Cubic magic clusters of rhodium stabilized with eight-center bonding: Magnetism and growth

Young-Cho Bae,[1] Vijay Kumar,[2,3,4] Hiroki Osanai,[1] and Yoshiyuki Kawazoe[2]
[1]*CODEC Co. Ltd., Kawasaki 215-0033, Japan*
[2]*Institute for Materials Research (IMR), Tohoku University, Aoba-ku, Sendai 980-8577, Japan*
[3]*Research Institute for Computational Sciences (RICS), National Institute for Advanced Scientific and Industrial Research (AIST), AIST Central 2, Umezono 1-1-1, Tsukuba 305-8568, Japan*
[4]*Dr. Vijay Kumar Foundation, 45 Bazaar Street, K. K. Nagar (West), Chennai 600 078, India*
(Received 27 May 2005; published 21 September 2005)

Ab initio calculations on Rh_n ($n=8-64$) clusters surprisingly show simple cubic structures to be most favorable up to $n\sim 27$. These are stabilized by eight center bonding and lie significantly lower in energy than the icosahedral isomers found in previous studies. With increasing size cuboctahedral, decahedral, and icosahedral isomers become preferred, showing a reversal of the growth behavior compared with the well-known icosahedral $\rightarrow$ decahedral $\rightarrow$ cuboctahedral transitions. The low-coordination cubic structures have *lower* magnetic moments than the dense packed icosahedral isomers and which agree closely with experiments. Our results resolve a long standing discrepancy between theory and experiments and provide a new direction in the understanding of the properties of transition metal clusters.

DOI: 10.1103/PhysRevB.72.125427 PACS number(s): 73.22.−f, 61.46.+w, 36.90.+f, 36.40.Cg

I. INTRODUCTION

The occurrence of magnetism in clusters of nonmagnetic transition metals such as rhodium[1–3] has attracted much attention[4–6] both from a fundamental point of view and technological importance. However, a proper understanding still remains elusive. Earlier calculations[3–6] show icosahedral growth to be most favorable for Rh_n clusters. But, the calculated magnetic moments are much higher than the observed values[2] and the origin of the discrepancy has been a puzzle. Here we report our finding of eight-center bonding in Rh_n clusters that favors low coordination simple cubic (SC) structures and lead to an unusual behavior of the bond lengths. These isomers lie significantly lower in energy than the icosahedral ones up to $n\sim 27$ and have *lower* magnetic moments in contrast to the general expectation of increasing moments with decreasing coordination. As the cluster size increases, structural transitions occur to cuboctahedral, decahedral, and icosahedral isomers showing a reversal of the growth behavior from the often found[7] icosahedral $\rightarrow$ decahedral $\rightarrow$ cuboctahedral transitions.

Rhodium clusters were found[1,2] to have magnetic moments with n up to $\sim$60 in the temperature range of 60–300 K although bulk Rh is a nonmagnetic metal. Clusters of magnetic elements Fe, Co, and Ni also have increased magnetic moments[8,9] relative to the bulk. Primarily this enhancement occurs due to the fact that clusters are intermediate forms of matter between atoms and bulk with reduced mean coordination and their magnetic moments tend to approach the atomic limit, which is often a higher value than in bulk. However, the magnetic properties of matter are structure dependent and the determination of the structure-property relations in clusters is an important and challenging task particularly when the cluster size becomes moderately large. Even for a $\sim$10-atom cluster it can be difficult as our results will demonstrate. Therefore, even though several *ab initio* calculations have been performed on Rh_n clusters,[3–6] most of these are limited to small sizes (n up to $\sim$13). Moreover, the predicted magnetic moment of, e.g., $1.62\mu_B$/atom on Rh_{13} in the icosahedral structure, differs significantly from the measured value[2] of $0.48\pm 0.13\mu_B$ /atom and no satisfactory explanation could be found so far. Recently, a cage-like isomer of Rh_{13} has been found[10] to be 0.30 eV lower in energy than an icosahedron but the calculated magnetic moment ($1.31\mu_B$/atom) is still significantly higher, leaving the discrepancy unresolved. Also recently a bilayer structure of Rh_{13} has been shown[11] to be 0.13 eV lower in energy than an icosahedron. However, the magnetic moment in the bilayer structure is $1.31\mu_B$/atom which is again significantly higher than the measured value.

In Sec. II we give our method of calculation while in Sec. III we present our results and discussion. A summary of our conclusions is given in Sec. IV.

II. METHOD OF CALCULATION

We performed *ab initio* calculations on Rh_n clusters in a wide range of sizes ranging from $n=2$ to 64 using ultrasoft pseudopotential[12] plane wave method and spin-polarized generalized gradient approximation for the exchange-correlation energy. The clusters were placed in a large cubic box of side up to 18 Å and Γ point was used for the Brillouin zone integrations. The cut-off energy for the plane wave expansion was taken to be 205.5 eV. Several isomers were optimized for each size using the conjugate gradient method without any constraint. Furthermore, several spin isomers were optimized for each low lying structural isomer. The total energy was converged with a tollerence of 10^{-4} eV while the force on ion was converged to an accuracy of 10^{-3} or less. The results for small clusters with $n\leqslant 9$ are the same as reported in Ref. 10. However, for larger clusters completely new isomers have been found and are discussed in the next section together with some selected low lying or well known other structures. A comparison is provided with respect to the lowest energy isomers reported in Ref. 10

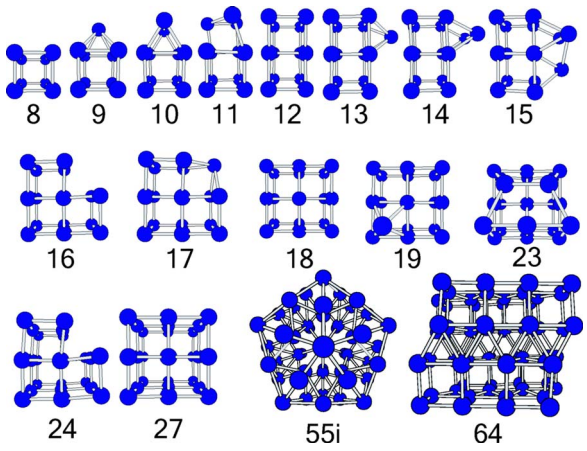


FIG. 1. (Color online) Optimized lowest energy isomers of Rh_n clusters. These results show simple cubic growth to be most favored for n up to 27. Numbers show the size (n) while 55i is the icosahedral isomer of Rh_{55}. The simple cubic isomer of Rh_{64} gets distorted.

which are the lowest energy isomers known before to the best of our knowledge for small sizes of rhodium clusters.

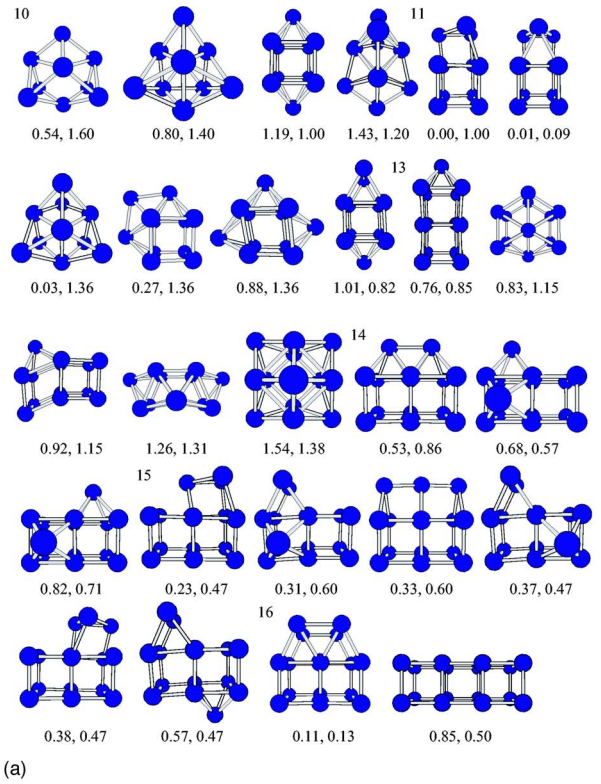
III. RESULTS AND DISCUSSION

A. Atomic structures

Our results strikingly show low coordination SC structures to be lowest in energy for rhodium clusters in the intermediate size of $n=8-27$. Starting from a perfect cube[10] for Rh_8, the cubic growth continues (Fig. 1) with a face capping such that Rh_{12} is a double cube. It lies 1.5 eV or more lower in energy than many other noncubic isomers we examined and has $0.67\mu_B$/atom magnetic moment, in excellent agreement with the measured value[2] of $0.59\pm0.12\mu_B$/atom. Continuing capping on a side face of Rh_{12}, we obtain Rh_{16} and Rh_{18} with SC structures having three and four cubical units (Fig. 1), respectively. Their magnetic moments, 0.50 and $0.22\mu_B$/atom, respectively, also agree well with the measured values of $0.64\pm0.10\mu_B$/atom and $0.35\pm0.12\mu_B$/atom. Another cubic isomer (Fig. 2) of Rh_{16}, with two neighboring faces of Rh_{12} on the same side capped by dimers, lies only 0.11 eV higher in energy while three cubes in a row lies 0.85 eV higher in energy. Though the latter structure is quite symmetric, it indicates that structures based on three cubes in a row are not favored. Indeed as we shall show later, our results on larger clusters further support this conclusion. Most interestingly, several often-considered close-packed isomers of Rh_{18} (Fig. 2) such as a cuboctahedron with one capping atom missing, a decahedron with all the seven faces capped and an atom at the center, a double icosahedron with a capping atom missing (it is nearly degenerate with a double icosahedron in which one of the center atom is missing), and a capped double decahedral isomer with two atoms at the centers lie 1.42, 2.26, 3.12, and 3.13 eV higher in energy, respectively. Therefore, in this size range, close-packed structures are quite unfavorable.

In the intermediate sizes of $n=9-11$, different capping of the faces of Rh_8 show a cube bicapped on a face (Fig. 1) to be most favorable for Rh_{10} with $1.2\mu_B$/atom magnetic moment. It lies 0.24 and 1.19 eV lower in energy compared with a bicapped tetragonal antiprism ($1.4\mu_B$/atom) (see Ref. 10) and a cube with two opposite faces ($1.0\mu_B$/atom) capped (Fig. 2), respectively. Therefore, isomer with capping of a cube on opposite faces is quite unfavorable. Close-packed structures, such as a tricapped pentagonal biprism, a tetracapped prism, and an isomer with two interpenetrating pentagonal biprisms (see Fig. 2) have 0.54, 0.80, and 1.43 eV higher energies and 1.6, 1.4, and $1.2\mu_B$/atom magnetic moments, respectively. These are unlikely to be present in experiments. Rh_{11} also has a cubic structure with three atoms capping a face (Fig. 1) of Rh_8. There are two nearly degenerate spin isomers with 1.0 (Fig. 1) and $0.09\mu_B$/atom magnetic moments (Fig. 2) that are 0.33 eV lower in energy than the previous best result,[10] while an isomer (Fig. 2) with two atoms capping a face and an atom capping the opposite face of a cube lies 1.01 eV higher in energy. However, a threefold symmetric isomer with three adjacent faces of a cube capped (Fig. 2) is only 0.03 eV higher in energy, with $1.36\mu_B$/atom magnetic moment. We expect this isomer to be present in experiments and give rise to a higher mean value of the magnetic moment in agreement with the measured value[2] ($0.8\pm0.2\mu_B$/atom).

For Rh_{13}, capping of a side face of Rh_{12} (Fig. 1) is favored with $0.69\mu_B$/atom magnetic moment. This is the best agreement with the experimental value[2] of $0.48\pm0.13\mu_B$/atom among all the theoretical results obtained so far. A hexagonal isomer[10] and a cube with five faces capped (Fig. 2) lie 1.09 and 1.54 eV higher in energy and have 0.85 and $1.38\mu_B$/atom magnetic moment, respectively. The formerly best icosahedral isomer[3–6] lies 1.34 eV higher in energy. The lowest energy non-icosahedral isomer of Rh_{13} reported in Ref. 10 lies 1.05 eV higher in energy as compared to our lowest energy cubic isomer. The biplanar isomer (Fig. 2) reported in Ref. 11 though lies 0.08 eV lower in energy than the icosahedral isomer with $1.31\mu_B$/atom magnetic moment, it is 1.26 eV higher in energy as compared to our lowest energy cubic isomer. Two other relatively open isomers (Fig. 2) lie 0.83 and 0.92 eV higher in energy than the best cubic isomer. Thus, our findings show a completely different growth pattern than known before with much lower energy isomers. Interestingly, an isomer with an atom capping the top of the double cube (Fig. 2) lies 0.76 eV higher in energy, with $0.69\mu_B$/atom magnetic moments. This result suggests that structures with continued three-dimensional cubic growth may be favorable. Indeed Rh_{14} is a bicapped (on a side face) double cube (Fig. 1) similar to Rh_{10}. It has $0.43\mu_B$/atom magnetic moment, in good agreement with the experimental value[2] of $0.5\pm0.12\mu_B$/atom. Other cubic isomers (Fig. 2) with different ways of capping lie more than 0.50 eV higher in energy with a preference for capping of two adjacent faces. The previously best, hexagonal isomer[10] lies $\sim$1 eV higher in energy. Continuing the SC growth, Rh_{15} is obtained from Rh_{14} by capping a neighboring face with an atom (Fig. 1). It has $0.47\mu_B$/atom magnetic moment, compared with the experimental value of $0.71\pm0.09\mu_B$/atom. A few other isomers (Fig. 2) with different capping of faces lie within 0.4 eV, while the previous best isomer[10] lies 0.76 eV higher in energy, suggesting low preference for closed-packed structures.



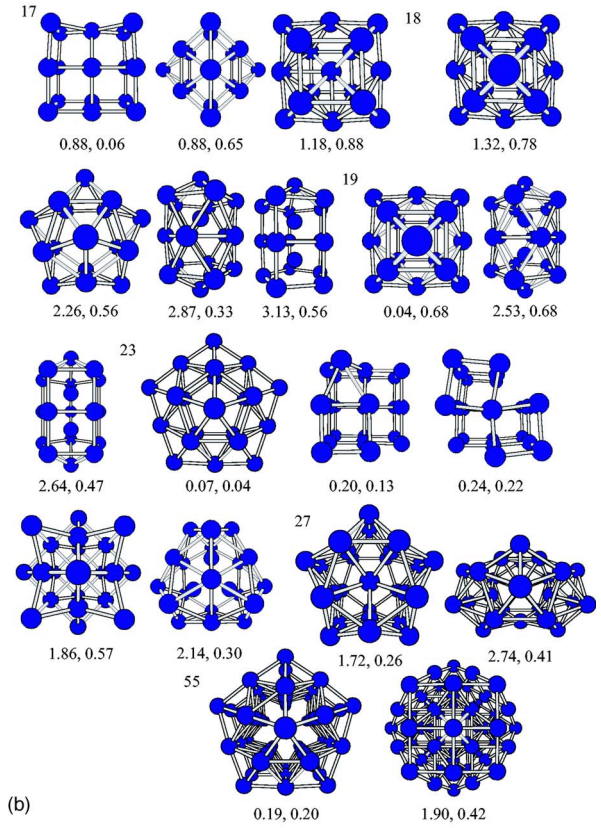


FIG. 2. (Color online) A few selected isomers of Rh_n clusters. The number on the top left indicates the size (n) of the following isomers while the number below the figure indicate the energy (eV) compared to the lowest energy isomers shown in Fig. 1 and the magnetic moment (μ_B/atom).

Rh_{17} is obtained from Rh_{16} by capping an atom on the step so that the two cubes are linked (Fig. 1). It has only $0.06\mu_B$/atom magnetic moment, compared with the measured value[2] $0.39\pm0.12\mu_B$/atom. However, spin isomers with 0.18, 0.29, and $0.41\mu_B$/atom magnetic moment lie only 0.015, 0.024, and 0.096 eV higher in energy, respectively, and are likely to be present in experiments leading to a higher observed value of the magnetic moment. A few other cubic isomers (Fig. 2) as well as a cuboctahedron with two capping atoms missing symmetrically as shown in Fig. 2 lie 0.88, 0.88, and 1.18 eV higher in energy, respectively and are unlikely to be observed. For Rh_{19}, an isomer with capping of a face of Rh_{18} (Fig. 1) has the lowest energy and $0.16\mu_B$/atom magnetic moment. A spin-isomer with $0.26\mu_B$/atom magnetic moment lies only 0.044 eV higher in energy and could result in a higher observed value. Most interestingly, a cuboctahedron (Fig. 2) is only 0.040 eV higher in energy and has $0.68\mu_B$/atom magnetic moment, which is close to the observed value[2] of $0.61\pm0.08\mu_B$/atom while a double icosahedron and a decahedron (Fig. 2) lie 2.53 and 2.64 eV higher in energy, respectively. Thus the well-known close-packed icosahedral and decahedral isomers are not favored in this size range, and a cuboctahedral isomer becomes competitive at $n=19$, indicating a possible change in the growth pattern.

In order to check the structural transitions with increasing size, we studied SC isomers for $n=27$ and 64, as well as cuboctahedral, decahedral, and icosahedral isomers for $n=23$ and 55. The binding energy in Fig. 3(a) shows that the SC structures are preferred for $n=23$ and 27, with 0.39 and $0.31\mu_B$/atom magnetic moments, respectively. These values compare well with the measured values[2] 0.13 ± 0.13 and $0.20\pm0.13\mu_B$/atom, respectively. For $n=23$, the observed value could be lower also, because at least three other isomers (Fig. 2) lie within 0.24 eV and have lower magnetic moments. A decahedral isomer (Fig. 2) with 0.07 eV higher energy and $0.04\mu_B$/atom magnetic moment is likely to be present in experiments and lead to significantly reduced magnetic moments. However, an icosahedron and a cuboctahedron (Fig. 2) of Rh_{23} lie 2.14 and 1.86 eV higher in energy, respectively, with 0.30 and $0.57\mu_B$/atom. Similarly, for Rh_{27}, an icosahedral and a decahedral isomer (Fig. 2) lie 2.75 and 1.72 eV higher in energy than the lowest-energy SC structure, ruling out icosahedral or decahedral growth. However, for $n=55$, an icosahedral isomer (Fig. 1) becomes lowest in energy, with $0.13\mu_B$/atom magnetic moment. The decahedral isomer (Fig. 2) lies only 0.19 eV higher in energy with $0.2\mu_B$/atom, while a cuboctahedral isomer (Fig. 2) lies 1.90 eV higher in energy and has $0.42\mu_B$/atom magnetic moment indicating a transition from simple cubic growth. The SC isomer for $n=64$ (three cubes in each direction) also distorts[13] and a transition occurs to closer-packed structure at least in the interior of the cluster (Fig. 1). These results show a reversal of the growth behavior compared with the well-known icosahedral→decahedral→cuboctahedral isomers with increasing cluster size and the possibility of distorted cubic structures for large clusters.

The binding energy, as well as the highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) gap [inset Fig. 3(a)], show local maxima for clusters with com-

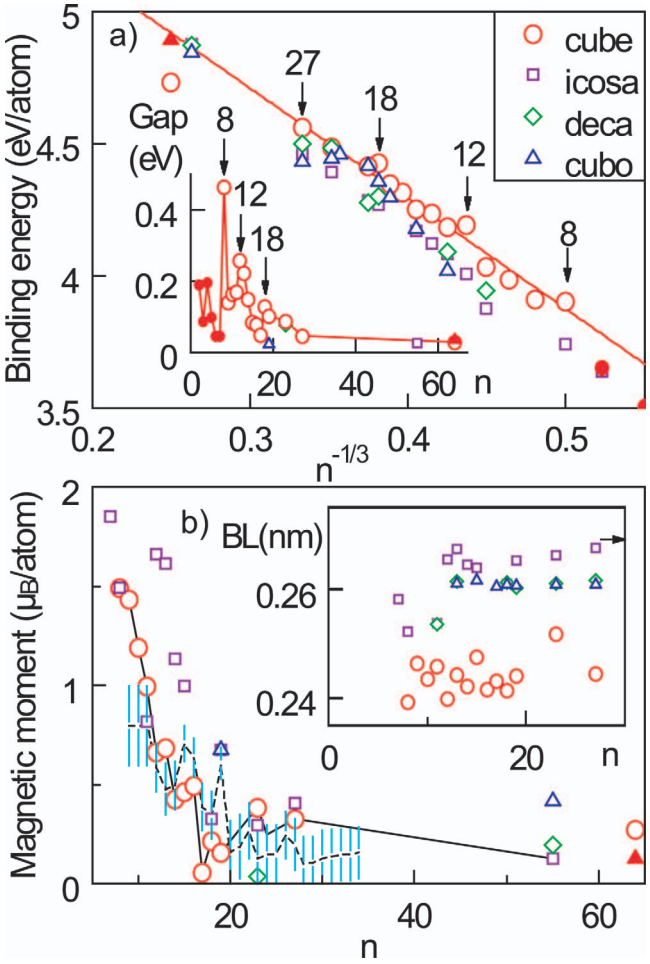


FIG. 3. (Color) (a) Binding energy of rhodium clusters. Inset shows the HOMO-LUMO gap. Filled red triangle is for the distorted cubic cluster for $n=64$. Filled red circles correspond to the lowest energy isomers for small clusters. Line represents least-square fit to the energies of simple cubic isomers. Upon extrapolation we get bulk cohesive energy of 5.96 eV/atom that agrees well with the experimental value of 5.75 eV/atom. (b) Calculated magnetic moments (values for the lowest energy isomers connected by a line) show good agreement with the experimental results[2] (broken curve with error bars in cyan color). Inset shows the mean bond length (BL). Right arrow shows the bulk value 0.269 nm.

plete cubic units such as for $n=8$, 12, and 18. These are therefore magic. Most importantly, the magnetic moments [Fig. 3(b)] show overall very good agreement with experiments, in contrast to all previous studies, and clarify that the lower observed values are due to structures that were hitherto unknown for rhodium clusters. Magic clusters of metals such as Nb_8 have been found[14] to have low reactivity. For these clusters the HOMO-LUMO gap is large[15] such as 0.78 eV for Nb_8. However, for magic clusters of Rh the HOMO-LUMO gaps are much smaller (Fig. 3). Though the reactivity of clusters depends on many factors and is generally specific to particular molecule, the relatively smaller HOMO-LUMO gaps may not show strong variations in reactivity of Rh clusters. Indeed experiments[16] on interaction of D_2 and N_2 do not show any strong magic behavior though the reactivity slows down in the range of $n=5-17$.

B. Eight-center bonding, electronic, and magnetic behaviors

In order to understand the nonintuitive result of low magnetic moments in the low-coordination SC structures and the bonding nature, we find that the bond lengths in SC isomers are significantly shorter [near 0.245 nm, see inset in Fig. 3(b)] compared with ~0.265 nm in the bulk and a similar value for the closed-packed cuboctahedral, decahedral, and icosahedral isomers. A contraction in the bond length with decreasing coordination is expected, but one would also expect an increase in the magnetic moment. More surprisingly, in Rh_{12} the bonds joining the two cubes (between atoms with coordination 4) are shorter (0.237 nm) than the bonds joining the corner atoms with coordination 3 (Fig. 4). A similar feature is seen in Rh_{18}, in which the bonds between the two square faces of Rh_{18} and those linking the cubes are shorter (about 0.235 nm), but in Rh_{27} no such short bonds are present. To our knowledge such a behavior in metal clusters has not been reported before.

These results are understood from novel eight-center bonding in SC isomers. As it can be seen from Fig. 4(a), the lowest-energy electronic state of Rh_8 has strong *d* bonding character, in contrast to the normally found *sp* character in metal clusters (note the charge density for the cuboctahedral isomer of Rh_{19} that shows typical metallic bonding [Fig. 4(f)] with the lowest electronic state having strong *sp* character). It represents eight-center bonding with charge density lobes pointing along the cube diagonals [Fig. 4(b)]. Two electrons share this state. The partial charge density isosurfaces of a few other low-lying electronic states also show maximum density along the bonds. Such covalent bonds tend to reduce magnetic moments. The shorter bond lengths in Rh_{12} and Rh_{18} arise due to the forces resulting from eight-center bonding that act in the same direction [Figs. 4(d) and 4(e)]. But, for Rh_{27}, the eight-center bonding is weaker due to increased coordination of atoms, leading to elongation of the central bonds. These results also suggest why SC growth becomes unfavorable with increasing *n* as for Rh_{64} in which the central atoms tend to form a closer packing but the corner cubes retain their identities. For larger sizes, bulk metallic bonding should emerge, at least in the central regions of clusters, and favor closer-packed structures.

The magnetic ordering in Rh_8 [Fig. 4(c)] is ferromagnetic, but for Rh_{27} the magnetic moments on off-corner sites become quite small [Fig. 4(g)]. However, antiferromagnetism is not responsible for the occurrence of isomers with low magnetic moments. Similar variation in the spin polarization is seen in other smaller cubic clusters (two nearly degenerate isomers of 11, and the lowest energy isomers of 12, 13, 14, 15, and 19) as shown in Fig. 5. On the other hand for the cuboctahedral isomer of 19 [Fig. 4(f)], the polarization is more uniform. However, for Rh_{55}, the polarization is more on the surface shell while for the inner atoms the polarization is reduced significantly. These results also indicate that surface polarization may occur even for larger clusters.

IV. SUMMARY

In summary, we have found, quite unexpectedly, simple cubic growth in Rh_n clusters to be most favorable up to a size

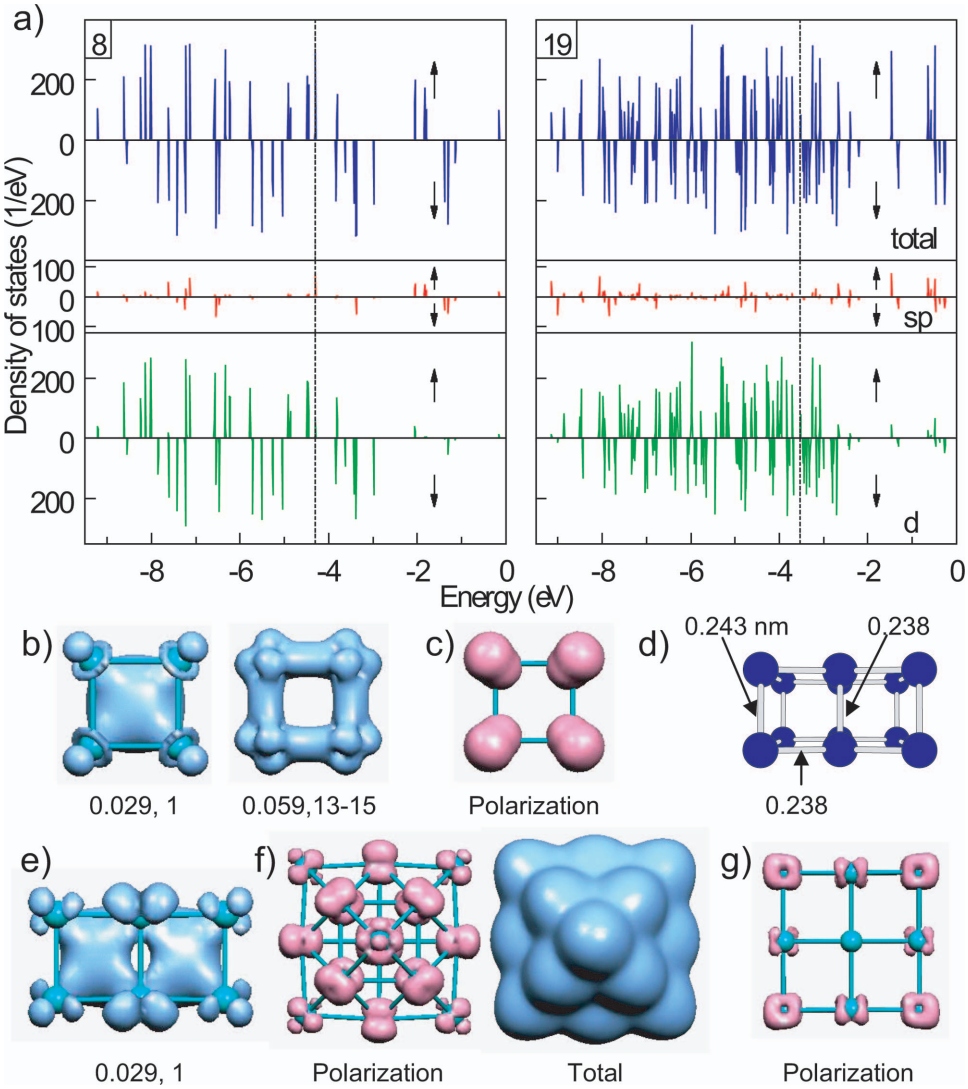


FIG. 4. (Color) (a) Total and angular momentum decomposed up- and down-spin density of states for cubic Rh_8 and cuboctahedral Rh_{19} clusters. (b) Charge density isosurface for the lowest energy state numbered 1 (below the picture) shows eight-center bonding while a representative isosurface from 13-15 (degenerate) states shows charge accumulation around the bonds. The value of the density is given below the pictures in units of $e/Å^3$. (c) Spin-polarization density isosurface for cubic Rh_8 shows ferromagnetic coupling. (d) Bond lengths, and (e) charge density isosurface for cubic Rh_{12}. (f) Spin-polarization and total density isosurfaces (value $0.148e/Å^3$) for cuboctahedral Rh_{19}. (g) Same as in (c) but for cubic Rh_{27}. The spin-polarization isosurfaces are at the value of $0.148/Å^3$.

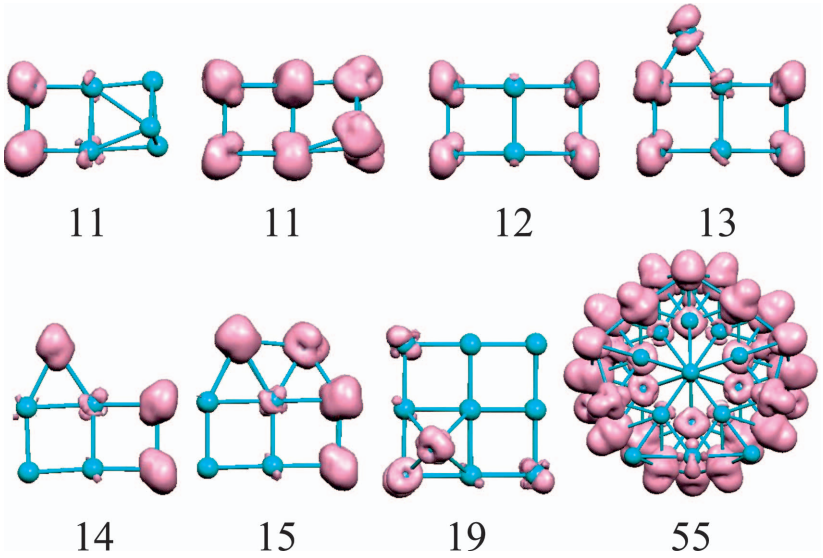


FIG. 5. (Color) Spin polarization as in Fig. 4 for the two nearly degenerate isomers of 11 (low and high spin) and the lowest energy isomers of 12, 13, 14, 15, 19, and 55. The spin-polarization isosurfaces are at the same value as in Fig. 4.

of $n \sim 27$. These are stabilized by eight-center bonding that also leads to an unusual bond length contraction in clusters with $n=12$ and 18. Cuboctahedral and decahedral isomers become competitive at $n=19$ and 23, respectively, and for Rh_{55}, icosahedral/decahedral isomers are nearly degenerate and have lowest energy, showing a reversal of the growth pattern from what is commonly known. The magnetic moments in the low coordination simple cubic isomers are also lower than in close packed structures and agree closely with the observed values explaining the origin of a long-standing experimental result. The good agreement of the calculated magnetic moments with experiments suggests that our atomic structures are the true minima of these clusters at least in the size range of up to around 20. As it is well known, one can never be sure of the lowest energy structures and there may be more than one isomer coexisting in experimental conditions. However, our results show new structures and growth behavior in Rh clusters that was not known before and we believe that these results would lead to a new direction in the understanding of atomic structures of clusters as well as lead to a better understanding of magnetism and reactivities[17–19] of transition-metal clusters. Our results could also pave way for the development of new catalysts based on rhodium and other transition metals. It is to be noted that recently for Pt clusters also cubic and relatively open structures have been found[20] to be lowest in energy. Therefore clusters of late transition metals have much surprise in store. These are catalytically among the most important ones and we hope that our results would generate renewed interest in further understanding of the properties of these clusters.

ACKNOWLEDGMENTS

We thank G. Baskaran for insightful discussions on the bonding in these clusters, K. Goretta for helpful comments and the staff of the Center for Computational Materials Science of IMR for the use of the Hitachi SR8000/64 supercomputing facilities. V.K. gratefully acknowledges hospitality at IMR and RICS as well as partial support from the Asian Office of Aerospace Research and Development, and the NAREGI Nano Science Project at RICS from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

[1] A. J. Cox, J. G. Louderback, and L. A. Bloomfield, Phys. Rev. Lett. **71**, 923 (1993).
[2] A. J. Cox, J. G. Louderback, S. E. Apsel, and L. A. Bloomfield, Phys. Rev. B **49**, 12295 (1994).
[3] B. V. Reddy, S. N. Khanna, and B. I. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993).
[4] B. V. Reddy, S. K. Nayak, S. N. Khanna, B. K. Rao, and P. Jena, Phys. Rev. B **59**, 5214 (1999).
[5] V. Kumar and Y. Kawazoe, Eur. Phys. J. D **24**, 81 (2003).
[6] Yang Jinlong, F. Toigo, and W. Kelin, Phys. Rev. B **50**, 7915 (1994); C. Barreteau, R. Guirado-Lopez, D. Spanjaard, M. C. Desjonqueres, and A. M. Oles, *ibid.* **61**, 7781 (2000); R. Guirado-Lopez, M. C. Desjonqueres, and D. Spanjaard, *ibid.* **62**, 13188 (2000).
[7] V. Kumar, K. Esfarjani, and Y. Kawazoe, in *Clusters and Nanomaterials*, edited by Y. Kawazoe, T. Kondow, and K. Ohno (Springer, Heidelberg, 2002), p. 9.
[8] I. M. L. Bilas, A. Chatelian, and W. A. de Heer, Science **265**, 1682 (1994).
[9] I. M. L. Billas, J. A. Becker, A. Chatelian, and W. A. de Heer, Phys. Rev. Lett. **71**, 4067 (1993).
[10] Y.-C. Bae, H. Osanai, V. Kumar, and Y. Kawazoe, Phys. Rev. B **70**, 195413 (2004).
[11] C. M. Chang and M. Y. Chou, Phys. Rev. Lett. **93**, 133401 (2004).
[12] G. Kresse and J. Fürthmuller, Phys. Rev. B **54**, 11169 (1996).
[13] A cubic isomer with $0.28\mu_B$/atom magnetic moment is stable but the distorted isomer lies 10.25 eV lower in energy with $0.12\mu_B$/atom.
[14] H. Kietzmann, J. Morenzin, P. S. Bechthold, G. Ganteför, and W. Eberhardt, J. Chem. Phys. **109**, 2275 (1998).
[15] V. Kumar and Y. Kawazoe, Phys. Rev. B **65**, 125403 (2002).
[16] M. R. Zakin, D. M. Cox, and A. Kaldor, J. Chem. Phys. **89**, 1201 (1988).
[17] J. Wei and E. Iglesia, J. Catal. **225**, 116 (2004).
[18] A. T. Bell, Science **299**, 1688 (2003).
[19] M. Frank, S. Andersson, J. Libuda, S. Stempel, A. Sandell, B. Brena, A. Giertz, P. A. Brühwiler, M. Bäumer, N. Mårtensson, and H.-J. Freund, Chem. Phys. Lett. **279**, 92 (1997); **310**, 229(E) (1999).
[20] L. Xiao and L. Wang, J. Phys. Chem. A **108**, 8605 (2004).