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Magnetization of Gd_{13} cluster: Anomalous thermal behavior

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Abstract. Theoretical studies of the temperature (T) dependence of magnetization of Gd_{13} clusters have been carried out within a classical Heisenberg model using Monte-Carlo simulations. It is shown that for a broad range of values of γ, defined as the ratio between competing ferro and anti-ferro magnetic couplings, the cluster magnetization increases with T in the low T region, as seen in experiment. The clusters are also shown to exhibit a wide distribution of moments at a given T, which broadens significantly with increasing T. It is suggested that this may affect the observed magnetic behavior of magnetic clusters in Stern-Gerlach experiments.

PACS. 31.15.Ar Ab initio calculations – 36.40.-c Atomic and molecular clusters – 71.24.+q Electronic structure of clusters and nanoparticles

Studies of atomic clusters over the last decade have shown that there are significant changes in the behavior of matter as one reduces the size from bulk to small clusters [1]. The changes arise due to the finite size, preponderance of low coordinated surface sites as well as geometrical arrangements which are different from those in bulk. These can profoundly modify the electronic structure which affects various properties. One of the most intriguing developments occur in the magnetic behavior [2]. For example, clusters of conventional itinerant ferromagnetic metals like Fe, Co, and Ni have been found to exhibit superparamagnetic relaxations [3–5]. The magnetic moments are generally enhanced over the bulk, but exhibit large variations with size for smaller clusters [6]. It is also found that clusters of Rh [7,8] which is non-magnetic in bulk, and those [9] of Mn which has an antiferromagnetic bulk phase, exhibit ferromagnetic order with large moments (ferromagnetic order here refers to the ferromagnetic alignment of the atomic moments).

An interesting case of the novel magnetic order in clusters has been that of Gd. Bulk Gd is ferromagnetic with a moment of $7.55\mu_B$ per atom [10]. A Gd_2 molecule has been found to have a spin moment of $8.82\mu_B$ per atom with ferromagnetic coupling [11]. The Gd_n clusters containing 10 to 30 atoms were, however, found to have magnetic moments between $(2.94 \pm 0.35 - 3.88 \pm 0.47)\mu_B$ per atom [12], therefore considerably below the bulk value. A Gd atom has 7 unpaired f-electrons and one unpaired d-electron. To obtain a moment of less than $6\mu_B$ per atom in a cluster, either some of the f-electron spins (in a given atom) have to be paired or the magnetic coupling between the atoms modified. Note that the f-spins are unpaired in the molecule and in the bulk where the exchange splitting is around 12 eV. It is therefore highly unlikely that they could be paired in clusters. This puzzle was recently resolved by Pappas *et al.* [13], who argued that like bulk Gd, small clusters are marked by indirect RKKY type exchange interactions which oscillate as a function of the distance between two magnetic atoms. Assuming a nearest neighbor *ferromagnetic*, and a non-nearest neighbor *antiferromagnetic* interaction within a Heisenberg model [14], they studied the spin configuration in Gd_{13} clusters. These studies showed that for a range of interaction strengths, the atomic spins assume configurations where the surface spins are canted (see Fig. 1). This leads to lower net magnetization and accounts for the observed anomalously low moments of the clusters.

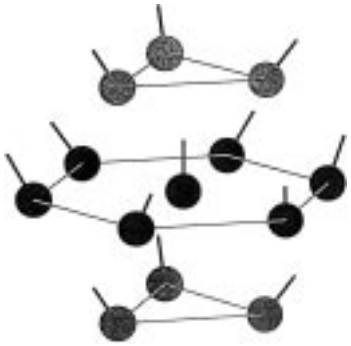

Fig. 1. Gd_{13} cluster. Spins are oriented to have D_{3h} symmetry. Atoms belonging to the lower, middle and upper planes are connected (except the middle one).

Experiments on Gd clusters also show another interesting new feature. Studies of clusters as a function of temperature show that the measured magnetization increases

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with temperature. This feature has also been recently seen in Gd nanoparticles [15] where the measured magnetization shows an increase with temperature for certain range of temperatures. These later experiments on a range of particle sizes further show that while the magnetization as a function of field saturates at high temperatures, it does not saturate at low temperatures. It is suggested [15] that these effects could be understood by assuming that the spins near the surfaces are not in alignment with the interior spins. While such a picture would be consistent with the ground state spin configurations for Gd_{13} found by Pappas *et al.* [13], no study of the temperature dependence of magnetization is available.

In this paper we present what we believe are the first theoretical investigations of the effect of temperature on the magnetic properties of small Gd_n clusters. The key issues we wish to focus are:

(1) how does the magnetization change with temperature and how is this related to the details of the coupling?
(2) at a given temperature, what is the distribution of magnetic moments amongst different clusters?

We show that the presence of competing ferromagnetic and anti-ferromagnetic couplings can lead to situations where the magnetization initially increases with temperature and then decreases. This behavior is linked to the excitations from the canted configuration to the ferromagnetic excited states. We also show that the clusters can have a wide distribution of magnetic moments. This could lead to a broadening of the cluster beams in Stern-Gerlach deflection experiments. We would like to point out that while our studies are carried out on Gd_{13} clusters, we believe that the results have a more wider applicability.

The system is described by a Hamiltonian H,

$$H = J\left(-\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j+\gamma\sum_{\langle i,j\rangle}{}'\,\mathbf{S}_i\cdot\mathbf{S}_j\right), \qquad (1)$$

where $\mathbf{S}_i$'s are the spins of the Gd atoms, the prime sign in the second sum denotes summation over all pairs of spins that are *not* nearest neighbors, and, $\gamma \geq 0$. J determines the energy scale, and, thus, we assume $J = 1$. The quantity we have calculated is the magnetization per atom M, defined as $M = (1/13)\sqrt{\sum_{i,j}\mathbf{S}_i\cdot\mathbf{S}_j}$. If all the moments are oriented parallel to each other $M = 1$. In a previous study [13] we had examined the ground state geometry of Gd_{13} clusters using *ab initio* electronic structure calculations and had shown that the hexagonal closed packed arrangement had the highest binding energy. In this work we have therefore assumed a hexagonal closed packed structure shown in Figure 1.

For $0 \leq \gamma < 0.29$, the ground state is ferromagnetic, *i.e.* all spins are aligned in the same direction. When the value of γ is further increased beyond 0.29, competition between ferro- and antiferro-magnetic interactions leads to a spin canting. The symmetry of the ground state is consequently reduced from the symmetric S_{13} to the canted C_{3v} symmetry [13]. The new symmetry, together with invariance under simultaneous rotation of all spins, is still sufficiently high to allow very accurate determination of the ground state. By rotating all spins such that the central spin is oriented along the z-axis of the cluster, and rotating all spins around the z-axis until spins outside the middle plane are in vertical symmetry planes, (1) can be expressed as a function of only three angles. First is the angle θ_u between spins outside the middle plane and the central spin, and other two angles (θ, ϕ) that determine the orientation of one of the spins in the middle plane. Values of other 21 angles are then fully determined from the symmetry, and, (1) becomes

$$\begin{aligned} H(\theta_u,\theta,\phi) = 3[&1-\gamma-(1+\gamma)\cos(2\phi)\\ &+\cos^2\theta(-2+4\gamma+(1+\gamma)\cos(2\phi))\\ &-2\cos\theta_u+3(-1+\gamma)\cos^2\theta_u\\ &+2\cos\theta(-1+(-2+4\gamma)\cos\theta_u)\\ &-2(1+\gamma)\sin\theta(\sqrt{3}\cos\phi-\sin\phi)\sin\theta_u]. \end{aligned} \qquad (2)$$

Calculation of the exact minimum of (2) is a simple computational task for any given value of γ. However, in order to confirm the symmetry of the ground state, we have minimized (1) first without assuming any symmetry, by using simulated annealing. Near-global minima were obtained and compared with the results of minimization of (2). The latter always had slightly lower energy, while the former always had almost C_{3v} symmetry. Thus, the symmetry of the ground state can be understood as a fine modification of the near-global energy minima into the exact one. This holds when the ground state is ferromagnetic as well, and, it can be used for an accurate determination of the transition point between ferromagnetic and canted ground states.

We notice that if the ground state had only C_{3v} symmetry, additional angle θ_d would have been needed to define the angle between one of the lower three spins and the middle spin, while θ_u would have been used only for the upper three spins. We have assumed that ground state has $\theta_u = \theta_d$. We have ensured that this assumption is correct by minimizing $H(\theta_u, \theta, \phi, \theta_d)$. This means, however, that the full symmetry of the ground state is D_{3h} instead of C_{3v}.

When $\gamma > 0.37$, the ground state remains canted but the symmetry changes to a mirror symmetry defined by one plane (C_2 group), and, the magnetization of the ground state changes discontinuously at the transition point [13]. Number of relevant degrees of freedom (angles) now becomes 12, and, therefore, finding exact ground states by using symmetry considerations is a considerably more difficult task than in the previous case.

Finite temperature magnetization has been calculated by using the parallel tempering Monte-Carlo (PTMC) algorithm [16]. The method consists of applying usual Metropolis Monte-Carlo (MC) steps (spin flips in our case) on a set of systems at different temperatures β_i, followed by a sequence of additional swaps of the ith and the jth system with a probability $\min(1, \exp(-(\beta_j - \beta_i)(E_i - E_j)))$. The swaps are performed sequentially between two

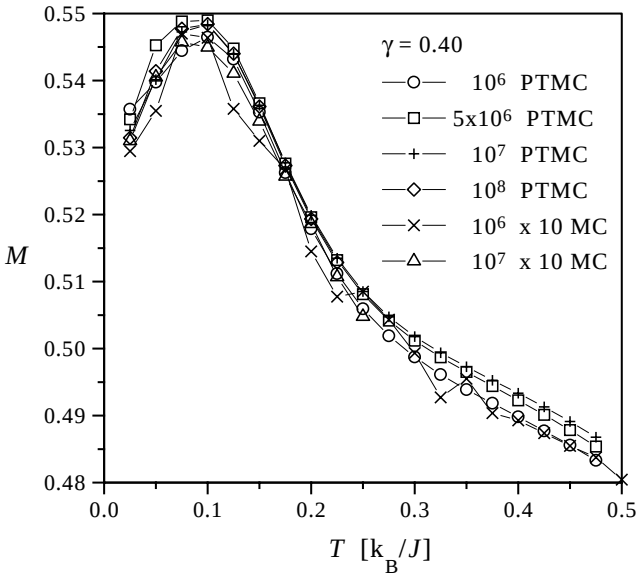

Fig. 2. Results of PTMC and MC simulations for various number of time steps. In the case of MC simulations, the result is an average over ten independent simulations.

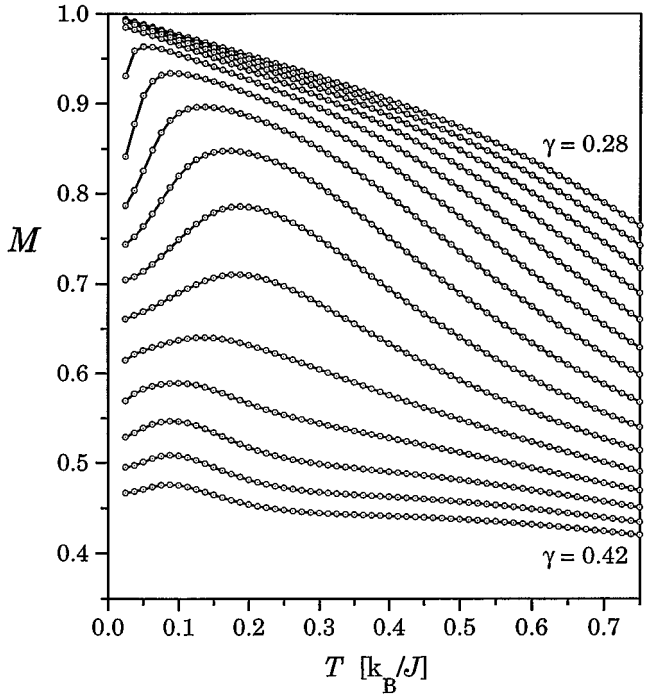

Fig. 3. Magnetization *vs.* temperature for different values of γ. Difference in γ for two neighboring curves is 0.01. The error in the low T regime is of the size of the circles (0.005) and is smaller for higher T.

systems at the neighboring temperatures, beginning from the pair at the high temperature end. Systems at higher temperatures explore more system configurations in the course of simulation, and, from the point of view of a system at some lower temperature, a swap allows the latter system to make a jump from one configuration to the another one with similar energy but which is much harder to access through usual MC steps. As a result, the system samples configuration space more efficiently.

Thermalization was monitored by recording the distributions of all 26 angles for each of the configurations one system goes through at the given temperature during the simulation. Due to the finite size of the system, global SO(3) symmetry of spin configurations cannot be broken, and, thus, every orientation of the spins has to be equally probable once the thermal equilibrium has been reached.

Figure 2 shows $M(T)$ for several MC and PTMC simulations, for a particular value of γ (= 0.4). In the case of MC, results are averages over ten independent simulations. All the results for M (except for $10^6 \times 10$ MC) are within 0.005 of each other for low T, and slightly smaller for higher T.

The temperature dependence of magnetization is given in Figure 3, and distributions of magnetization for three different values of γ are presented in Figure 4. Results are calculated performing 10^7 PTMC steps per point. When the ground state is ferromagnetic ($\gamma < 0.29$), magnetization decreases with the temperature, as expected. When γ increases beyond this critical value, the ground state changes from a ferromagnetic state to a canted ferromagnetic state which has a D_{3h} symmetry. One therefore expects to see some qualitative change in the temperature (T) dependence of magnetization M. We can clearly see that M increases with T from its zero temperature value for γ equal to or greater than 0.31.

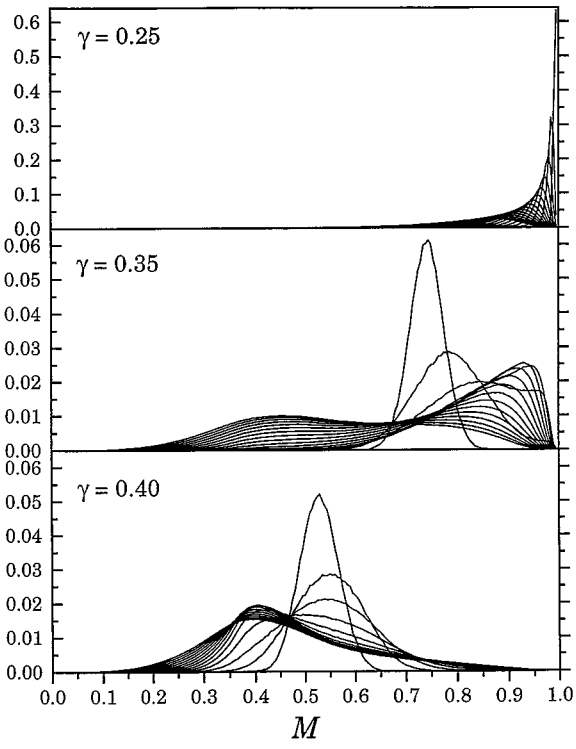

Fig. 4. Distribution of magnetization for three different values of γ. Lowest temperature is 0.025, and, the temperature step is 0.025. Broader curves correspond to higher temperatures.

It is possible that this increase is present for values of γ just above 0.29. But our finite T Monte-Carlo simulations cannot address this question because the lowest temperature of our simulation is 0.025. However, if we take the position of peaks in M for $\gamma = 0.31$, 0.32, and 0.33 and extrapolate towards $T = 0$, we see that it extrapolates to the value 1. This suggests that a peak in M might appear but at a very low T as soon as one crosses $\gamma = 0.29$, the critical value. Proving this point using MC simulations however appears quite difficult. The increase in M with T can be understood by noting that the thermal fluctuations lead to excitations of the system to other configurations with higher magnetization than the ground state. For $\gamma = 0.36$, highest relative increase in magnetization (compared to the ground-state value) is about 13%. Similar behavior occurs when the ground state has mirror symmetry, for the lower values of γ, but the magnitude of this increase is smaller, due to reduction in the level of competition between ferro and canted (low moment) configurations which get thermally excited. Finally, for large values of γ this effect disappears, and the magnetization again slowly decreases with the temperature, but the temperature dependence is rather weak.

As pointed out above, the observed low magnetic moments of Gd_n clusters were earlier explained as due to canting of the surface spins. Using the experimentally measured magnetic moments on Gd_n clusters and the calculated magnetization as a function of γ in [13], one obtains a value of γ in the range 0.35–0.4. It is interesting to note that for these values of γ, Figure 3 shows that the magnetization initially slightly increases with temperature. Following our initial theoretical work, Gerion *et al.* [17] have recently measured the temperature dependence of magnetization in Gd_n ($n = 13$, 21, and 22) clusters. For Gd_{13}, they estimate a $\gamma = 0.365$. For this γ their measured values for the temperature dependence of M are in very good agreement with our predictions [17]. Note, however, that the quantitative change depends on γ which depends on the electronic structure. This shows that the temperature dependence would depend on the cluster size. What is most surprising is that the clusters have a distribution of moments (see Fig. 4) at a given temperature, and the distribution depends sensitively on T. The experimental measurements of moments in clusters are carried out by passing size selected clusters through the gradient field in Stern-Gerlach magnets [6]. Variation of moments amongst clusters would lead to broadening of the deflection profiles in the experiment. The recent experiments [17] on Gd_n indeed observe very broad profiles compared to earlier experiments on transition metal clusters [3]. It is important to note that the broadening would be more pronounced if the passage time through the magnet is shorter than the relaxation times for the moments [6].

To summarize, we have shown that the observed increase in magnetization in Gd clusters can be understood using a simple Heisenberg model with competing interactions. The variation of magnetization with temperature are linked to the nature of the excited states and the presence of ferromagnetic excited states can lead to the observed increase. These theoretical results are consistent with recent experiments by Gerion *et al.* [17]. We would like to point out that although the present studies are carried out on Gd_{13} clusters, the results are applicable to other systems as well. For example, Hehn *et al.* [18] have recently obtained an array of cobalt dots on Al_2O_3 substrate and have observed the presence of canted configurations including vortices. This is similar to the case of Gd clusters and it will be interesting to study the temperature variations of magnetization in these magnetic arrays.

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