

Nonicosahedral growth and magnetic behavior of rhodium clustersYoung-Cho Bae,¹ Hiroki Osanai,¹ Vijay Kumar,^{2,3} and Yoshiyuki Kawazoe²¹CODEC Co., Ltd., Kawasaki 215-0033, Japan²Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980-8577, Japan³Dr. Vijay Kumar Foundation, 45 Bazaar Street, K. K. Nagar (West), Chennai 600 078, India

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Ab initio pseudopotential calculations of the atomic structures and magnetic behavior of Rh_n ($n \leq 15$) clusters using the generalized gradient approximation for the exchange-correlation energy, reveal new lowest energy structures that are noncompact and have no atom at the center upto $n=13$, leading to a nonicosahedral growth. An eight-atom cluster has cubic structure and is magic. Some clusters beyond 13 atoms also do not have close packed structures due to some covalent character in the bonding. The calculated magnetic moments are generally lower and in better agreement with experiments than obtained before. Further studies on Ru_{13} and Pd_{13} clusters show that the lowest energy isomers of these clusters are also nonicosahedral. These findings of the novel behavior of technologically important transition metal clusters provide new ground for a better understanding and design of new catalysts.

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I. INTRODUCTION

The occurrence of magnetism in clusters of nonmagnetic elements^{1,2} Ru, Rh, and Pd has attracted much attention in recent years³⁻⁸ but it is still not well understood. These elements lie in the periodic table just below the magnetic elements Fe, Co, and Ni, respectively, whose clusters have been found⁹ to have enhanced magnetic moments as compared to bulk due to reduced coordination of atoms and localization of electrons. Such an enhancement in magnetic moments also occurs on surfaces¹⁰ of magnetic elements where the coordination of atoms is again lower than in the bulk. The magnetic moments in these cases lie in between the values for the atom and the bulk. In clusters also, a large fraction of atoms lie on the surface and this leads to the development of magnetic moments in Ru, Rh, and Pd clusters. Earlier studies³⁻⁷ on clusters of these elements overestimated the magnetic moments as compared to the measured values¹ and obtained an icosahedral growth. However, here we report the finding of nonicosahedral growth in Rh clusters. These isomers generally have lower magnetic moments as compared to those reported before leading to a better agreement with experiments.

In addition to the fundamental interest in magnetism and bonding nature as well as their correlation with the atomic structures of nanoclusters, Rh clusters are important for catalysis¹¹ and it is necessary to know the atomic structures and magnetic properties properly to understand their role in reactions. Experiments¹ in the temperature range of 60–300 K suggest Rh_n clusters to be magnetic upto about $n=60$ with a value of $0.48 \pm 0.13 \mu_B/\text{atom}$ for Rh_{13} . *Ab initio* calculations have been done mostly on clusters having upto about 13 atoms. Studies using a tight binding model⁸ on clusters with n upto about 200 also showed icosahedral isomers to be lowest in energy. A spin-polarized density functional study^{3,4} of Ru, Rh, and Pd clusters having upto 147 atoms showed large magnetic moments on small clusters and icosahedral growth to be lowest in energy. For Ru and Rh the magnetic moments were found to decrease much

faster as compared to Pd with an increase in the cluster size. The magnetic moment on Rh_{13} in an icosahedral structure has been calculated to be 1.62 and $1.15 \mu_B/\text{atom}$, respectively, by Reddy *et al.*⁵ and Reddy *et al.*⁶ Jinlong *et al.*⁷ also obtained $15 \mu_B$ magnetic moment on Rh_{13} using the discrete variational method while Kumar and Kawazoe⁴ obtained $21 \mu_B$ magnetic moment on this cluster. However, it was shown⁴ that isomers with lower magnetic moments such as the one with $15 \mu_B$ lie only about 0.04 eV higher in energy and therefore lower magnetic moment isomers are expected to be present in experimental conditions. These results generally show that the calculated values are significantly higher than those obtained from experiments. Reddy *et al.*,⁶ obtained structures using a parametrized model potential without spin polarization. The resulting structures were reoptimized using density functional calculations. Guirado-Lopez *et al.*⁸ kept the symmetry of the clusters fixed. Our *ab initio* calculations surprisingly reveal noncompact and nonicosahedral structures to be energetically more favorable opening a new possibility in the understanding of this important class of clusters. A non-icosahedral growth has also been obtained¹² for Nb clusters. Therefore, we performed further checks on the structures of Ru_{13} and Pd_{13} clusters. Interestingly we find an icosahedron for Ru_{13} to be much higher in energy as compared to the non-compact structure while for Pd_{13} the noncompact structure is lower in energy but it is nearly degenerate with an icosahedron.

II. METHOD

The calculations have been performed using the *ab initio* ultrasoft pseudopotential plane wave method.^{13,14} The cutoff energy for the plane wave expansion is taken to be 205.5, 203.6, and 199 eV for Rh, Ru and Pd, respectively. The generalized gradient approximation (GGA)¹⁵ with spin polarization has been used for the exchange-correlation energy and the Γ point, for the Brillouin zone integrations. Several structures have been fully optimized using the conjugate gradient

method such that the force on each ion became less than 0.005 eV/\AA . The energy is converged to an accuracy of 0.0001 eV . In most cases the low lying isomers are further checked for different spin-isomers using a constraint on the net magnetic moment and the reoptimization of the atomic structure. The binding energy (BE) of Rh_2 is calculated to be 2.04 eV/atom with the bond length of 2.20 \AA . The magnetic moment reduces to $2\mu_B/\text{atom}$ from the atomic value of $3\mu_B$. There is a large scatter in the available theoretical values for a dimer. We compare our results with those obtained by using GGA. Our BE (bond length) is slightly higher (shorter) as compared to 1.88 eV/atom (2.34 \AA) obtained⁶ by using DMOL and GGA. Also our BE is higher than the experimental value¹⁶ of 1.46 eV/atom but the bond length is in better agreement with the experimental value of 2.28 \AA . The bulk cohesive energy and lattice constant for Rh are calculated to be 6.06 eV/atom and 3.83 \AA that are in good agreement with the experimental values of 5.75 eV/atom and 3.80 \AA , respectively. Therefore, we expect a better prediction of the BEs of clusters with increasing size but an overall slight overestimation.

III. RESULTS

A. Structures

The low lying isomers of Rh_n clusters with $n=4-12$ are shown in Fig. 1. The BEs, magnetic moments, and mean nearest neighbor bond lengths of the lowest energy isomers are given in Table I. Earlier studies^{6,7} have reported a tetrahedral structure for Rh_4 with $4\mu_B$ magnetic moment. This is nearly degenerate with a nonmagnetic tetrahedral isomer. We find a bent (nearly 90°) rhombus (side 2.41 \AA , angles 71.9° and 70.4° , and diagonals 2.78 and 2.83 \AA) to be lowest in energy with $6\mu_B$ magnetic moment while a square (side 2.33 \AA) lies 0.15 eV higher in energy with $4\mu_B$ magnetic moment. A tetrahedron (side 2.45 \AA) lies 0.19 eV higher in energy and is nonmagnetic. This is the first result for transition metal clusters that an open structure has lowest energy. For Rh_5 , we obtain a square pyramidal structure (bond lengths 2.42 \AA in the base and 2.54 \AA from vertex to base) with $5\mu_B$ magnetic moment to be 0.31 eV lower in energy than a trigonal bipyramid (bond lengths 2.65 \AA in the base and 2.50 \AA from vertex to base) that has $7\mu_B$ magnetic moment. A similar result was obtained earlier.⁶ For Rh_6 a slightly distorted prism with mirror symmetry (bond length varying between 2.36 to 2.47 \AA with the mean value of 2.43 \AA) and an octahedron (bond length varying from 2.50 to 2.66 \AA with the mean value of 2.54 \AA) each with $6\mu_B$ magnetic moment are nearly degenerate while a bi-capped tetrahedral structure lies 0.31 eV higher in energy with $10\mu_B$ magnetic moment. A nonmagnetic octahedral isomer lies only 0.05 eV higher in energy than the $6\mu_B$ isomer and therefore in this octahedral isomer the magnetic behavior is very weak and can be easily destroyed even at quite low temperatures. However, the nonmagnetic prism isomer lies 0.22 eV higher in energy and therefore it is unlikely to be observed at room temperature. An isomer with the capping of the lowest energy Rh_5 pyramid structure lies 0.55 eV higher in energy with $4\mu_B$ magnetic moment. We also calcu-

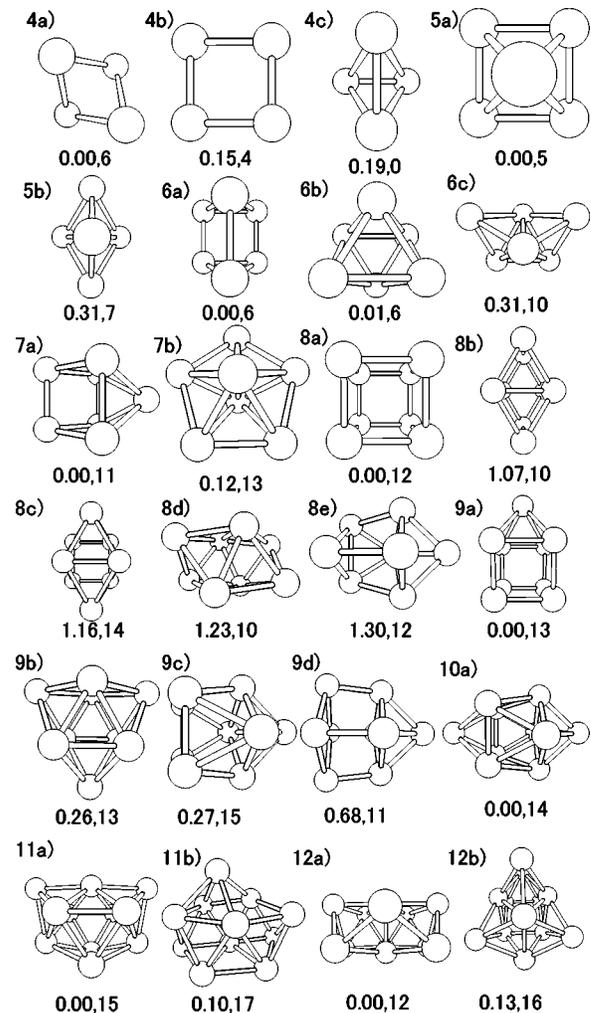


FIG. 1. Atomic structures of Rh_n clusters with $n=4-12$. Isomer (a) has the lowest energy which is taken as reference. The relative energies (eV) of other isomers are given below each structure along with the magnetic moment in the unit of μ_B . The structure of 12a has six atoms in each layer. There is one atom in the center of the upper layer to which two side atoms are connected. The front atom in this layer is connected with two atoms in the lower layer. The latter also has one atom behind the central atom. The smaller the size of the ball, the deeper is the position.

lated a planar triangular structure and a hexagon. These lie 2.08 and 3.38 eV higher in energy with 8 and $0\mu_B$ magnetic moments, respectively than the lowest energy isomer. Therefore, these low dimensional structures lie significantly higher in energy for $n=6$. Earlier an octahedral structure was obtained for this cluster. However, our finding of the prism structure is important as for Rh_7 also we find a square capped prism structure with $11\mu_B$ magnetic moment to be 0.12 eV lower in energy than a pentagonal bipyramid ($13\mu_B$) obtained before.^{6,7} An isomer in which a triangular face of the prism is capped lies 0.48 eV higher in energy with $7\mu_B$ magnetic moment.

Another surprising finding is that Rh_8 has a perfect cubic structure with 2.40 \AA side and $12\mu_B$ magnetic moment. The bond length is quite short and it reflects the strong covalent bonding in this cluster. It lies about 1 eV lower in energy

TABLE I. The binding energy (BE), magnetic moment (M), and mean nearest neighbor bond lengths (d) in the lowest energy isomers of Rh clusters.

n	Structure	BE (eV/atom)	M (μ_B)	d (Å)
4	Bent rhombus	3.12	6	2.41
5	Square pyramid	3.40	5	2.48
6	Prism	3.57	6	2.43
7	Capped prism	3.71	11	2.50
8	Cube	3.96	12	2.40
9	Capped cube	3.97	13	2.47
10	Bicapped tetragonal antiprism	4.02	14	2.56
11	Fused pentagonal pyramids	4.06	15	2.57
12	Bilayers	4.12	12	2.55
13	Cage	4.16	17	2.57
14	capped hexagonal prism-like	4.23	16	2.55
15	Hexagonal	4.26	19	2.62

than many other isomers [8(b)–8(e) in Fig. 1] such as two prisms fused on a square face, a bicapped prism, a D_{2d} type structure, and a capped pentagonal bipyramid that are 1.07, 1.16, 1.23, and 1.30 eV higher in energy with 10, 14, 10, and $12\mu_B$ magnetic moments, respectively. As we shall show later, this cluster shows magic behavior. Among transition metal clusters, eight-atom cluster of Nb has also been found¹² to be magic but the lowest energy structure of Nb_8 is a bicapped octahedron. These results indicate that the close packed structures of Rh clusters are not of the lowest energy and the growth behavior in this size range does not follow the partial icosahedral structure route. In fact the capped pentagonal bipyramid structure lies highest in energy among these isomers. Furthermore a tetrahedron with four faces capped and a hexagonal bipyramid of Rh_8 lie 2.09 and 2.92 eV higher in energy with 12 and $0\mu_B$ magnetic moments, respectively.

The above growth behavior is continued further and Rh_9 is a capping of cubic Rh_8 with $13\mu_B$ magnetic moments. It is quite different from a bicapped pentagonal bipyramid obtained earlier.⁶ We obtain a capped tetragonal antiprism (9c) to be 0.27 eV higher in energy. It has $15\mu_B$ magnetic moment. This can also be considered as a pentagonal prism capped with a triangle on one side. A capped tetragonal prism type isomer (9d) lies 0.68 eV higher in energy and is unlikely to be present in experiments. We also obtained a tricapped prism (9b) which is 0.26 eV higher in energy and has $13\mu_B$ magnetic moments. Therefore, our results are the lowest spin isomers. However, for Rh_{10} , our result of bicapped tetragonal antiprism (10a) ($14\mu_B$ magnetic moments) is the same as obtained before.⁷ A bicapped distorted hexagonal biprism lies 0.30 eV higher in energy with $16\mu_B$ magnetic moments whereas a bicapped (opposite faces) cube and two interconnected pentagonal bipyramids lie significantly higher (0.95 and 1.19 eV) in energy with 10 and $12\mu_B$ magnetic moments, respectively. Several different cappings of a

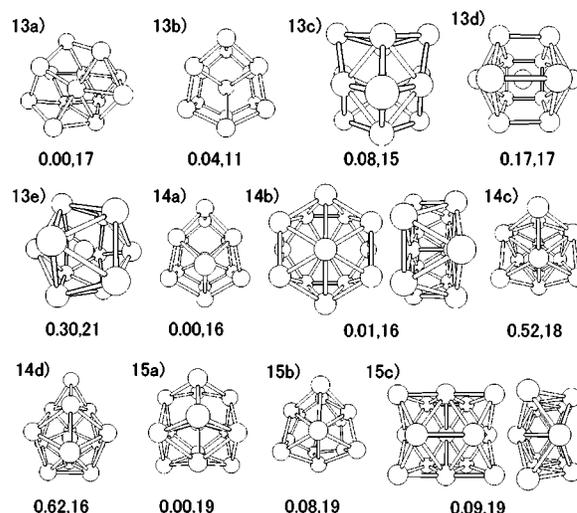


FIG. 2. The same as in Fig. 1 but for $n=13-15$.

pentagonal bipyramid were also optimized and these lie 0.5 eV or higher in energy, supporting the non-icosahedral growth in these clusters.

The lowest energy isomer of Rh_{11} (11a) can be viewed as two capped pentagons joined by an atom. It has $15\mu_B$ magnetic moments. Another low lying isomer (11b) can be viewed as capped two layers of five atoms each (five atoms in a triangular packing in one layer and a pentagon in another). It lies only 0.10 eV higher in energy and has $17\mu_B$ magnetic moments. It is likely to be present in experiments. This structure is a precursor to the lowest energy structures of Rh_{12} and Rh_{13} . There is no atom at the center. Similarly for $n=12$, a two layer structure (12a) has the lowest energy. It has mirror symmetry and $12\mu_B$ magnetic moments. Increasing or decreasing the magnetic moments of this cluster by $2\mu_B$ makes only a small change in energy of about 0.1 eV and therefore, the magnetic moments can be easily affected by temperature. There are slightly different isomers. One is shown in Fig. 1 (12b) and it lies only 0.13 eV higher in energy and should also be present in experiments. It also has a mirror symmetry with the magnetic moments of $16\mu_B$. So in this case, it can be possible that there is an increase in the magnetic moments with an increase in temperature.

The most important result is obtained for Rh_{13} . Earlier an icosahedron has been reported to be lowest in energy.⁴⁻⁷ We carried out optimizations for icosahedron, cuboctahedron, decahedron, and capped cubic structures as well as several other isomers. A few low lying isomers are shown in Fig. 2. Surprisingly a cage structure (13a) with $17\mu_B$ magnetic moment and no atom at the center is 0.30 eV lower in energy than an icosahedron (13e) with $21\mu_B$ magnetic moment as obtained before.⁴ (An icosahedral isomer with $17\mu_B$ magnetic moment is only about 0.01 eV higher in energy and is almost degenerate.) It has a pentagon (in the middle), a rhombus on one side, and a near square on the other. These results indicate that in general, Rh clusters prefer relatively open structures. Several other atomic and spin isomers lie close in energy. This will also lead, in general, to spin isomers with lower magnetic moments to be present in experiments. There is an isomer (with mirror symmetry) (13b)

which is only 0.04 eV higher in energy and has $11\mu_B$ magnetic moments. This will be also abundant in experimental conditions and will give rise to an average lower magnetic moment on this cluster and therefore a better agreement with the experimental¹ value of $0.48 \pm 0.13\mu_B/\text{atom}$. This is in contrast to the value of $1.62\mu_B/\text{atom}$ obtained by Reddy *et al.*⁵ using the local density functional theory while Jinlong *et al.* as well as Reddy *et al.*⁶ obtained $1.15\mu_B/\text{atom}$ for this cluster. As we shall show later, there is some directionality in bonding in isomer (13b). This is also seen from the fact that a nearly hexagonal prism isomer with an atom at the center lies 0.44 eV higher in energy with $15\mu_B$ magnetic moment than isomer (13b). The latter is important as Rh_{14} is obtained from it. We also show two more isomers (13c and 13d) that are 0.08 eV [with $15\mu_B$ magnetic moments and somewhat similar to (13a)] and 0.17 eV (decahedral with $17\mu_B$ magnetic moment) higher in energy than the isomer (13a). Many other isomers were also studied but these are higher in energy.

A few optimized structures for Rh_{14} are shown in Fig. 2. The lowest energy isomer of Rh_{14} is obtained from isomer (13b) by capping a hexagonal face. It has $16\mu_B$ magnetic moments. A hexagonal anti-prism with each hexagon having an atom at the center (14b) is nearly degenerate with $16\mu_B$ magnetic moments. In this case there is no atom at the center. Another isomer with three-fold symmetry and no atom at the center (14c) lies 0.52 eV higher in energy with $18\mu_B$ magnetic moments. A capped icosahedron (14d) lies 0.62 eV higher in energy, again showing that icosahedral growth is not favored. A cubic isomer with capping of the six faces lies 0.52 eV higher in energy and has $18\mu_B$ magnetic moments. The lowest energy structure of Rh_{15} is derived from the lowest energy isomer of Rh_{13} . It has an atom at the center of a bent hexagon with a tetramer on either side and $19\mu_B$ magnetic moments. There are several other isomers that have lower or equal magnetic moments and which will be present in experiments below room temperature and give rise to a lower estimation of the magnetic moments on this cluster. Two such isomers are shown in Fig. 2. The isomer (15b) is derived from (14a) with both hexagonal (the six atoms are not in a plane) faces capped while (15c) has two layers with no atom at the center. These results show that relatively open (noncompact structures) are more favored by Rh clusters. Some of the properties of the lowest energy isomers of $n=13-15$ clusters are given in Table I.

In general we find an abundance of rhombii in the lowest energy structures of Rh clusters. Starting from Rh_4 , one can consider the growth process to follow from addition of an atom to an existing cluster with significant relaxations. This way one can account for the growth upto $n=10$. Rh_{11} can be considered to be a symmetrical capping by two atoms on a Rh_9 cluster having a capped tetragonal antiprism structure. However, the capped tetragonal antiprism isomer of Rh_9 lies significantly higher in energy. So the growth process can be quite complex and in the cases where more than one isomer are nearly degenerate, there could be different routes for the growth of these clusters.

B. Cagelike structure

The result that icosahedron is not of the lowest energy for Rh_{13} and that a relatively open cage structure has lower en-

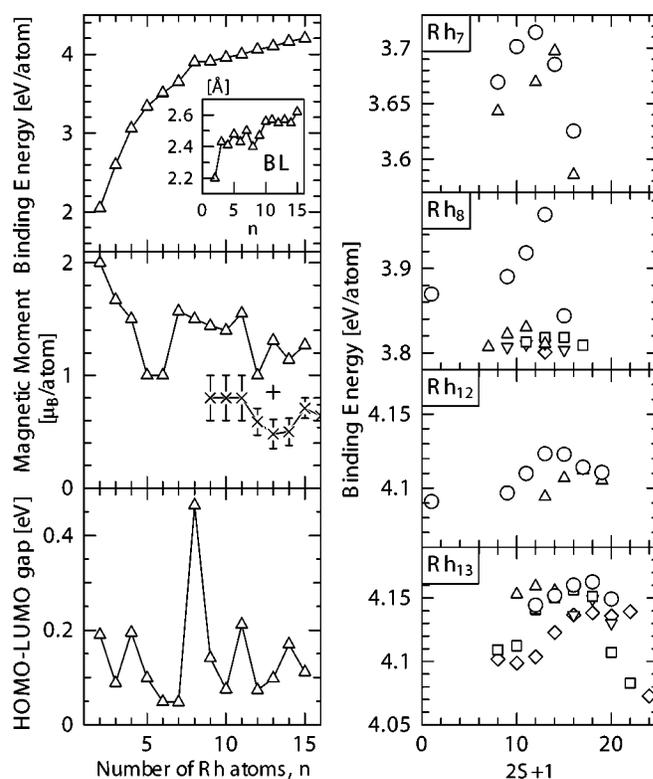


FIG. 3. Binding energies, magnetic moments, and HOMO-LUMO gaps of Rh_n clusters are plotted in the left panel. A plus (+) shows the magnetic moment of the isomer (13b) which gives a much better agreement with the overall trend found in experimental results which are shown by crosses with error bars. Inset shows the mean nearest neighbor bond lengths. The energies of the spin isomers are shown for $n=7, 8, 12,$ and 13 in the right panel. S equals half the value of the total magnetic moment. Circles, triangles, squares, reverse triangles, and diamonds represent, respectively, the isomers (a)–(e) in Figs. 1 and 2.

ergy is significant in understanding the growth behavior of transition metal clusters. In fact non-icosahedral growth was also reported earlier¹² for Nb clusters. In order to check if a similar behavior would be found in clusters of Pd and Ru that are neighboring elements to Rh in the periodic table, we performed calculations for Pd_{13} and Ru_{13} . It is found that in these cases also an icosahedron is not of the lowest energy. For Ru_{13} the second best isomer (13b) of Rh_{13} has the lowest energy with $4\mu_B$ magnetic moments while the one with the structure of the best isomer (13a) of Rh_{13} lies 1.56 eV higher in energy with $2\mu_B$ magnetic moments. Changing the spin in these isomers costs little energy (see Fig. 3 for Rh clusters) and therefore the magnetic moments can be easily suppressed in these clusters. The icosahedral isomer lies 2.25 eV higher in energy and has a large magnetic moment of $12\mu_B$. Therefore icosahedral structure is very unfavorable for Ru and our results explain the nearly nonmagnetic behavior found in these clusters in experiments.¹ For Pd_{13} the best structure of Rh_{13} also has the lowest energy with $8\mu_B$ magnetic moments but an icosahedral isomer reported earlier³ lies only 0.05 eV higher in energy with $8\mu_B$ magnetic moment. Therefore for Pd_{13} these two isomers are nearly degenerate. The bonding in

Pd clusters is much weaker as delocalization of $4d$ electrons occurs slowly and this could explain why icosahedral structure becomes more favorable in Pd. The lowest energy isomer of Ru_{13} [(13b) in Fig. 2] lies 0.81 eV higher in energy for Pd and has $6\mu_B$ magnetic moments. Therefore, the behaviors of Pd and Ru clusters are quite different. A decahedron of Pd_{13} lies 0.34 eV higher in energy and has $8\mu_B$ magnetic moments. These results show that Pd_{13} has the same magnetic moments in quite different structures.

C. Calculated properties

The BE is shown in Fig. 3 for the lowest energy isomers of Rh clusters. It increases monotonically as the cluster size increases and has a small peak at $n=8$. Interestingly there is also a significant highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) gap for Rh_8 making it behave like a magic cluster. In most of the other clusters the HOMO-LUMO gap is generally small and shows an oscillatory behavior. There is an overall decrease with an increase in size. This is expected as bulk Rh is a metal. The magnetic moments per Rh atom (Fig. 3) show an oscillatory behavior as a function of the cluster size but overall there is a decreasing trend as the bulk is nonmagnetic. The magnetic moment is nearly constant in the range of $n=7-11$ and for $n=12$ there is a significant drop. These results agree well with the experimental data¹ that show $0.8 \pm 0.2\mu_B/\text{atom}$ magnetic moment for $n=9-11$ and then $0.59 \pm 0.12\mu_B/\text{atom}$ for $n=12$. Also our result of $0.85\mu_B/\text{atom}$ magnetic moment for the isomer (13b) agrees well with an experimental decrease in the magnetic moment from $n=12$ to 13 and then for $n=14$ and 15, there is an increase in the magnetic moment again in agreement with the trend found in experiments (experimental values being 0.50 ± 0.12 and $0.71 \pm 0.09\mu_B/\text{atom}$ for $n=14$ and 15, respectively). The overall good agreement with the experimental results gives us confidence that our calculated lowest energy structures are close to the experimental findings. The experimental values of the magnetic moments are nearly uniformly lower and this could be due to the fact that theoretical results are at zero temperature while experimental results correspond to temperatures in the range of 60–300 K. We have also shown the variation in the energy of the spin isomers considering the cases of clusters with $n=7, 8, 12,$ and 13. This is generally small as the total spin is changed to a lower value while the energy decreases more sharply for higher spin isomers. As mentioned before, this could account for the observed lower magnetic moments because isomers with lower magnetic moments would also be present. Our finding of a new isomer of $n=13$ is particularly noteworthy and this could explain the much lower magnetic moments observed for Rh_{13} .

It is worth to point out here that in our studies we have ignored orbital contribution to the magnetic moments. In recent years there are efforts¹⁷ to include the orbital contribution as well as the magnetic anisotropy in clusters. The orbital contribution would increase the total magnetic moment and therefore would lead to a larger difference with the experimental results. Guirado-Lopez *et al.*¹⁸ have calculated the orbital magnetic moments for Rh clusters using a self-

consistent tight-binding method and representative face center cubic structures with bulk nearest neighbor bond lengths. The average orbital magnetic moments have been reported to lie in the range of $0.1-0.24\mu_B/\text{atom}$ for $n \leq 19$ with strong oscillations as a function of n . The orbital contribution to the magnetic moments is expected to be sensitive to the structures of clusters and as our results show, the structures of Rh clusters are generally very different from the high symmetry structures considered by these authors. We shall expect that the significantly lower symmetry in most cases of Rh clusters would lead to a reduced contribution from orbital magnetic moments. Further, in order to find a correlation between the magnetic moments and the bond lengths or the coordination number, we calculated the local magnetic moments around each ion for a few clusters. However, we do not find a systematic trend. In general a higher coordination or a short bond length reduces magnetic moments due to the increased hybridization. This can be seen from the lowest energy isomer of Rh_6 . In this isomer there is one bond which is shortest (2.36 \AA) and the local magnetic moments on the two atoms are the smallest ($\approx 0.8\mu_B$) while on the remaining atoms the magnetic moments are $\approx 1.1\mu_B$. In this case the coordination of each atom is 3 and therefore the short bond is responsible for the reduced moment. However, in the case of the lowest energy isomer of Rh_{13} , an atom with coordination 7 has magnetic moments of $0.97\mu_B$, whereas the other two atoms with coordination 7 have 1.45 and $1.17\mu_B$ magnetic moments. Therefore, there does not appear to be a straightforward correlation with the coordination number. Similarly in the case of the lowest energy isomer of Rh_{11} , most of the atoms have coordination 5 and two atoms have coordination 4 while one atom has coordination 6. In this case the local magnetic moments have values lying in between 1.22 and $1.59\mu_B$. Atoms with coordination 4 are symmetrically located and have $1.22\mu_B$ magnetic moments while two symmetrically placed atoms with coordination 5 have the highest local magnetic moments of $1.59\mu_B$. An atom with coordination 6 has the local magnetic moments of $1.44\mu_B$. Further calculations on Rh_{14} show that an atom with coordination 3 has the highest magnetic moment of $1.39\mu_B$. For this atom the nearest neighbor bond lengths have values of about 2.61, 2.61, and 2.65 \AA while a few other atoms with coordination ranging from 3 to 5 have reduced local magnetic moments of about $1.02\mu_B$ due to the short nearest neighbor bonds of about 2.44 \AA . The atom with the highest coordination of 8 has the local magnetic moment of $1.08\mu_B$. We also studied the local moments in the case of the lowest energy isomer of Rh_{15} . Two symmetrically placed atoms with coordination 6 have the lowest local magnetic moments of $0.98\mu_B$ while the atom at the center with coordination 8 has the local magnetic moments of $1.05\mu_B$. On other atoms the local magnetic moments lie in the range of $1.23-1.41\mu_B$ though the coordination changes from 3 to 5. These results show the complex nature of the magnetic moments in these clusters, though in all cases we obtain ferromagnetic coupling.

The calculated mean bond lengths for Rh clusters are shown in the inset of Fig. 3 and the values are also given in Table I. For small clusters there is significant contraction and the bond length approaches towards the calculated bulk value (2.71 \AA) in an oscillatory manner. Rh_8 has short bond

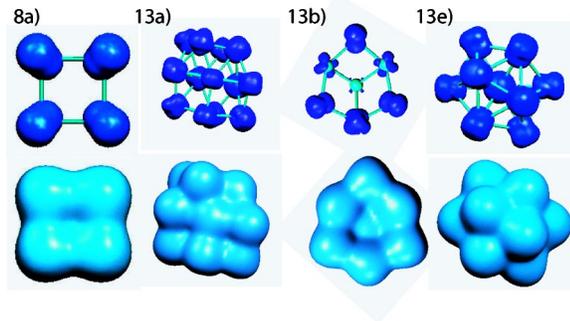


FIG. 4. (Color online) Spin-polarization (upper) and isosurfaces (lower) of the total charge density for isomers (8a), (13a), (13b), and (13e).

lengths which have the lowest value after $n=2$. Also in some clusters such as isomer (13b), there are many short bonds [bond lengths 2.39, 2.41, 2.44, 2.46 Å as compared to the mean bond length of 2.57 Å in isomer (13a)] which indicate directional bonding and covalent character in these clusters. We also calculated the mean coordination in these clusters and for the lowest energy isomers of Rh_n with $n=4-15$, the values are 2, 3.2, 3, 3.71, 3, 3.56, 4.8, 4.91, 4.67, 4.92, 4.14, and 4.67. Some clusters have low mean coordination such as $n=8$ and 14. Also the second lowest energy isomer of $n=13$ has the mean coordination of 3.69. These reflect covalent character of bonding in these clusters. It is more clearly seen from the isosurfaces of the magnetic polarization and the charge densities shown in Fig. 4 for a few selected isomers of Rh_{13} and the lowest energy isomer of Rh_8 . In the case of isomers (13a) and (13e) the polarization is nearly uniformly distributed over the whole cluster, while in the case of the isomer (13b) the central atom and four atoms at the surface of the cluster have much less polarization than the rest of the atoms. These atoms have higher coordination. The bond lengths are short (2.51 Å with four symmetric atoms and 2.58 Å with two atoms from the center) but not the shortest. The central atom has the highest coordination and

the lowest polarization. So a higher coordination reduces the magnetic moments significantly but short bond lengths are also responsible for much reduced magnetic moments in this cluster. This leads to much more hybridization between the $sp-d$ states which is also seen from the plots of the angular momentum decomposed density of states (Fig. 5). Also for the isomers (13a) and (13e) the charge densities are more uniformly distributed [though isomer (13a) appears to have some covalent character] while for isomer (13b), the covalent character is quite clear. In Rh_8 the charge density and polarization are symmetric reflecting the underlying symmetry of the cluster, but the directional bonding does not appear to be very strong. These results are important revelations of the nature of bonding and unexpected relatively open structures in clusters of these transition metals. The angular momentum decomposed and gaussian broadened densities of states show (Fig. 5) that the $sp-d$ hybridization in the case of the isomer (13b) is more significant than in isomer (13a). Also the HOMO lies in a large gap in the up-spin states of the isomer (13a) though the other states are generally uniformly distributed due to the low symmetry of this cluster. On the other hand for the isomer (13b) the HOMO lies in a very small gap and there are many unoccupied states in the up-spin energy spectrum.

IV. SUMMARY

We have studied from first principles the atomic and electronic structures of small Rh clusters and found for the first time relatively open structures to be lower in energy than the icosahedral structures obtained before. In general these isomers have lower magnetic moments and this result is in better agreement with the available experimental data. In particular clusters with 13 or less number of atoms have no atom at the center. Though an atom goes at the center for clusters having more than 13 atoms, the structures are not the closest packed. We find an isomer of 13-atom cluster which is nearly degenerate with the lowest energy isomer and has a

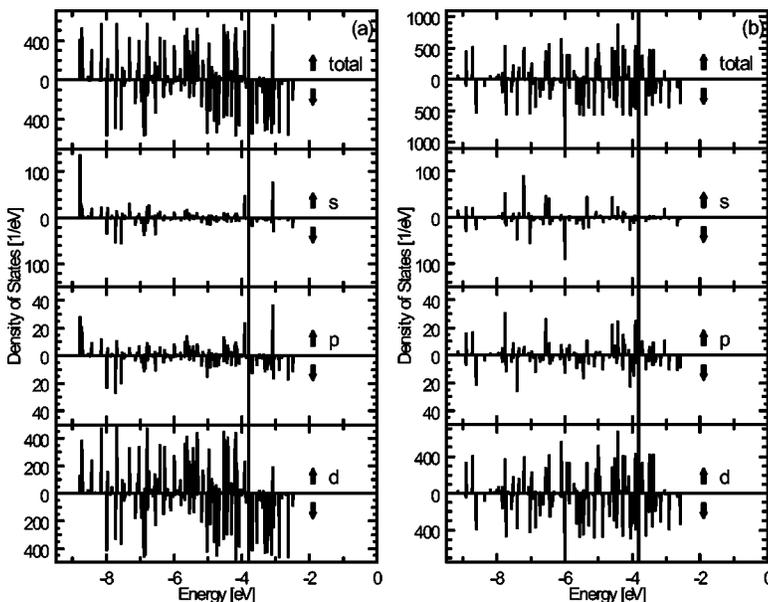


FIG. 5. Gaussian broadened total and angular momentum decomposed electronic states of (13a) and (13b) isomers. The vertical line shows the HOMO.

significantly lower magnetic moment. The latter is in better agreement with the experimental result. In general we find several isomers which lie close in energy and therefore, it is very likely that in experiments one has these isomers unless these are performed at very low temperatures. Our results also show that there is some covalent bonding character in these clusters that is responsible for the relatively open structures. Rh_8 is found to be magic. Further, our preliminary studies on Ru and Pd clusters show that similar structures are lower in energy for Ru clusters than those based on the icosahedral growth while for Pd clusters, the two growth modes may be nearly degenerate. Our results thus open a

new chapter in the study of this important class of transition metal clusters. This would lead to a better understanding of the physicochemical properties of these clusters and reactions and to a better design of catalysts.

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- ¹A.J. Cox, J.G. Louderback, and L.A. Bloomfield, Phys. Rev. Lett. **71**, 923 (1993); A.J. Cox, J.G. Louderback, S.E. Aspel, and L.A. Bloomfield, Phys. Rev. B **49**, 12 295 (1994).
²V. Kumar, K. Esfarjani, and Y. Kawazoe, in *Clusters and Nanomaterials*, edited by Y. Kawazoe, T. Kondow, and K. Ohno, Springer Series in Cluster Physics (Springer-Verlag, Heidelberg, 2002), p. 9.
³V. Kumar and Y. Kawazoe, Phys. Rev. B **66**, 144413 (2002).
⁴V. Kumar and Y. Kawazoe, Eur. Phys. J. D **24**, 81 (2003).
⁵B.V. Reddy, S.N. Khanna, and B.I. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993).
⁶B.V. Reddy, S.K. Nayak, S.N. Khanna, B.K. Rao, and P. Jena, Phys. Rev. B **59**, 5214 (1999).
⁷Y. Jinlong, F. Toigo, and W. Kelin, Phys. Rev. B **50**, 7915 (1994).
⁸C. Barreateau, R. Guirado-Lopez, D. Spanjaard, M.C. Desjonqueres, and A.M. Oles, Phys. Rev. B **61**, 7781 (2000); R. Guirado-Lopez, M.C. Desjonqueres, and D. Spanjaard, *ibid.* **62**, 13 188 (2000).
⁹I.M.L. Bilas, A. Chatelian, and W.A. de Heer, Science **265**, 1682 (1994).
¹⁰O. Eriksson, A. M. Boring, R. C. Albers, G. W. Fernando, and B. R. Cooper, Phys. Rev. B **45**, 2868 (1992); M. Alden, S. Mirbt, H. L. Skriver, N. M. Rosengaard, and B. Johansson, *ibid.* **46**, 6303 (1992).
¹¹J. Wei and E. Iglesia, J. Catal. **225**, 116 (2004).
¹²V. Kumar and Y. Kawazoe, Phys. Rev. B **65**, 125403 (2002).
¹³G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
¹⁴G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996); Comput. Mater. Sci. **6**, 15 (1996).
¹⁵J.P. Perdew, in *Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
¹⁶K.A. Gingerich and D.L. Cocke, J. Chem. Soc., Chem. Commun. **1**, 536 (1972).
¹⁷R. A. Guirado-Lopez, J. Dorantes-Davila, and G. M. Pastor, Phys. Rev. Lett. **90**, 226402 (2003); A. N. Andriotis and M. Menon, *ibid.* **93**, 026402 (2004); J.T. Lau, A. Föhlich, R. Nietubyc, M. Reif, and W. Wurth, *ibid.* **89**, 057201 (2002); X. Wan, L. Zhou, J. Dong, T.K. Lee, and D.-S. Wang, Phys. Rev. B **69**, 174414 (2004).
¹⁸R. Guirado-Lopez, P. Villasenor-Gonzalez, J. Dorantes-Davila, and G.M. Pastor, Eur. Phys. J. D **24**, 73 (2003).