Spin Configuration of Gd_{13} Clusters

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The structure and spin configuration of a Gd_{13} cluster has been examined using theoretical electronic structure calculations and a Heisenberg model. The structure calculations show that the ground state geometry of the cluster has an hcp arrangement with a slightly reduced nearest-neighbor distance compared to bulk and an average moment of $7.8\mu_B$/atom. The Heisenberg model is calculated using an RKKY-like interaction. The effects of competing ferromagnetic and antiferromagnetic coupling for the nearest- and next-nearest-neighbor interaction, respectively, is investigated. It is shown that for a range of interaction strengths the spins assume a canted configuration. This effect leads to lower net magnetization of the cluster, and accounts for the anomalous low moments of Gd_n clusters which have been experimentally observed. [S0031-9007(96)00355-9]

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The field of small atomic clusters is drawing considerable attention since their properties are being discovered to be very different from bulk. The difference arises due to the preponderance of surface atoms as well as the reduced size. This leads to atomic arrangements as well as electrical, magnetic, optical, and chemical properties that are different from the bulk [1]. These properties change with size and composition and this has raised the possibility of forming new materials by properly assembling selected clusters [2]. One of the most intriguing developments in clusters relates to their magnetic behavior. The magnetic measurements are usually carried out by passing size selected clusters through a Stern-Gerlach experiment. Initial results [3–4] on transition metals, i.e., Fe and Co, showed that these clusters deviated uniformly in the same direction and had magnetization per atom far below the bulk. The reduced magnetization was contrary to theoretical predictions [5] that lowering the coordination enhances local moments and hence clusters should be more magnetic than bulk. This contradiction was resolved by the proposition [6] that the clusters were undergoing superparamagnetic relaxations (even though the bulk is ferromagnetic) with the total cluster moment sampling the configuration space as the cluster traveled through the gradient magnet. The intrinsic moments [7] calculated using the superparamagnetic model were indeed higher than bulk as predicted by theory. Another surprising development was the prediction [8] and the subsequent discovery [9] of magnetism in small clusters of Rh, which is nonmagnetic in the bulk.

Despite this progress in the understanding of transition metal clusters, the magnetic behavior of rare-earth clusters remains an unsolved problem [10]. Stern-Gerlach experiments [10–11] on size selected clusters in beams indicate that their behavior depends on size. While clusters of certain sizes deviate uniformly like transition metal clusters, for other sizes the beam spreads into a broad deflection. A nonuniform deflection can arise when the moment is fixed to the lattice, and is therefore unable to relax. The two behaviors can be understood as being due to the differences in the anisotropy energy with size. What is surprising is the measured moment per atom. For Gd clusters [10–11] exhibiting superparamagnetic relaxations, the measured moments are $0.5–3.0\mu_B$ per atom; far below the bulk value of $7.55\mu_B$ per atom. Note that a Gd atom has 7 unpaired *f*-spins and one *d*-electron. To obtain a moment of less than $6\mu_B$, either some of the *f*-spins would have to be paired or the coupling between the Gd atoms would have to be modified. The *f*-orbitals are highly localized and the Gd ions maintain these unpaired *f*-spins in the bulk [12] with an exchange splitting of 12 eV. A Gd_2 molecule has also recently been found to have a moment of $8.82\mu_B$ per atom [13] with ferromagnetic (FM) coupling. If the seven $4f$ spins are unpaired in the molecule and even in the bulk, it is unlikely that they will be paired in clusters. Another puzzling result is the temperature dependence of the moment [10–11]. The calculated moment is found to increase with temperature. To explain this, it has been suggested that some of the atomic moments are coupled antiferromagnetically at low temperature and ferromagnetically at high temperatures. A quantitative explanation using such a picture would require the presence of a large number of inequivalent sites with strongly varying coupling, which is unlikely in small, 13 atom clusters which are mostly symmetric [8,14].

In this Letter we propose a different picture for the magnetism in small Gd clusters via a study of the spin coupling. We first carry out nonrelativistic self-consistent local spin density calculations on a Gd_{13} cluster and show that the ground state is an hcp structure and that all of the $4f$ electrons are unpaired. As mentioned above, the magnetism in rare-earth metals arises due to $4f$ electrons localized at the ions and coupled via indirect exchange RKKY interactions mediated by the conduction electrons. The interaction oscillates as a function of distance, which leads to various helical

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magnetic structures which are apparent in some of the $4f$ rare-earth metals. For Gd, which is normally FM, it is found that at the (001) surface there is a magnetic reconstruction [15]. Antiferromagnetic coupling at the surface was predicted along with a 6.3% expansion of the first layer spacing in recent calculations [16]; however, subsequent IV-LEED studies [17] show that the first layer spacing is actually contracted by 2.4%, with a 1% second layer spacing expansion. Another reasonable explanation of this effect is that the nearest-neighbor coupling J of Gd remains FM, while the next-nearest-neighbor interaction, K favors AFM (antiferromagnetic) alignment. Because of the reduced coordination at the surface a relatively weak value of K relative to J may affect the alignment of the spins. In clusters, where the majority of the atoms lie at the surface, an oscillating interaction can also be expected to result in a canted spin arrangement. In this Letter, we examine the spin configuration in small clusters using an RKKY-like interaction for nearest- and next-nearest-neighbor interactions. In our model a FM nearest-neighbor interaction is used, in accordance with experimental Gd_2 and Gd surface results [13]. We show that these competing FM and AFM couplings lead to a ground state marked by canted spins. The cluster moment in any direction, determined by projecting the atomic moments on the z axis, is therefore much less then the sum of the atomic moments. The anomalous Stern-Gerlach deflections which are determined by the z component of the total cluster magnetization, are therefore measuring a low moment even though the intrinsic moments on the atoms are comparable to those of the bulk.

In order to first determine the ground state structural properties of Gd, a first-principles electronic structure calculation was carried out using a linear combination of atomic orbitals approach [18]. The exchange correlation effects were included within a local spin density functional [19]. The atomic orbitals entering the cluster wave function were generated from free atom calculations and included the $4f^7 5d^{0.99} 6s^2 6p^{0.01}$ as valence orbitals, with the core frozen. The Kohn-Sham equations were solved by calculating the Hamiltonian matrix elements numerically on a mesh. For details we refer the reader to earlier articles [20,21]. The ground state of the cluster was obtained by starting from icosahedral and hcp arrangements and optimizing the geometrical parameters to minimize the energy. The hcp structure was found to be 1.4 eV more stable than the icosahedral arrangement. The hcp lattice parameters are $c = 12.88$ and $a = 6.82$ a.u., which corresponds to a 6.7% reduction of the c axis relative to bulk and no change in the hexagonal plane. A global Mulliken population analysis showed that the average moment per atom of the cluster is $7.85\mu_B$, and that all of the 4-f spins were unpaired. This shows that the experimentally measured moment of $0.5-3.0\mu_B$ per atom cannot be explained by a reduction of the $4f$ moment in each atom. Could it be that the spins are canted as on surfaces? This possibility cannot be examined within a local spin density calculation because in this approximation the spins can only be either up or down.

To examine this possibility, we therefore propose to use the Heisenberg model

$$H = \sum_{ij} J_{ij} s_i \cdot s_j .$$

This is a reasonable model for Gd clusters because of the localized $4f$ spins and the fact that the calculated Fermi energy of the band structure is in a continuum of the density of states, showing that a metallic character is already present. To determine the spin configuration, the Hamiltonian is solved within the quasiclassical approximation with the Gd spins considered as vectors. In the present model we use two different interactions, one between an atom and its nearest neighbors J, and one between an atom and the rest of the atoms in the cluster to be K. An extended model including all five inequivalent exchange integrals is tractable in this formalism; however, the use of many parameters to determine one measured quantity, i.e., the reduced moment, results in a highly overdetermined system. In this work we examine the spin configuration with respect to the parameter $\gamma = K/J$.

In the following the c axis is chosen to be along the Z direction with the coordinate system as shown in the inset of Fig. 1. The orientation of the spins can be described using spherical coordinates, so that for the ith atom θ_i corresponds to the angle relative to the c axis (z direction) and ϕ_i the angle in the basal plane. The moment on the central atom is chosen to lie along the z axis only for convenience, thus $\theta_0 = 0$.

To obtain the ground state spin configuration, the angles θ_i and ϕ_i are determined via an iterative process. Basically, it is assumed that the local moment orients

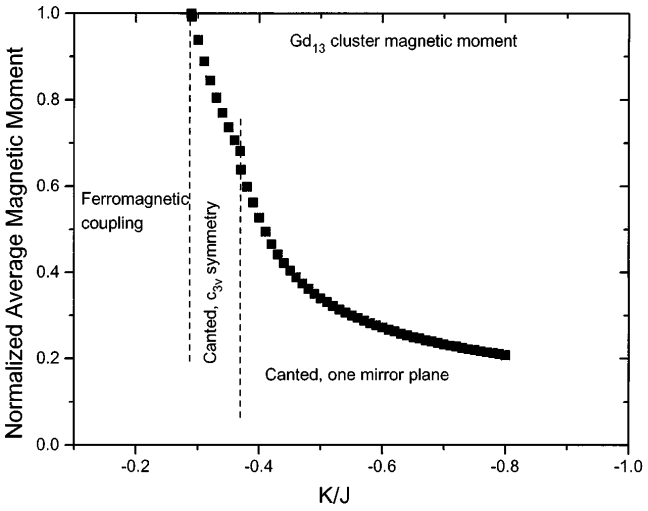

FIG. 1. Average magnetization per atom (normalized to the intrinsic moment) as a function of the parameter $\gamma = K/J$ (K = next-nearest-neighbor coupling, J = nearest-neighbor coupling strength).

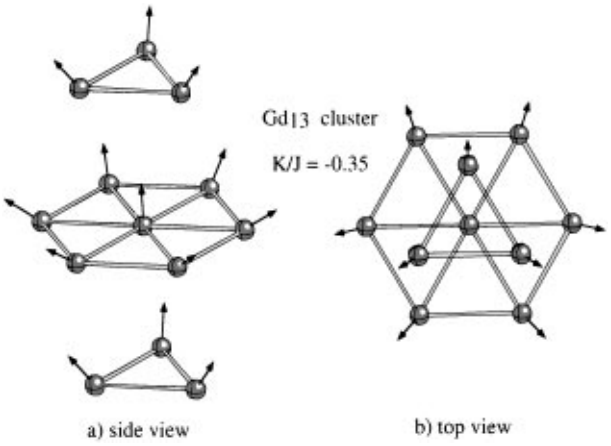

FIG. 2. Canted C_{3v} state for $\gamma = -0.35$.

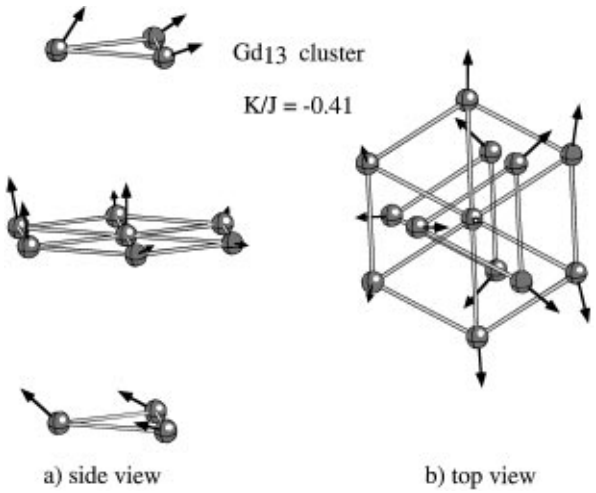

FIG. 3. Canted spin configuration for $\gamma = -0.41$.

in the direction of the molecular field created by the remaining atoms. One starts with random orientations for all the spins, and θ_i and ϕ_i are calculated iteratively until convergence. We found that, depending on the initial configuration, the cluster ended in several local minima. We calculated the energy for these minima and the minimum energy configuration was selected as the ground state. In Fig. 1 we show the calculated average moment for various values of $\gamma = K/J$. We have also marked the resulting spin configurations. For $\gamma > -0.29$, the ground state was found to be FM. An interesting transition takes place as γ is reduced below -0.29. For $-0.37 < \gamma < -0.29$, the ground state does not correspond to parallel spins. The spins are canted but are symmetric with respect to a 120° rotation about the z axis. The ground state has a C_{3v} symmetry that we refer to as the "symmetric mode," and is shown in Fig. 2. The transition is smooth and the magnetization gradually decreases from the bulk value as γ is decreased.

A second transition takes place as γ is further reduced. For $\gamma < -0.37$ another spin state becomes more stable. The symmetry C_{3v} is broken and the SC (spin configuration) has a lower symmetry. The cluster averaged moment jumps discontinuously from 0.68 to 0.64 (see Fig. 1). The only remaining symmetry corresponds to a reflection in a vertical plane. The resulting spin structure is shown in Fig. 3. Note that the decrease in γ also results in a further decrease of the average moment. An average atomic moment of $3.5\mu_B$ is achieved at $\gamma = -0.4$.

The above results show that the observed low moment in Gd_n clusters does not imply a reduction in the isolated atomic moments or a drastically modified nearest-neighbor interaction from the bulk. Rather, for a certain range of the nearest-neighbor FM and next-nearest-neighbor AFM couplings, the ground state corresponds to the canted spin configuration. This indicates the presence of an RKKY-like oscillatory exchange coupling in Gd that manifests itself in clusters and possibly at surfaces due to the reduced coordination. The Stern-Gerlach experiment, which measures the z component of the total magnetization, therefore leads to low moment per atom. Using the calculated Gd moment per atom, e.g., $7.8\mu_B$, a value of $\gamma = -0.4$ would reduce the normalized magnetization per atom by a factor of 2, and hence can account for the experimental finding. While we have restricted this work to 13 atom clusters as an example, similar canting due to an oscillatory exchange coupling could be used for any cluster size, in agreement with experiment, as well as to explain the magnetic reconstruction at the Gd(0001) surface [15].

The other issue corresponds to the anomalous temperature dependence of the cluster magnetization [11]. An increase in temperature will modify the mean field of the cluster due to spin fluctuations, modifying γ, and thus the spin configuration. In fact, since the next-nearest-neighbor AFM interactions are the weaker, they are first overcome and the system is likely to undergo an increase in the spin alignment, resulting in the increase of the moment that is observed experimentally. An investigation of these effects has to await a detailed *ab initio* investigation.

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