Magnetic ordering in clusters of the group 3 transition elements: Sc_n, Y_n, and La_n

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The magnetic properties of isolated clusters composed of scandium, yttrium, and lanthanum containing 5–20 atoms have been investigated in a Stern–Gerlach molecular-beam deflection experiment. The molecular-beam profiles for most clusters in this size range display either high-field deflections indicative of superparamagnetism or symmetric broadening indicative of locked moment behavior. The magnitude of the deflections for those clusters exhibiting high-field seeking behavior indicate susceptibilities that are significantly larger in magnitude than those expected based on the extrapolation of the susceptibility of the bulk solids, signifying that these species are magnetically ordered. Magnetic moments for Sc_n and Y_n, evolve with size in patterns that are strikingly similar to one another. Several clusters stand out as *bona fide* high-spin molecular magnets: Sc_{13} $(6.0\pm0.2\mu_b)$, Y_8 $(5.5\pm0.1\mu_b)$, Y_{13} $(8.8\pm0.1\mu_b)$, and La_6 $(4.8\pm0.2\mu_b)$.

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I. INTRODUCTION

Transition metal clusters containing fewer than $\sim 10^2$ atoms can exhibit magnetic ordering not displayed by the corresponding bulk solids.[1–4] Stern–Gerlach molecular-beam deflection techniques have proven to be useful for uncovering such behavior, since chemically pure metal clusters can be prepared and studied in isolated form, thus removing the perturbing effects of substrates, matrices, and stabilizing ligands. Using such techniques, Cox *et al.* have shown that bare rhodium clusters ($Rh_{9\text{-}60}$) display magnetic moments[1,5] as high as 0.8 μ_b per atom (Rh_9-Rh_{11}) indicative of ferromagnetic or ferrimagnetic ordering, even though bulk rhodium is a Pauli paramagnet at all temperatures.[6] Bloomfield and co-workers[2] measured magnetic moments for Cr_8-Cr_{156} that ranged from ~ 0.5 to $\sim 1.0\mu_b$ per atom, clearly indicating that these clusters do not display antiferromagnetic ordering as in bulk chromium, but rather ferromagnetic or ferrimagnetic ordering. Knickelbein[3,4] has shown that manganese clusters ($Mn_{5\text{-}99}$) display substantial nonzero moments indicative of ferrimagnetic ordering.[3,4] Recently, de-Heer and co-workers[7] have found evidence for magnetic ordering in palladium clusters using molecular-beam deflection techniques.

Anomalous magnetism in low-dimensionality transition metals can be attributed to the enhancement of densities of *d* states at the Fermi level resulting from spatial confinement.[8] For transition metal systems, the effects of spatial confinement on magnetic properties can be put on a quantitative framework using the Stoner model of itinerant ferromagnetism. This model, despite its simplicity, is a remarkably useful predictor of spontaneous magnetization in bulk transition metals, successfully predicting ferromagnetic ordering in iron, cobalt, and nickel (and only those transition metals).[9–11] According to this model, the paramagnetic susceptibility χ is determined by the density of *d* states at the Fermi level $N(E_f)$ and the exchange function *J*,

$$\chi = \frac{\mu_0 \mu_b^2 N(E_f)}{1 - JN(E_f)},$$

where μ_0 is the permeability of free space and μ_b is the bohr magneton. The *Stoner enhancement* term given by $[1-JN(E_f)]^{-1}$ increases rapidly as $JN(E_f)\rightarrow 1$, and for $JN(E_f)\geqslant 1$, χ (formally) becomes negative, signifying a ferromagnetic instability and thus spontaneous magnetic ordering.[11] The Stoner model thus provides a simple framework with which to predict the emergence of "unexpected" magnetic ordering in the transition elements as spatial dimensions are reduced: The *d*-band narrowing that typically accompanies spatial confinement[8] produces an enhancement in $N(E_f)$ which, if sufficiently large, can lead to ferromagnetic instability: Spontaneous magnetic ordering occurs.

Like most transition elements, scandium, yttrium, and lanthanum are paramagnetic in their bulk phases. However, their relatively high paramagnetic susceptibilities,[11–13] as compared to those of their neighbors in the Periodic Table, suggests that these metals are on the verge of ferromagnetic instability, and may be induced to display ordering by spatial confinement. In this paper, we present the results of magnetic deflection experiments that confirm that all scandium clusters and most yttrium and lanthanum clusters in the range $n=5$–20 are elemental molecular magnets.

II. EXPERIMENTAL METHODS

The experimental methods have been provided in detail previously.[4,14] The experiment was performed using a four-stage differentially-pumped molecular-beam apparatus, shown schematically in Fig. 1. Scandium, yttrium, and lanthanum clusters were produced via pulsed laser vaporization from the surfaces of cylindrical targets of the corresponding pure metals: Sc (99.9%, Rare Metallic Company Ltd., Tokyo), Y (99.9%, Goodfellow Corp.), and La (99.99%, Ames Materials Preparation Center, Ames, Iowa).[15] The metal targets were housed in laser vaporization sources through which helium flowed continuously. The laser vaporization source was coupled to a high aspect ratio flow tube (9 cm length $\times$ 0.3 cm inner diameter) held whose temperature could be controlled between 55 K and 300 K. The residence time of the clusters within the flow tube $\sim$4 ms was

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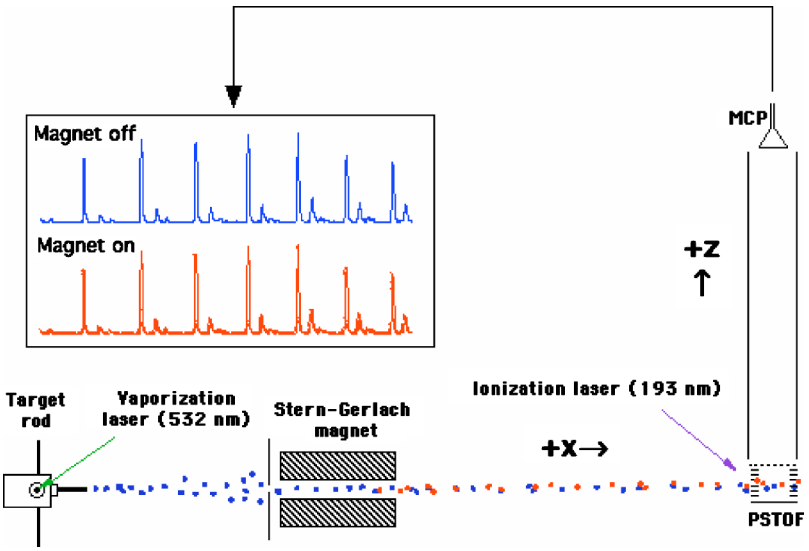

FIG. 1. (Color online) Schematic of the experiment. PSTOF mass spectra are recorded sequentially, first with the Stern–Gerlach magnet on and then again with the magnet off.

sufficient to ensure that they were equilibrated to the flow tube temperature prior to expansion into a vacuum though a 1.2 mm diameter orifice at the end of the flow tube.[16] Under these mild expansion conditions, very little supersonic cooling of the clusters' vibronic degrees of freedom is expected,[17] so that the postexpansion cluster temperature is estimated to be close (within ~5 K) to that of the flow tube. The expanding jet was skimmed into a molecular beam, which passed through a gradient dipole magnet[18] capable of producing B fields of up to ~1.2 T and gradients ($\partial B/\partial z$) up to ~210 T m^{-1} in the center of the gap. The clusters were then ionized with a spatially expanded ArF excimer laser ($\lambda = 193$ nm), with the resulting singly ionized clusters detected via position-sensitive time-of-flight (PSTOF) mass spectrometry,[14,19,20] a technique which allows field-induced deflections or broadening of cluster beams to determined with a spatial sensitivity of about 20 μm. This technique allows the spatial distributions of clusters in a molecular beam to be mapped onto the time domain and thus recorded using a digital oscilloscope. The spatial deflections or broadening of each cluster size in the beam was independently measured by quantitatively comparing the field on versus field off PSTOF peak profiles. Magnetic moments were determined via analysis of the beam broadening and deflection profiles, as described in detail below.

III. RESULTS AND DISCUSSION

Magnified portions of PSTOF spectra showing Y_6 and Y_8 mass peaks recorded with the deflection field off versus on, is shown in Fig. 2. These PSTOF mass peak profiles illustrate the two types of beam deflection behavior observed for Sc_n, Y_n, and La_n clusters at 58±2 K. The symmetric broadening of the beam about the center line of the beam axis ($z=0$) is displayed by Y_5, Y_6, La_5, and all Sc_n clusters except Sc_{10} and Sc_{20}. By contrast, the beam profiles of $Sc_{10-20}, Y_{7-10,13-18}$, and $La_{6-9,11,13-20}$ shift uniformly to later arrival times upon application of the gradient field, corresponding to a spatial shift in the $+z$ direction (high-field-seeking behavior). The magnitude of the broadening and shifting is significantly larger than would be expected based on the susceptibilities of the corresponding bulk elements, implying that these clusters are not simply small fragments of the corresponding paramagnetic solids, but rather are molecular magnets.

High-field-seeking beam deflection behavior has been observed in previous studies for clusters of the ferromagnetic transition metals, Fe_n,[21–23] Co_n,[22,24] Ni_n,[14,21,25] as well as for clusters of certain transition metals that are not normally ferromagnetically ordered in any of their bulk phases, such as Mn_n (Ref. 3) and Rh_n (Ref. 1). Such behavior is consistent

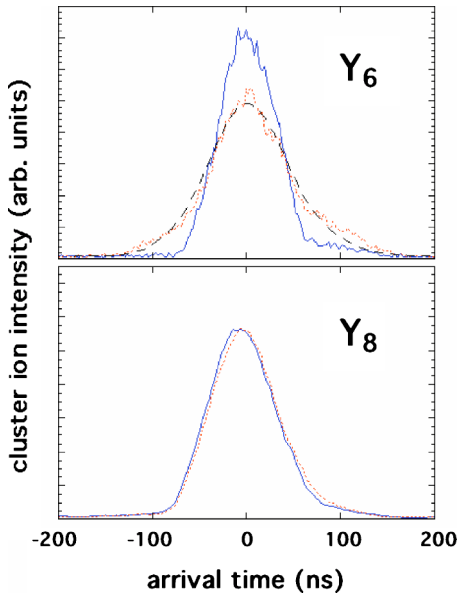

FIG. 2. (Color online) Magnified portions of yttrium cluster time-of-flight spectra showing the PSTOF profiles for Y_6 and Y_8. Solid traces: $B, \partial B/\partial z = 0$; dotted traces: $B = 0.78$ T, $\partial B/\partial z = 160$ T m^{-1}. For Y_6, the adiabatic rotor model (dashed curve) was fitted to the field-broadened profile, in this instance yielding a total moment of 2.25μ_b ($\bar{\mu} = 0.38$ μ_b per atom). The moments reported in the present work are the average of 10–20 such determinations.

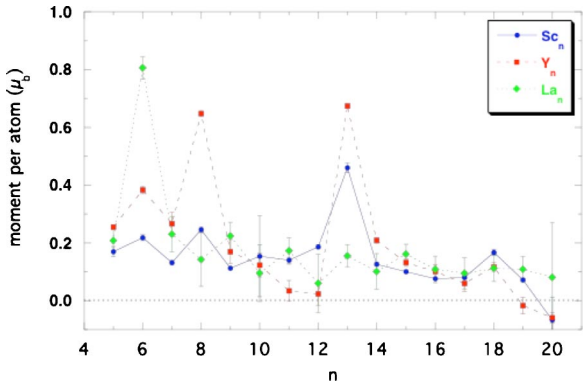

FIG. 3. (Color online) Magnetic moments per atom, $\overline{\mu}$, for Sc_n, Y_n, and La_n (n=5–20) measured with the cluster source maintained at 58±2 K.

with superparamagnetism resulting from ordered spins, and indicates that intramolecular spin relaxation[26] occurs on a time scale shorter than the flight time of the clusters through the magnetic field (~0.4 ms). In this case, the induced magnetization $\langle M_z \rangle$ of the ensembles of clusters displaying high-field-seeking behavior can be calculated from the magnitude of the beam deflection Δz as computed from the change in PSTOF mass peak first moments recording with the magnetic field on versus off:[14,21,27]

$$\langle M_z \rangle = C\Delta z m v^2 \left(\frac{\partial B}{\partial z} \right)^{-1}, \tag{1}$$

where m is the cluster mass, v is the molecular beam speed, $\partial B/\partial z$ is the field gradient, and C is an apparatus constant. For a magnetic system in thermal equilibrium, magnetization $\langle M_z \rangle$ is related to the intrinsic moment μ exactly via the Brillouin function $\mathcal{B}(T)$:[10]

$$\langle M_z \rangle = \mu \mathcal{B}(T). \tag{2}$$

At temperatures T in which the condition $\mu B \ll kT$ holds, as is the case in the present experiment, the Brillouin function can be approximated by the Curie law:[21,26–29]

$$\langle M_z \rangle \approx \frac{\mu^2 B}{3kT}. \tag{3}$$

It is readily shown[10,26] that the apparent magnetic moments for a system of angular momentum J derived from $\langle M_z \rangle$ using the Curie law are upper bounds to the true moments, exceeding the true moments by the factor $\sqrt{J(J+1)}/J$ and thus approach the actual values of μ [as given by Eq. (2)] asymptotically as $J \to \infty$ Because J is unknown (but clearly small) for the clusters studied in these experiments, we will apply the Curie Law with the caveat that the moments so derived are upper limits to the true moments. The mean per-atom magnetic moments $\overline{\mu}=\mu/n$, determined using the Curie Law expression for those clusters displaying high-field deflections, are shown in Fig. 3.

The beam profiles of certain clusters display symmetric field-induced broadening such that at sufficiently high fields, their profiles exhibit distinct Lorentzian-type "wings" (see Fig. 2). This type of field-broadened profile is characteristic of clusters whose moments μ are locked rigidly to their molecular frameworks as they tumble through the magnet.[4,30–32] Accordingly, the field-broadened peak profiles for $Sc_{5\text{-}9,11\text{-}19}$, $Y_{5\text{-}6}$, and La_5 were analyzed using the adiabatic rotor model of Bertsch and Yabana[30] which assumes locked-moment behavior in a thermal ensemble of isolated, spherical rotors characterized by a rotational temperature T_{rot}. Under conditions in which $\mu B \ll kT_{rot}$ and in the limit of high rotational quantum numbers, the distribution function of moments $R(\mu_z)$ takes on a simple analytical form that is independent of T_{rot}:[30]

$$R(\mu_z) = \frac{1}{2\mu} \ln \left(\frac{\mu}{|\mu_z|} \right), \tag{4}$$

In practice, μ was determined by convoluting the unbroadened beam profile with the distribution function R, and least-squares fitting the resulting convolution to the field-broadened beam profile. Details of this convolution and fitting procedure are described elsewhere.[4] Because $R(\mu_z)$ is independent of $\mu B/kT_{rot}$ when $\mu B \ll kT_{rot}$ knowledge of T_{rot} is not required in the fitting procedure. At fields for which $\mu B \approx kT_{rot}$, the shape of the moment distribution becomes dependent on $\mu B/kT_{rot}$ with the overall distribution becoming asymmetrical, shifting to higher μ_z.[30–32] Such behavior is not observed in the present experiments. An example of a best-fit convolution profile for Y_6 (T=58 K) obtained using the adiabatic rotor model is shown in Fig. 2 along with the experimental field-broadened PSTOF profile. Although the moments reported here were obtained for clusters generated at 58±2 K, the same results (within experimental error) were obtained for clusters generated at various source temperatures, up to 290 K, confirming the temperature independence of $R(\mu_z)$. The per-atom moments $\overline{\mu}$ derived using the adiabatic rotor analysis for $Sc_{5\text{-}9}$, $Sc_{11\text{-}19}$, $Y_{5\text{-}6}$, and La_5 are shown in Fig. 3, along with the Curie law values obtained for the superparamagnetic clusters. The beam profiles for $Y_{11,12,19,20}$ and $La_{12,20}$ display no measurable deflection or broadening (beyond statistical uncertainty) even at the highest fields; accordingly their moments are taken to be $<0.1\mu_b$ per atom.

As shown in Fig. 3, the moments for most Sc_n, Y_n, and La_n clusters are quite small ($<0.3\mu_b$ per atom). Notable exceptions are Sc_{13}, Y_8, Y_{13}, and La_6, with total moments of 6.0, 5.5, 8.8, and 4.8μ_b, respectively, thus putting these clusters in the class of true high-spin molecular magnets. The size variation of the per-atom moments of scandium clusters and yttrium clusters display many of the same features (e.g., local maxima at n=6, 8, 13, and 18), with the moments yttrium cluster tending to be slightly larger. This similarity may imply a common structural motif for these two series of clusters [bulk Sc and Y both adopt hexagonal close packed (hcp) packing]. By contrast, the moments of lanthanum clusters evolve with a different pattern than those displayed by scandium and yttrium cluster, suggesting that they adopt a different structural motif (unlike Sc and Y, bulk La adopt double hcp packing). Whether the structures of Sc_n, Y_n, and La_n clusters bear any resemblance to each other or to those

of the corresponding bulk solids is unclear, as there are currently no first-principles calculations of the equilibrium structures of these species. Note that the size dependencies of the total cluster moments do not follow a simple odd-even pattern (e.g., between 0 and $1\mu_b$) indicative of alternating singlet and triplet states, as was recently reported for niobium clusters.[33] Because the present experiment measures only the *total* magnetic moment of the clusters, there is no direct indication of the nature of the magnetic ordering displayed by these cluster systems—i.e., whether they are ferromagnetic, ferrimagnetic, or a more complex ordering. Unlike the situation in bulk transition metals, orbital contributions may be significant in small transition clusters.[23,34,35]

There are currently no first-principles calculations of the magnetic properties of group 3 clusters to provide guidance as to the nature of their magnetic ordering. We can, however, provide estimates for the upper limits of moments assuming ideal ferromagnetic ordering of local *atomic* moments computed using simple electronic structure considerations combined with Hund's rules. Spedding and Croat have provided evidence supporting a localized moment of $1.65\mu_b$ in bulk scandium based on Curie-Weiss analysis of susceptibilities.[36] In our local moment analysis, we make the approximation that the atoms comprising Sc_n, Y_n, and La_n are in $ns(n-1)d^2$ electronic configurations. It is further assumed that the *s* electrons are bonding in nature and contribute no net spin (and thus no magnetism) as is the case for the ferromagnetic transition metals[9] so that the effective atomic core can be as described as a $^3F_2$ term. In this case, the Landé *g* factor is computed to be 0.66 and thus the moment $\mu_z = gJ$ is $1.33\mu_b$ per atom. This value reflects *intra-atomic* antiferromagnetic coupling of spin and orbital atomic angular momenta as predicted by Hund's third rule for less-than-half-filled atomic shells.[10] If, on the other hand, the orbital moments are completely quenched in small clusters as is the case in the bulk transition metal ferromagnets (Fe, Co, and Ni), then the only available contribution to magnetism is the spin *S* contributed by the two *d* electrons, assumed to be ferromagnetically coupled (Hund's first rule). In this case, $S=1$, and because $g=2.00$ in the absence of orbital angular momentum, the predicted atomic moments are given by $gS=2.00\mu_b$ per atom. The same set of calculations performed assuming a $ns^2(n-1)d$ electron configurations yields $gJ=1.20\mu_b$ (orbital momentum fully included) and $gS=1.00\mu_b$ (orbital momentum quenched). The per-atom moments for Sc_n, Y_n, and La_n reported in the present study are significantly lower than the ideal (Hund's rules-based) upper limits computed with either $ns(n-1)d^2$ or $ns^2(n-1)d$ orbital populations, suggesting that the ordering is not strictly ferromagnetic, but rather ferrimagnetic or perhaps a more complex (e.g., noncollinear) arrangement of spins. Accurate first-principles calculations of geometry-optimized clusters will be required in order to understand both the magnitude of the orbital contributions to the overall moments and the nature of the ordering.

The current theoretical understanding of the paramagnetic properties of bulk scandium, yttrium, and lanthanum comes from electronic structure calculations of the extended solids.[11,37–43] We will focus first on scandium and yttrium and we will refer to the study of Matsumoto *et al.*[39] as a recent representative of such studies, as it treats both Sc and Y on an equal theoretical footing, thus allowing meaningful quantitative comparison between systems. These workers employed a relativistic spin-polarized band structure method to compute the paramagnetic susceptibilities of hcp Sc and Y. They obtained substantial Stoner enhancement factors $[1-JN(E_f)]^{-1}$ of 4.1 and 4.3 for Sc and Y, respectively, thus accounting for the relatively high paramagnetic susceptibilities measured for these metals.[36,44] In both metals, the key quantity responsible for the substantial Stoner enhancements was the high value of $N(E_f)$. Notably, the paramagnetic spin anisotropy (*c* axis versus *a* axis) computed for hcp Y was a factor of 10 larger than that for hcp Sc. This result runs counter to the present finding that all scandium clusters in the $n=6$–22 range studied display locked-moment behavior (reflecting high magnetocrystalline anisotropy) whereas the majority of yttrium cluster display superparamagnetic behavior (reflecting low anisotropy), with only Y_5 and Y_6 displaying locked moment behavior. However, these calculations are for extended hcp solids in which magnetocrystalline anisotropy effects are significant. It is not expected that the structures of finite Sc_n and Y_n clusters bear any resemblance to those of the corresponding extended solids, but rather display their own unique structure-dependent internal magnetic anisotropies. Although several band structure calculations have been performed on dhcp and face-centered-cubic phases of lanthanum,[40–43] none of the derived electronic properties (e.g., susceptibilities) hint at spontaneous magnetic ordering for either phase. The appearance of magnetic ordering in small lanthanum clusters clearly implies electronic structures unlike the bulk phases.

IV. CONCLUSIONS

The present results were obtained for isolated clusters. Whether anomalous magnetism as is observed here for isolated clusters is also observed in condensed phase cluster-assembled magnetic materials[45,46] remains an open question having important technological implications. As the characteristic length scales of magnetic materials are pushed into the nanometer regime, it can be anticipated that normal magnetic behavior (e.g., as exhibited by conventional iron or cobalt ferromagnetic particles) may give way to unusual unanticipated confinement-induced magnetic behavior, including anomalous magnetic ordering in nominally nonmagnetic elements. Efforts in probing such phenomena in condensed phase samples of size-selected clusters are currently underway in our laboratory and will be reported in the future.

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