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# Magnetism in clusters of non-magnetic elements: Pd, Rh, and Ru

## Magnetism in clusters of non-magnetic elements

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**Abstract.** We have carried out *ab initio* calculations on clusters of Pd with 2–23, 55, and 147 atoms using ultrasoft pseudopotential plane wave method and spin-polarized generalized gradient approximation for the exchange-correlation energy. It is found that these clusters have an icosahedral growth and size dependent oscillatory magnetic moments. Atomically closed shell 13, 55, and 147 atom clusters have large moments of 8, 26, and 60 $\mu_B$, respectively. But cubic $Pd_{55}$ has a small moment of 10 $\mu_B$ only. This shows the importance of the icosahedral structure in the development of magnetism in Pd clusters. The magnetic energy is, however, small and the moments get quenched by H adsorption. Similar studies have been carried out on Rh and Ru clusters. In the atom these have large moments as compared to zero for Pd and therefore, the moments on clusters are also large. However, the moments decrease rapidly as the size grows.

**PACS.** 36.40.Cg Electronic and magnetic properties of clusters – 71.15.Nc Total energy and cohesive energy calculations

## 1 Introduction

The study of magnetism in clusters of 4*d* elements, Ru, Rh, and Pd has attracted much attention [1] as in bulk these are non-magnetic. These metals are used as catalysts but the size dependence of the properties of their clusters as well as the changes due to adsorption are not well understood. In bulk, Pd is close to fulfilling the Stoner criterion of magnetism with high paramagnetic susceptibility and only 6% lattice expansion induces bulk ferromagnetism in it [2]. Also it is now well-known that small clusters such as those of 3*d* magnetic elements, Fe, Co, and Ni show enhanced moments [3] due to narrow band widths that arise from a lower mean coordination in clusters as compared to bulk and the increased localization of electrons. Another important factor that makes clusters different from bulk is the possibility of non-crystallographic icosahedral (i) or decahedral (d) structures. The high symmetry of i clusters could have important consequences for magnetism. The different bond lengths in clusters in the interior and near the surface of a cluster could show interesting layer dependent variation in magnetic moments in such clusters.

Pd atom has a closed shell $4d^{10}5s^0$ electronic configuration while Rh and Ru have open 4*d* shell with magnetic moments of 3 and 4 $\mu_B$, respectively. However, all are non-magnetic in bulk. Therefore, the approach to bulk behavior is likely to be different for Pd as compared to Rh and Ru. Aggregation of atoms should lead to delocalization of electrons. For Pd, one would, therefore, expect a depletion of the 4*d* states that could initially give rise to magnetism in clusters. On the other hand, the delocalization of electrons in Rh and Ru should lead to lowering of the moments as compared to atom. The closed shell behavior of Pd atom also leads to weak bonding in its small clusters. However, Rh and Ru clusters are expected to be quite reactive. Experiments have given conflicting results as far as magnetism in Pd clusters is concerned. Early Stern-Gerlach experiments [4] showed zero magnetic moments in Pd clusters with temperatures in the range of 60 K or above. Photoemission studies [5] suggested Ni-like magnetic behavior for $Pd_N$ with $N = 3{-}6$, whereas non-magnetic Pt-like for $N > 15$. Measurements at 1.8 K in the range of 50−70 Å particle size, however, reported [6] magnetic moment of $0.23 \pm 0.19$ $\mu_B$ per surface Pd atom. For Rh clusters, giant magnetic moments with ferromagnetic ordering were reported [4]. Subsequent studies showed large moments of about 1 $\mu_B$/atom in small clusters which decrease towards the zero value of bulk as the size increases. For Ru clusters the moments have been found to be close to zero.

Theoretical studies [7] on $Pd_{13}$ using the local spin density approximation showed an i isomer to be more favorable than cubic (c) isomer with a magnetic moment

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of 0.12 $\mu_B$ per surface atom and 0.43 $\mu_B$ at the central atom. A self-consistent tight-binding calculation [8] with $N = 2-201$ showed either non-magnetic or only weak magnetic behavior, *keeping the symmetries* such as equilateral triangle, tetrahedron, octahedron etc. of the clusters. In another related study [9], the clusters were relaxed, but only the 4*d* electrons were considered. First principles calculations [10] on small Pd clusters with $N = 2-7$ and 13 gave significant moments. For $Rh_{13}$ and $Ru_{13}$, i structures were reported [7] to have lower energy than a cuboctahedron with a giant magnetic moment of 21 $\mu_B$ on $Rh_{13}$ with an antiferromagntic coupling between the spins on the central and the vertex atoms. A similar behavior was obtained for $Ru_{13}$ with slightly lower magnetic moments. These values are significantly higher than obtained experimentally. In a few other studies [11,12] on Rh clusters with up to 13 atoms, i clusters or fragments were found to be of lowest energy. On the other hand Piveteau *et al.* [13] obtained fcc structure to be favorable for $Rh_{13}$ and $Ru_{13}$. Li *et al.* [14] studied selected clusters having up to 43 atoms with fixed symmetries. Here we report results of *ab initio* calculations on the magnetic behavior of Pd, Rh, and Ru clusters having up to 147 atoms. Preliminary results are also reported on the effect of H adsorption on the magnetic behavior of clusters. Results of magnetism in Pd clusters have been presented in more detail in reference [15].

## 2 Computational approach

We use ultrasoft pseudopotential plane wave method [16] with a cut-off of 14.63, 15.11 and 14.96 Ry to expand the wave functions for Pd, Rh, and Ru, respectively. A norm-conserving pseudopotential is used for H with a cut-off of 25.68 Ry for the plane waves. The clusters are placed in a simple cubic supercell of side up to 30 Å. For such large cells the Brillouin zone integrations are carried out using only the $\Gamma$ point. The exchange-correlation energy is calculated within the spin-polarized generalized gradient approximation (GGA) [17]. Selected structures are optimized without any symmetry constraint using the conjugate gradient method. For a dimer of Pd, we obtain a magnetic moment of 2 $\mu_B$ and the binding energy (BE) to be only 0.611 eV/atom. However, the bonding is not Van der Waals type as there is a contraction in the bond length (2.48 Å) when compared with the calculated bulk value of 2.8 Å. The highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) gap for the dimer is small (0.34 eV) and therefore, aggregation is likely to be favored. Rh and Ru dimers each has a magnetic moment of 4 $\mu_B$ that agrees with earlier calculations on Rh [11]. The bond length of $Rh_2$ is 2.2 Å which compares well with the experimental value of 2.28 Å [18]. $Ru_2$ has the bond length of 2.04 Å.

## 3 Results

The BEs and magnetic moments of the lowest energy structures are shown in Figure 1. Our results [15] on Pd clusters with $N \leq 7$ and 13 are similar to those in [10] within GGA. Clusters with $N = 3-5$ are triangle, tetrahedron and trigonal bipyramid, each with 2 $\mu_B$ magnetic moment. $Pd_6$ is an octahedron and it is non-magnetic. A tetrahedral structure changes to a distorted prism and lies 0.331 eV higher in energy with a magnetic moment of 2 $\mu_B$. $Pd_7$ has a pentagonal bipyramid (PBP) structure with 2 $\mu_B$ magnetic moment. A capped prism and a capped octahedron lie only 0.063 and 0.051 eV higher in energy, respectively and have zero magnetic moment. In experiments, all these isomers are likely to be present and lead to an underestimation of the moment on this cluster. $Pd_8$ has a $D_{2d}$ type structure that is 0.219 eV lower in energy than a capped PBP. Both have 2 $\mu_B$ magnetic moment. For other clusters, i isomers or fragments of an icosahedron have lower energies than a few other structures we have studied. The energy differences between the isomers are generally small.

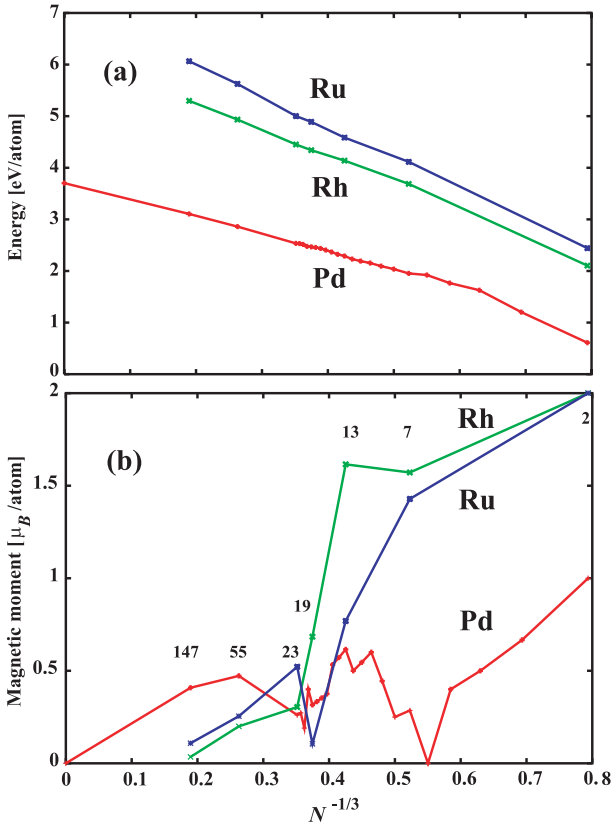


**Fig. 1.** (a) Binding energy per atom and (b) magnetic moment in $X_N$, X = Pd, Rh, and Ru, clusters. The numbers show the size of the clusters. The points are connected to aid the eye.

For $Pd_9$, capping of adjacent faces on the same side of a PBP is most favorable. A tricapped prism lies 0.241 eV higher in energy while another isomer with capping of two adjacent faces on opposite sides of the basal plane of a PBP lies 0.285 eV higher. The latter was obtained from optimization of a capped tetragonal antiprism. All these isomers have 4 $\mu_B$ magnetic moment. $Pd_{10}$ is a tricapped (adjacent faces on the same side) PBP with 6 $\mu_B$ magnetic moment. A bicapped tetragonal antiprism converges to an

isomer with two interlocked PBPs. It lies only 0.062 eV higher in energy and has 4 $\mu_B$ magnetic moment. It is likely to be abundant in experiments and again lead to an underestimation of the moments. On the other hand, a tetracapped prism lies 0.505 eV higher in energy and has 4 $\mu_B$ magnetic moment. $Pd_{11}$ and $Pd_{12}$ are incomplete icosahedra each with 6 $\mu_B$ magnetic moment. An i isomer with 8 $\mu_B$ magnetic moment is lowest in energy for $Pd_{13}$ in agreement with an earlier GGA study [11], but it is different from the result of 2 $\mu_B$ [8] using a tight binding method and also by Reddy *et al.* [7] within LDA. The LDA BE in the latter paper was also low (1.56 eV/atom) as compared to our GGA value of 2.322 eV. Experimental studies [4] have reported zero moment on $Pd_{13}$. This could be due to the relatively high temperatures (60 to 380 K) of the clusters. An upper limit for the magnetic moments in $Pd_{13}$ was suggested to be 0.4 $\mu_B$/atom which is close to 0.61 $\mu_B$/atom we have obtained. A c isomer is also found to have 8 $\mu_B$ magnetic moment, but it transforms to the i isomer upon relaxation keeping the same moment. A d isomer with 8 $\mu_B$ magnetic moment lies 0.312 eV higher in energy. There is a large gap of 1.639 eV in the up-spin electronic spectrum of the i isomer and it plays an important role in the lowest spin state of this cluster.

$Pd_{14}$ is a capping of i-$Pd_{13}$ on a 3-fold site while for $Pd_{15}$ bicapping on adjacent faces is favored. Both of these have 8 $\mu_B$ magnetic moment. A capped hexagonal antiprism, often a low lying isomer for 15 atom metal clusters, has 6 $\mu_B$ moment and lies 0.247 eV higher in energy. Also a body centered c structure with 8 $\mu_B$ magnetic moment lies 0.231 eV higher in energy. Therefore, our results show that the i growth is most favored in Pd clusters. Continued capping of the i isomer up to $N = 19$ leads to a double icosahedron. All these clusters with $N = 16$ to 19 have 6 $\mu_B$ magnetic moment. Further capping leads to three interpenetrating icosahedra for $Pd_{23}$. The magnetic moments for 20 to 23 atom clusters are 8, 4, 6, and 6 $\mu_B$, respectively. The surface atoms in $Pd_{23}$ have 0.23−0.32 $\mu_B$ magnetic moment while the 3 central atoms, 0.19 $\mu_B$. The moment on each atom is calculated by using Voronoi construction and by integrating the polarization.

For $N = 55$ and 147, spin unpolarized calculations gave the Mackay icosahedra to be of lowest energy with the c isomers lying, respectively, 0.212 and 0.63 eV higher. The d isomers lie 0.628 and 0.869 eV higher in energy. Spin polarized calculations further lowered the energies of i-$Pd_{55}$ and i-$Pd_{147}$ by 0.465 and 1.847 eV with a total moment of 26 and 60 $\mu_B$, respectively. The c-$Pd_{55}$ isomer has a significantly lower magnetic moment of 10 $\mu_B$. Therefore, *the* i *structure plays an important role in the development of magnetism in Pd clusters.* Other spin states with 14, 18, 24 and 34 $\mu_B$ moments lie, respectively, 0.124, 0.121, 0.015, and 0.95 eV higher in energy. The energy differences for the 14 and 18 $\mu_B$ states are quite small and could lead to lower spin isomers to be abundant in experimental conditions of finite temperatures. On the other hand, it costs significantly higher energy to create a higher moment isomer. For $Pd_{147}$, the gap in the up-spin spectrum becomes quite small and therefore, the energy differences between the different spin isomers are also likely to be quite small. Therefore, a proper understanding of the magnetic behavior may need quite low temperatures. The BE of Pd clusters increases monotonically towards the bulk value with a weak bonding in the small region. For large clusters, it shows nearly a linear behavior that extrapolates to the calculated bulk value closely.

The above results show that the magnetic moment per atom in Pd clusters varies in an oscillatory manner with size (Fig. 1b). The increase in the magnetic moment for i-$Pd_{55}$ as compared to i-$Pd_{23}$ is contrary to naive expectation of smaller moments for larger clusters. However, the moment per atom is smaller than the value for i-$Pd_{13}$. The moment of i-$Pd_{147}$ is also large, but again smaller than the value for i-$Pd_{55}$. Therefore, *the atomically closed shell clusters tend to have higher magnetic moments which decrease slowly with increasing size.* The icosahedral structure is the highest symmetry structure possible besides small distortions and would give rise to high density of states (DOS) at the HOMO and this could facilitate the development of ferromagnetism. Also we find that in i isomers, the inner bonds are slightly contracted while the bonds at the surface are elongated. From the tendency of Pd to develop magnetic moments upon expansion, one could expect development of magnetic moments at the surface of Pd clusters. The spin polarizations of the charge densities in 13, 55, and 147 atom clusters was found [15] to be nearly uniform. The slow decrease in the moments with size suggests that larger i clusters will continue to have significant moments particularly in the surface region. This could support the experimental report [6] of surface magnetism in large Pd clusters at low temperatures. We also studied the effect of H adsorption on magnetism of Pd clusters by considering one H on a 3-fold site on i-$Pd_{13}$. It reduces the moment by 1 $\mu_B$. The Pd-H bond lengths are 1.82 and 1.83 Å whereas the BE of H on i-$Pd_{13}$ is 2.969 eV. Adsorption on a bridge site is 0.3 eV less favorable. Adsorption of eight H atoms in a cubic arrangement around i-$Pd_{13}$ quenches all the moments [15]. Therefore, impurities could be another source that can reduce the magnetic moments. The adsorption energy per H is nearly the same as for one H. There is a HOMO-LUMO gap of 0.42 eV.

In both $Pd_{55}$ and $Pd_{147}$, there is a compression of the inner atomic shells as compared to the calculated bulk nearest neighbor distance of 2.8 Å. A similar behavior was also found in Sr clusters [19] as a result of the optimization of strain between the surface atoms which are stretched due to the i packing. The expanded bond lengths at the surface could also lead to the development of magnetic moments in deeper layers. We find moments at least in the first 3−4 surface layers where the effect of the surface is the maximum. For Sr clusters that have icosahedral growth, we [19] suggested a correlation between compressibility and i growth in clusters. This is further supported by our results. However, a smaller energy difference in the i and c isomers should lead to an early transition to the fcc structure, in accordance with the lower compressibility of Pd than Sr.

Similarly for Ru and Rh clusters we find i growth to be generally the most favorable. There is a large magnetic moment in small clusters, but it decreases rapidly to very small or zero value at the size of 147 atoms. $Rh_{13}$ has a magnetic moment of 21 $\mu_B$ that is much higher than in the case of $Pd_{13}$. This value is close to the result of 22 $\mu_B$ obtained by Piveteau *et al.* [13] using the tight binding method with only d electrons. Lower magnetic moment states lie very close in energy. 19 $\mu_B$ state lies only 0.043 eV higher, while a 17 $\mu_B$ state lies only 0.021 eV higher in energy. An spin isomer with 15 $\mu_B$ magnetic moment lies 0.044 eV higher making the 15 and 19 $\mu_B$ spin isomers to be nearly degenerate. These magnetic moments are higher than the observed values. However, it is likely that low spin isomers would be abundant under experimental conditions of finite temperatures and lead to an effective underestimation of the moments. The c and d isomers have 19 and 5 $\mu_B$ moments, respectively and are nearly degenerate with about 0.5 eV higher energy than the i isomer. Therefore, i structures are important for high moments on these clusters also. The magnetic moment (25 $\mu_B$) on i-$Rh_{55}$ is close to the value of i-$Pd_{55}$. However, a d isomer with 11 $\mu_B$ magnetic moment becomes 0.308 eV lower in energy. For i-$Rh_{147}$, the magnetic moment becomes only 5 $\mu_B$ as compared to 60 $\mu_B$ for i-$Pd_{147}$. Therefore, there is a tendency for states of low magnetic moments to be of lowest energy. A similar behavior is obtained for Ru clusters with 12 and 14 $\mu_B$ moments on i-$Ru_{13}$ and i-$Ru_{55}$, respectively. However, a c isomer of $Ru_{13}$ with 10 $\mu_B$ magnetic moment lies significantly lower in energy, but i-$Ru_{55}$ has the lowest energy. Piveteau *et al.* [13] also obtained fcc structure to be lower in energy than the i structure but with a magnetic moment of 24 $\mu_B$ using a simplified tight binding model. In our calculations such a high spin isomer lies about 3 eV higher in energy. The magnetic isomer (16 $\mu_B$) of i-$Ru_{147}$ is only 0.115 eV lower in energy than the non-magnetic state. These results show that the delocalization of electrons is faster in Rh and Ru clusters as compared to Pd, leading to the disappearance of magnetism in these clusters faster (Fig. 1b). Though i structures are generally favored, there is a competition between the different structures and the magnetic moments in these clusters. A similar conclusion was obtained on Rh clusters using a simplified tight binding model [20]. A detailed report of these results and the effects of H interaction will be presented elsewhere [21].

## 4 Summary

In summary, we have presented results of *ab initio* calculations on the magnetic behavior of large Pd, Rh, and Ru clusters having up to 147 atoms. We find an oscillatory ferromagnetic behavior as a function of size and an i growth in Pd clusters. The i symmetry of the atomically closed shell 13, 55, and 147 atom clusters leads to high magnetic moments that decrease slowly with size for Pd. For Rh and Ru clusters, though i structures are generally preferred, there is a competition between the structure and the magnetic moment. There is a tendency for rapid delocalization of electrons and consequently a quite rapid decrease in the magnetic moments on their clusters. The magnetic moments are significant at least in the first 3−4 layers near the surface. The magnetic energy is generally small and even at liquid nitrogen temperature the moments can be significantly reduced or destroyed making their observation difficult in agreement with experimental results. Also it is found that H adsorption quenches the moments of Pd. Therefore, impurities could affect magnetic behavior significantly.

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