Experimental Observation of Magnetism in Rhodium Clusters

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We have observed giant magnetic moments in clusters of rhodium, Rh_n ($n = 12$–32), consistent with ferromagnetic ordering of the $4d$ electrons. Ferromagnetic behavior has not been reported previously in pure $4d$ transition metals. Rhodium clusters are superparamagnetic at 93 K, with magnetic moments of between 0.3 and $1.1\mu_B$ per atom. We find that Rh_{15}, Rh_{16}, and Rh_{19} have magnetic moments per atom that are significantly larger than those of adjacent cluster sizes.

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Recent experiments have failed to demonstrate magnetic ordering in clusters of normally nonmagnetic elements. While clusters of the bulk ferromagnets Fe, Co, Ni, Gd, Tb, and Dy were shown to be ferromagnetic or otherwise magnetically ordered [1–8], similar studies of the bulk nonferromagnets Al, Pd, V, and Cr did not find any magnetically ordered clusters [9,10]. Ferromagnetic ordering has been expected in clusters of nonferromagnetic materials because of their reduced dimensionality and high degree of symmetry [11,12]. These attributes narrow the widths of the electronic bands and offer the possibility of large spin multiplicities in the electronic ground states. But in spite of these predictions, no magnetic order was observed.

Similarly, ferromagnetic ordering of $4d$ and $5d$ transition metals is not seen in the bulk. Only a few of the $3d$ transition metals form magnetic solids. Pd is very close to the Stoner criterion for ferromagnetic ordering but remains only paramagnetic [13]. While they do not order spontaneously, $4d$ electrons in Pd can be oriented by the inclusion of dilute magnetic impurities such as Co and Fe and form giant induced moments [14–20]. Studies have shown that Fe impurities can induce local spin polarization in a Pd lattice with an extent of about 5 nm [18]. These giant induced moments are not found in other $4d$ metals, such as Rh. Ferromagnetic order has been seen in Rh monolayers on Fe [21] and is predicted theoretically in $3d$, $4d$, and $5d$ transition metal monolayers on noble metals [22].

In a recent paper, Reddy, Khanna, and Dunlap proposed an alternate mechanism for making $4d$ elements magnetic [23]. Using *ab initio* density functional theory, they proposed that thirteen atom clusters of Rh will be strongly magnetic because of the reduced coordination and the high symmetry. To explore such a possibility, we have carried out experimental studies on Rh_n ($n = 12$–32). We find that these clusters have giant magnetic moments of between 0.3 and 1.1 bohr magnetons per atom at 93 K. This is the first case where a nonmagnetic solid has been shown to be magnetic as a cluster. This is also the first case where a $4d$ or $5d$ element shows spontaneous magnetic order.

We have determined the magnetic moments of Rh clusters by measuring their deflection following passage through a gradient magnetic field. The experimental technique has been described previously [3–8,24], but is summarized briefly in the following paragraphs.

Clusters are formed by laser vaporization of a rhodium sample disk inside the cluster source. The second harmonic output of a pulsed Nd:YAG laser is focused onto the sample and creates a plume of metal vapor. This metal vapor is entrained and cooled by a pulse of helium carrier gas that is introduced into the enclosed volume above the sample disk just before the laser pulse. Clusters form and grow in this growth chamber, giving up heat to the surrounding gas and the walls of the chamber. The mixture of clusters and helium slowly bleeds out of the growth chamber through a conical nozzle and undergoes a supersonic free-jet expansion to form a molecular beam.

Clusters with long residence times in the growth chamber stop growing and come into thermal equilibrium with the source before they leave. We determine when equilibrium occurs by carefully following the clusters' magnetic properties with increasing residence time [4–6]. Once equilibrium has been reached, after approximately 1 ms, further increases in residence time have no effect on the magnetic behaviors of the clusters. This arrival at equilibrium is also accompanied by a virtual disappearance of metal atoms and very small clusters, indicating that cluster growth has ceased. Our temperature results are similar to results obtained in flow tube experiments, where laser-produced clusters carried in helium gas are found to come into thermal equilibrium with a narrow flow tube only if the tube is quite long, typically 5 cm or more [25,26].

To produce a cluster beam, the mixture of clusters and helium gas must undergo a supersonic, free-jet expansion into the vacuum. While this expansion produces a dramatic drop in the translational temperatures of the mixture, it has little effect on the vibrational temperatures of the clusters. Strong supersonic expansions of small organic molecules seeded in helium gas have been shown to be only moderately effective at cooling the vibrational temperatures of those molecules [27]. Large clusters of heavy metal atoms are thus unlikely to experience sig-

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nificant cooling in a helium expansion. Recently, weak supersonic expansions of small Nb clusters seeded in helium have been found to leave the clusters' vibrational temperatures unchanged [26].

We find that the weak free-jet expansion in our source has no measurable effect on the cluster vibrational temperatures [4–6]. As long as we use clusters that have reached thermal equilibrium with the source before they undergo free-jet expansion, the specific expansion conditions have no effect on the cluster magnetic properties. While there has been some controversy concerning this observation in the past [28], we have performed extensive experimental tests which indicate that clusters in our molecular beam have vibrational temperatures no colder than the source in which they formed [6,29]. In these experiments, we attempted to attach Ar and Xe atoms to the metal clusters during the supersonic expansion. Despite extensive variations in temperatures and expansion conditions, we were unable to detect any adsorption of rare gas atoms to the clusters. It is thus very unlikely that the clusters ever reach vibrational temperatures below the temperature of the source because the rare gas atoms adsorb preferentially to the source and not to the clusters.

All measurements reported in the present work were done on Rh clusters that were in thermal equilibrium with the source. The source itself is attached to a helium refrigerator and can be cooled to 93 K to produce clusters with that vibrational temperature.

Clusters leaving the source pass through a molecular beam skimmer and two 0.4 mm wide vertical slits, 851 mm apart. The second slit is 2.5 mm high. This narrow beam, 0.4 mm wide by 2.5 mm high, is chopped longitudinally by a rapidly rotating chopper disk, forming a packet several cm long.

The packet passes through a gradient field magnet with a quadrant of a quadrupole geometry and a peak magnetic field of between 0 and 1.5 T. A magnetic cluster experiences a transverse force as it passes through this magnet and it is deflected in the drift region following the magnet.

A narrow beam from a 193 nm ArF excimer laser ionizes the clusters as they fly through the source region of a time-of-flight mass spectrometer. The deflection profile for each cluster size is determined by scanning the narrow ionizing laser beam across the cluster beam and recording the mass spectrum found at each spatial location. Clusters that deflect can be found at locations other than on the beam axis.

All of the rhodium clusters are seen to deflect toward the strong field, the same behavior that was observed in Fe, Co, and Ni clusters [2–7]. Each cluster profile is merely shifted over, not broadened, indicating that the clusters of a single size deflect homogeneously. This homogeneous, single-sided deflection is the signature of a relaxation process that causes the clusters to forget their initial conditions as they pass through the magnet. We find experimental magnetic moments that increase linearly with the applied magnetic field and with the inverse of cluster vibrational temperature.

These observations in Rh clusters are consistent with their having giant magnetic moments which behave superparamagnetically [30]. Such superparamagnetism has been seen in isolated clusters of Fe, Co, and Ni and certain clusters of Gd, Tb, and Dy [4–8]. In superparamagnetism, the measured magnetic moment is actually the time-averaged projection of the true, internal moment on the external magnetic field. In a small monodomain particle, thermal energy can exceed the magnetocrystalline anisotropy energy and decouple the magnetic moment's orientation from that of the atomic lattice. The internal moment of such a particle fluctuates rapidly in orientation, under thermal influence. In the absence of an external magnetic field, all orientations of the magnetic moment are equally favorable and the magnetic moment is entirely masked at long time scales by the thermal averaging process.

It is only in a strong magnetic field and at a low temperature that the internal moment of a superparamagnetic particle becomes apparent. When the interaction energy between the internal magnetic moment and the external magnetic field becomes comparable to the thermal energy, the time-averaged magnetic moment begins to shift noticeably toward alignment with the external field. This response is similar to paramagnetic behavior but because it involves the giant moment of the entire particle it is called superparamagnetism [31].

Measuring the cluster's magnetic moment in our apparatus requires several hundred microseconds, its flight time through the 250 mm long gradient magnet. This measurement time is much longer than the nanosecond time scale of the thermal fluctuations, so we can observe only the time-averaged or effective magnetic moment of a superparamagnetic cluster and not the internal moment itself. The effective magnetic moment per atom μ_{eff} is reduced from the internal moment per atom μ by a factor of the Langevin function $\mathcal{L}$:

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

where N is the number of atoms, B is the external field, k is Boltzmann's constant, and T is the temperature of the cluster. Because an isolated cluster's angular momentum is conserved, rotational temperature does not participate in the thermal fluctuations. Instead, T is the cluster's vibrational temperature T_{vib}. For a superparamagnetic cluster, the magnetic moment per atom found by the experiment μ_{expt} is a measure of the effective magnetic moment per atom μ_{eff}.

At the magnetic fields and vibrational temperatures used in our experiment, $N\mu B/kT \ll 1$ and Eq. (1) reduces to

$$\mu_{\text{eff}} \approx \frac{N\mu^2 B}{3kT}. \quad (2)$$

Thus, the effective magnetic moment per atom μ_{eff} of a superparamagnetic cluster is proportional to the square of the internal magnetic moment per atom μ and increases linearly with the applied magnetic field B and the inverse of vibrational temperature $1/T_{\text{vib}}$.

This superparamagnetic dependence of experimental magnetic moment on applied magnetic field and vibrational temperature observed earlier in Fe, Co, and Ni clusters is also seen in Rh clusters. Rh cluster magnetic moments, measured at several temperatures and several values of the external magnetic field, are consistent with all the predictions of superparamagnetism. Using Eq. (2) and the measured magnetic moments per atom μ_{expt} for rhodium clusters, we obtain internal magnetic moments per atom μ which range from 0.3 to 1.1 bohr magnetons per atom at 93 K. These moments are reported in Table I.

In contrast to the nearly size-independent values for μ observed in Fe, Co, and Ni clusters [4–7], those we observe in Rh clusters depend significantly on cluster size. There are several special sizes, Rh_{15}, Rh_{16}, and Rh_{19}, that are unusually magnetic relative to adjacent clusters.

TABLE I. μ_{expt} are the measured magnetic moments per atom for Rh_n (n = 12–32) at T = 93 K and an applied magnetic field B = 1.034 T. μ are the internal magnetic moments per atom for Rh_n (n = 12–32) obtained from measured magnetic moments found at T = 93 K, B = 0.798, 0.906, 0.977, 1.034, and 1.2 T and at T = 113 K, B = 0.798, 0.906, and 0.977 T using Eq. (1) and assuming that the clusters are superparamagnetic. Many more data were used to obtain the μ listed below than appear as μ_{expt}.

Cluster	μ_{expt} (μ_B)	μ (μ_B)
Rh_{12}	0.027±0.009	0.92±0.16
Rh_{13}	0.025±0.009	0.88±0.16
Rh_{14}	0.009±0.009	0.66±0.33
Rh_{15}	0.017±0.009	1.02±0.16
Rh_{16}	0.025±0.009	1.09±0.17
Rh_{17}	0.016±0.009	0.45±0.17
Rh_{18}	0.016±0.009	0.68±0.19
Rh_{19}	0.022±0.009	0.95±0.15
Rh_{20}	0.007±0.009	0.38±0.38
Rh_{21}	0.011±0.009	0.49±0.20
Rh_{22}	0.012±0.009	0.53±0.20
Rh_{23}	0.011±0.009	0.40±0.20
Rh_{24}	0.007±0.009	0.43±0.20
Rh_{25}	0.007±0.009	0.37±0.17
Rh_{26}	0.014±0.009	0.50±0.16
Rh_{27}	0.016±0.009	0.50±0.15
Rh_{28}	0.011±0.009	0.45±0.18
Rh_{29}	0.007±0.009	0.41±0.20
Rh_{30}	0.012±0.009	0.42±0.16
Rh_{31}	0.012±0.009	0.43±0.16
Rh_{32}	0.014±0.009	0.35±0.11

There are also a few clusters that appear to be relatively nonmagnetic.

A total magnetic moment of $21\mu_B$ was predicted for Rh_{13} by Reddy *et al.*, using a linear combination of atomic orbitals approach within the density functional formalism [23]. While our observed value of μ for Rh_{13} is only $11.5\mu_B$, their theoretical prediction of giant magnetic moments in Rh clusters is clearly correct. The clusters are superparamagnetic at 93 K indicating that, despite the large spin-orbit coupling present in the 4*d* metals, these clusters do not have sufficient magnetocrystalline anisotropy to avoid the thermal averaging process. To date, the only clusters found to have magnetocrystalline anisotropies large enough to orient their magnetic moments relative to their atomic lattices are some of the rare earth clusters, Gd_n, Tb_n, and Dy_n [5,6,8].

Although we can measure their total magnetic moments, we cannot determine the type of magnetic ordering in these clusters. Reddy *et al.*, predict ferromagnetic ordering for Rh_{13}, a complete icosahedron [23], but it is uncertain what should happen in larger, less highly symmetric clusters. It is also not clear why the experimental magnetic moment of Rh_{13} is smaller than expected and why Rh_{15}, Rh_{16}, and Rh_{19} have such large magnetic moments.

Because of rhodium's large atomic weight and the modest magnetic moment per atom observed in these clusters, the Rh cluster beam deflections are small, even at low temperatures. Measuring the deflections of Rh clusters at higher temperatures is extremely difficult and we have not yet found the Curie temperature for these clusters. Despite experimental limitations, we expect to extend our present measurements to higher temperatures, larger clusters, and a broader range of magnetic fields in the near future. We are particularly interested in observing the transition from magnetic clusters to nonmagnetic bulk as the cluster size increases.

In conclusion, we have demonstrated that clusters of Rh (n = 12–32) are magnetic and have internal magnetic moments per atom that often exceed those of bulk Ni. This discovery verifies the prediction of Reddy *et al.*, that certain 4*d* transition metal clusters should have giant magnetic moments. Rh clusters are the first clusters of nonferromagnetic bulk elements to exhibit magnetic ordering and the first pure 4*d* or 5*d* metallic systems to exhibit spontaneous magnetic order. The clusters are superparamagnetic at 93 K, indicating that they have insufficient magnetocrystalline anisotropy to lock their magnetic moments to their atomic lattices. The internal magnetic moments per atom depend significantly on cluster size with several clusters exhibiting magnetic moments per atom that are significantly larger than those of adjacent sizes.

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