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Unusual Temperature Dependence of Magnetization and Possible Magnetic Noncollinearity in Tm and Pr Clusters

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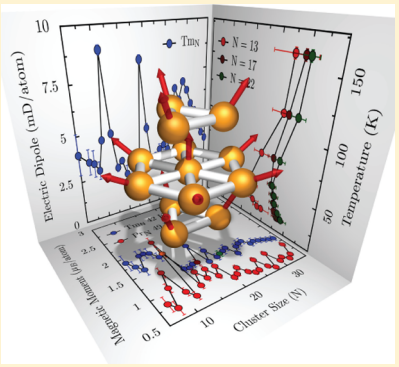
ABSTRACT: Rare-earth metals in their bulk form possess rather similar crystallographic structures, which is due to the very similar features of their outer electronic states. On the contrary, their magnetic properties are of rich variety, which is related to the specific form of the indirect magnetic exchange interaction between the inner electronic shells. In cluster form, this interplay may lead to very unusual magnetic structures. Here we show how the magnetic moments vary with size and temperature in Tm and Pr clusters. Although in Pr clusters clear atom-by-atom oscillations indicate antiferromagnetic ordering, smooth variation and anomalous temperature behavior in Tm is representative for an essentially noncollinear spin arrangement. Their electric behavior is also very different, with a metallic-like behavior of Pr and localized electronic states in Tm.



INTRODUCTION

Atomic clusters are the smallest pieces of matter where condensed matter properties gradually emerge with the number of constituent atoms.[1] Moreover, the physical and chemical properties of each cluster can vary strongly on an atom-by-atom level, leading to intriguing magnetic,[2,3] electric,[4] and catalytic[5] properties. It is these variations that lead to a strong interest in cluster physics both from the fundamental point of view and for the possibility of design of materials with *a-priori* selected properties.

Clusters made of rare-earth metal elements, moreover, represent an intriguing magnetic system. Indeed, the Ruderman−Kittel−Kasuya−Yosida (RKKY) mechanism,[6−8] which is invoked to explain the exchange coupling in the bulk, has obviously no application in clusters, where the *k*-vector is not defined. In addition, the rare-earth metals with partially filed 4f shells have large atomic moments and show a variety of interesting magnetic phases at low temperature, due to the oscillatory nature of the indirect exchange interaction.[9] These magnetic properties are highly sensitive to the lattice geometry, making it particularly interesting to investigate the rare-earth metals in cluster form, where the majority of atoms have unusual coordination numbers and interatomic distances.

Particularly interesting could be a comparison between light and heavy rare-earth metals. In the light ones, a relatively large radius of 4f shells means a sizable influence of the neighbors. As a consequence, in bulk praseodymium the crystal field interaction wins over the Hund's rules, leading to the disappearance of the atomic magnetic moment. On the contrary, in heavy rare-earth metals, 4f shells are of small radius and only indirectly interact with the environment.

In this paper we demonstrate that the clusters of 4f elements, surprisingly, both in the beginning of the row of the Periodic table (praseodymium) and at the end of it (thulium) show qualitatively similar behaviors, both with high temperatures of magnetic ordering and with nonferromagnetic arrangement of atomic magnetic moments. For Pr clusters, clear atom-by-atom oscillations of the total moment are consistent with the collinear antiferromagnetic configuration. In contrast, the evolution of magnetization in Tm clusters is much more smooth, indicative of noncollinear spin structure. Both systems show an unusual temperature behavior of the magnetization. In particular this relates to Tm clusters, where almost all sizes show an initial increase of the magnetic moment with temperature.

RARE EARTH METALS FROM BULK TO CLUSTERS

In most cases, the magnetic properties of the rare-earth metals can be understood in what is usually called "the standard model",[9] according to which the magnetic 4f-electrons in the metal have the same angular-momentum quantum numbers as in the free ion. They interact with the surrounding crystal field, and with each other through an indirect exchange mediated by the conduction electrons.

The particular form of the indirect exchange interaction in this case is of the RKKY type, which is thus an oscillatory coupling with the period given by the spanning vector of the (rather complicated) Fermi surface of the particular metal. When rare-earth metal atoms are assembled in a solid, the 4f

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electrons remain localized, whereas the external 5d and 6s electrons extend through the metal and form the conduction electron gas. These conduction electrons themselves make a negligible contribution to the magnetic moment, but by mediating the magnetic interactions, they play a crucial role in the determination of the magnetic properties. The interactions of the electronic states with the crystal fields make the magnetism of the rare-earth metals to be extremely sensitive to the atomic arrangement. The appearing magnetic structures of rare-earth metals are thus determined by the interplay between exchange, crystal field, and magnetoelastic contributions. The oscillatory nature of the RKKY exchange interactions is a driving force behind the complicated spiral structures and modulated magnetic moments.[10] The situation is somewhat simpler in the heavy rare-earth metals, where the 4f-shells are better protected from crystal field influences.

In thulium, at the Neel temperature of T_N = 56 K, the moments order along the *c*-axis with their values sinusoidally modulated.[11,12] The modulation squares up at lower temperatures once the amplitude begins to exceed the free-ion moment of 7.0 μ_B at roughly 40 K. At 32 K, a ferromagnetic component appears and at the lowest temperatures, an "antiphase" square wave structure is obtained with four layers having "up" spin (still along the *c*-axis) and three layers having "down" spin with an exact period of seven layers.[12]

For a number of years praseodymium has been a metal of particular interest; there has even been a controversy about the existence of magnetic ordering, with a conflict between the data from samples of different morphology.[13] An antiferromagnetic structure was found below 25 K on powder and polycrystalline samples,[14,15] with an average spontaneous moment of about 0.7 μ_B/atom. In contrast, no evidence of magnetic ordering in single crystals was found down to 0.4 K.[16,17] Even more intriguing, the fcc phase of Pr was suggested to be ferromagnetic below either 8.7[18] or 20 K,[15] with a saturation moment of 0.76 μ_B/atom.

It was finally agreed that the original atomic configuration of the Pr^{3+} ion (S = 1, L = 5, J = 4) is destroyed by the strong crystal field of the dhcp structure, so that it has a singlet ground state.[19] Magnetism can occur by induced-moment behavior, due to the mixing-in of the higher crystal-field levels through the exchange interaction.[19−21] Therefore, the effects of strain on the crystal fields could be responsible for magnetic ordering in polycrystalline samples. There is a considerable evidence that the exchange interaction in this system is close to the critical value for the induced moment to appear.[22]

Given the rich variety of the bulk properties, it should come as no surprise that rare-earth metal clusters also exhibit a rich variety of magnetic behaviors. From the beginning, these materials were promising for cluster studies due to the large atomic magnetic moments and strong magnetic anisotropies. Magnetic deflections of several of the heavy rare-earth metal clusters, such as Gd, Dy, Tb, and Ho, were studied. In fact, more questions were triggered than answers provided, by the observation of high Curie temperatures in very small clusters of Gd[23] or by the suggested field-induced antiferromagnet to ferromagnet transition in Dy clusters.[24] Surprisingly, the majority of the rare-earth metal clusters showed the locked-moment behavior[25−28] indicating huge magnetic anisotropy. Even taking into account strong crystal-field effects of the bulk rare-earth metals, such values of anisotropy were unusual. Tb and Ho clusters demonstrated a kind of "magic number" in their magnetic moments, these numbers being equal for the two metals.[29] All these findings have raised a question about the origin of magnetism in the rare-earth metal clusters, which remains unanswered to this point. That the mechanism of the exchange interaction may be drastically different from the bulk one, was indicated by the observation that in oxygen-doped clusters, in spite of clear modification of electronic properties, the magnetic moments stay unchanged.

To our knowledge, this is the first experimental study on the magnetic properties of Pr and Tm clusters. These two elements have a certain similarity of the atomic configuration of their 4f shells (two 4f-electrons in Pr versus two 4f holes in Tm); however, their bulk properties are drastically different due to different interaction of the "magnetic" electrons with the environment, as discussed above.

EXPERIMENTAL DETAILS

Neutral metal clusters were produced in a cryogenically cooled laser vaporization source. A 10 ns pulse of a doubled neodymium-doped yttrium aluminum garnet laser of 532 nm wavelength is focused onto a target rod of rare-earth metals. The laser pulse ablates a plasma of metal vapor that is subsequently quenched by a pulse of cryogenically cooled to 15 K helium gas. The metal vapor condenses into clusters and the clusters remain in the source long enough to ensure that they are at thermal equilibrium with the buffer gas. After this dwell time, the gas−cluster mixture is expanded through a nozzle into a vacuum. The nozzle expansion is skimmed and collimated into a narrow beam. The beam velocity is determined by the temperature of the buffer gas and is measured using a mechanical chopper.

To measure the magnetic response, the cluster beam is directed between the pole faces of a Rabi-type two-wire electromagnet, which applies an inhomogeneous magnetic field of 350 T/m in a direction transverse to the beam. To measure the electric response, the cluster beam is sent through a coaxial electric deflection plate, which applies an inhomogeneous electric field of up to 7×10^6 V/m and a gradient of 2×10^9 V/m^2. In both of these cases, the clusters experience a force and are deflected in a direction transverse to the beam. By measuring the deflections, we can determine the magnetic moment or electric dipole of the clusters.

We should note here that it is still a point of discussion, which exact mechanism relates the measured deflections with true magnetic moments of the clusters: internal spin relaxation[30] or via avoided crossings at the spin-rotational Zeeman diagram.[31,32] Both of them actually connect the cluster magnetic moment μ with the measured deflection M and the applied magnetic field B via the Langevin formula

$$M = \mu\left(\coth\left(\frac{\mu B}{k_B T}\right) - \frac{k_B T}{\mu B}\right) \approx \frac{1}{3}\frac{\mu^2 B}{k_B T} \quad (1)$$

the last approximation being valid at low fields and/or high temperatures. The major difference is thus which temperature should be taken to make the link: that of the rotational or vibrational system? The problem is avoided by using very gentle expansion conditions of the source, and the source temperature is used as a reference. Moreover, the temperature of the clusters was confirmed by the measurements of the velocity of the cluster beam.

After the deflection magnet, the clusters are mass separated and the deflections are measured with a position sensitive time-of-flight mass spectrometer,[33] which simultaneously measures

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their deflections d and their masses m. This is achieved by a defocusing of the mass spectrometer, where the linearity of the deflection is assured by an extra electrode. The clusters are ionized by an ArF excimer laser (193 nm/6.42 eV).

RESULTS AND DISCUSSION

Magnetic Moments. The magnetic deflection profiles or Pr clusters are shown in Figure 1, and the first thing that one

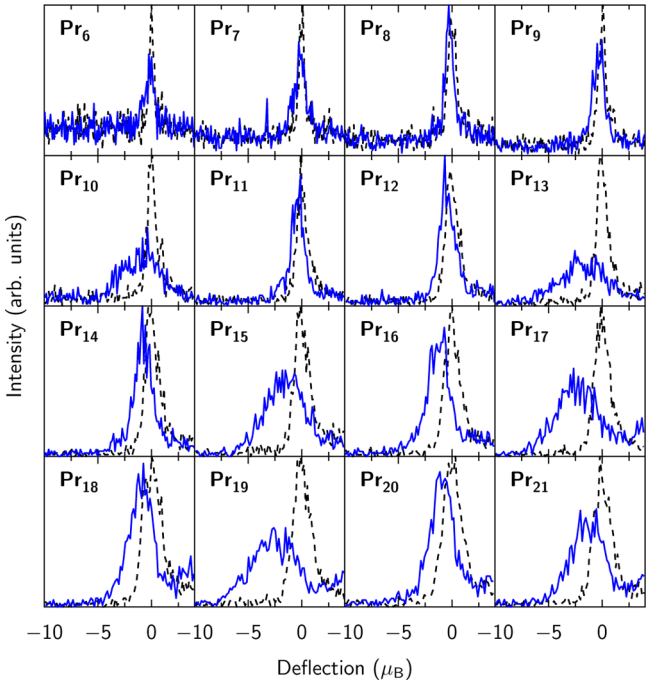

Figure 1. Magnetic deflection profiles of selected Pr_n clusters at 29 K: black dashed line, profiles in the absence of the applied magnetic field; solid blue line, field of 0.6 T applied.

notices is that Pr clusters are indeed magnetic. We remind the reader here that bulk Pr is typically nonmagnetic due to the large crystal field splitting present in bulk samples. Due to the reduced average coordination number of clusters, it is reasonable to expect that the crystal field splitting is also reduced.

From the deflection profiles the magnetic moments can then be extracted and are presented in Figure 2. From the moments per atom, we can see that changes from one size to another are nonmonotonous and highly depend on the number of atoms in the cluster. For example the cluster sizes Pr_n, n = 10, 13, 15, 17, 19, 22, 26, 29, and 33 have a higher moment per atom than their neighboring sizes. Also, when looking at the deflection profiles of the clusters (Figure 1), we can see that these "high-moment" clusters all are significantly broadened as well as shifted, thus undergoing a single-sided deflection. At n = 13−20 a clear odd−even effect can be seen, where odd clusters have a higher moment per atom. An odd−even oscillation could be indicative of an antiferromagnetic ordering within the cluster, where each subsequent atom aligns antiparallel to the previous one. In support of this, the amplitude of the oscillations of the total moment of the cluster (~4 μ_B) agrees reasonably well with the atomic moment of Pr (3.27 μ_B). The clusters are not ideally antiferromagnetic though, as there is a residual magnetic moment of about 1 μ_B per atom.

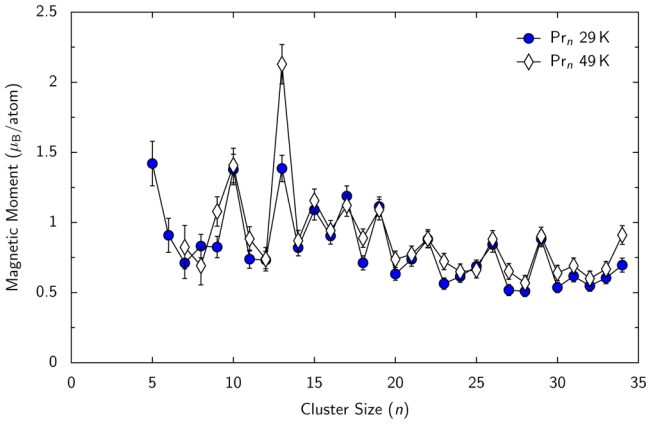

Figure 2. Magnetic moment per atom of Pr_n clusters at 29 and 49 K. Note the enhanced moment for Pr_{13}, and the distinct odd−even oscillations with increasing n for n = 12−20.

Other possible causes for the size dependence of the magnetic moment include either a change in the structure of the cluster or a change in the interaction strength between the local moments. Structural changes would have an indisputable influence on the magnetic ordering, exchange coupling, and anisotropy energy of the cluster through changes in the separation of the atoms and on the crystal field strength. The exchange interaction can also be affected by changes in the density of states of the valence electrons in the cluster. Here we should recall that although the bulk RKKY exchange mechanism as it is cannot be applied here, one or another form of the indirect exchange interaction, mediated by spin-polarized valence electrons, seems to be the only viable alternative. As the number of unpaired electrons in the system changes, the exchange interaction strength likely changes accordingly.

As several temperatures have been measured, it is also possible to investigate the effect of temperature on the magnetism of Pr clusters. In doing so, two effects can be seen: (i) the magnetic moment of Pr_{13} increases with temperature across the investigated range, and (ii) the magnetization width decreases with temperature for the clusters that exhibit significant broadening at 29 K, namely, n = 10, 15, 17, 19, 22, 26, 29, and 33.

First it is important to note that the moments shown in Figure 2 have already been corrected for temperature, and thus any (significant) differences in the value of the moment are a result of a reordering of the magnetic structure of the cluster. Interestingly, when considering the magnetic moments seen in Figure 2, one can see that the (temperature corrected) moments do not differ significantly with temperature for these cluster sizes. This would suggest that, even though the profile itself can be affected by temperature, there is no significant reordering of the magnetic structure with an increase in temperature. This decrease in broadening is consistent with the avoided crossing model,[4] where the deflection profile reflects the internal energy distribution of the cluster ensemble.

Apart from Pr, the magnetic moments of Tm clusters have also been measured at several temperatures, Figure 3. In considering the magnetic moment as a function of cluster size, one can see that, in general, there is no significant dependence on the number of atoms in the cluster, nor is there any odd−even oscillations. The moments per atom are, however,

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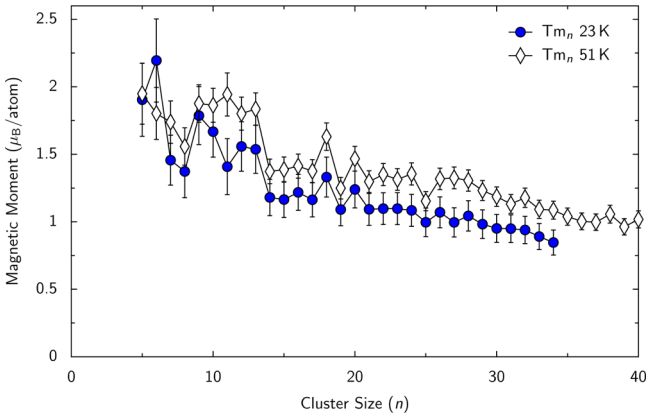

Figure 3. Magnetic moment per atom of Tm$_n$ clusters at 23 and 51 K. For some cluster sizes an odd−even effect can be seen, however, not as prominent as that in Pr clusters (Figure 2). Note that the magnetic moment depends on temperature.

significantly reduced from the atomic value of 7 μ_B, possibly indicative of canted or noncollinear moments.

Further, it is immediately seen that Tm, similar to some of the Pr clusters, exhibits an anomalous temperature dependence. For Tm this feature is much more general in the sense that practically all the clusters in the measured size range show an increase of magnetization in some temperature range.

The magnetization of Tm clusters and a limited number of Pr clusters thus show an unexpected temperature dependence; namely, the net magnetization increases with temperature across a certain range, as seen in Figure 4. This increase with temperature is predominant across most Tm clusters studied,

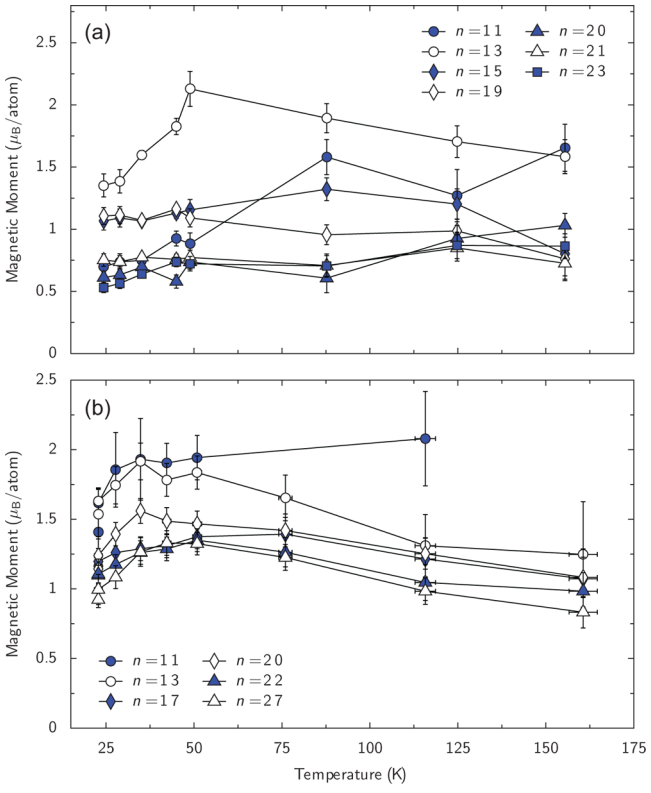

Figure 4. Temperature dependencies of the cluster atomic magnetic moment of selected Pr (a) and Tm (b) clusters.

and a small number of Pr clusters (most significantly Pr$_{13}$). This effect has also been observed previously in Gd clusters.[23] One possible explanation for this unusual temperature dependence was given by Cerovski et al.[34] (and later others[35]), where they attributed it to a canted magnetic ordering, first described for the case of Gd$_{13}$ by Pappas et al.[36] Similar results have been found using an Ising model, including the case of an antiferromagnetic cluster.[37]

Interestingly, as was already indicated above, whereas Tm shows an increase in magnetization with temperature for all cluster sizes investigated, only Pr$_{13}$ shows a significant increase in moment with temperature (Pr$_{15}$ shows a minimal effect). This could be the result of a differing exchange coupling strength for the next-nearest neighbors. An important question here is why the coupling strength, though not size dependent in Tm clusters, is size dependent in Pr clusters.

A separate note should be added here on the notation of the ordering (Curie) temperatures in the case of clusters. Of course, the bulk definition is not applicable here, in a strict thermodynamic sense. We thus use this term approximately, as above a certain range (around 150 K in both cases) it is difficult to experimentally distinguish between paramagnetic cluster saturated in the applied field, and a ferromagnetic one.

Electric Dipoles and Polarizabilities. A certain insight into this problem can be obtained from the electronic structures of the clusters. Unfortunately, very little has been done in the case of rare-earth metal systems. Minimum experimental data would be provided by the electric polarizability and dipole moment, such as, for example, in the case of Tb clusters doped with oxygen.[38]

Presented in Figure 5 are the polarizability and electric dipole of Pr and Tm clusters, respectively. First of all, the Pr clusters show an average polarizability of 10−15 Å^3/atom and an average electric dipole of 0.002−0.003 D/atom, both of which are relatively low and the clusters can thus be considered as having no anomalous electric properties. One could also consider them in principle as being "metallic". We should note here that the definition of the metallicity in such small clusters can be ambiguous as no continuous bands across the Fermi level exist here. For a recent discussion of these issues, see ref 39.

In contrast to Pr, the electric properties of Tm$_n$ show many anomalous, size-dependent effects, such as unusually large polarizabilities and permanent electric dipoles for sizes n = 10−12, 19, and 27−32. Note that a high permanent dipole can also cause an increase in the observed shift in the deflection profiles; thus it is possible that the observed high polarizability is a side effect of the large electric dipole moment present in certain Tm clusters.

One possible explanation for the size-dependent changes in the electric dipole of the clusters is structural in origin. One condition for metallicity is a periodic oscillation of the electrostatic potential in real space. In k-space, this relates to a dispersion relation with bands where the valence electrons would interact with the lattice, and bands where they are free. If a particular cluster size has a low symmetry such that there is no region in k-space where the electrons are free to move within the cluster, then charge mobility will be hindered.

A reduction in carrier mobility will result in the inability of the valence electrons to shield a local charge, thus resulting in the formation of an electric dipole across the cluster. (A reduction in the mobility of the free electrons in the cluster would actually result in a decrease in the polarizability. As peaks

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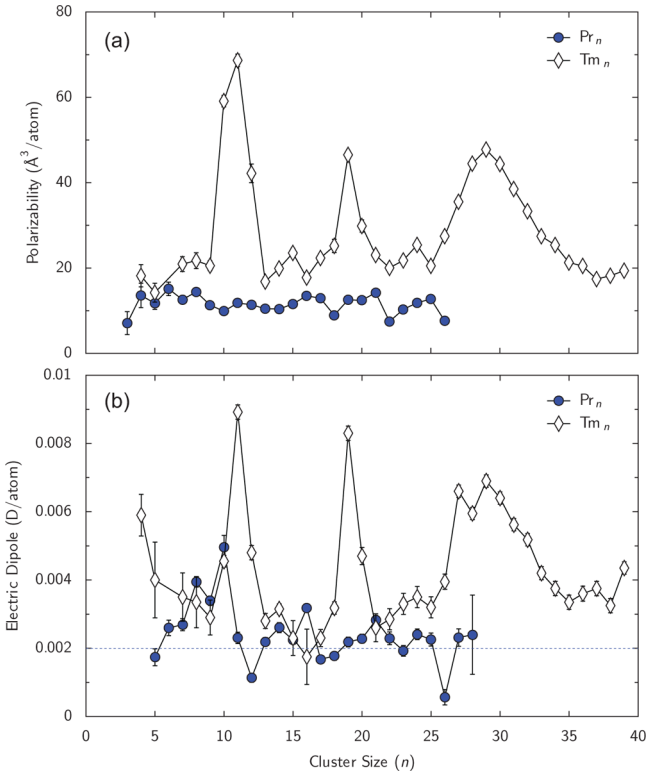

Figure 5. (a) Polarizability of Pr_n and Tm_n at 26 and 19 K, respectively. (b) Electric dipole of Pr_n and Tm_n clusters. The dashed line at 0.002 D/atom represents an approximate baseline for the measurement method.

in the dipole correlate with peaks in the polarizability, this points to a side effects in the measurement process.)

Another possible explanation for the size dependent electric properties is that all clusters actually have a charge localization within the cluster, but that this does not manifest as a net electric dipole due to the symmetry of the cluster. Therefore, the high-dipole clusters in this case are simply clusters that are asymmetric and thus charge localization does result in a net dipole.

When comparing the magnetic properties of the clusters from Figures 2 and 3 with the electric properties, one can see that there is little correlation between the peaks in each graph. That is to say, the polarizability and electric dipole have little effect on the magnetic properties of Pr clusters. This would imply that the changes seen from one size to another in the magnetic moment are not of electric origin. It is important to note, however, that the measured electric properties do not always reflect possible changes in the electronic structure of the cluster. It is therefore possible that, for example, the relative densities of the spin-up and spin-down electrons in the valence system do change with cluster size, but these changes do not have an effect on the measured polarizability. (Recall that it is the unpaired valence electrons that mediate the RKKY exchange interaction between the local 4f moments, not the total electron density.)

At higher temperatures, starting at 80 K, the deflection decreases and normal "metallic" behavior returns. This implies that there is a transition from the high-polarizability, high-dipole state at low temperatures, to a metallic state at higher temperatures. This behavior has been seen previously in Nb clusters[4] and was in that case related to the formation of a ferroelectric state at low temperatures.

A strong structure dependence of the magnetism has also been observed in the literature;[35] thus the answer could lie in differing preferred packing schemes. To elucidate this, a structural investigation of the rare-earth metal clusters is necessary. For example, geometrical conformations of Tb cation clusters were investigated with the help of infrared vibrational spectroscopy.[40] Such study, however, is still unique as far as rare-earth metals are concerned.

We remind readers here that the electronic configuration of trivalent Pr is $4f^2$ whereas the configuration of trivalent Tm, which is usually the bulk configuration for the majority of the rare-earth metals, is 4f.[12] Thus, we have the same spin and orbital moments in both systems, but with the opposite sign of the spin−orbit coupling. This leads to a considerably different total atomic magnetic moment in the 4f shells of these elements, with the orbital part ($5\ \mu_B$) dominating the spin one ($2\ \mu_B$) in both cases. Though we see (compare Figures 2 and 3) a certain difference in total average magnetic moments, serious theoretical study is required to make further conclusions on this. A starting point has been done recently by derivation of the valence stability of the electronic structures of rare-earth metal clusters.[41] In particular, Tm is interesting as a transition from divalent to trivalent state has been predicted at about six atoms size. This, however, still needs to be verified experimentally.

Broadening of the Magnetic Deflection Profiles. What is also directly visible in Figure 1 is the strong broadening of the deflected profiles. The broadening was intensively discussed in the past; see, for example, refs 30−32. Claims were made that the intrinsic spin relaxation in clusters is not able to explain the observed broadenings. In the model of Xu et al., where the broadening was explained by the avoided crossings on a spin-rotational Zeeman diagram, a relation has been derived between the observed amount of broadening ΔM and the cluster magnetic moment μ as

$$\Delta M = \frac{1}{3}\frac{\mu^2 B}{k_B T}\sqrt{\frac{1}{\nu_{DOS} - 1}} = M\sqrt{\frac{1}{\nu_{DOS} - 1}} \qquad (2)$$

where ν_{DOS} relates to the number of excited vibrational modes.[31,32] Note that this formula is valid in the limit $\nu_{DOS} > 1$ only. Simply speaking, one would expect the decrease in the broadening with temperature, due to an increase in the population of vibrational states ν_{DOS}.

We have analyzed the experimentally observed broadening for a number of cluster sizes; the obtained result is shown in Figure 6. Surprisingly, it is absolutely not what is expected: the broadening initially *increases* with temperature, up to about 50 K. This is neither in agreement with the intrinsic spin relaxation, where no broadening at all is expected, nor is it accounted for by the avoided crossings model. A simple explanation by the inhomogeneous magnetic field and/or its gradient does not work either, as then the broadening would monotonously increase with the magnetic moment of the clusters, and the observed increase is not in line with this picture.

One final possibility that could affect the amount of broadening of the deflection profile is a change in the strength of the interaction between crossed levels in the Zeeman diagram; however, it is not clear how this would change with cluster size. The problem thus stays open.

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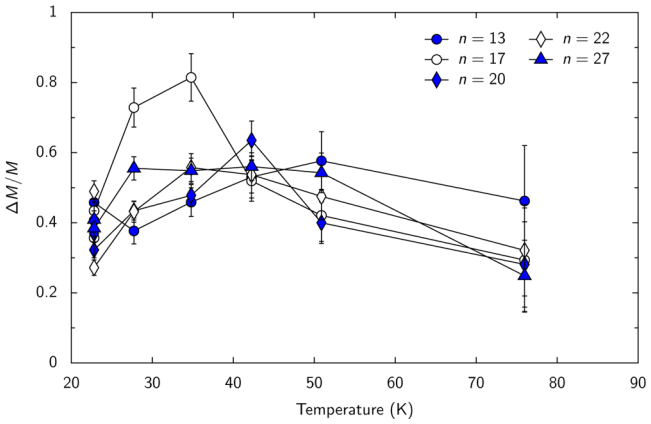

Figure 6. Amount of broadening ΔM, normalized by the absolute deflection amplitude M, observed on the deflection profiles for Tm clusters of various selected sizes as a function of temperature.

CONCLUSIONS

To summarize, in this work we have investigated the magnetic moments of Pr and Tm clusters. For both of them, the average magnetic moment per atom is significantly smaller than the bulk value. This is undoubtedly related to the nonferromagnetic configuration of the clusters. For Pr, this is most probably a relatively collinear antiferromagnetic arrangement, which is derived from a typical atom-by-atom oscillatory behavior of the magnetic moment. In contrast, in Tm clusters essentially noncollinear magnetism could be envisaged, this conclusion being supported by the observed increase of the magnetization with temperature.

The measurements of the electric polarizability and dipole moment show a strong difference between the Pr and Tm cluster: although the former are clearly "metallic", the latter show sizable electric dipole moments, which is a clear fingerprint of the localized electrons. At this moment, it is not clear how this affects the observed magnetic behavior. However, this makes a good starting point for the electronic structure calculations in the future.

On a separate note, the behavior of a magnetic cluster in a combination of a magnetic field plus its gradient still needs to be solved. Our measurements show that there is an unknown parameter that determines the value of the broadening. Therefore, the behavior of a cluster in external fields remains a challenge for future research.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) De Heer, W. A. The Physics of Simple Metal Clusters: Experimental Aspects and Simple Models. *Rev. Mod. Phys.* **1993**, *65*, 611−676.

(2) Billas, I. M. L.; Châtelain, A.; De Heer, W. A. Magnetism from the Atom to the Bulk in Iron, Cobalt, and Nickel Clusters. *Science* **1994**, *265*, 1682−1684.

(3) Xu, X.; Yin, S.; Moro, R.; Liang, A.; Bowlan, J.; De Heer, W. A. Metastability of Free Cobalt and Iron Clusters: A Possible Precursor to Bulk Ferromagnetism. *Phys. Rev. Lett.* **2011**, *107*, 057203.

(4) Moro, R.; Xu, X.; Yin, S.; De Heer, W. A. Ferroelectricity in Free Niobium Clusters. *Science* **2003**, *300*, 1265−1269.

(5) Lang, S. M.; Bernhardt, T. M.; Barnett, R. N.; Landman, U. Methane Activation and Catalytic Ethylene Formation on Free Au_2^+. *Angew. Chem., Int. Ed.* **2010**, *49*, 980−983.

(6) Ruderman, M. A.; Kittel, C. Indirect Exchange Coupling of Nuclear Magnetic Moments by Conduction Electrons. *Phys. Rev.* **1954**, *96*, 99−102.

(7) Kasuya, T. A. A Theory of Metallic Ferro- and Antiferromagnetism on Zener's Model. *Prog. Theor. Phys.* **1956**, *16*, 45−57.

(8) Yosida, K. Magnetic Properties of Cu-Mn Alloys. *Phys. Rev.* **1957**, *106*, 893−898.

(9) Jensen, J.; Mackintosh, A. *Rare Earth Magnetism*; Oxford University Press: New York, 1991.

(10) Sinha, S. K. Magnetic Structures and Inelastic Neutron Scattering: Metals, Alloys and Compounds, In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; North Holland: Amsterdam, 1978.

(11) Koehler, W. C.; Cable, J. W.; Wollan, E. O.; Wilkinson, M. K. Magnetic Structures of Thulium. *Phys. Rev.* **1962**, *126*, 6172−6178.

(12) Brun, T. O.; Sinha, S. K.; Wakabayashi, N.; Lander, G. H.; Edwards, L. R.; Spedding, F. H. Temperature Dependence of the Periodicity of the Magnetic Structure of Thulium Metal. *Phys. Rev. B* **1970**, *1*, 1251−1253.

(13) McEwen, K. A. Magnetic and Transport Properties of the Rare Earths. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; North Holland: Amsterdam, 1978.

(14) Cable, J. W.; Moon, R. M.; Koehler, W. C.; Wollan, E. O. Antiferromagnetism of Praseodymium. *Phys. Rev. Lett.* **1964**, *12*, 553−555.

(15) Birgeneau, R. J.; Als-Nielsen, J.; Bucher, E. Neutron Scattering from fcc Pr and Pr_3Tl. *Phys. Rev. B* **1972**, *6*, 2724−2729.

(16) Lebech, B.; McEwen, K. A.; Lindgärd, P. A. Magnetism in Praseodymium-Neodymium Single-Crystal Alloys. *J. Phys. C* **1975**, *8*, 1684−1696.

(17) Houmann, J. G.; Chapellier, M.; Mackintosh, A. R.; Bak, P.; McMasters, O. D.; Gschneidner, K. A. Magnetic Excitations and Magnetic Ordering in Praseodymium. *Phys. Rev. Lett.* **1975**, *34*, 587−590.

(18) Bucher, E.; Chu, C. W.; Maita, J. P.; Andres, K.; Cooper, A. S.; Buehler, E.; Nassau, K. Electronic Properties of Two New Elemental Ferromagnets: fcc Pr and Nd. *Phys. Rev. Lett.* **1969**, *22*, 1260−1263.

(19) Bleaney, B. Crystal Field Effects and the Cooperative State. II. The Cubic Compounds. *Proc. R. Soc. London, Ser. A* **1963**, *276*, 28−38.

(20) Trammell, G. T. Magnetic Ordering Properties of Rare-Earth Ions in Strong Cubic Crystal Fields. *Phys. Rev.* **1963**, *131*, 932−948.

(21) Cooper, B. R. Phenomenological Theory of Magnetic Ordering: Importance of Interactions with the Crystal Lattice. In *Magnetic Properties of Rare Earth Metals*; Elliott, R. J., Ed.; Plenum: London, 1972; Chapter 2.

(22) Johansson, T.; Lebech, B.; Nielsen, M.; Bierrum-Moiler, H.; Mackintosh, A. R. Crystal Fields and the Magnetic Properties of Praseodymium and Neodymium. *Phys. Rev. Lett.* **1970**, *25*, 524−526.

(23) Gerion, D.; Hirt, A.; Châtelain, A. High Curie Temperature and Possible Canted Magnetism in Free Gd Clusters. *Phys. Rev. Lett.* **1999**, *83*, 532−535.

(24) Pokrant, S.; Becker, J. A. Magnetization Curves of Dy_N Clusters. *Eur. Phys. J. D* **2001**, *16*, 165−168.

DOI: 10.1021/jp511926y
J. Phys. Chem. C 2015, 119, 11153−11159

(25) Pokrant, S. Evidence for Adiabatic Magnetization of Cold Dy_N Clusters. *Phys. Rev. A* **2000**, *62*, 051201.
(26) Douglass, D. C.; Bucher, J. P.; Bloomfield, L. A. Magic Numbers in the Magnetic Properties of Gadolinium Clusters. *Phys. Rev. Lett.* **1992**, *68*, 1774−1777.
(27) Douglass, D. C.; Cox, A. J.; Bucher, J. P.; Bloomfield, L. A. Magnetic Properties of Free Cobalt and Gadolinium Clusters. *Phys. Rev. B* **1993**, *47*, 12874−12889.
(28) Cox, A. J.; Douglass, D. C.; Louderback, J. G.; Spencer, A. M.; Bloomfield, L. A. Magnetic Properties of Rare-Earth Clusters. *Z. Phys. D* **1993**, *26*, 319−321.
(29) Bowlan, J.; Van Dijk, C. N.; Kirilyuk, A.; Liang, A.; Yin, S.; Rasing, Th.; De Heer, W. A. Size Dependent Magnetic Moments and Electric Polarizabilities of Free Tb, Ho, and Tm Clusters. *J. Appl. Phys.* **2010**, *107*, 09B509.
(30) Knickelbein, M. B. Spin Relaxation in Isolated Molecules and Clusters: The Interpretation of Stern-Gerlach Experiments. *J. Chem. Phys.* **2004**, *121*, 5281−5283.
(31) Xu, X.; Yin, S.; Moro, R.; De Heer, W. A. Magnetic Moments and Adiabatic Magnetization of Free Cobalt Clusters. *Phys. Rev. Lett.* **2005**, *95*, 237209.
(32) Xu, X.; Yin, S.; Moro, R.; De Heer, W. A. Distribution of Magnetization of a Cold Ferromagnetic Cluster Beam. *Phys. Rev. B* **2008**, *78*, 054430.
(33) De Heer, W. A.; Milani, P. Large Ion Volume Time-of-Flight Mass Spectrometer with Position- and Velocity-Sensitive Detection Capabilities for Cluster Beams. *Rev. Sci. Instrum.* **1991**, *62*, 670−677.
(34) Cerovski, V. Z.; Mahanti, S. D.; Khanna, S. N. Magnetization of Gd_{13} Cluster: Anomalous Thermal Behavior. *Eur. Phys. J. D* **2000**, *10*, 119−122.
(35) López-Urías, F.; Díaz-Ortiz, A.; Morán-López, J. L. Magnetism at Finite Temperature in Heavy Rare-Earth Clusters. *Phys. Rev. B* **2002**, *66*, 144406.
(36) Pappas, D. P.; Popov, A. P.; Anisimov, A. N.; Reddy, B. V.; Khanna, S. N. Spin Configuration of Gd_{13} Clusters. *Phys. Rev. Lett.* **1996**, *76*, 4332−4335.
(37) Viitala, E.; Merikoski, J.; Manninen, M.; Timonen, J. Antiferromagnetic Order and Frustration in Small Clusters. *Phys. Rev. B* **1997**, *55*, 11541−11551.
(38) Van Dijk, C. N.; Kirilyuk, A.; Rasing, Th.; Bowlan, J.; Liang, A.; De Heer, W. A. The Effect of Oxygen Doping on the Magnetism of Tb and Pr Clusters. *J. Appl. Phys.* **2010**, *107*, 09B526.
(39) Aguado, A.; Vega, A.; Lebon, A.; Von Issendorf, B. Insulating or Metallic: Coexistence of Different Electronic Phases in Zinc Clusters. *Angew. Chem., Int. Ed.* **2014**, *53*, 2111−2115.
(40) Bowlan, J.; Harding, D. J.; Jalink, J.; Kirilyuk, A.; Meijer, G.; Fielicke, A. Communication: Structure of Magnetic Lanthanide Clusters from Far-IR Spectroscopy: Tb_n^+ (n = 5−9). *J. Chem. Phys.* **2013**, *138*, 031102.
(41) Peters, L.; Di Marco, I.; Litsarev, M. S.; Delin, A.; Katsnelson, M. I.; Kirilyuk, A.; Johansson, B.; Sanyal, B.; Eriksson, O. Valence Stability and Spectral Properties of Rare-Earth Clusters. Manuscript to be published.

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J. Phys. Chem. C 2015, 119, 11153−11159