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Icosahedral growth, magnetic behavior, and adsorbate-induced metal-nonmetal transition in palladium clusters

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Studies of the atomic and electronic structures of Pd clusters with 2-23, 55, and 147 atoms have been carried out using the ultrasoft pseudopotential plane wave method and the spin-polarized generalized gradient approximation for the exchange-correlation energy. We find predominantly an icosahedral growth in these clusters, and size dependent oscillatory magnetic moments that are not confined just to the surface atoms. Atomically closed shell 13-, 55-, and 147-atom clusters have large moments of $0.61\mu_B$/atom, $0.47\mu_B$/atom, and $0.41\mu_B$/atom, respectively. But cubic Pd_{55} isomer has a low moment of $0.18\mu_B$/atom only, indicating the importance of the icosahedral structure in the development of magnetism in Pd clusters. The evolutions of the sp-d hybridization, the magnetic moment and the electronic structure are discussed as a function of the cluster size. The magnetic energy is found to be small. Further studies on the adsorption of H and O show that though both an increase as well as a decrease of the moment are possible, often there is a reduction in the magnetic moments of Pd clusters. A hydrogen induced metal to nonmetal transition is predicted in Pd_6H_8 and $Pd_{13}H_8$ clusters.

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I. INTRODUCTION

The possibility of magnetism in clusters of $4d$ elements Ru, Rh, and Pd has facinated researchers,[1–4] as in the bulk these elements are nonmagnetic. Pd is widely used as a catalyst, but the size dependence of its cluster properties as well as the changes due to the adsorption of gases are not well understood. In bulk, Pd is close to fulfilling the Stoner criterion of magnetism. It has a high paramagnetic susceptibility and a lattice expansion of only 6% induces bulk ferromagnetism.[5] Clusters of $3d$ magnetic elements Fe, Co, and Ni immediately above these $4d$ elements in the Periodic Table show enhanced magnetic moments[6] due to narrower bandwidths that arise from a lower mean coordination than in the bulk and the increased localization of electrons. As the cluster size decreases, the moment approaches the atomic limit which is, in general, significantly higher than the bulk value. An important factor that makes clusters different from the bulk is the possibility of noncrystallographic icosahedral (i) or decahedral (d) structures in which the bond lengths vary significantly. Icosahedral high symmetry and low mean coordination in clusters together with elongation in bond lengths could lead to important changes in the electronic structure with significant consequences for the magnetic behavior of Pd clusters.

Unlike Fe, Co, and Ni, the palladium atom has no magnetic moment due to the $4d^{10}5s^0$ closed shell electronic configuration. This also leads to weak bonding in its small clusters. The aggregation of atoms, however, leads to a delocalization of electrons and a depletion of the $4d$ states due to sp-d hybridization that could give rise to local moments and magnetism in clusters. Experiments have, however, given conflicting results. Early Stern-Gerlach deflection experiments[2] showed no magnetic moment in Pd clusters with temperatures in the range of 60 K or above. Photoemission studies[4] suggested a Ni-like magnetic behavior for Pd_N with $N=3-6$, and a nonmagnetic Pt-like behavior for $N>15$. The temperature of the clusters was, however, not specified. Contrary to this, measurements at 1.8 K in the range of 50–70 Å particle size reported[7] a magnetic moment of $(0.23\pm0.19)\mu_B$ per surface atom. Other studies[8] on low-dimensional structures, such as Pd layers on Ag(001), showed no magnetic moment for one layer, but a bilayer was found[9] to be ferromagnetic with a net magnetic moment of $0.17\mu_B$/atom. Therefore, the observation of magnetic moment in large clusters was thought to arise from surface effects. However, palladium surfaces are nonmagnetic.

Theoretical studies[3] on Pd_{13} using the local spin density approximation showed an i isomer to be more favorable than a cubic (c) isomer, with magnetic moments of $0.12\mu_B$ per surface atom and a higher moment of $0.43\mu_B$ at the central atom. A self-consistent tight-binding calculation[10(a)] with $N=2-201$ showed either a nonmagnetic or only a weak magnetic behavior, *keeping the symmetries* such as equilateral triangle, tetrahedron, octahedron etc. of clusters. In another related study,[10(b)] clusters were relaxed, but only the $4d$ electrons were considered. First principles calculations[11] on *symmetric* body centered cubic Pd_{15} and face centered cubic Pd_{19} clusters gave $0.53\mu_B$/atom and $0.32\mu_B$/atom moments, respectively. A nonmagnetic state of c-Pd_{19} was also reported to lie close in energy. However, in this study no effort was made to explore the lowest energy atomic structures of these clusters. Small Pd clusters with $N=2-7$ and 13 were recently studied[12] using symmetry unrestricted optimizations of selected structures. Significant moments were obtained on these clusters and it was concluded that an ensemble of Pd_7 may even show an increase in magnetic moment with temperature. Also a study[13] of 55-, 135-, and 140-atom clusters within the local density approximation (LDA) gave 55- and 135-atom clusters to favor i isomer while c isomer was more favorable for $N=140$. In these calculations the clusters were, however, treated to be nonmagnetic. Here we report results of *ab initio* calculations on the evolution of the atomic and electronic structures as well as magnetism in large Pd clusters having upto 147 atoms, and the changes in the magnetic behavior of clusters due to H and O adsorption. An interesting finding is the hydrogen-induced metal-nonmetal transition in palladium clusters.

II. COMPUTATIONAL DETAILS

We use the ultrasoft pseudopotential plane wave method[14] with a cutoff of 14.63 Ry for the plane wave expansion in the case of pure Pd clusters, 25.68 Ry for calculations with H adsorption and 29.10 Ry for those with O adsorption. The clusters are placed in a simple cubic supercell of side up to 30 Å. For such large cells Brillouin zone integrations are carried out using only the Γ point. The exchange-correlation energy is calculated within the spin-polarized generalized gradient approximation (GGA).[15] Calculations for bulk Pd give the cohesive energy and lattice constant to be 3.718 eV/atom and 3.96 Å, in good agreement with the experimental values of 3.89 eV/atom and 3.89 Å, respectively as compared to the LDA values of 4.974 eV/atom and 3.86 Å. For clusters, we optimize selected structures without any symmetry constraint using the conjugate gradient method. While such an approach generally converges to the nearest local minimum, it has been successfully used in a large number of cases of clusters[16–22] and in particular for clusters of transition metals as the simulated annealing approach becomes computationally intensive. In the small size range, it is possible to consider several isomers including the ones known for metal clusters, and this often leads to the lowest energy atomic structure. However, the additional problem of spin isomers in magnetic clusters makes the search more difficult.[23] For small clusters it is possible to consider several spin isomers of some low lying atomic structures, but for large clusters with several tens of atoms this becomes very demanding. In general, *c*, *d*, and *i* isomers are among the most likely candidates for metal clusters in the larger size range of few tens of atoms. We, therefore, limit our search to these isomers for 55- and 147-atom clusters. We believe that our results should give a fair representation of the growth behavior in these clusters. For small clusters, we optimize a few atomic structures in each case and, in the intermediate range of 14–23-atom clusters, we predominantly study the *i* isomers as studies of other isomers in a few cases suggested preference for *i* structures. In general we started with a smearing of the eigenstates to obtain the self-consistency. Subsequently the smearing parameter was reduced to a very small value so that all states had integer occupancy. In most cases this approach led to the lowest spin isomer as we find from studies of different spin isomers of a few clusters. However, in some cases the energy differences between the different spin isomers are quite small and, therefore, calculations were also performed on a few spin isomers in such cases to obtain the lowest energy state.

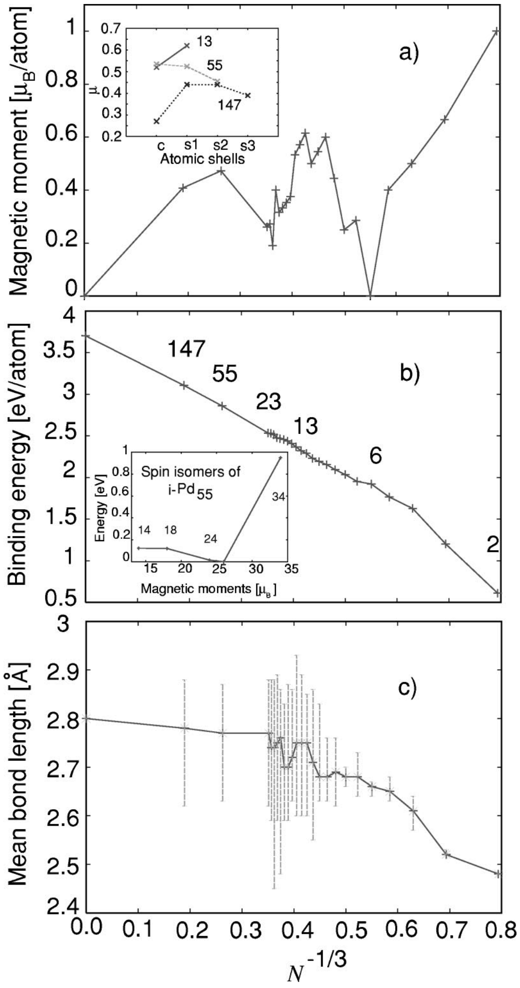

FIG. 1. (a) Magnetic moment per atom, (b) binding energy per atom, and (c) the mean nearest neighbor bond length in Pd_N clusters. The numbers in (b) show the size of the clusters. The points are connected to aid the eyes. The inset in (a) shows the mean magnetic moment per atom in successive atomic shells of icosahedral 13-, 55-, and 147-atom clusters. The inset in (b) shows the energies of the spin isomers of i-Pd_{55} with respect to the ground state of $26\mu_B$.

III. RESULTS

A. Pure clusters

Pd_2 - Pd_{13}

The magnetic moments, binding energies (BE's), and mean bond lengths of the lowest energy structures are shown in Fig. 1. These results as well as some other isomers are also listed in Table I. Our results of structures and magnetic moments of clusters with $N \leqslant 7$ and 13 are similar to those in Ref. 12 within the GGA, but differ for Pd_6. For a dimer, we obtain a magnetic moment of $1\mu_B$/atom, and the BE is only 0.611 eV/atom. This is about 16% of the bulk value. 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 2.80 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. Figure 2 shows the total and angular

TABLE I. BE, magnetic moment *M* on clusters, and mean nearest neighbor bond length *d*. PBP, TAP, HAP, and DIC represent a pentagonal bipyramid, a tetragonal antiprism, a hexagonal antiprism, and a double icosahedron, respectively. Octahedron1 and octahedron2 are the isomers of Pd_7 shown in Figs. 3(c) and 3(d), while PBP1 and PBP2 are isomers of Pd_9 shown in Figs. 3(g) and 3(i), respectively.

N	Cluster	BE (eV/atom)	M (μ_B)	d (Å)
2	Dimer	0.611	2	2.48
3	Triangle	1.203	2	2.52
4	Tetrahedron	1.628	2	2.61
5	Trigonal bipyramid	1.766	2	2.65
6	Octahedron	1.922	0	2.66
	Octahedron	1.919	2	2.66
	Tetrahedral	1.867	2	2.67
	Distorted Prism	1.832	2	2.65
7	PBP	1.953	2	2.68
	Capped octahedron1	1.946	2	2.65
	Capped octahedron2	1.944	0	2.65
	Capped octahedron	1.926	4	2.66
	PBP	1.917	0	2.70
8	Bicapped octahedron	2.036	2	2.68
	Capped PBP	2.009	2	2.70
9	Capped PBP1	2.094	4	2.69
	Tricapped prism	2.067	4	2.68
	Capped PBP2	2.062	4	2.70
	Capped TAP	2.033	4	2.67
10	Capped PBP	2.155	6	2.68
	2 interlocked PBPs	2.149	4	2.71
	Bicapped TAP	2.119	4	2.68
	Tetracapped prism	2.104	4	2.68
11	Icosahedral	2.192	6	2.68
12	Icosahedral	2.231	6	2.71
13	Icosahedral	2.290	8	2.75
	Decahedron	2.266	4	2.71
14	Capped icosahedron	2.322	8	2.75
15	Bicapped icosahedron	2.368	8	2.75
	Bicapped HAP	2.362	6	2.77
	Body centered cubic	2.353	4	2.68
16	Capped icosahedron	2.406	6	2.75
17	Capped icosahedron	2.437	6	2.72
18	Capped icosahedron	2.456	6	2.70
19	DIC	2.467	6	2.76
20	Capped DIC	2.477	8	2.75
21	Capped DIC	2.514	4	2.74
22	Capped DIC	2.531	6	2.74
23	Polyicosahedron	2.534	6	2.77
55	Mackay icosahedron	2.860	26	2.77
	Mackay icosahedron	2.859	24	2.77
	Mackay icosahedron	2.858	18	2.76
	Mackay icosahedron	2.858	14	2.77
	Mackay icosahedron	2.852	0	2.77
	Mackay icosahedron	2.843	34	2.77
	Cuboctahedron	2.850	10	2.74
	Cuboctahedron	2.849	12	2.74
	Cuboctahedron	2.848	6	2.74
	Cuboctahedron	2.848	4	2.74
	Cuboctahedron	2.848	0	2.74
	Decahedron	2.841	0	2.75
147	Mackay icosahedron	3.106	60	2.78
	Mackay icosahedron	3.093	0	2.78
	Cuboctahedron	3.089	0	2.76
	Decahedron	3.087	0	2.76
Bulk	fcc	3.718	0	2.80
	Experimental values	3.890	0	2.75

momentum decomposed densities of states. This has been obtained by expanding the wave function into angular momentum components within spheres of radius 1.434 Å around each Pd ion. As significant charge lies outside the spheres, this decomposition is only representative and is expected to give the main character of each state. It is seen that the up-spin $4d$ states are fully occupied, while the down-spin states are depleted due to sp-d hybridization such that one electron has a predominantly s character. The up-spin s state lies just below the HOMO, while the down-spin s state is unoccupied and lies just above the HOMO. The p character of states in the occupied portion is negligible. It should be noted that the sum of the partial densities of states is expected to be less than the total density of states. This is particularly so for the s and p states as much of the charge lies outside the spheres.

Clusters with $N=3-5$ are Jahn-Teller distorted triangle, tetrahedron and trigonal bipyramid, each with $2\mu_B$ magnetic moment (triplet state). The lowest energy structure of Pd_6 is a singlet with an octahedron structure. A spin isomer with $2\mu_B$ magnetic moment lies only 0.017 eV higher in energy. Moseler *et al.*[12] found this magnetic isomer to be the ground state. However, the energy difference is rather small and the two spin isomers can be treated to be nearly degenerate. The temperature at which the higher energy isomer may become observable can be estimated from $2(E_{GS}-E_{isomer})/(3N-6)k_B$, where E_x is the energy of the x specie which is either the ground state or the isomer and k_B is the Boltzman constant. For the two spin isomers of Pd_6, this temperature is only 32.8 K. Therefore, under the experimental conditions of temperatures of 60 K or above, both the isomers are likely to be present in an ensemble of these clusters. In our calculations, Pd_6 is the only cluster that has a non-magnetic isomer to be of the lowest energy. A tetrahedral structure of Pd_6 [Fig. 3(a)] lies 0.331 eV higher in energy. Also an initially prism structure distorts [Fig. 3(b)] and lies 0.538 eV higher in energy. Both of these isomers have a $2\mu_B$ magnetic moment, but are unlikely to be observed. For Pd_7, a pentagonal bipyramid (PBP) has the lowest energy with a $2\mu_B$ magnetic moment. The nonmagnetic solution lies 0.191 eV higher in energy. However, a capped prism and a capped octahedron [Fig. 3(c)] lie only 0.063 and 0.051 eV higher in energy, and

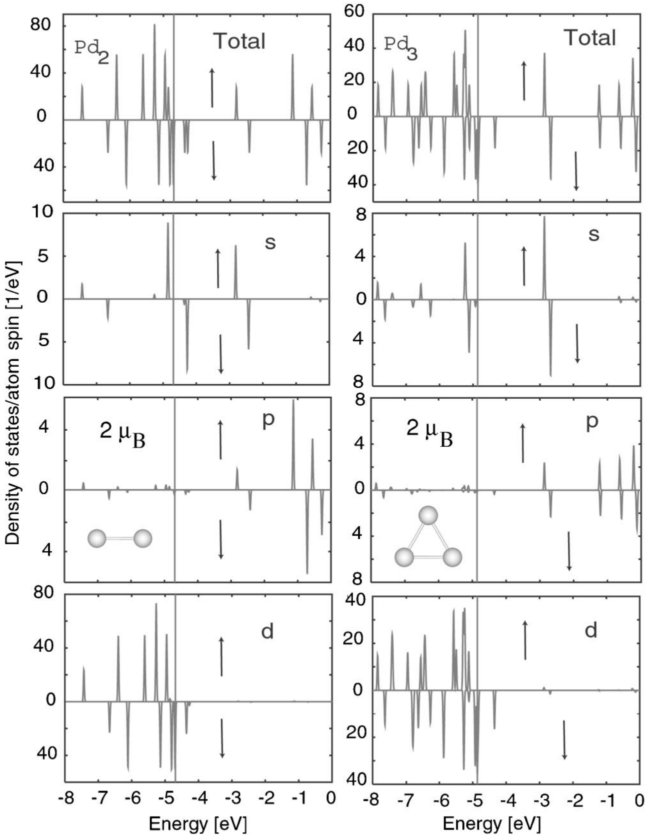

FIG. 2. Gaussian broadened (width 0.02 eV) total and angular momentum decomposed electronic energy spectra of Pd_2 and Pd_3. The vertical lines denote the HOMO.

have zero and $2\mu_B$ magnetic moments, respectively. The capped prism structure distorts and becomes an edge capped octahedron [Fig. 3(d)]. We also considered a spin isomer of capped octahedron with a $4\mu_B$ magnetic moment as obtained in Ref. 12. It lies only 0.127 eV higher in energy than the lowest energy isomer. These results suggest that, in experiments at room temperature, these isomers are likely to be present. Therefore, in addition to the higher moment spin isomer that will be observable at increasing temperatures as suggested in Ref. 12, there would also be abundance of isomers with zero spin. This result agrees with the suggestion[4] based on the photoemission data that Pd_7 may be a closed shell specie with zero magnetic moment. The density of states curves show that the *s*-*d* hybridization increases as the size of the cluster grows from 3 to 7 (Figs. 2, 4, and 5), while the *p* character remains quite small in the occupied portion of the states. The *s* states shift to higher binding energies as the size grows due to increased delocalization of electrons. The up-spin density of states has a significant HOMO-LUMO gap for all these clusters except for Pd_6 giving them half-metallic character.

For Pd_8, a tetragonal antiprism relaxes to a bicapped octahedron [Fig. 3(e)] and lies 0.219 eV lower in energy than a capped PBP [Fig. 3(f)]. Both are triplet states. For larger clusters, *i* isomers or fragments of an icosahedron have lower energies than other structures. The energy differences between the isomers are, however, small. For Pd_9, a capping of adjacent faces on the same side of a PBP [Fig. 3(g)] is most favorable. A tricapped prism [Fig. 3(h)] lies 0.241 eV higher in energy, while another isomer [Fig. 3(i)] with capping of two adjacent faces on opposite sides of the basal plane of a PBP lies 0.285 eV higher. A capped tetragonal antiprism [Fig. 3(j)] lies 0.550 eV higher in energy. All these isomers have a $4\mu_B$ magnetic moment. For Pd_{10}, similarly, a tricapped (adjacent faces on the same side) PBP [Fig. 3(k)] has the lowest energy with a $6\mu_B$ magnetic moment. Its nonmagnetic isomer lies 0.384 eV higher in energy. An isomer with

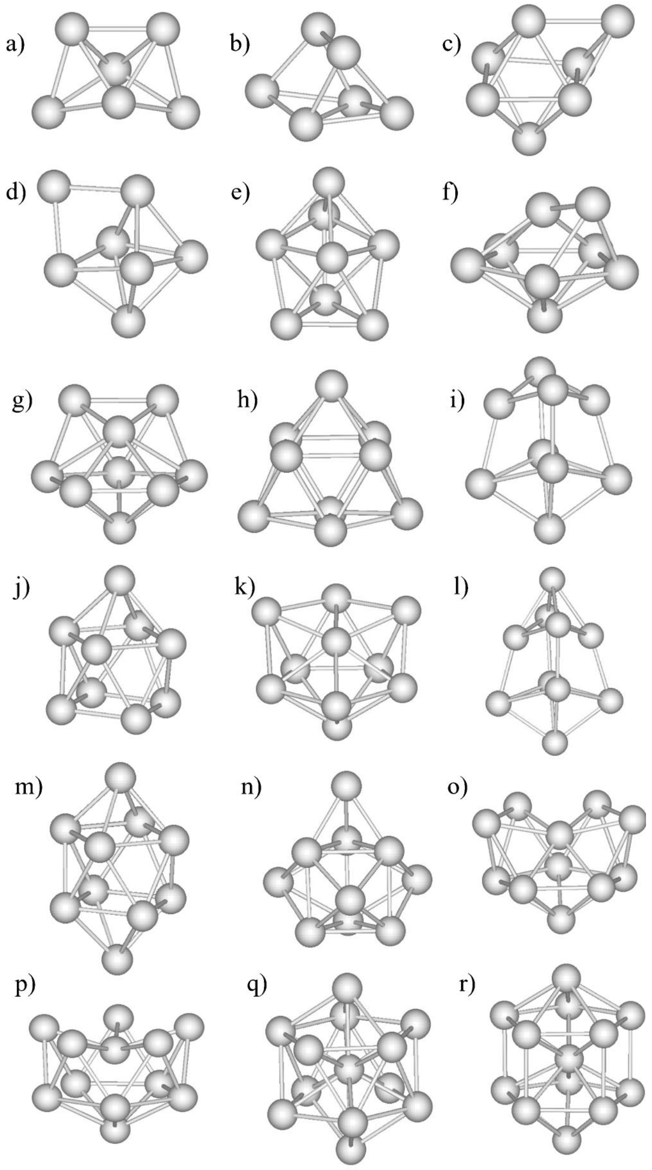

FIG. 3. Isomers of small Pd_N ($N=6-13$) clusters. (a) Tetrahedral and (b) distorted prism isomers of Pd_6, (c) and (d) capped octahedra of Pd_7, (e) bicapped octahedron and (f) capped PBP for Pd_8, (g) capped PBP1, (h) tricapped prism, (i) bicapped PBP2 and (j) capped tetragonal antiprism for Pd_9, (k) capped PBP, (l) two interlinked PBPs, (m) bicapped tetragonal antiprism, and (n) tetracapped trigonal prism for Pd_{10}, (o) icosahedral Pd_{11}, (p) icosahedral Pd_{12}, (q) icosahedron and (r) decahedron for Pd_{13}. Bonds with lengths less than 2.8 Å are connected.

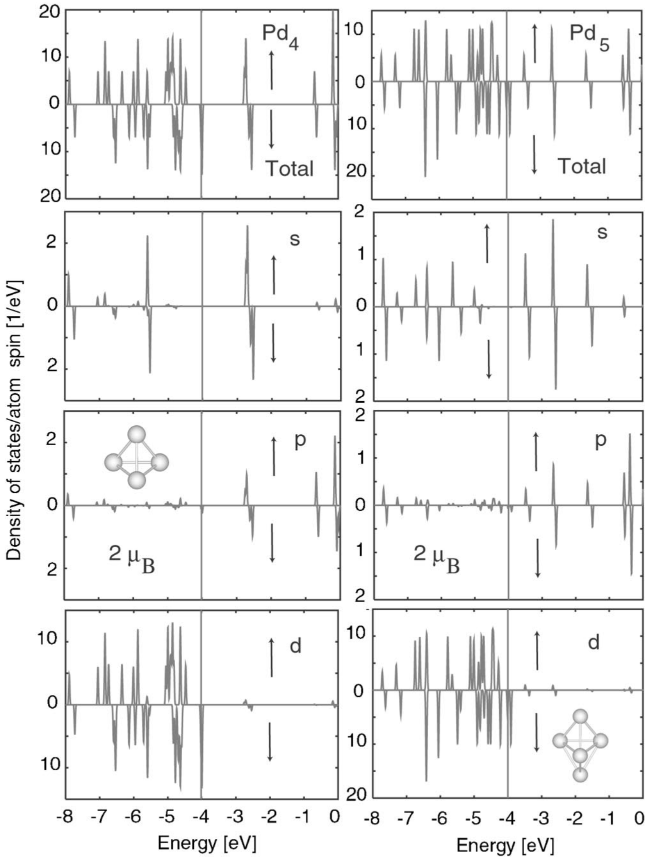

FIG. 4. Same as in Fig. 2, but for Pd_4 and Pd_5.

two interlocked PBP's [Fig. 3(l)] lies only 0.062 eV higher in energy and has a $4\mu_B$ magnetic moment. It is likely to be abundant in experiments at around 60 K and again lead to an underestimation of the moment. Its nonmagnetic isomer lies 0.281 eV higher in energy. This may become accessable at around room temperature. A bicapped tetragonal antiprism [Fig. 3(m)] lies 0.363 eV higher in energy and has a $4\mu_B$ moment while a tetracapped prism [Fig. 3(n)] lies 0.505 eV higher in energy and has a $4\mu_B$ magnetic moment. These are unlikely to be present in experiments at room temperature. Pd_{11} [Fig. 3(o)] and Pd_{12} [Fig. 3(p)] are incomplete icosahedra each with a $6\mu_B$ magnetic moment.

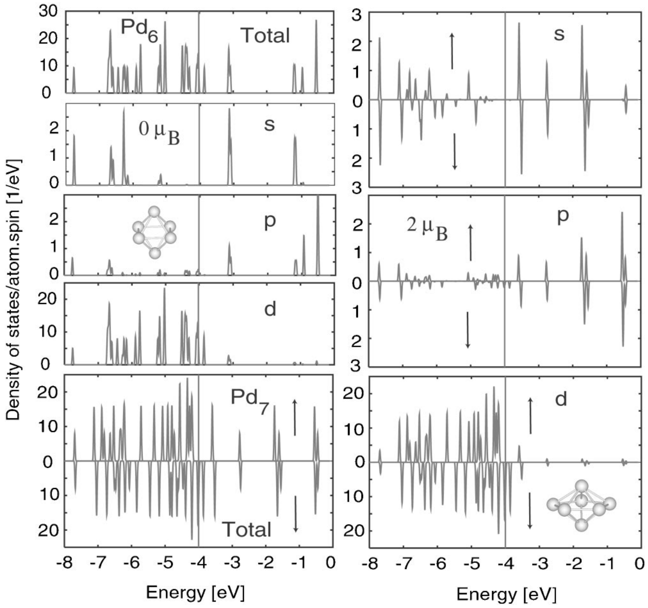

FIG. 5. Same as in Fig. 2, but for Pd_6 and Pd_7.

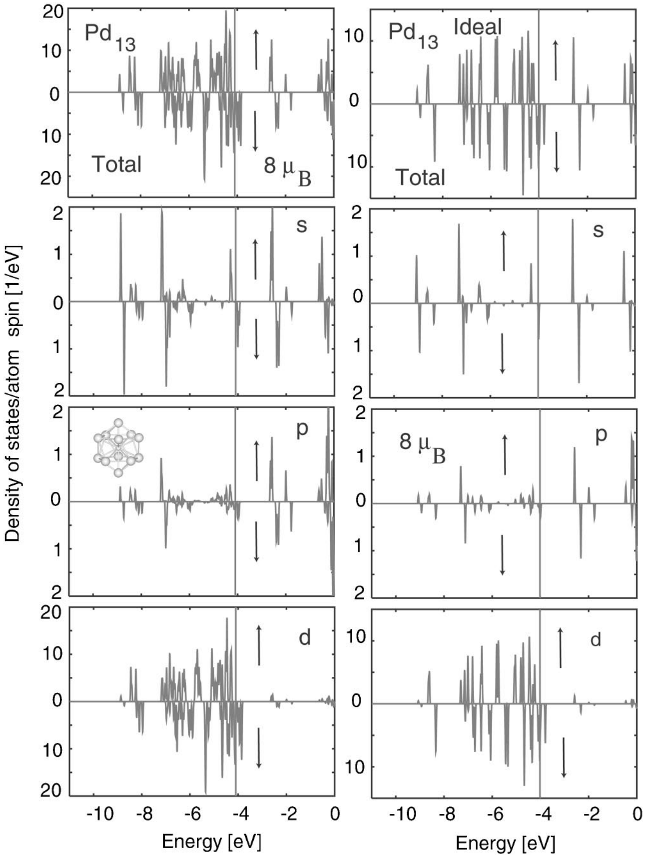

FIG. 6. Same as in Fig. 2, but for Pd_{13} clusters. The relaxed structure (left) and an ideal *i* structure (right) with the center to vertex bond length of 2.61 Å.

For Pd_{13} an *i* isomer [Fig. 3(q)] with an $8\mu_B$ magnetic moment is found to have the lowest energy in agreement with an earlier GGA study,[12] but it is different from the result of $2\mu_B$ using a tight binding method,[10(a)] and also that found by Reddy *et al.*[3] within the LDA. The latter also reported the LDA BE of 1.56 eV/atom as compared to our GGA value of 2.322 eV/atom. The central atom in our calculations has a magnetic moment of $0.52\mu_B$ while the surface atoms have moments in the range of $(0.6–0.65)\mu_B$ due to Jahn-Teller distortions. The moments on each atom are calculated by using the Voronoi construction and by integrating the polarization. Experimental studies[2] reported a zero moment on Pd_{13} that 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, that is close to $0.61\mu_B$/atom we have obtained. A *c* isomer is also found to have an $8\mu_B$ magnetic moment, but it transforms to the *i* isomer upon relaxation keeping the same moment. This is also in agreement with the similar finding in Ref. 12. A *d* isomer [Fig. 3(r)] also with an $8\mu_B$ magnetic moment lies 0.312 eV higher in energy. The total and angular momentum decomposed densities of states of the *i* isomer are shown in Fig. 6. There is a large gap of 1.639 eV in the up-spin electronic spectrum, giving it a half-metallic character. It plays an important role in the lowest spin state of this cluster. The up-spin *d* states are fully occupied while the down-spin states are depleted. Besides the *s* states which have significant polarization, there is also a significant increase in the *p* component as the central atom has a coordination of 12. We further ask if the electronic spectra of these clusters can be understood in terms of the hybridization between the 4*d* states and a jellium spectrum arising from the *sp* electrons as clusters of the next element in the Periodic Table, namely, silver, show a magic behavior similar to alkali metal clusters.[1] For this we studied an ideal case of Pd_{13} with perfect *i* symmetry. This also has an $8\mu_B$ magnetic moment, and its density of states is shown in Fig. 6. It is found that the energy spectrum of the relaxed Pd_{13} cluster is quite similar to the ideal case, except for the splitting of the states due to the reduction in symmetry. However, a jellium description does not seem to be appropriate.

Pd_{14} - Pd_{23}

Pd_{14} is a capping of i-Pd_{13} on a threefold site,[24] while for Pd_{15} bicapping on adjacent faces is favored. Both of these have an $8\mu_B$ magnetic moment. A capped hexagonal antiprism, often a low lying isomer for 15-atom metal clusters, has a $6\mu_B$ moment and lies 0.247 eV higher in energy. Also a body centered cubic structure with an $8\mu_B$ magnetic moment lies 0.231 eV higher in energy. The magnetic moment on this cluster agrees with the result in Ref. 11, but it is not the lowest energy isomer. However, both these isomers are likely to become accessable in experiments at around 150 K. These results again show that the *i* growth is most favored in Pd clusters. Therefore, we continued capping of the *i* isomer up to $N=19$ to form a double icosahedron. All these clusters with $N=16$–19 have $6\mu_B$ magnetic moments. Further capping leads to three interpenetrating icosahedra (polyicosahedron) for Pd_{23}. The magnetic moments for 20–23-atom clusters are $8\mu_B$, $4\mu_B$, $6\mu_B$, and $6\mu_B$, respectively. The surface atoms in Pd_{23} have a $(0.23$–$0.32)\mu_B$ magnetic moment while the three central atoms have a moment of $0.19\mu_B$. Therefore, there is a significant decrease in the local moments as compared to the values for Pd_{13}. The density of states for Pd_{23} is shown in Fig. 7. In this case the band becomes slightly wider and the up-spin *d* states are not fully occupied. Consequently the gap in the up-spin spectrum becomes very small. The *s* and *p* characters of the states grow further, but the *p* character remains quite small.

Pd_{55} and Pd_{147}

For $N=55$ and 147, we first performed spin unpolarized calculations that gave Mackay icosahedra to be the lowest in energy. These are not perfect icosahedra, but the deviations are small. The *c* isomers lie, respectively, 0.212 and 0.63 eV higher in energy. Interestingly the *d* isomers lie 0.628 and 0.869 eV higher in energy. This is in contrast to clusters of other metals such as Sr, for which *d* isomers are lower in energy than the *c* isomers.[18] Spin-polarized calculations further lowered the energies of i-Pd_{55} and i-Pd_{147} by 0.465 and 1.847 eV, with total moments of $26\mu_B$ and $60\mu_B$, respectively. These energy gains due to magnetism in the clusters are rather small and even at around 70–100 K nonmagnetic isomers will become accessible. We also studied other spin isomers of i-Pd_{55} with $14\mu_B$, $18\mu_B$, $24\mu_B$, and $34\mu_B$ moments. The $24\mu_B$ spin isomer is only 0.015 eV higher in energy [see the inset in Fig. 1(b)], while the spin isomers with $14\mu_B$, $18\mu_B$, and $34\mu_B$ moments lie, respectively, 0.124, 0.121, and 0.950 eV higher in energy. The energy differences for the $14\mu_B$ and $18\mu_B$ spin isomers are quite small, and make the magnetic order rather fragile. Under experimental conditions of room temperature or even less, isomers of lower magnetic moments would be accessible. This could be a possible reason for the experimental results of either zero or quite small moments at finite temperatures. Our results suggest that the energy cost to flip a spin in these clusters is quite small, and consequently it is possible that the magnetic order can be lost or the moments significantly reduced even at low temperatures. On the other hand, it costs significantly higher energy to create a higher magnetic moment state [inset of Fig. 1(b)]. Further, the c-Pd_{55} isomer has a low magnetic moment of $10\mu_B$ only. The nonmagnetic state lies only 0.159 eV higher in energy than the ground state of a cuboctahedron. This shows that the *c* isomers in this size range have significantly lower magnetic moments and that the difference in energy from the non-magnetic state is quite small. The $4\mu_B$, $6\mu_B$, and $12\mu_B$ isomers lie only 0.078, 0.070, and 0.012 eV higher in energy, respectively. These results show that *it is not only the reduced band width or the presence of a large number of surface atoms, but also the i structure that plays an important role in the development of magnetism in Pd clusters*. This result is not so obvious from calculations on Pd_{13} as both the *c* and *i* isomers have the same magnetic moment. The density of states for i-Pd_{55} is shown in Fig. 7. There is again a small HOMO-LUMO gap of 0.276 eV in the up-spin spectrum and the up-spin *d* states are nearly completely occupied (small depletion due to sp-d hybridization). This is due to the higher symmetry (besides Jahn-Teller distortions) of this cluster as compared to Pd_{23}. The gross features of the density of states are similar to those of Pd_{23}. In the case of i-Pd_{147}, the gap in the up-spin spectrum becomes quite small (Fig. 8). Following the results for Pd_{55}, we anticipate that the energy differences between the different spin isomers would also be quite small for Pd_{147}. Therefore, in an ensemble of such clusters under experimental conditions of finite temperatures of about 100 K or above several spin isomers with low magnetic moments are likely to be present and lead to an underestimate of the magnetic moment of this cluster.

The above results show that the magnetic moment per atom in Pd clusters varies in an oscillatory manner with size [Fig. 1(a)]. The increase in the magnetic moment for i-Pd_{55} as compared to i-Pd_{23} is contrary to naive expectation of lower moments for larger clusters. This is likely to be due to the higher symmetry of the i-Pd_{55} cluster. However, the moment per atom is smaller than the value for atomically closed

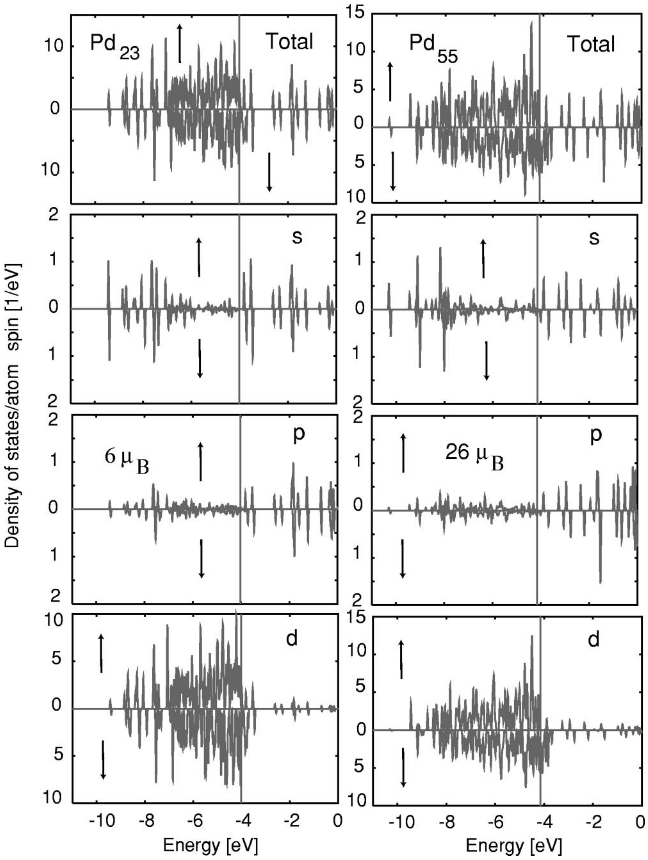

FIG. 7. Same as in Fig. 2, but for Pd_{23} and Pd_{55}.

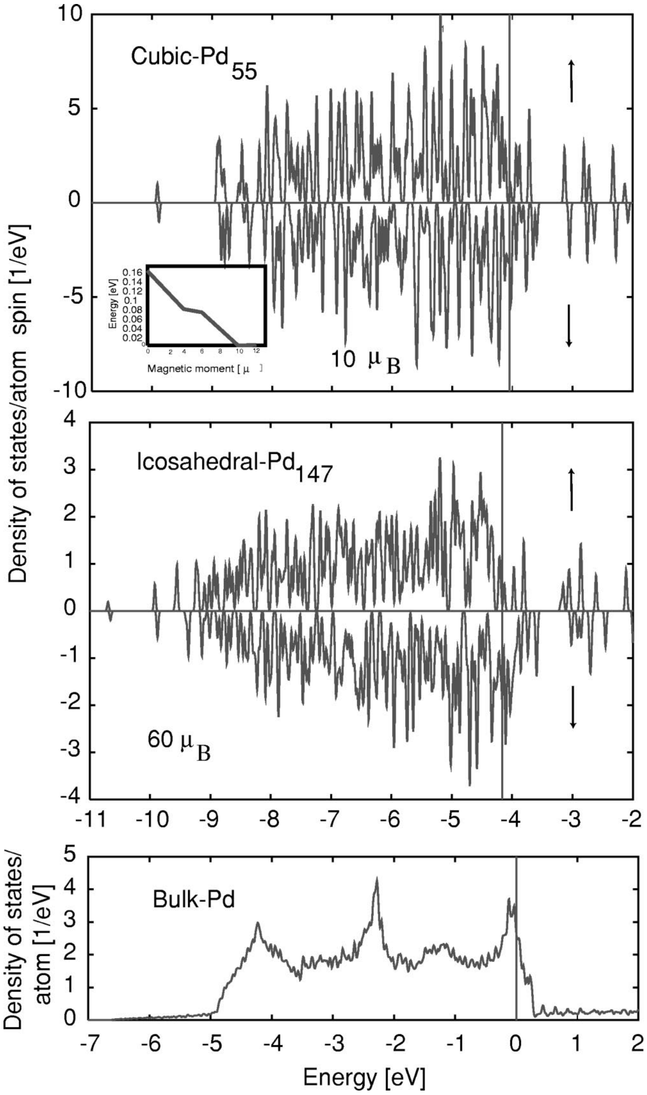

FIG. 8. Density of states for c-Pd_{55}, i-Pd_{147}, and bulk Pd. The inset shows the energies of different spin isomers of c-Pd_{55} with respect to the lowest energy spin isomer of $10\mu_B$.

shell i-Pd_{13}. The moment of i-Pd_{147} is also large, but again smaller than the value for i-Pd_{55}. Thus we conclude that *the atomically closed shell clusters tend to have higher magnetic moments which decrease slowly with size*. These are also the clusters with highest symmetry. The exchange splitting is generally small with values of about a few tenths of an eV in all cases. The density of states for i-Pd_{147} differs significantly from the bulk (see Fig. 8). Also the density of states of c-Pd_{55} is significantly different from the bulk. In this case the up-spin d states are more depleted as compared to the i-Pd_{55} isomer. These results suggest that much larger clusters would be needed to obtain a bulklike behavior.

Magnetic behavior and icosahedral structure

In order to further understand the magnetic behavior, we studied the change in bond lengths with an increase in size. It is found that in i isomers, the inner bonds are slightly contracted while the bonds at the surface are elongated. In Fig. 3 one can notice some missing bonds which are greater than 2.8 Å. From the tendency of bulk Pd to develop magnetic moments upon expansion, one could expect development of magnetic moments at the surface of Pd clusters. However, spin polarizations of the charge densities in 13-, 55-, and 147-atom clusters show (Fig. 9) that the polarizations are nearly uniform. Surprisingly *for i-Pd_{55} and i-Pd_{147}, the moments on the surface atoms are lower (mean values $\approx 0.455\mu_B/atom$ and $0.39\mu_B/atom$) than in the shell below (mean values $\approx 0.53\mu_B/atom$ and $0.44\mu_B/atom$, respectively)*. However, the moment is reduced to $0.26\mu_B$ [see the inset in Fig. 1(a)] at the central atom in i-Pd_{147} which has the shortest nearest neighbor bond lengths. This behavior is likely to be due to the Friedel oscillations of the charge density. Also the presence of significant moment at the central site in spite of compression is different from bulk, though the central atom has 12 nearest neighbors, as does the bulk. This could be due both to the proximity effect that the outer shells are magnetic as well as to the higher symmetry of Pd_{147}. 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[7] of surface magnetism in large Pd clusters at low temperatures.

As shown in Fig. 1(c), in general there is a slow and oscillatory increase in the bond lengths with an increase in the cluster size (also see Table I). Small clusters with $N < 10$ show only small deviations from the mean values. The closed atomic shell clusters with 13, 55, and 147 atoms have

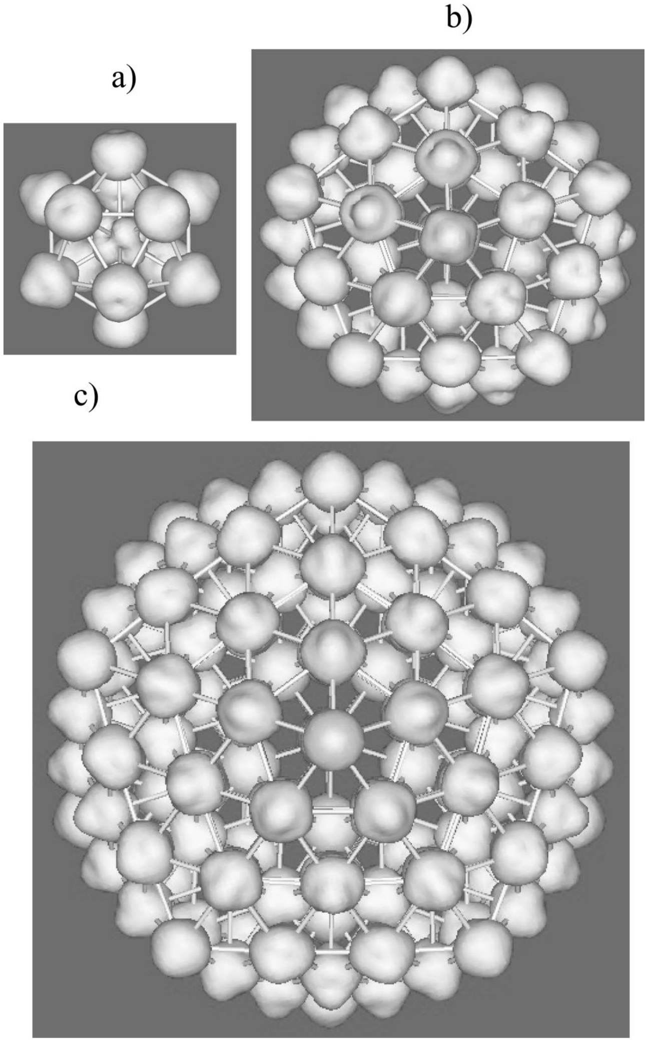

FIG. 9. Isosurfaces of spin-polarization for (a) 13-, (b) 55-, and (c) 147-atom icosahedral clusters with a value of 0.05. The nearly uniform distribution on all atoms is clearly seen.

longer mean bond lengths and smaller deviations as compared to other clusters in this size range. The distortions from the perfect *i* symmetry are also small. For i-Pd_{13} 6 bonds from the center (c) to vertex (v) are short (2.60 Å) while the other six bonds are 2.71 Å. The first neighbor v to v bonds vary in the range of 2.75–2.85 Å, the latter being slightly longer than the bulk value. Clusters with open atomic shells have some bond lengths significantly smaller than the mean bond length leading to large deviations. In the case of i-Pd_{55}, there is an expansion of the bonds in going from c to v along the 12 *i* directions where the atoms lie on top of each other [center to first shell $(s1)$ 2.63 Å and $s1$ to second shell $(s2)$, 2.65 Å]. The other bond lengths vary in the range of 2.66–2.87 Å. For Pd_{147}, it is, however, oscillatory. The c to $s1$ bond lengths vary between 2.64 and 2.65 Å, and then in the 12 directions, $s1$ to $s2$ slightly shorten to 2.62 Å and then a slight expansion to 2.63–2.64 Å between $s2$ and $s3$. In other directions the bond lengths vary in the range of 2.67–2.88 Å. In both Pd_{55} and Pd_{147}, there is a compression of the inner shell as compared to the calculated bulk nearest neighbor distance of 2.80 Å. A similar behavior was also found[18] in Sr clusters 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 also expose the deeper layers and could lead to the development of magnetic moments. While the development of magnetism in Pd clusters leads to a lowering of the energy and it goes well with the increased bond lengths in the surface region, it occurs at least in the first 3–4 surface layers where the effect of the surface is the maximum. Earlier we[18] suggested a correlation between compressibility and *i* growth in clusters. This is further supported by the present study. Our results show that a small 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. It is to be noted that cobalt clusters with about 1000 atoms are found[25] to have a fcc structure.

Binding energy and magic behavior

The results of the electronic states show that the HOMO-LUMO gap is quite small in all cases (less than 0.23 eV, except for 0.34 eV for Pd_2). Therefore, there may not be strong abundances for certain clusters as continuous aggregation is likely to be favored. Small clusters are very weakly bonded [Fig. 1(b)]. As the size grows, the BE increases monotonically toward the bulk value. In the region of large clusters it shows a nearly linear behavior when extrapolated to the calculated bulk value in the limit $N \rightarrow \infty$. The second order difference in energy shows 4-, 6-, 8-, 10-, 13-, 15-, 18-, 21-, and 22-atom clusters to be magic. This trend is different from the one observed in some other transition metals where a seven-atom cluster is often found to be magic.[1,18] To our knowledge, there is no abundance spectrum of Pd clusters. These results also show that there is no correlation between the magnetic moments and magic behavior of clusters.

B. Adsorption of H and O

As Pd clusters are important catalysts, we also studied the effects of H and O adsorption on magnetism of Pd_6 and Pd_{13}. The structures of all the studied cases are given in Fig. 10, and the results are summarized in Table II. Considering one H on a threefold site of octahedral Pd_6 [Fig. 10(a)], we find that the cluster has a magnetic moment of $1\mu_B$ (increase in the magnetic moment of Pd_6) and the BE of H on Pd_6 is 2.834 eV. H adsorption leads to an increase in the Pd-Pd bond lengths which lie in the range of 2.67–2.80 Å as compared to the values of 2.64–2.67 Å for Pd_6. The Pd-H bond length is 1.76 Å. We also considered interstitial H at the center of the octahedral cluster. The BE is, however, 0.386 eV less as compared to the value at the threefold site. Two H on Pd_6 are favorable on opposite faces [Fig. 10(b)], and the net moment on the cluster is zero. The BE is 2.791 eV per H which is slightly lower than the value for one H on Pd_6. The Pd-H (1.77 Å) and Pd-Pd (2.69–2.81 Å) bond lengths are

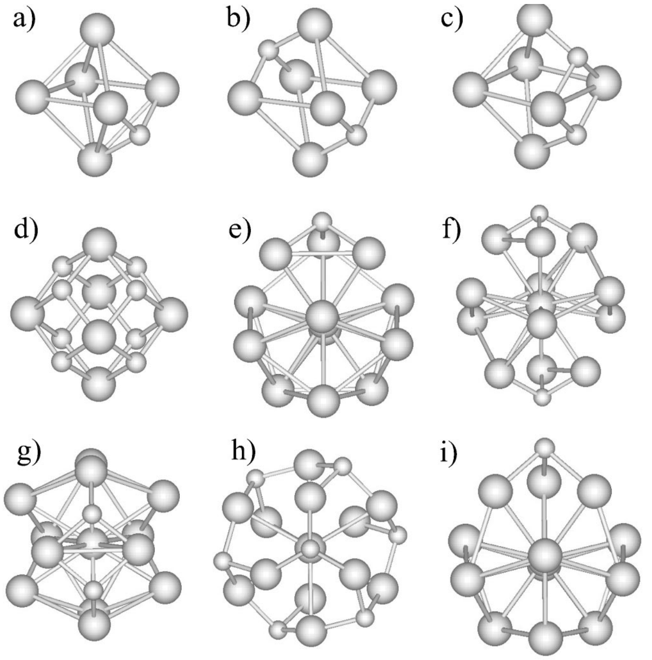

FIG. 10. Structures of H on Pd clusters. (a) H on a threefold site of octahedral Pd_6, (b) 2H on opposite faces of Pd_6, (c) 2H on neighboring faces of Pd_6, (d) 8H covering all the faces of Pd_6, (e) H on threefold site of i-Pd_{13}, (f) 2H on neighboring faces of Pd_{13}, (g) 2H on opposite faces of Pd_{13}, and (h) 8H in a cubic arrangement on Pd_{13} and (i) O on Pd_{13}. Pd-Pd bonds with lengths greater than 2.8 Å are not connected.

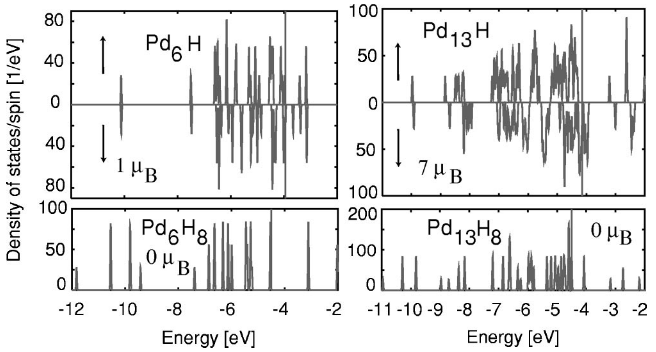

FIG. 11. The total density of states for H on Pd_6 and Pd_{13} clusters.

similar to the case of one H. For the case of two H on neighboring faces [Fig. 10(c)] the BE is 0.071 eV per H lower than in the case of farthest positions. The Pd-H (1.71 and 1.82 Å) and Pd-Pd (2.67–2.83 Å) bond lengths differ slightly. Further calculations on eight H covering all the faces of Pd_6 [Fig. 10(d)] lead to a significant increase in the Pd-Pd bond lengths which have the value of 2.93 Å whereas the Pd-H bond lengths are 1.82 Å. The magnetic moment on the cluster is zero and there is a large HOMO-LUMO gap of 1.427 eV. Therefore, *there is a metal to nonmetal transition in* Pd_6 *induced by H adsorption*. The BE is 2.671 eV per H on Pd_6. Thus an increase in the number of H atoms around Pd clusters generally reduces the BE of H. The densities of states for one and eight H are shown in Fig. 11. A comparison of these results with those shown for pure Pd_6 (Fig. 5) shows that H induces states at around 6 eV below the HOMO. This is similar to the behavior found for H on Pd surfaces.[26] The spectra for Pd_6H_8 has sharper features due to the perfect cubic symmetry, and has a state at even higher binding energy (≈ -11.8 eV).

TABLE II. BE (eV per H) of hydrogen, magnetic moment (μ_B) on the cluster, HOMO-LUMO gap (eV), and the nearest neighbor Pd-Pd and Pd-H bond lengths d in Å. int and nn represent H at the interstitial position and 2H on the neighboring faces, respectively.

Cluster	BE (eV)	M (μ_B)	Gap (eV)	d (Å)
Pd_6H	2.834	1	0.298	1.76, 2.67–2.80
Pd_6H (int)	2.448	1	0.308	1.93, 2.73
Pd_6H_2	2.791	0	0.193	1.77, 2.69–2.81
Pd_6H_2(nn)	2.784	0	0.241	1.71, 1.82, 2.67–2.83
Pd_6H_8	2.671	0	1.427	1.82, 2.93
$Pd_{13}H$	2.974	7	0.092	1.82, 1.83, 2.57–2.92
$Pd_{13}H_2$	2.950	6	0.036	1.77, 1.85, 2.60–2.89
$Pd_{13}H_8$	2.972	0	0.423	1.84, 2.69, 2.82, 2.86
Pd_6O	3.652	4	0.102	2.06, 2.07, 2.64, 2.73
$Pd_{13}O$	4.360	4	0.050	2.02, 2.03, 2.57–2.95

Studies of H adsorption on i-Pd_{13} show that one H on a threefold site [Fig. 10(e)] reduces its 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, which is slightly enhanced as compared to Pd_6. Similar to the case of Pd_6, there is a slight increase in the nearest neighbor Pd-Pd bond lengths in the vicinity of H. The values range between 2.58 and 2.71 Å for center to vertex and 2.74 and 2.92 Å for vertex to vertex as compared to the values of 2.60–2.71 and 2.74–2.86 Å, respectively for Pd_{13}. The up-spin spectrum of $Pd_{13}H$ has a large HOMO-LUMO gap of 1.423 eV similar to Pd_{13}, but for the down-spin electronic spectrum it is very small (Fig. 11). Adsorption on a bridge site is 0.3 eV less favorable. We also considered incorporation of H at a tetrahedral interstitial site. However, upon relaxation H comes out at the threefold site. Adsorption of 2H on neighboring faces of Pd_{13} [Fig. 10(f)] reduces its magnetic moment by $2\mu_B$. The BE is 2.950 eV per H, which is marginally lower than the value for one H. Again there is a large HOMO-LUMO gap of 1.08 eV in the up-spin spectrum, while for the down-spin spectrum it is nearly zero (0.036 eV). Adsorption on two opposite faces [Fig. 10(g)] is less favorable by 0.076 eV. Further calculations on eight H atoms in a cubic arrangement around i-Pd_{13} [Fig. 10(h)] show that the magnetic moment of Pd_{13} is completely quenched. There is a significant HOMO-LUMO gap of 0.423 eV (Fig. 11) leading to a metal to nonmetal transition due to H adsorption. Some states appear at higher binding energies (around -10 and -11 eV) than in i-Pd_{13}. The BE of H is 2.972 eV per H. This is a slight increase as compared to the low coverages and, therefore, this behavior is different from the results obtained for H on Pd_6. The Pd-Pd bond lengths increase slightly. The center to vertex bonds are 2.69 Å as compared to 2.60–2.71 Å for Pd_{13}, which shows both contraction as well as expansion in the

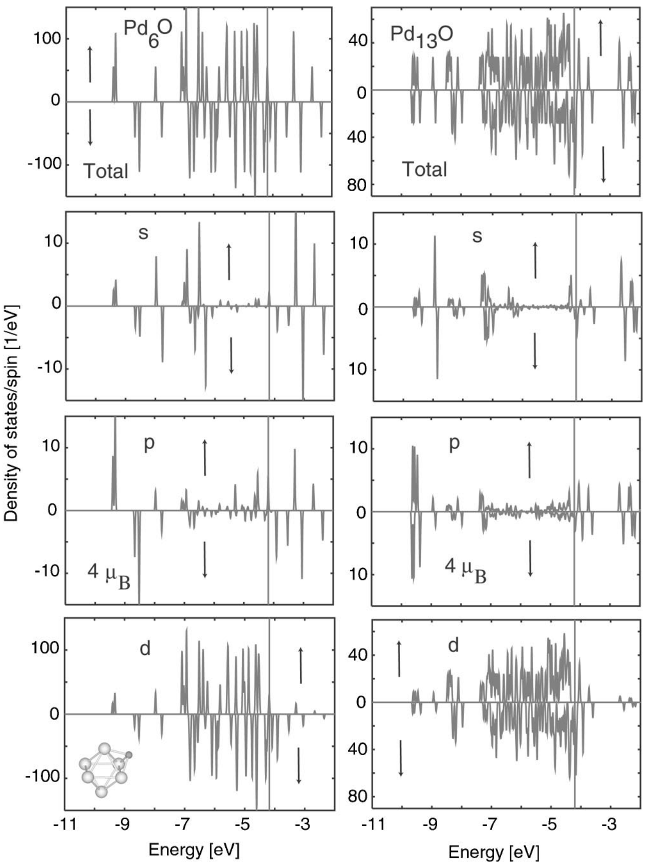

FIG. 12. The total and partial densities of states for oxygen on Pd_6 and Pd_{13} clusters. For Pd_6O, the small atom is O.

bonds. The other Pd-Pd bonds have values of 2.82 and 2.86 Å as compared to 2.74–2.86 Å for Pd_{13}. These results show that in general H adsorption leads to a decrease in the moments of Pd clusters and a slight increase in the Pd-Pd bond lengths. The latter may have important consequences for the H absorption behavior of palladium in the nanoform.

Similarly studies of oxygen adsorption on a threefold site of pd_{13} [Fig. 10(i)] show that O reduces the moment of Pd_{13} by $4\mu_B$. The BE of oxygen is 4.36 eV. The O-Pd bond lengths are 2.02 Å and the center to vertex and vertex to vertex Pd-Pd bond lengths lie in the range of 2.57–2.68 and 2.70–2.95 Å, respectively. As shown in Fig. 12, oxygen-induced states lie at around -9.5 eV. These arise predominantly from interaction between the oxygen p and Pd $4d$ states as one can see from the angular momentum decomposed density of states in Fig. 12. The total charge in these states is 6. However, oxygen is not likely to have a charge transfer of two electrons due to hybridization. In general the states are more distributed as compared to Pd_{13} or $Pd_{13}H$ due to more significant distortions of the cluster. Some of the up-spin d states of Pd get depleted and lie above the HOMO. Adsorption of two oxygen atoms on opposite faces of an icosahedron quenches all the magnetic moments. The BE of the second oxygen is 4.338 eV which is nearly the same as for one oxygen. The HOMO-LUMO gap is quite small, and therefore the character of the particles is metallic.

Oxygen adsorption on threefold site of Pd_6, however, increases the magnetic moment to $4\mu_B$. The structure and the density of states are shown in Fig. 12. The BE of oxygen is 3.652 eV, which is significantly lower than the value for Pd_{13}. The Pd-O bond length is 2.07 Å while the Pd-Pd bond lengths have values of 2.64 and 2.73 Å. The latter are for Pd-Pd bonds near the O atom. The O-Pd interaction is predominantly of p-d type. The exchange splitting is large as compared to the case of $Pd_{13}O$, and the up-spin states are fully occupied with a significant gap of 0.893 eV. Adsorption of two oxygen atoms on opposite faces reduces the magnetic moment to $2\mu_B$. The BE of the second oxygen is 4.043 eV. This shows that there is attractive interaction between the two oxygen atoms. The HOMO-LUMO gap is 0.230 eV.

IV. SUMMARY AND DISCUSSION

In summary, we have presented results of *ab initio* calculations on the growth and magnetic behavior of Pd clusters having up to 147 atoms. We find an icosahedral growth and a ferromagnetic behavior in these clusters. The moments vary in an oscillatory manner as a function of size. The c-Pd_{55} isomer is found to have a significantly lower moment of $10\mu_B$. Therefore, the i symmetry of the atomically closed shell 13-, 55-, and 147-atom clusters leads to higher magnetic moments that decrease slowly with an increase in size. There are local maxima for clusters with atomically closed shells. The magnetic moments are significant at least in the first 3–4 layers near the surface. However, the magnetic energy is small, and even at low temperatures of liquid nitrogen and above, isomers with lower moments will become accessible. While higher magnetic moment isomers are also possible, we find that, for Pd_{55}, the BE decreases more significantly than in the case of the lowering of the moments. The occurrence of several isomers should lead to more than one deflection in the Stern-Gerlach experiments. Our studies clarify the conflicting results obtained from experiments, and suggest that the magnetic behavior of clusters should be better observed much below the liquid nitrogen temperatures. We did not consider the possibility of noncollinear spins. We trust that the effect of this may be small as far as the energetics is concerned. However, this is an aspect that should be considered in future studies of Pd clusters. We also find that H and O adsorption generally reduces the magnetic moments of Pd clusters, and leads to an increase in the Pd-Pd bond lengths. However, both an increase and a decrease in magnetic moments are possible with adsorption. These results show that impurities and reactants on clusters could affect magnetic behavior significantly, and that the expansion in Pd-Pd bond lengths can have important consequences for hydrogen absorption in nanoform of palladium. An interesting result is the H-induced metal-nonmetal transition in Pd clusters. The binding energies for different structures suggest a transition to bulk fcc structure of clusters at a relatively small size as the energy difference for c-Pd_{147} is at most 17 meV/atom as compared to i-Pd_{147}.

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