Magnetism in 4*d*-transition metal clusters

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We present the results of a study of magnetism in rhodium, ruthenium, and palladium clusters. We report values for the magnetic moments of rhodium clusters which are free from a systematic error present in our previous measurements [Phys. Rev. Lett. **71**, 923 (1993)] and show that their magnetic moments decrease to the bulk value of zero as the cluster sizes increase. Ruthenium and palladium clusters are nonmagnetic.

Recent calculations have predicted magnetic ordering in low-dimensional systems of normally nonmagnetic materials.[1] In both clusters of atoms and monolayer films, the reduced coordination number and higher symmetry is expected to narrow the electronic bands, enhancing magnetization in already ferromagnetic materials and causing magnetization in nonmagnetic materials.[1,2] Clusters of bulk 3*d*-ferromagnetic metals do exhibit this enhanced magnetization, with magnetic moments per atom that are larger in clusters than they are in the bulk.[3–5] It has thus seemed likely that magnetic order would be found in low-dimensional systems of the appropriate nonmagnetic materials; perhaps in the nonmagnetic transition metals.

However, clusters of the nonferromagnetic 3*d*-transition metals vanadium and chromium do not exhibit ferromagnetic ordering.[6] There are also conflicting reports on whether vanadium monolayer films are ferromagnetic.[7–9] Several calculations predict ferromagnetism in 4*d* (ruthenium, rhodium, and palladium) and even 5*d*-transition metal monolayers grown epitaxially on magnetically inert substrates such as silver or gold.[10–12] However, experiments with rhodium and palladium films on gold and silver did not show the predicted magnetic ordering.[8,9] On the other hand, some 4*d*-transition metals on ferromagnetic substrates exhibit magnetic ordering. This magnetism is primarily a result of interactions between the ordered *d* bands of the ferromagnetic substrate and the 4*d* electrons of the monolayer. Rhodium monolayers on an iron substrate have a measured magnetic moment of $0.82\mu_B$ per rhodium atom.[13]

The situation changed when we found giant magnetic moments in rhodium clusters.[14] Rhodium is nonmagnetic in the bulk but is one of three nonferromagnetic 4*d*-transition metals, ruthenium, rhodium, and palladium, that were predicted to form magnetic clusters.[15,16] Our study of the magnetic moments in rhodium clusters of between 12 and 32 atoms observe magnetic ordering in a material which is nonmagnetic in the bulk. However, our report was preliminary and did not include ruthenium or palladium clusters. In this paper, we present a more extensive study of magnetism in the 4*d*-transition-metal clusters, along with values for the magnetic moments per atom in rhodium clusters. These values are free from a systematic error present in our previous results.[14]

Before presenting our results, we first review the predictions of magnetism in 4*d*-transition-metal clusters. Galicia used a molecular orbital approach to predict magnetism in a 13-atom rhodium cluster.[15] This calculation assumed the bulk crystal structure, fcc, and the bulk interatomic spacing for the 13-atom cluster. Thus, the calculation was performed on a 13-atom fragment of bulk rhodium rather than on a 13-atom cluster, which might have a different structure and interatomic spacing. Nevertheless, Galicia's spin-polarized calculations predicted that Rh_{13} has a moment of $13\mu_B$, or $1\mu_B$ per atom. However, Galicia noted that the method he used tends to overestimate magnetism.

Reddy, Khanna, and Dunlap, recently calculated the magnetic moments per atom for ruthenium, rhodium, and palladium 13-atom clusters with icosahedral and cubo-octahedral symmetry.[16] They predicted moments of $1.6\mu_B$ per atom for icosahedral Rh_{13}, $1.02\mu_B$ per atom for icosahedral Ru_{13}, and $0.12\mu_B$ per atom for icosahedral Pd_{13}. In these calculations, the equilibrium interatomic spacing was determined by minimizing the total energy via a variational method. However, the overall symmetry of the clusters, either icosahedral or cubo-octahedral, was maintained throughout each variational calculation. In all cases, the calculated binding energy was greater for the icosahedral structure than for the cubo-octahedral, so an icosahedron was assumed to be the ground state.

Reddy, Khanna, and Dunlap also calculated the magnetic moment for an fcc Rh_{13} cluster and found it to be $1.46\mu_B$ per atom, as compared to Galicia's $1\mu_B$ per atom. Since the equilibrium spacing in Galicia's 13-atom cluster is the bulk equilibrium spacing and larger than the spacing calculated by Reddy, Khanna, and Dunlap, it is surprising that Galicia predicts a smaller moment. This discrepancy reflects differences in the calculated energy shift between the majority and minority spin bands. Reddy, Khanna, and Dunlap calculated an exchange-induced energy shift of 0.9 eV while Galicia found one of only 0.6 eV. However, both calculations found that the spin density of states is large enough at the Fermi energy for the shift to lead to nonzero magnetic moments in 13-atom 4*d*-transition-metal clusters.

Our experimental apparatus is described in detail elsewhere.[4] Briefly, the experiment is a variation on

the classic Stern-Gerlach experiment, applied to clusters rather than individual atoms. Metal clusters, produced in a laser vaporization cluster source, leave the source in a supersonic expansion of helium gas and form a cluster beam. These clusters pass through a series of collimating slits and a rotating beam chopper before entering the gradient field magnet of the Stern-Gerlach experiment.

The beam chopper allows us to determine the cluster beam's velocity and to measure how long the clusters resided inside the source's growth region before entering the beam. Only after long residence in the source do the clusters come into thermal equilibrium with the source. By selecting only these later, equilibrated clusters, we are able to control their temperatures. We can adjust the temperature of our entire source with a cryorefrigerator and can thus control cluster temperatures over a range of about 60 to 380 K. This temperature control is essential to our interpretation of the data.

As they pass through the gradient magnet, magnetic clusters experience transverse forces and begin to deflect. This deflection continues until the clusters reach the ionization and detection region. There the clusters are photoionized by a narrowly collimated excimer laser beam and identified in a time-of-flight mass spectrometer. The ionizing laser beam is carefully scanned across the cluster beam profile to determine the extent to which the clusters were deflected by the magnetic field.

As reported previously, rhodium clusters do experience small, nonzero deflections in a gradient field.[14] The clusters all deflect in the direction of the high field and the peak profiles are narrow like those of the ferromagnetic $3d$-transition-metal clusters. The narrow peak profiles and uniform, homogeneous deflections to the high field side are characteristic of superparamagnetic behavior, the same behavior found in the ferromagnetic $3d$-transition-metal clusters.[17,4]

A superparamagnetic cluster has a single, large magnetic moment but one that is essentially free of the cluster's lattice. This orientational freedom allows the moment to align with an external magnetic field. However, thermal fluctuations prevent the magnetic moment from fully aligning with the external field for any length of time. Over a typical experimental time period, the magnetic moment explores the entire Boltzmann distribution of possible projections onto any external field. As a result, the effective magnetic moment per atom μ_{eff} is reduced from the internal magnetic moment per atom μ by the Langevin function:

$$\mu_{\text{eff}} = \mu \left[\coth\left(\frac{N\mu B}{kT}\right) - \frac{kT}{N\mu B} \right], \qquad (1)$$

where N is the number of atoms in the cluster, B is the magnetic field, and T is the temperature. It is this μ_{eff} that corresponds to the experimentally measured magnetic moment per atom, μ_{expt}.

In order to use Eq. (1) to obtain a cluster's internal magnetic moment per atom from its experimental moment per atom, the cluster's internal temperature must be known with considerable accuracy. As noted above, we use only those clusters that have remained inside the source long enough to come into thermal equilibrium with the source, so that their internal temperatures are those of the source. To be sure that we have waited long enough, we study the evolution of cluster magnetic behavior as a function of increasing residence time in the source until no further changes occur. While this technique has been the basis for controversy in the past, de Heer, the principal scientist discounting its validity,[18] has now implicitly conceded that our technique is valid by making extensive use of it himself.[5]

When $N\mu B/kT \ll 1$, Eq. (1) is accurately approximated by $\mu_{\text{eff}} \approx \frac{N\mu^2 B}{3kT}$. Thus, if μ does not change with N, B, or T, a plot of μ_{expt} versus $\frac{NB}{T}$ yields a straight line with a slope of $\frac{\mu^2}{3k}$. In the $3d$-transition metals, μ is relatively independent of N, B, and T.[4] Only at $N > 200$ does μ begin to decrease in iron clusters.[5,19]

However, in rhodium, μ depends strongly on the cluster size. We must therefore determine μ independently for each cluster. To do this, we plot μ_{expt} versus $\frac{NB}{T}$ for each cluster, obtaining in each case a straight line with a slope of $\frac{\mu^2}{3k}$. Over temperatures ranging from 60 to 300 K and external magnetic fields of up to 1.2 T, we see no deviations from the linear dependence of μ_{expt} on $\frac{NB}{T}$, characteristic of superparamagnetic behavior. Values of μ for Rh_n ($n = 9$ to 34) appear in Table I.

The values of μ listed in Table I are somewhat smaller than we originally report.[14] This discrepancy is due to an unanticipated and undetected systematic error in our original measurements. At the very high magnetic fields needed to observe appreciable deflections in the heavy

TABLE I. Magnetic moments per atom for Rh_9–Rh_{34}.

Cluster	μ/atom
Rh_9	$0.8\,\mu_B \pm 0.2\mu_B$
Rh_{10}	$0.8\,\mu_B \pm 0.2\mu_B$
Rh_{11}	$0.8\,\mu_B \pm 0.2\mu_B$
Rh_{12}	$0.59\mu_B \pm 0.12\mu_B$
Rh_{13}	$0.48\mu_B \pm 0.13\mu_B$
Rh_{14}	$0.50\mu_B \pm 0.12\mu_B$
Rh_{15}	$0.71\mu_B \pm 0.09\mu_B$
Rh_{16}	$0.64\mu_B \pm 0.10\mu_B$
Rh_{17}	$0.39\mu_B \pm 0.12\mu_B$
Rh_{18}	$0.35\mu_B \pm 0.12\mu_B$
Rh_{19}	$0.61\mu_B \pm 0.08\mu_B$
Rh_{20}	$0.16\mu_B \pm 0.16\mu_B$
Rh_{21}	$0.19\mu_B \pm 0.16\mu_B$
Rh_{22}	$0.27\mu_B \pm 0.14\mu_B$
Rh_{23}	$0.13\mu_B \pm 0.13\mu_B$
Rh_{24}	$0.15\mu_B \pm 0.15\mu_B$
Rh_{25}	$0.15\mu_B \pm 0.15\mu_B$
Rh_{26}	$0.25\mu_B \pm 0.12\mu_B$
Rh_{27}	$0.20\mu_B \pm 0.13\mu_B$
Rh_{28}	$0.10\mu_B \pm 0.14\mu_B$
Rh_{29}	$0.11\mu_B \pm 0.13\mu_B$
Rh_{30}	$0.13\mu_B \pm 0.14\mu_B$
Rh_{31}	$0.14\mu_B \pm 0.14\mu_B$
Rh_{32}	$0.15\mu_B \pm 0.13\mu_B$
Rh_{33}	$0.15\mu_B \pm 0.13\mu_B$
Rh_{34}	$0.16\mu_B \pm 0.13\mu_B$

rhodium clusters, our gradient magnet deformed approximately 25 microns toward a strong field, taking a collimating slit with it. This motion caused an apparent increase in each cluster's deflection and was incorporated in our earlier values for μ. We have since eliminated this magnet deformation and have repeated the measurements with much higher precision. While we are embarrassed at having missed this systematic error, we are relieved to report that rhodium clusters are still magnetic. These numbers lie about 2 error bars below our original values.

The size dependence of rhodium clusters' magnetic moments per atom is not so surprising. Since the magnetic moment must eventually diminish to the bulk value of zero with increasing cluster size, a decrease in moment with increasing size is expected. However, rhodium reaches the bulk value of its magnetic moment per atom at much smaller cluster sizes than do the $3d$-transition metals.[4,5] Rhodium clusters of more than about 60 atoms do not deflect enough for us to be certain that their moments are nonzero (Fig. 1).

In addition to this overall decrease in μ with increasing size, some rhodium clusters exhibit anomalously large values of μ (see Fig. 2 or Table I). In particular, Rh_{15}, Rh_{16}, and Rh_{19} appear to be unusually magnetic. The extraordinary size dependence of μ in rhodium clusters indicates that cluster structure itself is important in the enhancement of the magnetic moment. Such structural dependence is apparently absent in the $3d$-transition metals, where all clusters exhibit essentially the same value of μ.

It is natural to wonder whether the anomalously magnetic clusters have easily identifiable crystal structures. Unfortunately, the mass spectrum itself gives no information on the cluster structure. In many materials, structure in the abundance spectrum of the clusters can be used to infer structural information about the clusters. However, the mass spectrum of rhodium is essentially featureless, with no cluster significantly more abundant than any other. Thus the dependence of the magnetic behavior on cluster size offers some valuable assistance in identifying cluster structures. For example, Khanna has performed some preliminary calculations of magnetic

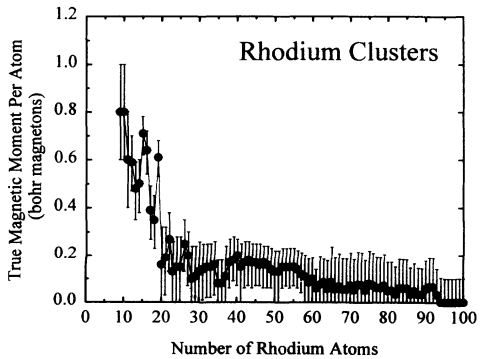

FIG. 1. Rhodium cluster magnetic moments per atom decrease with cluster size and are approximately zero, the bulk value, for $n \geq 60$.

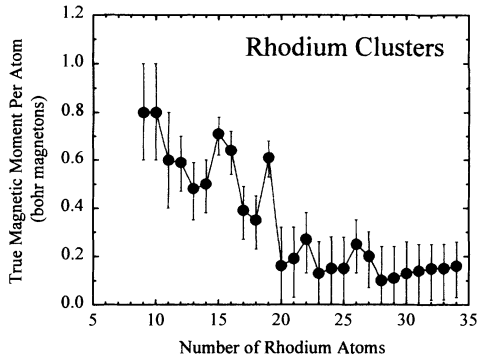

FIG. 2. Rhodium cluster magnetic moments per atom. Rh_{15}, Rh_{16}, and Rh_{19} exhibit anomalously large magnetic moments per atom.

moments in two possible configurations of the 15-atom rhodium cluster. He finds that Rh_{15} with a bcc structure should be nonmagnetic while Rh_{15} that is an icosahedron with two extra atoms should be quite magnetic.[20] Clearly, the dressed icosahedron is the more likely structure for the actual Rh_{15} clusters. It is also worth noting that the magnetic interactions within the clusters are strong enough to affect the clusters' spatial structures.

We find that Rh_{13} has a μ of $0.47 \pm 0.1\mu_B$ per atom, significantly smaller than the values of $1.6\mu_B$ per atom and $1\mu_B$ per atom calculated by Reddy, Khanna, and Dunlap[16] and Galicia,[15] respectively. However, by restricting their calculations to icosahedral and cuboctaheral symmetries, Reddy, Khanna, and Dunlap may have missed a less symmetric ground state that is also less magnetic than the pure icosahedron. Since they reduce degeneracies, slight distortions of the icosahedron will broaden the electronic bands and should reduce the cluster's magnetic moment.

We find that ruthenium and palladium clusters of from 12 to more than 100 atoms are nonmagnetic. The measured magnetic moments μ_{expt} were $0.000 \pm 0.004\mu_B$ per atom for ruthenium clusters and $0.000 \pm 0.005\mu_B$ per atom for palladium clusters in an applied magnetic field of 1.034 T. The clusters studied had remained in the source long enough that they should have reached thermal equilibrium with it. If these clusters were magnetic, it is very likely that they would exhibit superparamagnetism. In that case, their internal magnetic moments per atom μ are much larger than the experimentally observed value μ_{expt}. From μ_{expt}, we use Eq. (1) to calculate limits on the values of μ and list them in Table II. Pd_{13} has a magnetic moment of no more than $0.40\mu_B$/atom and Ru_{13} has a moment of no more than

TABLE II. Magnetic moments per atom for palladium and ruthenium clusters.

Clusters	T_{source}	μ_{expt}/atom	μ/atom
Pd_{13-105}	98 K	$0.000 \pm 0.005\mu_B$	$Pd_{13} < 0.40\mu_B$
			$Pd_{105} < 0.13\mu_B$
Ru_{10-115}	63 K	$0.000 \pm 0.004\mu_B$	$Ru_{10} < 0.32\mu_B$
			$Ru_{115} < 0.09\mu_B$

$0.29\mu_B$/atom. The predicted values of μ are $0.12\mu_B$ per atom and $1.02\mu_B$ per atom, respectively. While the predicted value of μ for Pd_{13} is too small for us to distinguish from zero, the predicted μ for Ru_{13} is outside our experimental uncertainty.

Although ruthenium and palladium clusters are not ferromagnetic, the rhodium results confirm the predictions of magnetic ordering in clusters of normally nonferromagnetic materials. The predictions of $1\mu_B$ and $1.6\mu_B$ per atom for Rh_{13} are higher than the observed value of $0.47\mu_B$ per atom. The varying magnetic moment as a function of cluster size should aid in determining the spatial structures of these clusters. We also observe that rhodium clusters gradually become less magnetic as their sizes increase and that they are nonmagnetic above about 60 atoms.

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