Magnetic Behavior of Superatom-Fullerene Assemblies

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ABSTRACT: It has recently been possible to synthesize ordered assemblies composed of magnetic superatomic clusters Ni₉Te₆(PEt₃)₈ separated by C₆₀ and study their magnetic behavior. We have carried out theoretical studies on model systems consisting of magnetic superatoms separated by non-magnetic species to examine the evolution in magnetic response as the nature of the magnetic superatom (directions of spin quantization), the strength of isotropic and anisotropic interactions, the magnetic anisotropy energy, and the size of the assembly are varied. We have examined square planar configurations consisting 16, 24 and 48 sites with 8, 12 and 24 magnetic superatoms respectively. The magnetic atoms are allowed 2 or 5 orientations. The model Hamiltonian includes isotropic exchange interactions with second nearest neighbor ferromagnetic and nearest neighbor anti-ferromagnetic couplings and anisotropic Dzyaloshinskii-Moriya interactions. It is shown that the inclusion of Dzyaloshinskii-Moriya interaction that cause spin canting is necessary to get qualitative response as observed in experiments.

INTRODUCTION

Magnetic nanoparticles are critical to memory storage, spintronics, and development of magnetic materials for a variety of industrial applications.¹–⁶ Starting from the bulk magnetic material, the decrease in size to smaller than a typical domain size results in a nanoparticle where the atomic moments are exchange coupled and the particle behaves like a giant magnet with a moment Nµ where N is the number of atoms and µ is the moment per atom. At small sizes, the magnetic anisotropy energy responsible for holding the magnetic moment沿 certain directions becomes comparable to the thermal energy.⁷,⁸ The thermal fluctuations can then lead to random flipping of the giant magnetic moment with time, leading to superparamagnetic relaxations and a thermally unstable magnetic order. The first step to stable magnetic order is then to control the magnetic anisotropy.⁹,¹⁰ We recently showed that one of the approaches to high anisotropy is to synthesize nanoparticles where the transition metal layers are separated by carbon.¹¹ Using wet chemical methods, we reported synthesis of iron-cobalt-carbide nanoparticles with blocking temperature, Tₘ, of 790 K for particles with a domain size as small as 5±1 nm. While the synthesis of nanoparticles with controlled anisotropy is an exciting development for applications such as memory storage, one of the questions is the magnetic behavior of an assembly of magnetic nanoparticles. For example, how can one develop soft or hard magnetic solids by controlling anisotropy and interaction between nanoparticles?

The purpose of this paper is to investigate the nature of collective response that emerges as one assembles clusters/nanoparticles. We study the progression of the collective behaviors as the particles are allowed to interact by isotropic and anisotropic interactions. We initially investigate the magnetic response as the particles interact via isotropic exchange interactions including ferromagnetic and anti-ferromagnetic couplings. In finite systems, the spin orbit coupling can lead to anisotropic exchange interactions including the well-known Dzyaloshinskii-Moriya (DM) interaction.¹² The DM interaction between interacting ions that lack inversion symmetry can lead to spin canting and is usually included at surfaces and in small particles characterized by outer sites that do not possess center of symmetry. The calculated magnetic behaviors are compared with those observed in recently synthesized ordered superatomic cluster solids.¹³,¹⁴ These solids consist of assemblies of individually synthesized chalcogenide superatoms that exchange charge with counter-ions to form ionic solids. One such assembly consists of Ni₉Te₆(PEt₃)₈ clusters with a Ni₉Te₆ core decorated with 8 tri-ethylphosphine (PEt₃) ligands attached to Ni sites. The cluster forms a rock-salt (NaCl) structure where the ligated cluster acts as an electron donor when combined with C₆₀ that acts as an electron acceptor. Experiments indicate that the ionic solid is magnetic and undergoes a ferromagnetic phase transition at low temperatures (4K) while it exhibits Curie-Weiss behavior at higher temperatures (above 10K). The SQUID measurements also indicate that the individual clusters behave as isolated localized magnets with a magnetic moment of around 5.4 μB per functional unit. The ferromagnetic phase and the hysteresis at 2K, require magnetic coupling between the superatoms. In a recent work we undertook an investigation of the magnetic moment and anisotropy in a Ni₉Te₆(PEt₃)₈ cluster using a first-principles approach.¹⁵ The theoretical studies indicate that the individual clusters have a spin magnetic moment of 5.3 μB in agreement with experiment. Further, the clusters are marked by low magnetic anisotropy energy (MAE) of 2.72 meV and a larger intracharge coupling exceeding 0.2 eV indicating that the observed paramagnetic behavior around 10K is likely due to superparamagnetic relaxations. The magnetic motifs separated by C₆₀ experience a weak superexchange and other interac-
tions that could stabilize a ferromagnetic ground state as observed around 2K. Experiments also indicate that the magnetization first increases and then decreases with increasing temperature in zero field cooled samples and increases with field at a given temperature. Our objective here is to investigate the variation of the magnetization in an assembly of magnetic clusters using a simple model that progressively includes ferromagnetic/antiferromagnetic interactions, magnetic anisotropy energy, and non-isotropic interactions. We further investigate assemblies of various sizes and allow magnetic species different space quantization. Our key objective is to demonstrate how the inclusion of various interactions affects the magnetic response and what combination of interactions could result in magnetic response reminiscent of the observed behavior in chalcogenide superatomic assemblies. In the next section, we outline the theoretical model used to investigate the collective behavior of assemblies of the magnetic clusters and then present our results followed by main conclusions.

METHODS

We employ a two-step model for the collective magnetic behavior of the metal cluster-fullerene superatomic clusters and solids. First, density functional theory calculations (DFT) have been carried out to calculate the magneto-crystalline anisotropy surface for an isolated metal cluster as well as the net magnetic moment using Vienna ab-initio simulation package (VASP). Details about density functional methods are given in our previous paper. Considering two metal clusters separated by a C60, we also evaluate the relative strength of the exchange coupling (J11/J12), i.e. the ratio of exchange coupling for 180° to that of a 90° metal-cluster-fullerene-metal cluster bond as well as the strength of the coupling (magnitude of J11 and J12). This information is used to construct the Hamiltonian for a larger assembly of metal clusters interacting through the fullerene by including the Heisenberg exchange energy between nearest and second nearest neighbors, magneto-crystalline anisotropy energy term for each cluster, and Zeeman energy for interaction between the cluster magnetic moment and the global magnetic field. We then go beyond the DFT predictions to modify the magnitude of the J11 coupling, include both the antiferromagnetic coupling (negative J12) and DM interaction whose strengths are estimated empirically. Comparison with observed behaviors indicates that the inclusion of DM interactions along with antiferromagnetic coupling is necessary to get qualitative trends of the experimentally observed magnitude of the magnetization and the manner in which it varies with temperature and magnetic field.

The optimized ground state structure of the ligated NiTe6(PET)8 is shown in Figure 1. The average Ni-Ni and Ni-Te distances are found to be 2.86 and 2.54 Å respectively. The NiTe6(PET)8 has the ground state of magnetic moment 6μB as obtained using SQUID measurements. We then calculated the energy difference as the spin moments on the two NiTe6(PH3)8 were aligned parallel and antiparallel to each other. We have defined the exchange energy “J” as follows

\[ J_{11} = E_{anti-ferro} - E_{ferro} \] (180° configuration)

\[ J_{12} = E_{anti-ferro} - E_{ferro} \] (90° configuration) (2)

The ferromagnetic state turns out to be ground state in each configuration. The values of J11 and J12 are found to be 7.7 and 3.92 meV respectively. Though, these results indicate the existence of weak exchange coupling between the clusters mediated by C60, as we will show, a model Hamiltonian that includes anisotropy and Zeeman energy corrections to Heisenberg model is essential for better understanding of magnetic phase transition. To model the collective magnetic response of the desired number of metal-clusters, we construct the Hamiltonian for finite systems consisting of metal clusters separated by C60 and arranged in a planar square configuration. The different planar cluster sizes for which the model Hamiltonian is calculated the change in total energy of NiTe6(PET)8 by constraining the magnetization along different (θ, ϕ) directions. The MAE is defined as the difference in total energy along the easy and hard axes. The MAE landscape shown in Figure 1 provides the variation in total energy for various values of (θ, ϕ). The calculated MAE of 2.72 meV corresponds to a relaxation time of 10^8 second using frequency of a GHz in a Neel model. This indicates the magnetic relaxation above 10K is likely due to superparamagnetic behavior. While the easy axis is along the body diagonal (Ni-Ni direction), the hard axis lies along the Ni-Te direction. The calculated orbital magnetic moments along easy and hard axes are found to be 0.194 and 0.205 μB, respectively. The small variation in orbital magnetic moment in going from easy to hard axes is consistent with the small values of MAE.

We now consider the low temperature ferromagnetic character of the superatomic solid. When the system is cooled in zero field or in applied magnetic fields, it shows a magnetic phase transition at 4K. Also, the presence of a hysteresis loop with coercive field of 400 Oe at 2K indicates a ferromagnetic phase. To develop a model Hamiltonian, we considered the nature of interaction between two ligated clusters separated by C60 as shown in Figure 2. These calculations were carried out by replacing PET ligands with PH3 due to limitations in our computational resources. We then calculated the energy difference as the spin moments on the two NiTe6(PH3)8 were aligned parallel and antiparallel to each other. We have defined the exchange energy “F” as follows

\[ F_{11} = E_{anti-ferro} - E_{ferro} \] (180° configuration)

\[ F_{12} = E_{anti-ferro} - E_{ferro} \] (90° configuration) (2)

The calculated change in total energy of NiTe6(PET)8 by constraining the magnetization along different (θ, ϕ) directions. The MAE is defined as the difference in total energy along the easy and hard axes. The MAE landscape shown in Figure 1 provides the variation in total energy for various values of (θ, ϕ). The calculated MAE of 2.72 meV corresponds to a relaxation time of 10^8 second using frequency of a GHz in a Neel model. This indicates the magnetic relaxation above 10K is likely due to superparamagnetic behavior. While the easy axis is along the body diagonal (Ni-Ni direction), the hard axis lies along the Ni-Te direction. The calculated orbital magnetic moments along easy and hard axes are found to be 0.194 and 0.205 μB respectively. The small variation in orbital magnetic moment in going from easy to hard axes is consistent with the small values of MAE.

Figure 1. Ground state structure of NiTe6(PET)8 and energy landscape for the magnetization direction as a function of ϕ and θ.
constructed is shown in Figure 3(a), (b) and (c). The different spin states considered is shown in Figure 3(d) and (e). As the number of clusters in the simulation increases, the model better approximates the behavior of a metal cluster-fullerene super solid. After setting up this Hamiltonian, the magnetization response corresponding to a specific magnetic field and temperature is calculated by assuming a Boltzmann distribution of the various possible spin configurations of the system. Different components of proposed model Hamiltonian are given as follows:

For an individual metal cluster the energy \( E^i \) corresponding to its magnetic moment pointing in a particular direction is evaluated by

\[
E^i = \sum_j E_{ij}^{\text{exchange}} + E_{ij}^{\text{anisotropy}} + E_{ij}^{\text{Zeeman}} + \sum_j E_{ij}^{\text{DMI}} \tag{3}
\]

Here, \( E_{ij}^{\text{exchange}} \) is described by the classical Heisenberg model to calculate the exchange energy between two nearest neighbor clusters as:

\[
E_{ij}^{\text{exchange}} = -J_i S_i S_j \cos \theta \tag{4}
\]

Here \( J_i \) is the exchange coefficient, such that \( J_{11} \) corresponds to a 180° metal-cluster-fullerene-metal cluster bond and \( J_{12} \) corresponds to a 90° metal-cluster-fullerene-metal cluster bond. The ratio \( J_{11} / J_{12} \) is calculated from DFT as 1.96. \( S_i \) and \( S_j \) are the magnitude of spin that we assumed equal to unity and \( \theta \) is the angle between the spin of the neighboring clusters. The sum is performed over first and second nearest neighbor metal clusters. We found that the ferromagnetic coupling alone cannot explain the low values of the moments and the observed peak at low temperatures. We therefore examined the case where \( J_{11} > 0 \) and \( J_{12} < 0 \) with the ratio of the magnitudes being the same as earlier. Our hypothesis is that since the first principles calculations were carried out using PH3 ligands instead of the much larger PEt 3 ligands, it is possible that the sign for \( J_{12} \) is negative for larger ligands. Here, \( J_{11} / J_{12} = -1.96 \). \( E_{anisotropy} \) is the magneto-crystalline anisotropy energy corresponding to the spin to the \( 'i' \)th metal-cluster pointing in a particular direction that can be calculated from the DFT estimate of the magneto-crystalline anisotropy surface. \( E_{Zeeman} \) is the energy of interaction between the cluster magnetic moment and the global magnetic field given by:

\[
E_{Zeeman} = -\mu_0 M. H = -\mu_0 M H \cos \theta \tag{5}
\]

Here \( M \) is the net moment of the metal-cluster system (that was considered to be 5.4 \( \mu_B \) and is consistent with both DFT and experimental results), \( H \) is the applied magnetic field and \( \theta \) is the angle between the global magnetic field and net magnetic moment of the cluster. Finally, to better explain the experimental data of both the value of the magnetic moments and their variation with field, we include the Dzyaloshinskii-Moriya (EDMI) interaction between two non-collinear nearest neighbor clusters given by:

\[
E_{DMI}^{ij} = -D_{ij} S_i S_j \sin \theta \tag{6}
\]

Here, \( S_i \) and \( S_j \) are the magnitude of spin that we assumed equal to unity and \( \theta \) is the angle between the spin of the neighboring clusters. \( D_{ij} \) is the interaction between two magnetic sites and is given by [12]:

\[
D_{ij} = \frac{D_0}{R_{ij}} \sum_n \frac{R_{in} R_{jn} (R_{in} \times R_{jn})}{(R_{in} R_{jn})^3} \tag{7}
\]

Here \( R_{in} \) and \( R_{jn} \) are the vector joining the magnetic sites \( i \) and \( j \) to the non-magnetic site \( n \) respectively. \( D_0 \) is proportional to the spin-orbit coupling and it is the measurement of the strength of the interaction. From equation 7 we can see that when \( R_{in} \) and \( R_{jn} \) are parallel the interaction is zero. Therefore we assume that for the 180° metal cluster-fullerene-metal cluster bond there will be no DM interaction whereas this term is important between clusters with the 90° metal-cluster-fullerene-metal cluster bond at the surface. Since the system studied is a powder with large surface to volume ratio, this term is important. The magnitude of \( D_0 \) term was taken empirically.

The total energy of the system for a particular spin configuration “q” is calculated as:

\[
E_{\text{system}} = \sum E_i \tag{8}
\]

The total energy of the system for every possible spin configuration can be calculated likewise.

In our model we considered 2 and 5 spin states. Consideration of only 2-spin states leads to a simple 2D Ising model. Here, the magneto-crystalline anisotropy cannot be incorporated as the two spin states shown in Figure 3(d) have degenerate magneto-crystalline anisotropy energy.
However, this model is amenable to be extended to a large number of clusters (for symmetry reasons we study number of clusters, n=12, 24). At n=24, the 2-spin state leads to $2^{24} \approx 10$ million spin configurations, which is still computationally feasible. However, we do consider 5 spin states shown in Figure 3(e), to understand the effect of magneto-crystalline anisotropy and gradual canting of spins due to the DM term. In this case, we were limited to 8 and 12 clusters due to prohibitive cost of computation of all (e.g. $5^n$, n=number of clusters) spin configurations.

At each given global magnetic field and temperature, the total energy of the system is calculated for each spin configuration and the magnetization of the system is calculated as follows:

$$M(H,T) = \frac{\sum_{q=1}^{N} E_q}{\sum_{q=1}^{N} M_q \times e^{\frac{-E_q}{kT}}}$$

Here $M_q$ and $E_q$ are respectively the net moment and total energy corresponding to the $q^{th}$ spin configuration and $N$ is the total number of possible spin configurations of the system.

RESULTS AND DISCUSSION

The theoretical model can predict the magnetization response of metal-cluster-fullerene superatomic supersolids with appropriately large number of such clusters. In particular, we studied magnetization vs. temperature at fixed magnetic fields.

1.1. Ferromagnetic behavior ($J_{11}/J_{12} > 0$)

(i) Effect of cluster size studied with a 2-spin model

Figure 4(a) shows the temperature dependence of magnetization at 200 Oe, 500 Oe and 1000 Oe magnetic fields for different cluster sizes. Clearly, with increasing number of clusters, it takes higher thermal energy to demagnetize the sample. This is expected as ferromagnetic behavior is a collective phenomenon and for small number of clusters the thermal effect is more significant. As we increase the temperature (for a fixed number of clusters) the superatomic solid loses collective magnetic interaction and hence displays paramagnetic behavior.

NOTE: A summary of the nominal values of the strengths of the different ferromagnetic, antiferromagnetic, DM coupling terms, magnetocrystalline anisotropy energy, etc. are given in Table-1.
(i) Effect of cluster size studied with a 2-spin model

Figure 4(c) shows the temperature dependence of magnetization at different fields with $J_{11}/J_{12} = -1.96$, which leads to anti-ferromagnetic ordering. This interaction and therefore higher thermal energy is required to break the antiferromagnetic coupling. This is the reason that the magnetization peak shifts to the right and the peak magnetization value decreases. As $J_{12}$ is reduced due to increase in the ratio, thermal and Zeeman energy have higher impact on the system.

(ii) Effect of the $J_{11}/J_{12}$ ratio (exemplified by 24 cluster 2-spin model)

Figure 4(e) shows the temperature dependence of magnetization at different fields for different $J_{11}/J_{12}$ ratios. In all of our calculations, we kept $J_{11}$ constant. Therefore, variation in $J_{11}/J_{12}$ ratio results in a variation in $J_{12}$. If we decrease the ratio, $J_{12}$ increases. Increasing $J_{12}$ increases the antiferromagnetic interaction and therefore higher thermal energy is required to break the antiferromagnetic coupling.

(v) Effect of Dzyaloshinskii-Moriya interaction (DMI)

Figure 4(h) shows DMI effect on a 8-cluster and 12-cluster system. As number of clusters increase, the blocking temperature will continue to shift to the right and the peak magnetization of 1000 Oe curve will fall down whether the peak of 200 Oe curve will remain same. It is because for high magnetic field, most of the spins occupy the nearest state to the applied field direction without a complete 180 degree flip that comes at the expense of a large increase in antiferromagnetic coupling. In each of these models (whether 2-spin or 5-spin), increasing the number of clusters makes the system less sensitive to temperature effects and leads to the trends explained earlier.

| Parameters                  | Values                          | Figures |
|-----------------------------|---------------------------------|---------|
| $J_{11}$                    | $0.9 \times 10^{-23}$ J         | (a)-(i) |
| $J_{11}/J_{12}$             | -1.96, -1, -1.96 and -4         | (a), (b), (i) |
| $D_{12}$                    | $1.5 \times 10^{-25}$ J         | (c)-(h) |
| $E_{MMAE}$                  | $3.04 \times 10^{-26}$ J        | (f)     |
| (easy axis-hard axis)       | (10 times $E_{MMAE}$, 100 times $E_{MMAE}$, 500 times $E_{MMAE}$) | (h)     |

Table 1: Values of different parameters used for simulations in Figr 4.
Figure 5 shows the temperature dependence of magnetization when we normalized the temperature axis by dividing temperature axis of each curve by its blocking temperature. We justify this by the observation that as the cluster numbers are increased (to a point where they model a true periodic solid) the blocking temperature shifts to the right and eventually match the experimental data better. In Figure 5(a) we can see that as we increase the anisotropy energy, the higher field curve tends to move towards the experimental data but lower field curve diverges from the experimental results. Therefore, we clearly see that we need to incorporate an effect that will bring the higher field magnetization curve closer to the experimental data by significantly lowering the magnetization but at the same time leave the low field magnetization curve relatively unperturbed. In Figure 5(b), the DMI interaction has been incorporated. We can see that, the reduction in magnetization at higher field is more significant than the reduction in magnetization for lower field, which is required in order to better match the experiment. Moreover, in Figure 5(c) we can see that as we increase the number of clusters the theoretical magnetization vs. temperature curve’s peak magnetization is lowered. This is because as the cluster numbers increase, the spin can gradually rotate over many clusters to form true Skyrmion-like states and decrease the net magnetic moment. We cannot go beyond 12-clusters due to computational limitations. Nevertheless, theoretical data appears to be on the track to converging with the experimental data as the cluster numbers are increased to a point where we can approximately model the behavior of a periodic superatomic solid.

CONCLUSIONS
With the inclusion of the DMI interaction, we have successfully been able to model and explain the collective magnetic behavior of a metal-cluster–fullerene-metal cluster system. This indicates that bulk Dzyaloshinskii-Moriya interaction could be important to the understanding of many of these systems.

ASSOCIATED CONTENT

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Notes
All the authors discussed the results and commented on the manuscript.

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