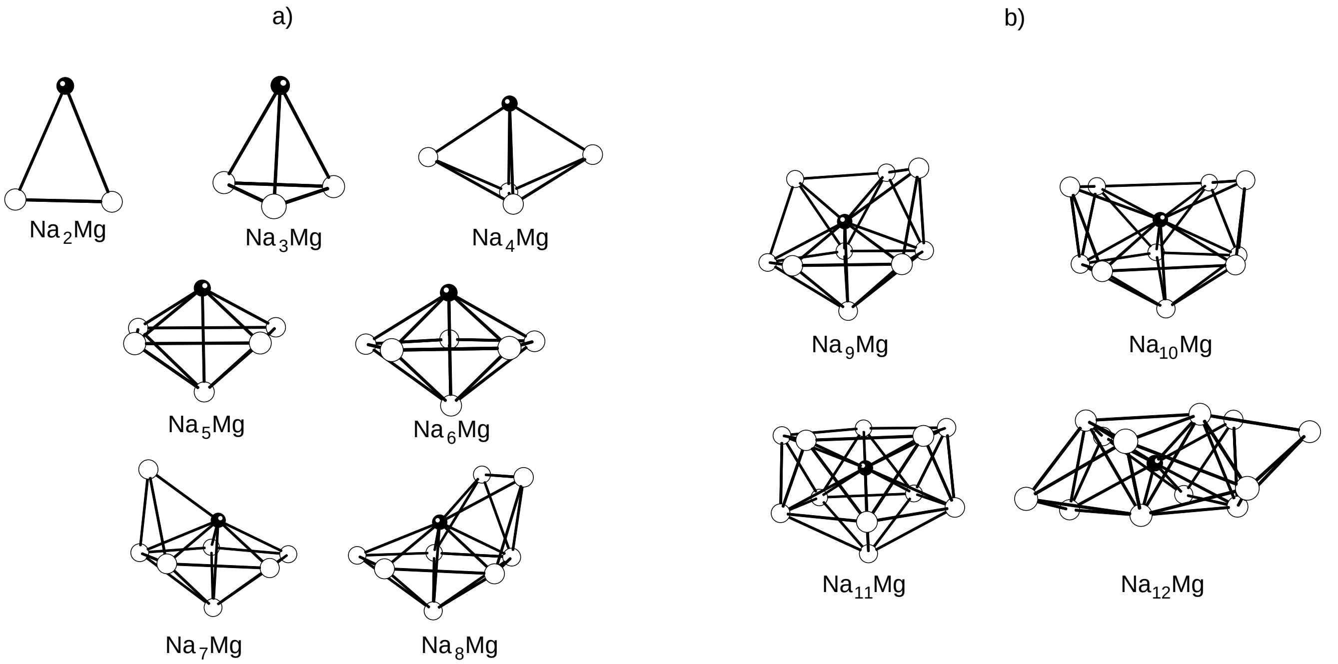

Fig. 1. (a) The ground-state geometries of Na_nMg ($n = 2$–8) clusters. (b) The ground-state geometries of Na_nMg ($n = 9$–12) clusters. (The dark circle represents a Mg atom and the white circle a Na atom.)

small distortions the ground-state geometries of Na_nMg clusters are similar to Na_nAl up to $n = 5$.

The geometries from $n = 6$ to $n = 11$ reveal the existence of a pentagonal ring as noted by Rothlisberger [17] *et al.* The growth of these can be considered as a successive capping of Na atom to each side of a pentagonal ring which leads to the formation of a second 5-fold ring and a subsequent trapping of Mg at $n = 11$. However the expected formation of an icosahedron for $Na_{12}Mg$ by addition of one more Na atom does not take place. It may be noted that such a growth path *via* a pentagonal ring formation is absent in case of Na_nAl clusters where the cluster of Na atoms grows in a symmetric fashion around a centrally situated impurity atom Al. Thus Al and Mg impurities in the same host Na give rise to different structures for $6 \le n \le 11$.

The lowest-lying structure for Na_6 is a pentagonal pyramid. The addition of impurity atom Mg changes this structure to a pentagonal bipyramid having C_{5v} symmetry. It may be noted that Na_6Mg having 8 valence electrons turns out to be the most stable cluster in this series. The stability is also confirmed on the basis of the energetics. This structure is very much different from Na_6Al. Trapping of a Mg atom inside the Na cage is not seen up to $n = 10$ for Na_nMg clusters. This can be understood on the basis of the bond strength between Na-Mg and Na-Al. The binding energy for Na-Mg dimer is 0.23 eV and for Na-Al dimer is 0.82 eV. The weaker binding between Na and Mg keeps the Mg atom as far as away from the Na cage for $n \ge 6$ clusters. The trend of capping of Na atoms to the pentagonal ring continues from $n = 7$ to $n = 10$ clusters resulting in trapped pentagonal bipyramid (PBP) structures (C_S symmetry) for all of them. For $Na_{11}Mg$ cluster the additional 5 Na atoms other than the PBP unit of Na_6Mg cluster cap all the triangular faces formed by the Mg atom and the two Na atoms belonging to the pentagonal ring resulting in an additional pentagonal ring. Interestingly, the addition of one Na atom does not make $Na_{12}Mg$ cluster icosahedral but is seen to be the distorted form of one of the low-lying structures of Na_{13}. The icosahedral structure is found to be 1 eV higher than the distorted structure.

The Na-Mg bond lengths (in a.u.) along with the total number of electrons in the system (N_e) are summarized in Table 1 for all the clusters studied. It can be seen that the shortest Na-Mg bond length gradually decreases from 5.9 to about 5.5 as the size increases indicating the strengthening of the bond.

In order to discuss the stability of the Na_nMg ($n = 1, 12$) clusters we have calculated their binding energies per atom, dissociation energies and the second difference in energy. We define the binding energy per atom $E_b[Na_nMg] = (-E[Na_nMg] + nE[Na] + E[Mg])/(n+1)$ and the second difference in energy as $\Delta^2 E[Na_nMg] = -2E[Na_nMg] + E[Na_{n+1}Mg] + E[Na_{n-1}Mg]$. The dissociation energy with respect to single Na dissociation is given by $\Delta E[Na_nMg] = E[Na_nMg] - (E[Na_{n-1}Mg] + E[Na])$.

The binding energy per atom as a function of the total number of atoms in the system is shown in Figure 2(a). The binding energy shows monotonic increase and a slight peak for Na_6Mg cluster indicating its stability. A comparison of the binding energies for Na_nAl [4] and Na_nMg clusters clearly indicates that Na-Mg bond is weaker than Na-Al bond. In Figure 2(b) we show the dissociation energy (solid line) and the second difference in energy (dotted line) for all the clusters. The graph shows

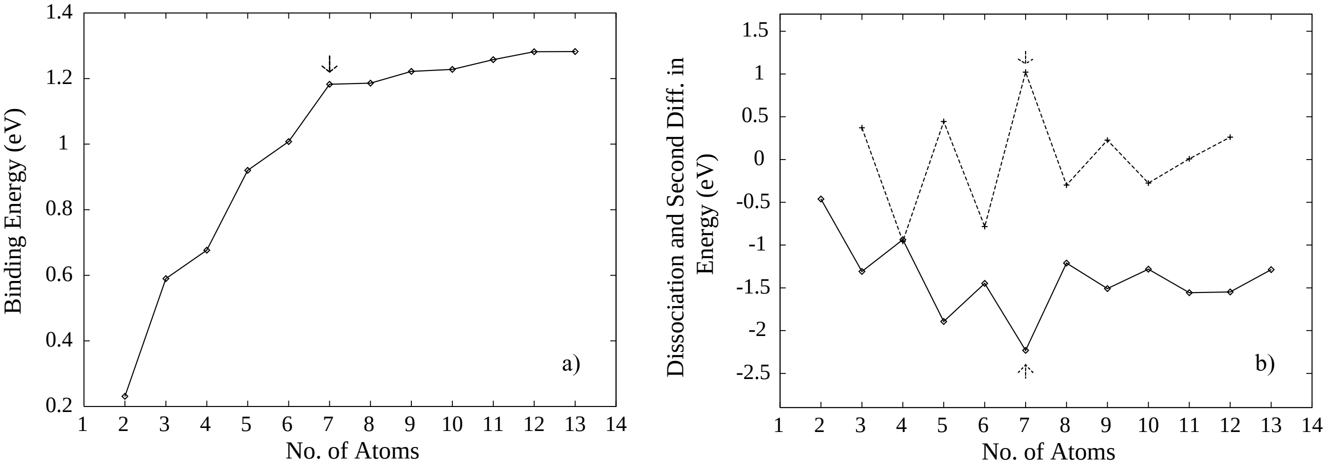

Fig. 2. (a) The binding energy (eV) per atom for the Na_nMg (n = 1–12) clusters shown as a function of the total number of atoms (N). (b) The dissociation energy (eV) (shown with solid line) and the second difference in energy (eV) (shown with dotted line) for Na_nMg (n = 1–12) clusters shown as a function of the total number of atoms (N). (The arrow indicates the most stable cluster.)

Table 1. The total number of electrons in the system (N_e), the bond length (in a.u) obtained using CPMD between Na-Mg for Na_nMg ($n = 1, 12$) clusters.

System	N_e	Na-Mg bond length (a.u.)
NaMg	3	5.93
Na_2Mg	4	7.02, 6.93
Na_3Mg	5	3 × 6.41
Na_4Mg	6	2 × 5.93 6.33, 6.38
Na_5Mg	7	4 × 5.60 6.06
Na_6Mg	8	5 × 5.82 6.28
Na_7Mg	9	3 × 5.65, 2 × 5.76 2 × 5.81
Na_8Mg	10	2 × 5.67, 2 × 5.78 2 × 5.94, 2 × 5.99
Na_9Mg	11	3 × 5.65, 5.79, 2 × 5.82 5.93, 2 × 5.97
$Na_{10}Mg$	12	2 × 5.71, 5.99, 6.04 6.08, 6.13, 6.31, 6.34 6.41, 6.43
$Na_{11}Mg$	13	5.59, 2 × 6.06, 3 × 6.12 4 × 6.16, 6.19
$Na_{12}Mg$	14	5.49, 5.51, 2 × 5.57 4 × 5.68, 2 × 9.44, 2 × 9.46

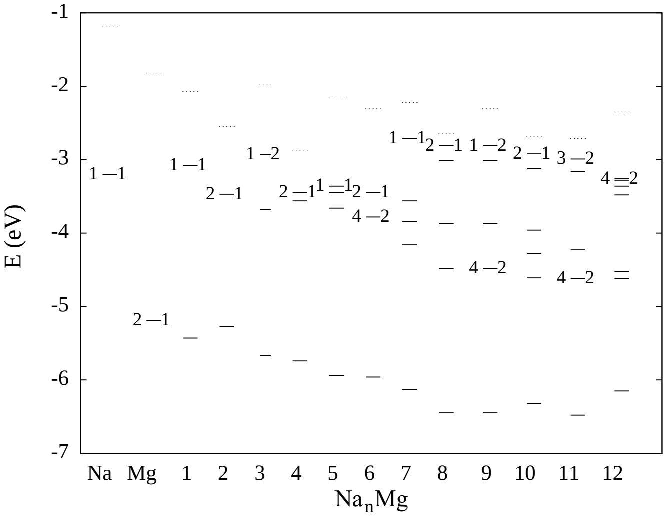

Fig. 3. Eigenvalue spectrum for Na, Mg and Na_nMg (n = 1–12). (Energies are in eV.) Unoccupied states are shown with dotted segments. For the highest occupied state and the lower occupied degenerate states the number on the right of a state denotes the degeneracy of a level while the number on the left denotes the total occupancy. All the other occupied states have occupancy 2.

remarkable even-odd pattern which is absent in the case of Na_nAl [4] clusters. The maximum in the second difference in energy and the minimum in the dissociation energy occurs for a seven-atom system, clearly showing Na_6Mg (8 valence electrons) to be the most stable.

It is of interest to examine the Kohn-Sham energy levels of clusters studied. Such an energy level diagram is shown in Figure 3 for all the clusters studied along with Na and Mg atomic levels. It is clear from the figure that the lowest eigenvalue (originating from Mg 3s level) is well separated from the higher lying states. The nature of the eigenvalue spectrum changes as we go from $n = 5$ to the stable system $n = 6$. The second and the third eigenstates of Na_5Mg combine to form a doubly degenerate state having lower energy in case of Na_6Mg and a partially filled state gets completely filled and is lowered giving maximum HOMO-LUMO gap for Na_6Mg.

Additional insight can be gained by examining systematically the isodensity surfaces for the HOMO of NaMg, Na_6Mg, Na_7Mg and Na_9Mg shown in Figure 4(a), 4(b),

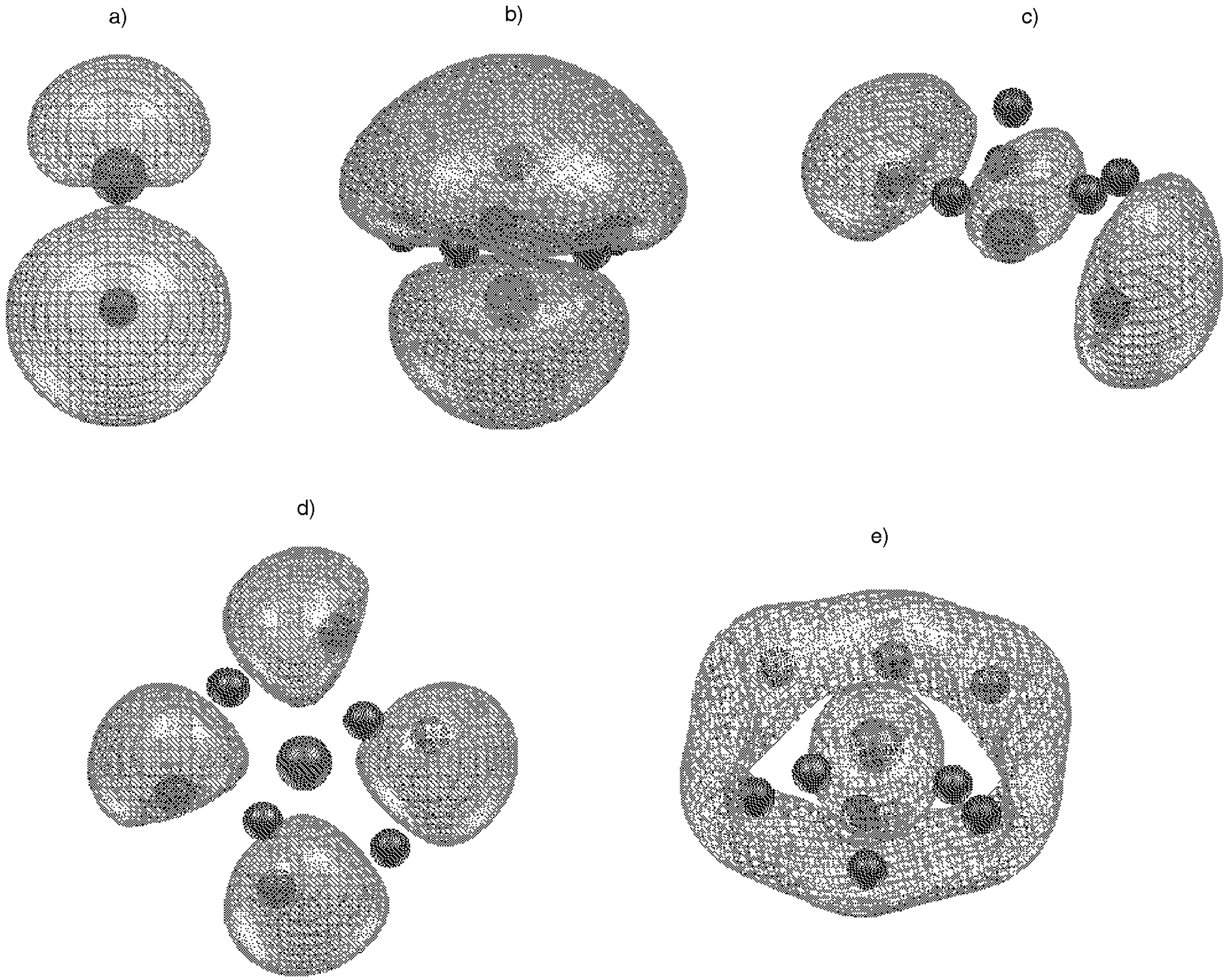

Fig. 4. (a) Isodensity surface corresponding to the highest occupied state for NaMg cluster. (b) Isodensity surface corresponding to the highest occupied state for $\mathrm{Na_6Mg}$ cluster. (c) Isodensity surface corresponding to the highest occupied state for $\mathrm{Na_7Mg}$ cluster. (d) Isodensity surface corresponding to the highest occupied state for $\mathrm{Na_9Mg}$ cluster. (e) Isodensity surface corresponding to the state just below the highest occupied state for $\mathrm{Na_9Mg}$ cluster.

4(c) and 4(d), respectively. The dimer density (Fig. 4(a)) shows "p_x" character and a nearly spherical charge density around Mg indicates a weak bonding of Mg with Na. The isodenses for $\mathrm{Na_6Mg}$ (Fig. 4(b)) show a delocalised "p_z" character for the HOMO (as expected) showing Mg atom bonding with all the Na atoms in the pentagonal ring. The shell filling so far is in conformity with the SJM (*i.e.* $1s^2$, $2p^6$). In order to investigate the further ordering of the states we have examined the isodensity surfaces for the HOMO of $9e^-$ (*i.e* $\mathrm{Na_7Mg}$) and $11e^-$ (*i.e.* $\mathrm{Na_9Mg}$) systems. The isodensity surface for the HOMO of $\mathrm{Na_7Mg}$ shown in Figure 4(c) is neither of pure "s" or pure "d" type but is an ad mixture. This is also stated by Rothlisberger [17] *et al.* However Figure 4(d) clearly indicates that for $\mathrm{Na_9Mg}$, the HOMO is mostly "d" type. In order to identify the nature of a previous state we have shown the isodensity surface for the state just below the highest occupied state of $\mathrm{Na_9Mg}$ cluster in Figure 4(e). It is "s" like. This indicates that the order of energy levels (*viz.* $1d^{10}$, $2s^2$) as stated by the SJM is reversed which has been also observed in the case of $\mathrm{Na}_n\mathrm{Al}$ [4] clusters.

4 Conclusion

In the present work, we have reported the ground-state geometries of magnesium-doped sodium clusters ($\mathrm{Na}_n\mathrm{Mg}$, n = 1–12). Our calculations were done using a combination of the DBMD method and the CPMD method to reduce the computational time. It is observed that the ground-state geometries are different from $\mathrm{Na}_n\mathrm{Al}$ for $n \geq 6$ clusters showing the dependence of geometries on the valence of the impurity atom added to the host. For $\mathrm{Na}_n\mathrm{Mg}$ clusters the impurity atom Mg does not occupy the interstitial position till n = 11. The earlier results based on *ab initio* CI calculations [18] assume that the

Mg atom occupies the central position of the cluster but it can be seen that the simulated annealing results for the ground-state geometries are different. The growth of the clusters from $n = 6$ to $n = 11$ can be considered as a successive capping of Na to each side of a pentagonal ring which leads to formation of a second 5-fold ring and a subsequent trapping of Mg at $n = 11$. However the expected formation of an icosahedron for $Na_{12}Mg$ by addition of one more Na atom does not take place. Thus the results indicate that a fivefold geometry is more favorable than a fourfold geometry for bigger clusters (n = 6–11). The extra stability of Na_6Mg (8 valence electrons) is confirmed from the energetics. The systematic analysis of isodensity surfaces shows that the order of energy levels (*viz.* $1d^{10}$, $2s^2$) as stated by SJM is reversed which is also observed in case of Na_nAl [4] clusters.

AJD greatfully acknowledges financial assistance from CSIR (New Delhi). DGK acknowledges partial financial assistance from the Department of Science and Technology (DST), Government of India. Authors are thankful to Dr. S. R. Gadre for providing NEWVIS software to plot isodensity surfaces. C. Majumder acknowledges S. K. Kulshrestha.

References

1. W.D. Knight, K. Clemenger, W.A. de Heer, W.A. Saunders, M.Y. Chou, M.L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).
2. M.Y. Chou, M.L. Cohen, Phys. Lett. A **113**, 420 (1986).
3. R. Car, M. Parrinello, Phys. Rev. Lett. **55**, 685 (1985).
4. Ajeeta Dhavale, Vaishali Shah, D.G. Kanhere, Phys. Rev. A **57**, 4522 (1998).
5. M. Pearson, E. Smargiassi, P.A. Madden, J. Phys. Condens. Matter **5**, 3221 (1993).
6. D. Nehete, V. Shah, D.G. Kanhere, Phys. Rev. B **53**, 2126 (1996).
7. V. Shah, D. Nehete, D.G. Kanhere, J. Phys. Condens. Matter **6**, 10773 (1994).
8. J.L. Martins, J. Buttet, R. Car, Phys. Rev. B, **31**, 1804 (1985); U. Rothlisberger, W. Andreoni, J. Chem. Phys. **94**, 8129 (1991).
9. V. Kumar, R. Car, Phys. Rev. B **44**, 8243 (1991).
10. H.P. Cheng, R.S. Berry, R.L. Whetten, Phys. Rev. B **43**, 10647 (1991).
11. I. Boustani, W. Pewestorf, P. Fantucci, V. Bonacic-Koutecky, J. Koutecky, Phys. Rev. B **35** 9437 (1987).
12. H. Cheng, R. Barnett, Uzi Landman, Phys. Rev. B **48**, 1820 (1993).
13. C. Majumder, G.P. Das, S.K. Kulshrestha, V. Shah, D.G. Kanhere, Chem. Phys. Lett. **261**, 515 (1996).
14. F. Hagelberg, S. Neeser, N. Sahoo, T. P. Das, Phys. Rev. A **50**, 557 (1994).
15. J. Giraud-Girard, D. Maynau, Z. Phys. D **32**, 249 (1994).
16. A. Bol, G. Martin, J. M. Lopez, J. A. Alonso, Z. Phys. D **28**, 311 (1993).
17. U. Rothlisberger, W. Andreoni, Int. J. Mod. Phys. B **6**, 3675 (1992); U. Rothlisberger, W. Andreoni, Chem. Phys. Lett. **198**, 478 (1992).
18. P. Fantucci, V. Bonacic-Koutecky, W. Pewestort, J. Koutecky, J. Chem. Phys. **89**, 4229 (1989).
19. M.M. Kappes, P. Radi, M. Schar, E. Schumacher, Chem. Phys. Lett. **119**, 11 (1985).
20. V. Bonacic-Koutecky, L. Cespiva, P. Fantucci, C. Fuchs, M.F. Guest, J. Koutecky, J. Pittner, Chem. Phys. **186**, 275 (1994).
21. G.B. Bachelet, D.R. Hamann, M. Schluter, Phys. Rev. B **26**, 4199 (1982).
22. W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1987).