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Magnetic studies of free nonferromagnetic clusters

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Recent calculations have indicated the possibility of large permanent magnetic moments for clusters of nonferromagnetic materials. Here we describe Stern-Gerlach measurements of aluminum, chromium, palladium, and vanadium clusters, none of which are ferromagnetic in the bulk. No deflections were observed in any of these systems. Upper limits of the magnetic moments are reported.

INTRODUCTION

Much experimental work has been done recently on the magnetic properties of free clusters of ferromagnetic materials.[1-4] However, nonferromagnetic clusters are also of interest. Theoretical calculations and thin-film experiments have indicated the possibility that small clusters of nonferromagnetic transition metals may possess large permanent moments.[5-7] In this paper, we discuss Stern-Gerlach-type deflection results for free clusters of chromium, palladium, vanadium, and aluminum. We were unable to observe any deflection of these clusters, within the resolution of our experiment.

Our experimental results are summarized in Table I. The cluster ranges observed and the temperature of the source for each element are included. The uncertainty of the observed magnetic moment is calculated for each element. In all cases the observed magnetic moment is $0.00\mu_B$.

Chromium is the only one of these four elements to have any magnetic ordering in the bulk state and is found to be antiferromagnetic. However, it is expected that both palladium and vanadium would become ferromagnetic[8,9] if one were able to increase their lattice spacing. Thin films of both elements deposited epitaxially on appropriate substrates should be ferromagnetic,[10,11] since the film will assume the lattice spacing of the substrate. This question is currently being investigated, and both positive and negative results have been obtained.[7,12,13] If these studies are able to demonstrate conclusively that the magnetic properties of these materials are indeed strongly dependent upon their lattice spacings, then measurements of the magnetic properties of clusters may yield some information on their spatial structures.

TABLE I. The measured magnetic moment per particle and the cluster range observed for each of the four elements. The temperature of the source during data acquisition is also reported here.

Element	Moment per atom	Size range	Source temp.
Aluminum	$0.000 \pm 0.003\mu_B$	15–48	88 K
Chromium	$0.000 \pm 0.014\mu_B$	9–31	86 K
Palladium	$0.000 \pm 0.014\mu_B$	100–120	86 K
Vanadium	$0.000 \pm 0.008\mu_B$	8–99	89 K

Aluminum clusters have already been the subject of one study.[14] Cox *et al.* examined Al_1 through Al_{25}, are reported that the magnetic moments vanish for clusters larger than nine atoms. Our measurements confirm these previous results.

EXPERIMENT

The experimental apparatus has been described elsewhere,[3] so only a brief overview is included here. The experiment consists of four basic pieces: three high-vacuum chambers and a magnet assembly. The cluster beam is formed in the first chamber by a laser vaporization cluster source (LVCS). In this LVCS, the second harmonic of a Nd:YAG laser (YAG is yttrium aluminum garnet) (532 nm) is focused on the face of a disk sample. The sample vapor jumps into a 0.5 cm^3 cavity, filled with helium by a modified General Valve valve. Cluster growth and cooling occur within the cavity. A cluster beam is formed as the vapor exists the source cavity through a conical nozzle. This beam enters the second chamber through a 2-mm-diam conical skimmer. The entire source assembly, including the helium valve, can be cooled to liquid-nitrogen temperature.

The second chamber contains the two 0.4-mm-wide collimating slits and a beam chopper. Together, they form a narrow cluster packet, 0.4 mm wide by 2.5 mm high. The beam then passes through a 250-mm-long gradient field magnet. The magnet reproduces one quadrant of a quadrupole field. These measurements were all made with a gradient of 310 T/m and an inductance field of 1 T. After the magnet, there is a 1-m-long deflection tube followed by a detection region in the third box. Deflections are measured by scanning a narrow (0.5 mm) excimer laser beam across the cluster beam to ionize the clusters. The resultant ions are mass analyzed by time-of-flight mass spectroscopy.

The beam chopper permits us to measure the cluster beam velocity to within a few percent, by establishing a starting time for its flight through the magnet to the detector. The chopper also allows us to measure the amount of time the clusters reside in the source. As reported earlier,[4] the measured moment of each cobalt cluster increases with increasing residence time τ_{res} until a

maximum is reached, and then the moment is constant with respect to further increases in τ_{res}. We attribute this effect to the cluster vibrational temperature coming into thermal equilibrium with the source. This equilibration process allows us a measure of control over the vibrational temperatures of the clusters. All measurements reported here were made using the liquid-nitrogen cooled source. Residence times were chosen to be as long as possible while still leaving a reasonably intense signal, so that the vibrational temperature was as close as possible to the source temperature.

Moments are determined from the deflections and the velocities according to the formula

$$\mu_{\text{expt}} = \frac{dmv^2}{(dB/dz)(DL + L^2/2)},$$

where d is the measured deflection, m is the mass of a single atom of the sample element, v is the cluster velocity, dB/dz is the magnetic gradient, D is the distance from the magnet to the ionization region, and L is the length of the magnet. Thus, the resolution of μ is governed by our ability to measure the deflection d, the cluster beam velocity v, and the field gradient. μ_{expt} is measured in Bohr magnetons per atom.

We have found that clusters of different elements tend to be formed under slightly different conditions of the source, and the beam velocities tend to reflect this. Also, the collimation slits for both the cluster beam and the excimer laser beam were narrower for aluminum and vanadium than they were for chromium and palladium, due to greater signal intensity. The different atomic masses of the samples also limit the resolution of μ_{expt}. This is why we report different values of the uncertainty in the moment for the different species (see Table I).

THEORY

We would expect ferromagnetic phases of transition elements to behave as do clusters of cobalt and iron. This behavior has been identified as superparamagnetism.[4,15] Superparamagnetic clusters have an effective magnetic moment given by the true moment μ times the Langevin function

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

where μ is the true moment per atom, N is the number of atoms in the cluster, B is the magnetic-field strength, k_B is the Boltzmann constant, and T is the temperature. In the limit where $N\mu B/k_B T \ll 1$, this reduces to

$$\mu_{\text{eff}} = N\mu^2 B/3k_B T.$$

These size, field, and temperature dependences have been verified experimentally in the case of cobalt.[4] μ_{eff} has units of Bohr magnetons per atom.

These equations are valid as long as the superparamagnetic relaxation time is small compared to the time the clusters spend in the magnet. The deflection d can be measured from the center of the deflected beam profile, as the statistical averaging produces nearly the same deflection for all clusters of the same size.

Another possibility is that the magnetic moment is rigidly coupled to the cluster lattice. We have previously observed this behavior in rare-earth systems.[16] In this case, a particular cluster will, in general, undergo very complex motion that can only be followed by a computer. The time-averaged projection of the cluster's magnetic moment on the field gradient (μ_{eff}) will depend strongly on that cluster's initial angular momentum vector **L**, its initial magnetic moment vector, and the applied magnetic field **B**. In the limit where the magnetic energy is much less than the rotational kinetic energy, then μ_{eff} is simply the projection of the true moment onto **L** projected onto **B**. There are no restrictions in the direction of either $\boldsymbol{\mu}$ or **L**, so μ_{eff} can in general vary from $-\boldsymbol{\mu}$ to $+\boldsymbol{\mu}$. This means that different clusters that are the same size can have extremely different deflections. We cannot simply measure the center of the deflected beam profile to determine the true moment per atom μ, but rather we must fit the entire observed profile to a computer-generated deflection profile that accounts for all possible initial cluster conditions.

In the case of paramagnetic transition metals, the exchange interaction is no longer strong enough to produce a single domain spontaneous magnetization, and the magnetic moments are described by Pauli paramagnetism,

$$\mu_{\text{eff}} = \boldsymbol{\chi} \cdot \mathbf{B} = \frac{D(E_F)}{1-\alpha} \mu_B^2 B,$$

where $D(E_F)$ is the density of states per atom at the Fermi level and $\alpha = ID(E_F)$ is the Stoner factor. The temperature dependence of $D(E_F)$ is usually small, except in palladium. For paramagnetic metals at ordinary fields of about 1 T, deflections are expected to be several orders of magnitude below those obtained for cobalt.

As the lattice spacing is increased, bulk vanadium and palladium are expected to become ferromagnetic.[8,9] The overlap of atomic integrals is such that the Stoner criterion $ID(E_F) > 1$ is satisfied. This may be realizable in thin films grown epitaxially on appropriate substrates. By choosing a substrate with a well-defined lattice spacing that is larger than that of vanadium or palladium, one may create artificially favorable conditions for the Stoner criterion to be satisfied. However, investigations of supported clusters indicate a lattice contraction rather than a lattice expansion.[17,18]

CHROMIUM

Clusters of chromium have been the subject of several theoretical efforts.[6,19,20] In particular, Cr_{15} has been predicted to have a moment per atom of $0.78\mu_B$,[6] or $0.33\mu_B$.[19] Pastor, Dorantes-Dávila, and Bennemann[19] also calculate moments of several smaller clusters. For Cr_9 in a bcc structure, they expect a very large moment per atom of $3.89\mu_B$, although larger clusters should have much less. Cr_8, on the other hand, is predicted to have a moment per atom of either $2.25\mu_B$ or $0.50\mu_B$, depending on the structure. More recently, Reddy and Khanna[20] have predicted that small ($N = 15$) chromium clusters in a field of 1 T will have moments that are less than $0.01\mu_B$.

The large moments predicted by Salahub and Messmer[6] and Pastor, Dorantes-Dávila, and Bennemann[19] should be observable in our experiment, although the small moments predicted by Reddy and Khanna are not.

If we assume that chromium clusters with permanent magnetic moments behave superparamagnetically, then we can place upper bounds on their true magnetic moments. By equating the upper limit of the uncertainty in the measured μ_{expt} given in Table I with μ_{eff} given by superparamagnetic theory, and knowing both the applied field and the vibrational temperature of the cluster, we can extract an upper limit on the true magnetic moment. With an applied field of 1 T and assuming that the clusters are in thermal equilibrium with the source at 86 K, then our measurements indicate that upper bounds on the true magnetic moments per atom vary from $0.77\mu_B$ for $N=9$ atom cluster to $0.42\mu_B$ for an $N=31$ atom cluster. We find that Cr_{15} has a true moment per atom of less than $0.6\mu_B$.

At finite temperatures, superparamagnetism is the most effective mechanism we have found for masking the true size of a cluster's internal magnetic moment. The statistical fluctuations and time averaging of superparamagnetism reduce the observable moment to a relatively small fraction of the true internal value. Other models, including the locked moment model, are not so effective at hiding the true magnetic moment of the cluster. Regardless of model, the uncertainty in our measurement of the observable magnetic moment corresponds to an uncertainty in the size of the true internal moment. That uncertainty is largest for the superparamagnetic model and is less for other models, such as the locked-moment model. Thus, while Cr_9 that behaves superparamagnetically has a moment that is $0.00\pm0.77\mu_B$/atom, chromium clusters that behave locked moment have a much more stringent limit of $0.000\pm0.014\mu_B$/atom regardless of size.

In either the superparamagnetic or the locked-moment case, however, the low upper bounds on the true magnetic moments are consistent with Reddy and Khanna's calculations. They are also consistent with what should be expected from a paramagnetic particle. Using the bulk room-temperature paramagnetic susceptibility of 3.34×10^{-6} emu/g,[21] one finds an induced μ_{eff} of $0.0003\mu_B$/atom in a field of 1 T. This value is considerably below our detection limit.

PALLADIUM

Palladium is paramagnetic in the bulk state at all temperatures. However, it is isolectronic with nickel, which is ferromagnetic. Calculations have indicated that upon expansion of the lattice by 10% palladium should become ferromagnetic, with $\mu=0.35\mu_B$.[8] Thin-film calculations indicate the possibility of ferromagnetism,[22] but have not been confirmed experimentally.[12] Detailed cluster calculations are not yet available.

We can again equate the uncertainty in μ_{expt} from Table I with μ_{eff} given by the superparamagnetic theory. Assuming the vibrational temperature is 86 K, then in a 1 T field the maximum true moment per atom for a 110-atom cluster is less than $0.22\mu_B$. A moment of $0.35\mu_B$/atom would certainly be observable.

This null result is again consistent with paramagnetism. Bulk palladium is paramagnetic at all temperatures, with a peak in its susceptibility at about 80 K. At this temperature, the susceptibility χ_g is about 7.4×10^{-6} emu/g,[21] so in a 1-T field one would expect an induced magnetic moment per atom μ_{eff} of about $0.0014\mu_B$, an order of magnitude below our resolution limit.

VANADIUM

Various experiments exploring the magnetic properties of vanadium have been conducted. Akoh and Tasaki observed magnetism in 90 to 300Å particles, which they attributed to ferromagnetic surface layers.[23] More recent experiments on thin films have yielded both positive and negative results for magnetism in the surface layer.[7,12] In clusters, calculations indicate that, assuming the bulk lattice spacing, a 15-atom cluster should be nonmagnetic, as in the bulk.[5,6] However, both the lattice spacing and the geometry of the cluster are critical to the magnetic properties. Assuming a bcc structure, Salahub and Messmer[6] have calculated the moment of the 15-atom cluster as a function of lattice spacing, finding that a moment appears when the lattice parameter is increased from the bulk value. Liu, Khanna, and Jena[5] have done similar calculations for the 9-atom cluster, and found the moment goes abruptly to zero when the lattice spacing falls below about 0.9 times the bulk lattice spacing. At the bulk spacing, they calculated an average magnetic moment of about $2.89\mu_B$/atom for V_9.

The maximum true moment per atom consistent with our uncertainty in μ_{expt}, again assuming superparamagnetism and a cluster vibrational temperature equal to the source temperature, is $0.59\mu_B$ for V_9 and $0.18\mu_B$ for V_{99}. This small value for V_9 is considerably below the calculated value of Liu *et al.*, and may indicate that the lattice spacing is less than the bulk value. These results are again more consistent with paramagnetism than ferromagnetism.

Bulk vanadium, like palladium, is paramagnetic at all temperatures, with a relatively temperature-independent susceptibility of about 5.8×10^{-6} emu/g (Ref. 21) at room temperature. The induced moment per atom in a 1-T field would then be $0.0005\mu_B$, well below our detection limit.

ALUMINUM

Aluminum is also observed to be paramagnetic in the bulk, with a susceptibility at 300 K of 0.6×10^{-6} emu/g.[21] This susceptibility is also relatively temperature insensitive. The induced moment per atom in a 1-T field would be $3\times10^{-5}\mu_B$, again below our detection limit.

As mentioned previously, Cox *et al.*[14] have studied small aluminum clusters. They did not obtain the entire beam profile for all cluster sizes, however. Instead, they observed the intensity at the maximum of the undeflected beam as a function of applied gradient and measured the axial depletion of the cluster signal. They found that by $N=9$ there was very little if any depletion of the cluster

beam, and hence no observable magnetic moment.

Unfortunately, we were unable to study the smaller clusters from $n=2$ to $n=14$. Our results for the larger clusters are in complete agreement with the previous observations.

CONCLUSION

The lack of any observable deflections of these particles is similar to what we expect from the bulk magnetic behavior of these elements. We do not mean to imply that these clusters are completely bulklike, however. Our experience with cobalt indicates that this is not necessarily true. The small moments for chromium and vanadium, when compared to theory, may indicate either that the interatomic spacings of these clusters are less than the bulk lattice constants or that the geometries are different from those assumed in the calculations.

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