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Magnetic properties of rare earth clusters

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Abstract. We report results of Stern-Gerlach deflection experiments on terbium clusters, which resemble earlier results for gadolinium clusters. As in gadolinium, we observe two distinct behaviors: clusters that are superparamagnetic and clusters that are described by a locked-moment model. The magnetic behavior is highly size dependent. Certain clusters make a transition from locked-moment to superparamagnetic behavior with increasing temperature and, in this process, exhibit an intermediate behavior. Both superparamagnetic and locked-moment clusters have magnetic moments per atom well below the bulk value. We show that oxygen atoms attached to the clusters have little effect on the clusters' magnetic properties and are not responsible for the two distinct behaviors observed in rare earth clusters. We also present preliminary results from studies on dysprosium clusters.

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1. Introduction

The origin of bulk magnetism in rare earth metals is quite different from that in transition metals, as is the magnetic structure of the respective metal clusters. Transition metal clusters of iron and cobalt deflect in the direction of the strong field [1,2], a behavior accurately explained by a superparamagnetic model in which the magnetic moment is orientationally independent of the cluster lattice and exhibits thermal, statistical behavior in an external field[2,3]. On the other hand, the magnetic properties of gadolinium clusters are highly dependent on the cluster size[4]. Certain gadolinium clusters fit the superparamagnetic model, while other clusters are well described by a second model which assumes a magnetic moment rigidly locked to the cluster lattice. In reporting terbium and preliminary dysprosium results, we examine magnetic properties common to rare earth metals and monitor the effect of attached oxygen atoms on the magnetic behavior of rare earth metals.

2. Experiment

The experimental design is described in detail elsewhere[5], so we will describe it below only briefly. Rare earth clusters, produced via a laser vaporization cluster source (LVCS), leave the source as a beam undergoing supersonic expansion. Before entering the gradient magnet, the beam passes through two collimating slits and a beam chopper. The beam chopper serves two important functions: it allows us to determine the cluster beam velocity and it gives us an accurate measure of the time the clusters reside in the source, τ_{res}. After leaving the magnet, the neutral clusters are ionized with an excimer laser and then detected via a Milani-deHeer time-of-flight mass spectrometer (TOFMS) [6] with a dual microchannel plate detector. In order to measure cluster deflections, the narrow (0.5mm FWHM) ionizing laser beam scans across the cluster beam as the signal intensity for each cluster is recorded, producing a peak profile. The magnetic moment per atom μ_{expt} measured from the deflection d and velocity v of a cluster is

$$\mu_{\text{expt}} = \frac{Gmv^2d}{(dB/dz)} \tag{1}$$

where m is the mass of a single atom, dB/dz is the magnetic field gradient, and G is a constant geometrical factor.

3. Results and Discussion

3.1. Superparamagnetic clusters

Rare earth clusters passing through the gradient magnet show two different responses depending on their size. One behavior, seen in transition metal clusters, is characterized by a sharp peak profile, while the other behavior is characterized by a broad peak. The rare earth clusters which exhibit the former behavior, superparamagnetism, at all temperatures, are Gd_{22}, Tb_{17}, Tb_{22}, Tb_{27}, Dy_{22}, and Dy_{27}.

Table 1. Internal magnetic moment per atom of superparamagnetic clusters.

T_{vib}	μ_B per atom				
	Tb_{22}	Tb_{27}	Dy_{22}	Dy_{27}	Gd_{22}
73K	2.81±.20	2.40±.18	2.40±.31	2.38±.26	
98K	2.93±.20	2.38±.19	2.40±.24	2.50±.25	2.94±.35
148K	3.41±.28	3.00±.22	3.06±.40	2.90±.29	3.33±.40
198K	3.70±.28	3.00±.26	3.24±.65	3.00±.60	3.65±.44
248K	4.39±.32	3.17±.35			3.88±.47
303K	4.42±.52		3.50±1.0	3.2±1.0	

As described by the superparamagnetic model, the magnetic moment associated with these clusters can point in any direction independent of the cluster lattice and is thereby free to align with the external field. The effective magnetic moment per atom μ_{eff} is reduced from the internal moment per atom μ by the Langevin function:

$$\mu_{\text{eff}} = \mu \left(\coth \left(\frac{N\mu B}{kT} \right) - \frac{kT}{N\mu B} \right), \tag{2}$$

where N is the number of atoms in the cluster, B is the magnetic field, and T is the temperature. In order to use this relationship, the temperature or, more specifically, the vibrational temperature of the clusters must be well defined. As the residence time τ_{res}, of the clusters in the source increases, the deflections of the superparamagnetic clusters saturate. This saturation indicates the clusters are in thermal equilibrium with the source and the cluster vibrational temperature is equal to the source temperature.

For $N\mu B/kT \ll 1$, Eq. (2) is accurately approximated by $\mu_{\text{eff}} \approx N\mu^2 B/3kT$. In all of the clusters mentioned above, the magnetic moment per atom μ, obtained by substituting the measured magnetic moment per atom μ_{expt} for μ_{eff} in Eq. (2), is constant as a function of field. Thus, a least squares fit of a line through the data points at a given temperature gives the internal magnetic moment per atom associated with a particular cluster. For Tb_{17}, the true magnetic moment is also independent of temperature, as in the case of transition metal clusters. At all temperatures and fields, μ is $3.49 \pm .21\mu_B$ per atom. However, for the other superparamagnetic clusters the internal magnetic moment per atom increases with increasing temperature, as seen in Table 1. These clusters, although superparamagnetic, have an internal moment that is a function of temperature, which implies that there is an additional mechanism responsible for the magnetic behavior of these clusters. Antiferromagnetic coupling of the atomic moments within the cluster may explain the increasing moment with increasing temperature.

3.2. Locked-moment clusters

The rest of the clusters exhibit a different behavior characterized by broad peaks that appear over a large range of deflections. These clusters deflect in the strong and also the weak field direction. Figure 1, a peak profile of Tb_{23}, as compared with Tb_{17}, illustrates this broad profile. Note that there is a sharp, virtually undeflected peak superimposed on the profile. This sharp peak centered around zero corresponds to superparamagnetic behavior, indicating that approximately 10 – 20% of Tb_{23} clusters are superparamagnetic.

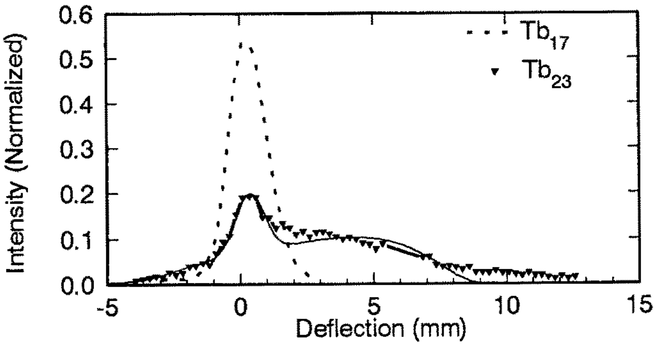

Fig. 1. Peak profile of Tb_{23} with a superparamagnetic peak, Tb_{17}, included for comparison. The data was taken at 98K and a field of .267T and a gradient of 101.3 T/m. The smooth curve is a locked-moment model fit.

For locked-moment clusters, the magnetic moment is no longer free to align directly along the magnetic field but instead rotates with the cluster, precessing and nutating in the field. The dynamics of the cluster motion are governed by the magnetic energy and the rotational energy. With an adiabatic entry into the magnetic field, a cluster's trajectory through the magnet will be highly dependent on initial conditions. For a given field, the statistical distribution of initial conditions is characterized by the rotational temperature and magnetic moment of the clusters. Including the superparamagnetic component of each peak, the model has only three fit parameters: the rotational temperature, the magnetic moment, and the fraction of superparamagnetic clusters The smooth curve in Fig. 1 is such a fit with an internal magnetic moment of $2.81\mu_B$ per atom and a T_{rot} of 4 K. The supersonic expansion of the cluster beam does efficiently cool the rotational temperature[7], not the vibrational temperature.

Locked moment clusters of terbium have internal magnetic moments per atom μ in a range of $0.5\mu_B$ to almost $4\mu_B$ per atom, well below the bulk value of $9.25\mu_B$ per atom. Similarly, the internal moments per atom of gadolinium clusters, ranging from $0.5\mu_B$ to $3\mu_B$ per atom, are less than the bulk value of $7.55\mu_B$ per atom. For both gadolinium and terbium locked-moment clusters, the magnetic moment increases with increasing field and with decreasing temperature.

3.3. Transition

Some of the clusters with locked-moments at low temperatures have unlocked moments at higher temperatures, as seen with Tb_{26}. In Fig. 2, Tb_{26} clusters are compared with a typical superparamagnetic (Tb_{17}) and locked-moment (Tb_{23}) cluster. Tb_{26} and Gd_{17} are the most dramatic examples of this transition, but Tb_{21}, Tb_{25}, and other clusters also show this behavior. As

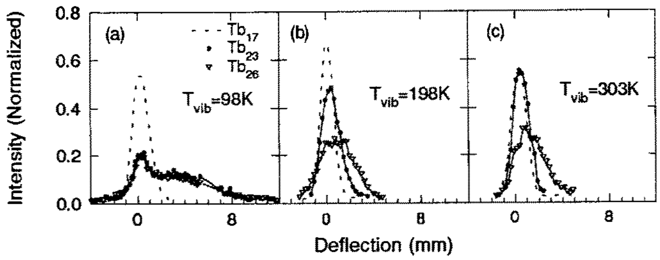

Fig. 2. The transition of Tb_{26} as a function of temperature in comparison with Tb_{17} and Tb_{23}. Increasing temperatures require increasing fields for comparable deflections. Thus, for (a) B=.267 T, dB/dz=101.3 T/m; (b) B=.540 T, dB/dz=194.9 T/m; and (c) B=.673 T, dB/dz=234.2 T/m.

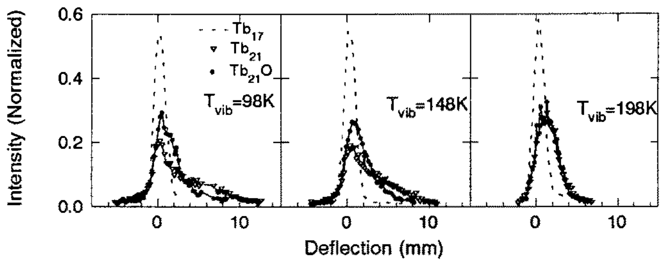

Fig. 3. Tb_{21} in comparison with $Tb_{21}O$, with Tb_{17} for reference. At 98K, B=.267T, 148K, B=.405T and at 198K, B=.540T.

the vibrational temperature increases, the moment, previously locked to the cluster lattice, becomes unlocked and free to align with the field.

During this transition, the profiles of these clusters do not fit the locked-moment or superparamagnetic model. In the superparamagnetic case, a large solid angle is available to the moment for reorientation independent of the cluster lattice. However, in the locked-moment case, the solid angle is negligibly small since the moment is coupled to the lattice. With increasing temperature, a transition occurs as the solid angle which the moment can explore increases. Therefore, during a transition from one behavior to another, we would expect to see an intermediate behavior, as in Fig. 2(b), where, at 198K, the size of this solid angle is between the two extremes.

3.4. Oxygen atoms

Because terbium is mono-isotopic and Tb_n and Tb_nO can be resolved for $n < 40$, we can examine the effect of oxygen atoms on the magnetic behavior of terbium clusters. At temperatures above 200K, there is no significant difference in the behavior of a cluster when an oxygen atom is attached to it. However, for the lowest temperatures studied, certain oxygen contaminated clusters behave differently than the associated clean clusters. In particular, $Tb_{21}O$ and $Tb_{25}O$ exhibit different peak profiles, characterized by a smaller deflection, from their clean locked-moment counterparts. Figure 3 illustrates this for Tb_{21} and $Tb_{21}O$. Similar to the intermediate or transition behavior of Tb_{26} at 198K in Fig. 2(b), the peak profile for $Tb_{21}O$ does not fit either model well. Both Tb_{21} and Tb_{25} also exhibit this intermediate behavior at temperatures above 200K. As seen in Fig. 3 above, the peak profiles of Tb_{21} and $Tb_{21}O$ are the same at 198K and continue to match with increasing temperature. For Tb_{25}, the clean and oxygen contaminated peaks show no significant differences for temperatures greater than 248K. In both of these instances, the intermediate behavior appears at a lower temperature with the addition of an oxygen atom, indicating that the oxygen atom may aid in partially unlocking the magnetic moment at a lower temperature.

On the other hand, the addition of an oxygen atom causes the superparamagnetic peak Tb_{22} to become a partially locked-moment cluster at lower temperatures. At all temperatures, Tb_{22} is predominately superparamagnetic, while $Tb_{22}O$ goes through a transition similar to Tb_{26} as discussed above. At low temperatures, it exhibits the intermediate behavior, while at high temperatures, it is predominately superparamagnetic. With the exception of the particular clusters mentioned above at low temperatures, the addition of an oxygen atom does not alter the magnetic properties of the clusters.

4. Conclusions

The magnetic behavior of rare earth clusters is highly size dependent. The clusters that are superparamagnetic show different behaviors: Tb_{17} has a constant magnetic moment, while the magnetic moments of other superparamagnetic clusters *increase* as the temperature *increases*. Non-superparamagnetic clusters have a moment that is best modeled as being locked to the crystal lattice. However, a number of the clusters do not fit either model well, exhibiting an intermediate behavior. From the terbium data, we find that the presence of an oxygen atom on the cluster does not change the magnetic behavior of that cluster, apart from the exceptions noted above. The magnetic moments of each of the rare earth clusters are well below the bulk values for the given rare earth metal.

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