Magic Numbers in the Magnetic Properties of Gadolinium Clusters

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Gadolinium clusters ($N=11$–92) in a molecular beam exhibit dramatic size dependences in their magnetic properties. Two principal behaviors are observed: rigid rotor precession and nutation when the magnetic moment is tightly locked to the lattice by crystal anisotropy, and superparamagnetism when the moment is approximately free. Partially locked behavior is also seen. Magnetic moments of about $3\mu_B$ per atom are observed, with Curie temperatures substantially above the bulk value. Moments that remain locked above 300 K may permit ultrahigh density magnetic memory.

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Recent studies of magnetic behavior in transition-metal clusters have found that iron and cobalt clusters all deflect toward strong field when they pass through a gradient magnet [1,2]. This strong-field-seeking behavior has been identified as superparamagnetism, where each cluster has a single large magnetic moment which fluctuates rapidly in orientation under the influence of the cluster's vibrational temperature [2,3]. This single "super" moment will have some time-averaged alignment with any applied magnetic field; hence the name "superparamagnetism." Above a certain vibrational temperature, sufficient thermal energy is available to unlock the moment from any easy axis of the cluster and to permit such free movement. The small crystal anisotropies in the transition metals permit the moments to become free at fairly low temperatures [4] and have restricted present studies of isolated transition-metal clusters to the superparamagnetic regime. Nonetheless, there should be a very low vibrational temperature regime in which the magnetic moments are locked to the cluster lattices. Unable to find such behavior in transition metals above 80 K, we turned to the rare earths, which have large magnetic anisotropy energies in the bulk.

In this paper, we report measurements of the magnetic behavior of gadolinium clusters ($N=11$–92) at 105 K. We find that their magnetic properties are dramatically size dependent. While some cluster sizes behave superparamagnetically, others exhibit a qualitatively different behavior that includes deflection toward weaker magnetic field. This behavior has never been observed before and we have determined that it is due to rigid rotor precession and nutation of clusters with their magnetic moments locked to their lattices. The very-low-vibrational-temperature behavior that we could not find in the transition metals has been found in the rare earths.

The experimental details have been discussed previously [2,5] and will be reviewed here only briefly. We grow the Gd clusters in a helium-filled source from atoms produced by pulsed laser vaporization of a sample disk. The clusters are retained in the source for nearly a millisecond, during which time they stop growing and thermalize with the walls. The entire source assembly, including the helium gas, is cooled to 105 K. The helium and cluster mixture then undergoes free-jet expansion into a vacuum chamber to form a supersonic molecular beam.

The beam is collimated by two slits, 0.4 mm wide by 2.5 mm high, and passes through a 250-mm-long gradient magnet with a quadrant of a quadrupole geometry. Any time-averaged projection of a cluster's magnetic moment on the field will produce a transverse force and a subsequent deflection. The clusters drift for 1183 mm after the magnet and are then photoionized by a 193-nm ArF excimer laser beam. A time-of-flight mass-spectrometer analyzes and detects the cluster ions. We collimate the laser beam so that it is 0.5 mm wide and scan it across the cluster beam in order to determine the deflection profiles.

A rotating chopper wheel, located near the cluster source, plays two important roles. First, it is a velocity selector since only clusters that travel from the chopper aperture to the mass spectrometer in a set amount of time will be detected. Velocity selection is needed to determine the magnetic moments. Second, it establishes the time at which the detected clusters left the source. The residence time τ_{res} between the vaporizing laser pulse and the moment the clusters leave the source determines the vibrational temperatures of the clusters. The longer τ_{res}, the closer the vibrational temperature of the clusters will be to the source temperature.

While there has been a long-standing belief that free-jet expansions are moderately effective at cooling vibrational temperatures in clusters, we see no evidence for such cooling in our expansion [2]. Recent measurements of photoinduced thermionic emission in small clusters of refractory metals have also found that vibrational temperature can be established only by long residence in the source and that free-jet expansions produce only negligible vibrational cooling [6]. Therefore, if the clusters are allowed to reach thermal equilibrium with the source, their vibrational temperature T_{vib} will remain at the source temperature T_{source} as they travel through the molecular beam. In contrast, there is very little heat capacity in the rotational degrees of freedom and we expect substantial cooling of each cluster's rotational temperature T_{rot} during the expansion. For the expansion conditions in our source, we expect T_{rot} to be approximately 5% of the source temperature or about 5 K [7].

All of the measurements reported in this paper were

made with $\tau_{res}=884$ μs, long enough for the clusters to reach thermal equilibrium with the source. We verify this equilibrium by measuring the magnetic moment of a superparamagnetic cluster, Gd_{22}, as a function of τ_{res}. Beyond $\tau_{res}=884$ μs, no increase in moment is observed. The clusters have reached thermal equilibrium with the source so that $T_{vib}=T_{source}=105\pm3$ K.

Figure 1(a) shows a structureless spectrum of Gd clusters observed directly on the beam axis with the gradient magnet turned off and the apparatus optimized to observe clusters near Gd_{25}. As soon as the gradient magnet is turned on, the clusters deflect and the spectrum changes considerably. On the beam axis, Fig. 1(b), the abundances of most clusters fall significantly but several sizes remain quite intense. Most of the missing Gd clusters are deflected in the direction of strong magnetic field, Fig. 1(c), but some are deflected to weak magnetic field, Fig. 1(d). The detailed behavior of each cluster size can only be determined by mapping out its entire deflection profile for several different magnetic fields. We have performed this exercise for the clusters Gd_{11} through Gd_{92} and find that most clusters exhibit mixtures of two specific behaviors.

The first behavior is superparamagnetism, as was seen in the transition metals. During the measurement time, a superparamagnetic cluster explores the entire Boltzmann distribution for the projection of its moment on the applied magnetic field. Thus, its observed behavior is characterized completely by three parameters: the magnitude of its magnetic moment, its vibrational temperature, and the applied magnetic field. There is no dependence on initial orientation and all clusters with the same moment and vibrational temperature will deflect identically. The signature of superparamagnetic behavior is a small deflection of the beam that does not broaden its profile and that is linear in both the applied field and the field gradient.

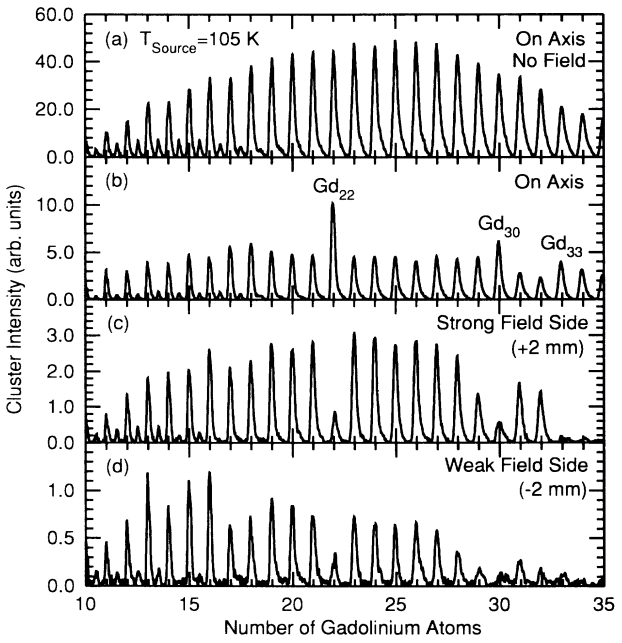

FIG. 1. Mass spectra of Gd clusters, with the apparatus optimized around Gd_{25}. (a) A spectrum of clusters on the undeflected beam axis without any magnetic field. (b)–(d) Spectra of clusters when a field of 0.132 T and a gradient of 50 T/m is applied: (b) on axis, (c) 2 mm to strong field, and (d) 2 mm to weak field. No clusters are seen 2 mm away from the axis when the magnetic field is off. Double ionization, responsible for the extra peaks at low mass, was avoided during actual data collection and analysis.

The second behavior has not been observed before and is characterized by a dramatic spreading of the cluster beam. Such spreading does not occur in superparamagnetism. Most of the clusters deflect toward strong field, but a significant fraction deflect toward weak field when the applied magnetic field is small. In order for clusters of the same mass and rotational and vibrational temperatures to exhibit such a broad range of magnetic moments, they must retain information about their initial conditions. We believe that these spreading clusters have their magnetic moments locked to their lattices, preventing the relaxation processes that yield superparamagnetism.

The fraction of clusters exhibiting each of these two behaviors is extremely cluster-size dependent. Some clusters, such as Gd_{22}, Gd_{30}, and Gd_{33}, have very large superparamagnetic components. Because this component deflects only slightly, it is still visible on the beam axis in Fig. 1(b) but is not seen far off the axis in Figs. 1(c) and 1(d). Gd_{22} is 70% superparamagnetic and has a magnetic moment of $(3.15\pm0.30)\mu_B$ per atom at 102 ± 3 K.

The two adjacent sizes Gd_{21} and Gd_{23} have almost no superparamagnetic component. These clusters spread to both strong and weak field, as can be seen in Figs. 1(b)–1(d). Figure 2 shows deflection profiles for Gd_{21} at four values of the magnetic field. These profiles are representative of all the nonsuperparamagnetic clusters. At very small applied fields and small cluster sizes, the beam spreads almost symmetrically to both weak and strong fields. As we increase the applied field or the cluster size, the profile shifts toward strong field and finally forms a ramp that increases from zero near the beam axis to a maximum value at a large strong-field deflection before dropping off abruptly.

Let us suppose that this spreading behavior is due to clusters with magnetic moments that are locked to their lattices. We can treat these clusters classically because they have very large angular momentum and spin quantum numbers. We consider a particular cluster size and model each cluster as a sphere with moment of inertia I, body-fixed magnetic moment $\boldsymbol{\mu}$, and angular momentum $I\boldsymbol{\omega}$, that is precessing and nutating in an applied magnetic field $\mathbf{B}$. Each cluster has a magnetic potential energy $U_{mag}=\boldsymbol{\mu}\cdot\mathbf{B}$ and a rotational kinetic energy $U_{rot}=I\omega^2/2$. If $U_{mag}\ll U_{rot}$, the angular momentum vector will simply precess around $\mathbf{B}$. If $U_{mag}\gg U_{rot}$, the cluster will oscillate

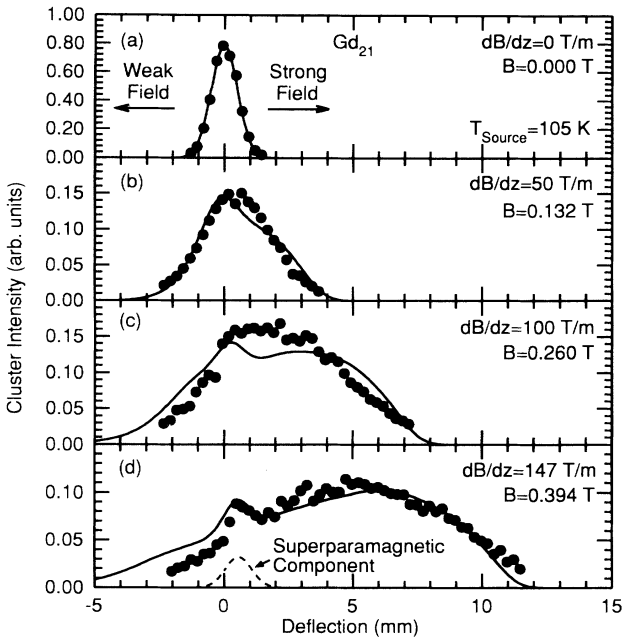

FIG. 2. Deflection profile of Gd_{21} as a function of magnetic field. The solid curves are the predictions of the rigid rotor with body-fixed magnetic moment model using $T_{rot}=5.8$ K, $\mu=2.56\mu_B$ per atom, and 4% of the clusters behaving superparamagnetically. The narrow peak in the solid curve near zero deflection in (d) is the 4% superparamagnetic component, shown separately as the dashed curve.

like a pendulum, in and out of alignment with **B**. When $U_{mag}\simeq U_{rot}$, the cluster will undergo very complex precession and nutation that can only be followed by a computer.

The time-averaged projection of a cluster's magnetic moment on the field gradient, μ_{eff}, will depend strongly on that cluster's initial angular momentum vector, its initial magnetic moment vector, the applied magnetic field, and how it enters that magnetic field. The applied magnetic field is ours to choose and the entry into that field is adiabatic [8]. However, many initial angular momentum and magnetic moment vectors are possible and must be considered. The magnitudes of these vectors are set by the rotational temperature of the supersonic cluster beam and total magnetic moment of a cluster, but there are no restrictions on the initial angles.

Since different initial conditions will yield different values for μ_{eff}, we must examine a statistical ensemble of initial configurations in order to determine the probability of observing a particular μ_{eff} and thus a particular deflection. At each applied field, a statistical ensemble is characterized by its rotational temperature T_{rot} and its magnetic moment μ. To produce a theoretical deflection profile for a particular choice of these two parameters, we numerically integrate the equations of motion for 10^7 different initial cluster configurations and fold in the experimental spatial resolution.

The model has only three adjustable parameters: rotational temperature, magnetic moment per atom, and the fraction of clusters that are superparamagnetic. A best-fit family of theoretical profiles, calculated at the four values of applied field, appear as solid curves in Figs. 2(a) to 2(d). The fit is very good, supporting the locked-moment model. Moreover, the model predicts that the width of the deflection profile should be approximately proportional to $|\nabla B|$, in agreement with the observed results. The values of the parameters obtained from the fitting process are $T_{rot}=5.8$ K, close to the value we expected for our free-jet expansion, $\mu=2.56\mu_B$ per atom, approximately the same value seen for the superparamagnetic clusters, and 4% as the fraction of clusters that are superparamagnetic.

Varying the parameter μ principally affects the width of the theoretical deflection profile, varying T_{rot} changes its overall shape, and changing the superparamagnetic fraction changes the height of the narrow peak near zero deflection [see Fig. 2(d)]. Modest changes in these parameters substantially worsen the fit to the data so that we determine $T_{rot}=5.8\pm2.0$ K, $\mu=(2.56\pm0.30)\mu_B$ per atom, and a superparamagnetic fraction of (4 ± 2)%, including systematic errors.

Data for other clusters with spreading components are in similar good agreement with theoretical profiles based on the same rotational temperature and approximately the same magnetic moment per atom. For small clusters or low fields, $U_{mag}<U_{rot}$ and clusters with locked moments should spread almost symmetrically. The applied field is only a small perturbation on these clusters and the equal probability of the moment pointing with or against the field leads to the symmetric spreading. The relatively large number of small clusters seen on the weak-field side in Fig. 1(d) reflects a symmetric spread, in agreement with the model.

For large clusters or high fields, $U_{mag}>U_{rot}$ and the model predicts that the deflection profiles should shift to the strong-field side. For such clusters, precession and nutation in the applied field dominate their dynamics and they spend much of their time aligned with the field. Adiabatic entry into the magnet also tends to align each cluster's magnetic moment with the field by converting magnetic potential energy into translational kinetic energy. To understand this effect, consider a nonspinning cluster that enters the magnet with its moment at some angle to the field. It behaves as a spherical pendulum, oscillating rapidly in and out of alignment with the field. Because the field increases while it is aligned with the field, the cluster is unable to fully return to its original angle of misalignment. The cluster gradually becomes more aligned with the field. To conserve energy, the cluster accelerates as it enters the magnet. When the adiabatic entry process is included in the locked-moment model, the predicted deflection profiles agree with the observed profiles.

Thus, we attribute the spreading behavior to clusters with magnetic moments locked to their lattices. Such

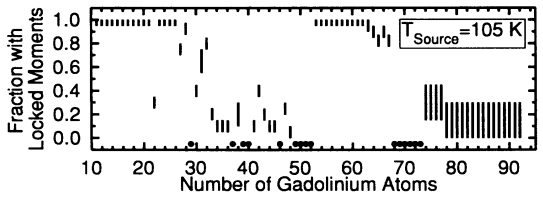

FIG. 3. Fraction of Gd clusters with their magnetic moments locked to their lattices at 105 K. Bars indicate experimental uncertainty. The remaining fraction is superparamagnetic. Sizes marked with a solid dot exhibit behavior consistent with moderate confinement of their moments to the lattice and become completely superparamagnetic by 300 K.

locked-moment behavior was anticipated but had never been seen before in free clusters. The fraction of clusters with locked moments depends critically on size (see Fig. 3) and gives rise to magnetic magic numbers in the spectrum of Gd clusters. Cluster sizes exhibiting both locked-moment and superparamagnetic behaviors could indicate that there are different isomers in the beam. However, it is more likely that each cluster size is a single isomer with a complicated crystal anisotropy energy surface that traps some orientations of the magnetic moment in potential minima while permitting other orientations to circulate almost freely around the cluster in potential troughs. A cluster with its moment tightly confined in a sharp angular minimum will exhibit locked-moment behavior, while an otherwise identical cluster with its moment loosely confined by a trough or shallow angular minimum may appear superparamagnetic.

As the vibrational temperature of a cluster increases, its moment explores larger regions of solid angle. A potential minimum may no longer tightly confine the moment, which may even begin to tunnel through barriers during the 500-μs measurement time. When confinement of the moment has become sufficiently weak, we would expect to see intermediate behavior, neither superparamagnetic nor locked moment. Several cluster sizes, each indicated by a solid dot in Fig. 3, have deflection profiles that are intermediate between the narrow peak of a superparamagnet and the broad slope of a locked-moment cluster and probably have such moderately confined magnetic moments at 105 K. When the source is operated at 300 K, these clusters are superparamagnetic. The additional thermal energy has unlocked their moments.

Not all clusters lose their locked-moment component at 300 K. Clusters still clearly exhibiting spreading behavior include Gd_{12-16}, Gd_{19-21}, Gd_{23}, Gd_{26}, and Gd_{55}. Several clusters that have locked moments at 105 K show intermediate behavior at 300 K (Gd_{11}, $Gd_{24,25}$, and $Gd_{53,54}$) while others are completely superparamagnetic (Gd_{17}).

We can study very hot clusters by choosing a τ_{res} that is far too short to ensure thermal equilibrium and using superparamagnetic Gd_{22} as a rough thermometer. At 800 ± 200 K, all of the Gd clusters are found to be superparamagnetic. We have not yet exceeded their Curie temperature. In contrast, the bulk Curie temperature for Gd is 293 K. We also note that all of the observed magnetic moments, both locked and unlocked, are $(3 \pm 2)\mu_B$ per atom, far less than the bulk limit of $7\mu_B$ per atom.

Many Gd clusters exhibit locked-moment behavior at and above room temperature and could be used to produce ultrahigh-density magnetic memory. Clusters formed in a cw source could be filtered by a gradient magnet and deposited in an inert matrix.

In summary, we find that Gd clusters exhibit both superparamagnetic and locked-moment behaviors. At 105 K, most cluster sizes show some mixture of the two. As vibrational temperature increases, magnetic moments become more weakly confined and locked-moment behavior evolves into superparamagnetism. All the observed Gd clusters are superparamagnetic well above the bulk Curie temperature. Clusters with locked magnetic moments can be used to measure their own rotational temperatures. We find that free-jet expansions can effectively cool cluster rotational temperatures.

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[1] W. A. de Heer, P. Milani, and A. Chatelain, Phys. Rev. Lett. **65**, 488 (1990).

[2] J. P. Bucher, D. C. Douglass, and L. A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991).

[3] S. N. Khanna and S. Linderoth, Phys. Rev. Lett. **67**, 742 (1991).

[4] G. Xiao, S. H. Liou, A. Levy, J. N. Taylor, and C. L. Chien, Phys. Rev. B **34**, 7573 (1986).

[5] J. P. Bucher, D. C. Douglass, P. Xia, B. Haynes, and L. A. Bloomfield, Z. Phys. D **19**, 251 (1991).

[6] A. Amrein, B. Collings, D. Rayner, and P. Hackett (unpublished).

[7] D. R. Miller, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford Univ. Press, New York, 1988), pp. 14–43.

[8] At $T_{rot} = 5.8$ K, the clusters rotate many thousands of times during the approximately 3 μs in which they enter the magnetic field. Since the applied field changes very little during each rotation, the cluster's entry into the field is adiabatic.