Giant Magnetic Moments in 4*d* Clusters

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Electronic structure of 13-atom clusters of 4*d* nonmagnetic solids Pd, Rh, and Ru has been studied using a linear combination of atomic orbitals molecular-orbital approach within the density functional formalism. Pd_{13}, Rh_{13}, and Ru_{13} are all found to have nonzero magnetic moments. Unexpectedly, the ground state of Rh_{13} is found to have 21 unpaired electrons and thus a magnetic moment of $21\mu_B$. These 4*d*-element magnetic moments are a result of the reduced dimensionality and the enhanced electronic degeneracy due to the symmetry of the cluster. The effect of impurities on the moments is examined through calculations on $FePd_{12}$, $FeRh_{12}$, $RhPd_{12}$, and $RuPd_{12}$ clusters.

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Although 3*d*, 4*d*, and 5*d* transition metals, all have unfilled localized *d* states, it is only certain 3*d* metals which form magnetic solids. None of the 4*d* or 5*d* solids are magnetic. These elements are, however, characterized by significant spin-orbit coupling and, if they could be made magnetic, they might provide a new class of magnetic materials with enhanced magnetocrystalline anisotropy. That it is indeed possible to magnetize groups of 4*d* atoms was demonstrated by the discovery of giant induced moments in Pd [1]. It was observed [2,3] that 3*d* impurities implanted in Pd induce host spin polarization extending up to the fourth shell of Pd atoms. For Fe impurities, these magnetic domains have a giant moment of around $(10-12)\mu_B$. Theoretical studies [4] have established that surrounding Pd atoms acquire an induced moment with Pd sites closest to Fe having moments of around $0.2\mu_B$ per site. This induced host spin polarization is, however, specific to Pd. Theoretical calculations [5] on *Rh*Fe have yielded zero moments at the Rh sites surrounding the Fe impurities. Recent theoretical calculations predict that the Rh monolayers grown on Fe [6] or Ag [7] substrates may be magnetic.

In this Letter we show that 13-atom gas-phase clusters of 4*d* elements are magnetic as are small clusters of the iron-group elements immediately above them in the periodic table. The individual moments on the atoms in the cluster are aligned (but not locked in a particular spatial direction as in a macroscopic ferromagnet) due to the reduced size of the cluster [8]. Our studies of 13-atom clusters of Pd, Rh, and Ru show that they all have large magnetic moments. The most dramatic is the case of Rh, where our calculations yield a giant moment of $21\mu_B$ for the cluster, which is almost 3 times the $8\mu_B$ moment of the corresponding icosahedral 13-atom nickel cluster [9]. Furthermore, the magnetic moment of the Rh_{13} cluster corresponds to a moment of $1.6\mu_B$ per atom, which is also nearly 3 times that of magnetic moment $0.56\mu_B$ per atom of bulk nickel. These results are particularly remarkable because bulk rhodium is not ferromagnetic while bulk nickel is ferromagnetic. The rhodium cluster has roughly the same magnetic moment per atom as bulk cobalt. These large moments are a result of two unique properties of small clusters, namely, reduced coordination and/or icosahedral symmetry. To examine if these large moments could be further enhanced by introducing Fe impurities as in case of solid Pd, we also present results on 13-atom clusters containing a central Fe surrounded by 12 Pd and Rh atoms. While the Pd sites did acquire a modest increase in moment as the case of solid, no enhancement was found for Rh.

All our studies are based on a linear combination of atomic-orbital and molecular-orbital approach within the density functional formalism. Basically, the molecular orbitals are expanded in a linear combination of atomic orbitals $\phi(r-R_j)$ centered at the atomic sites R_j, i.e.,

$$\psi_i(r)=\sum_j C_{ij}\phi_j(r-R_j)\,, \tag{1}$$

where C_{ij}'s are the variational coefficients obtained by solving the one electron Kohn-Sham equations [10]

$$\left(-\tfrac{1}{2}\nabla^2+V_{\text{ion}}+V_H+V_{\text{xc}}^{\alpha}\right)|\psi_n^{\alpha}\rangle=\epsilon_n^{\alpha}|\psi_n^{\alpha}\rangle\,, \tag{2}$$

where the first term is the kinetic energy operator, V_{ion} is the ionic potential, V_H is the Hartree potential, V_{xc}^{α} is the exchange correlation potential for spin α, and $|\psi_n^{\alpha}\rangle$ is the *n*th molecular orbital.

In this work we have used two different approaches to solve the Kohn-Sham equations. Most of our results are based on the discrete variational method (DVM) [11,12]. Here the basis functions are numerical atomic orbitals obtained by solving the atomic equation on a set of radial points. The secular equation (2) is solved by determining the various matrix elements numerically on a three-dimensional grid of points using the diophatine method. These calculations used the von Barth-Hedin [13] form for the exchange-correlation contributions. We also carried out theoretical calculations on the Rh_{13} cluster using an alternate approach where the basis functions are Gaussian functions centered at the atomic sites. These studies were carried out using two different forms of exchange correlation contributions, proposed by Perdew and Zunger [14] and by Vosko, Wilk, and Nusair [15]. The spin multiplicity of Rh_{13} was found to be the same irrespective of the method or the exchange correlation used. Further, as we will show, the DVM binding energy and bond length are close to those based on Gaussians.

We start by discussing the results based on the DVM method. The numerical orbital basis functions for Pd, Rh, Ru, and Fe were obtained from excited-state atomic calculations on states having the configuration $4d^{9.9}5s^{0.1}$, $4d^{8.9}5s^{0.1}$, $4d^{7}5s^{1}$, and $3d^{6.54}4s^{1.49}4p^{0.01}$, respectively. The Hamiltonian matrix elements were obtained by integrating over a mesh containing about 1000 points per atom. With this number of points per atom, the calculated cluster multiplicities converged. The details of the method have been described in earlier papers [11,12] and we refer the reader to these for details. The orbital basis set for our parallel linear-combination of Gaussian type orbitals (LCGTO) calculations on Rh_{13} is a $17s/11p/8d$ basis [16] augmented with a p exponent [17] of 0.81 bohr^{-2}. The orbital basis set was contracted to 4,5/3, 3/1,4, where for each angular momentum the number of contracted atomic functions and uncontracted diffuse Gaussians are separated by a comma. Their contraction coefficients were determined from the same-orbitals-for-different-spins fractional-occupation-number [18] (FON) ground-state configuration, $5s_{\uparrow}^{0.513}4d_{\uparrow}^{5.000}4d_{\downarrow}^{3.497}$. The binding energy is referenced to a completely unrestricted FON LCGTO calculation with ground-state configuration $5s_{\uparrow}^{0.493}4d_{\uparrow}^{5.000}4d_{\downarrow}^{3.507}$. The $17s$ functions were scaled by 2 and $\frac{2}{3}$ to generate the spherically symmetric parts of the charge density and exchange-correlation auxiliary fitting bases, respectively [19]. To fit angular variations around each atom, $5p$ and $5d$ fitting exponents were used with exponents 0.04, 0.2, 0.6, 2.0, and 10.0 bohr^{-2}. The bond-centered functions with exponents 1.0 and 0.33 bohr^{-2} were also included in the charge density and exchange-correlation basis, respectively.

As mentioned above, we have carried out calculations on pure Pd_{13}, Rh_{13}, and Ru_{13} clusters, and on $FePd_{12}$ and $FeRh_{12}$ obtained by replacing the central atom in pure 13-atom clusters by Fe. For each cluster the geometry was optimized by carrying out calculations on octehedrally and icosahedrally symmetric arrangements and allowing radial relaxation to minimize the energy. The magnetic moment at a given site was determined by integrating the projected local density of states. Again we refer the reader to our earlier paper [12] for details.

TABLE I. Magnetic moment (μ_B) at the central and outer sites of cuboctahedral and icosahedral 13-atom clusters of Pd, Rh, and Ru.

Cluster	Geometry	Radial dist. (a.u.)	$E_{\rm bin}$ (eV)	Moments Central	Outer
Pd_{13}	Cubo	5.20	19.8	0.0	0.0
	Icos	5.12	20.3	0.43	0.12
Rh_{13}	Cubo	4.90	41.3	1.54	1.45
	Icos	4.84	42.6	1.58	1.62
Ru_{13}	Cubo	4.86	55.5	−0.28	1.19
	Icos	4.81	56.0	−0.29	1.02

In Table I we give our calculated equilibrium DVM spacings, cluster binding energy, and the magnetic moments at the central and outer atoms in 13-atom Pd, Rh, and Ru clusters in icosahedral and octahedral geometries. In all cases we find that the icosahedral clusters are more stable than the fcc octahedral clusters. For Pd, this is consistent with the experimental indications [20] that small Pd clusters are icosahedral. We also find that there is a small contraction in the interparticle distance compared to the bulk interparticle distance. This is also consistent with results obtained in most metallic clusters [21] where one obtains a contraction in interparticle distance compared to the bulk. For Pd_{13}, Rh_{13}, and Ru_{13} we find a binding energy per atom of 1.56, 3.27, and 4.31 eV, respectively compared to the corresponding bulk cohesive energies of 3.89, 5.75, and 6.74 eV. These calculations used 0.05 eV Lorentzian broadening to determine the occupation number near the Fermi energy. As mentioned before, we have also carried out LCGTO calculations on Rh_{13} to ensure that the results are independent of the basis set. We found that the FON (equivalent to setting the broadening parameter to zero) LCGTO binding energy per atom in Rh_{13} is 4.66 eV, somewhat larger than but consistent with corresponding DVM binding energy. The LCGTO Rh_{13} electronic configuration is $a_{g\uparrow}^{14}a_{g\downarrow}^{14}$, $t_{1g\uparrow}^{15}t_{1g\downarrow}^{12}$, $t_{1u\uparrow}^{54}t_{1u\downarrow}^{51.25}$, $h_{g\uparrow}^{90}h_{g\downarrow}^{85}$, $h_{u\uparrow}^{35}h_{u\downarrow}^{30}$, $t_{2g\uparrow}^{6}t_{2g\downarrow}^{3}$, $g_{g\uparrow}^{28}g_{g\downarrow}^{28}$, $t_{2u\uparrow}^{33}t_{2u\downarrow}^{33}$, $g_{u\uparrow}^{28}g_{u\downarrow}^{25.75}$ which corresponds to a spin multiplicity of 22 and is identical to that obtained in the DVM calculation. The LCGTO radial bond distance of 4.9 bohr is again almost identical to the DVM bond distance of 4.84 a.u. (Table I).

Our results on the magnetic moment are most fascinating. We find that Pd_{13}, Rh_{13}, and Ru_{13} all have nonzero magnetic moments unlike the bulk which are nonmagnetic. For Pd_{13} we obtain a small moment of $0.12\mu_B$/atom. The experiments [22] on Pd clusters containing 100–120 atoms, however, find them to be nonmagnetic (within $\pm 0.014\mu_B$). This indicates that the moment in Pd quickly decays as the cluster size is increased. As opposed to Pd, the Rh clusters have a large magnetic moment of $1.62\mu_B$ per atom for the surface atoms. In Ru clusters, while the moment on the central atom is aligned antiferromagnetically to the outer atoms and has a value of only $-0.29\mu_B$, the outer atoms have a large moment of $1.02\mu_B$. A similar antialignment occurs for iron, the element immediately above Ru in the periodic table. The antialignment in Fe_{13} can directly be seen by comparing the moments of icosahedral Fe_{12} and Fe_{13} clusters [23].

The highest moment is thus obtained for Rh clusters. This moment is even larger than the moment of $0.6\mu_B$ per atom in bulk Ni, and is comparable to the bulk moment of $1.6\mu_B$ in Co. To understand the origin of this giant moment we show in Fig. 1 the density of electronic states (DOS) in an icosahedral Rh_{13} cluster obtained by broadening each electronic level by a Lorentzian of width 0.05 eV. Our corresponding DOS for unpolarized Rh_{13} show that the Fermi energy lies in a sharp peak and the cluster has a very high density of states at the Fermi energy. This is different from the bulk [24] where the Fermi energy lies in a dip of the density of states. There are two factors which contribute to this high DOS at the Fermi energy. First the DOS in the cluster is marked by sharp peaks characteristic of the enhanced degeneracy due to the icosahedral symmetry of the clusters [25]. Second the band is narrowed compared to the bulk due to the preponderance of surface atoms with reduced coordination [26] (the cluster has a bandwidth of around 4.5 eV compared to a bulk value of around 7.0 eV). Both these factors lead to an enhancement of the DOS at the Fermi energy and the cluster acquires a large multiplicity and a consequent magnetic moment of $21\mu_B$. Figure 1 also shows that the exchange splitting in the cluster is around 0.9 eV.

As mentioned before [2,3], experiments have shown that Fe impurities in bulk Pd induce host polarization through an exchange enhancement of the host due to the magnetic impurity. To explore if such an effect would persist in clusters and if the moments of the pure cluster would be further increased via such an effect, we carried out calculations on 13-atom octahedral and icosahedral clusters consisting of a central Fe surrounded by 12 Pd or 13 Rh atoms. The results are given in Table II. In all cases, the icosahedral clusters are more stable than the octahedral clusters. We start by discussing our results on the $FePd_{12}$ cluster in Table II. The introduction of Fe increases the moments at the outer Pd atoms from $0.12\mu_B$ in Pd_{13} to $0.23\mu_B$. This Pd moment is comparable to the moments at the Pd sites surrounding the Fe impurity in bulk [4] Pd which are estimated to be around $(0.2\text{–}0.4)\mu_B$. From the density of states at the Pd sites in Pd_{13} and in $FePd_{12}$ we found that the introduction of Fe increases the exchange splitting at the Pd site from around 0.08 eV in Pd_{13} to 0.15 eV in $FePd_{12}$ indicating that the increase in moment is due to exchange enhancement. The situation is, however, different for Rh where the introduction of Fe slightly reduces the moment. We found that the Fe sites in $FeRh_{12}$ gain around $1e$. The charge transfer moves the Fermi energy from the high peak and reduces the DOS at the Fermi energy.

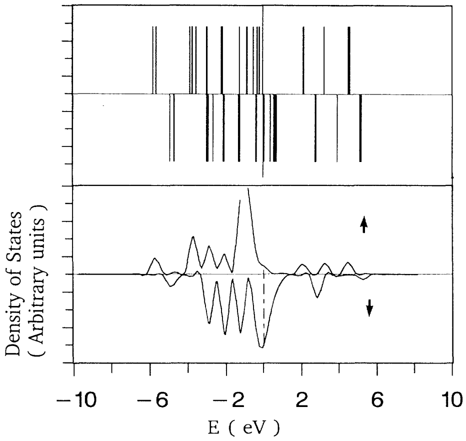

FIG. 1. One-electron levels and the corresponding spin density of states (obtained by broadening each level by a Lorentzian of half-width 0.05 eV) in an icosahedral Rh_{13} cluster.

It is important to note that while bulk $4d$ elements are nonmagnetic, the $4d$ atoms have nonzero spin multiplicities. Further, as we have shown above, clusters of $4d$ elements are magnetic. The question then arises whether the exchange enhancement in Pd can also be brought about by introducing atoms of $4d$ elements instead of Fe. To investigate whether this is indeed possible, we also present results on 13-atom clusters containing a central Rh or Ru surrounded by 12 Pd atoms. These results are given in Table II. We note that the Pd sites in $RhPd_{12}$ and $RuPd_{12}$ have moments of $0.24\mu_B$ identical to the case of $FePd_{12}$. An analysis of the DOS in these clusters shows Pd bands split by 0.15 eV which is the same as in the case of $FePd_{12}$. Further the Rh and Ru sites in these clusters have moments of $1.59\mu_B$ and $2.96\mu_B$, respectively. These results again show that Rh or Ru behave like ferromagnetic $3d$ elements at small sizes. We believe that this result may hold a potential clue to the recent observation [27] of induced moments around Rh impurities in bulk Pd. Note from Table II that the moment at the Pd sites in the cuboctahedral clusters is larger for Fe than for Rh. Since the bulk Pd is fcc, one expects smaller moments around Rh impurities in Pd than in the case of Fe. This is in agreement with the above experiments which predict induced moments of $(5\text{–}7)\mu_B$ around Rh sites, compared to moments of $(10\text{–}12)\mu_B$ around Fe sites.

TABLE II. Magnetic moments (μ_B) at the central and outer sites of 13-atom cuboctahedral and icosahedral clusters containing a central impurity surrounded by 12 Pd or 12 Rh atoms.

Cluster	Geometry	Radial Dist. (a.u.)	E_{bin} (eV)	Moments Central	Outer
Fe_1Pd_{12}	Cubo	5.11	24.3	3.99	0.33
	Icos	5.02	25.8	3.91	0.23
Fe_1Rh_{12}	Cubo	4.84	45.0	3.62	1.36
	Icos	4.79	45.8	3.64	1.46
Rh_1Pd_{12}	Cubo	5.20	21.2	1.45	0.26
	Icos	5.15	22.7	1.59	0.24
Ru_1Pd_{12}	Cubo	5.20	22.8	2.97	0.42
	Icos	5.15	24.0	2.96	0.25

To sum up, we have shown that small $4d$ clusters have nonzero magnetic moments. Most remarkably, the Rh_{13} cluster has moment per atom which is larger than even bulk Ni. The $4d$ atoms have a large spin-orbit coupling and their orbital moments are quenched in the solid. The situation in clusters is, however, unclear, but one expects these clusters to behave differently from the clusters of ferromagnetic materials [8] which exhibit superparamagnetism. Further, Rh is known to be an important catalyst and one wonders if these small clusters may have catalytic applications. We have also shown that $4d$ atoms produce the same effect as Fe when surrounded by Pd, thus confirming that in small clusters the $4d$ elements are magnetic.

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Note added.—Stimulated by these predictions, Bloomfield and co-workers [28] have experimented with Rh_n clusters in the 13-atom size range. They find significant magnetic moments.

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