Using graphene to control magnetic anisotropy and interaction between supported clusters

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Abstract

Stabilization of magnetic order in clusters/nanoparticles at elevated temperatures is a fundamentally challenging problem. The magnetic anisotropy energy (MAE) that prevents the thermal fluctuations of the magnetization direction can be around 1–10 K in free transition metal clusters of around a dozen atoms. Here we demonstrate that a graphene support can lead to an order of magnitude enhancement in the anisotropy of supported species. Our studies show that the MAE of supported Co\textsubscript{5} and Co\textsubscript{13} clusters on graphene increase by factors of 2.6 and 25, respectively. The enhancement is linked to the splitting of selected electronic orbitals that leads to the different orbital contributions along the easy and hard axis. The conductive support enables a magnetic interaction between the deposited species and the nature of the magnetic interaction can be controlled by the separation between supported clusters or by vacancies offering an unprecedented ability to tune characteristics of assemblies.

1. Introduction

The principal quantity controlling the applications of magnetic clusters/nanoparticles is the magnetic anisotropy energy (MAE) [1–3] that determines the minimum energy for disorienting the direction of magnetization [4, 5]. For small clusters containing around dozen atoms, the MAE is only of the order of few kelvins and one of the customary approaches to increase the MAE is then to deposit clusters on substrates like Pt marked by strong spin–orbit interaction (SOI) [4, 6]. In this work, we propose an alternate approach that enhances intrinsic anisotropy of individual clusters and further allows assemblies with magnetic interaction between them. These features emerge on a substrate that is neither magnetic nor has significant SOI. We show that Co\textsubscript{5} and Co\textsubscript{13} clusters, that have a low magnetic anisotropy of 0.9 meV (10.4 K) and 0.12 meV (1.4 K) respectively, undergo substantial enhancement of MAE when supported on graphene. The enhancement is driven by the modest interaction that changes the atomic structure and couples to selected orbitals to stabilize the orientation of the magnetic moment via the intrinsic SOI. The present work complements a recent development where metal-carbon nanoparticles with size \(\approx 8\) nm have been found to have blocking temperature (TB) in excess of 570 K [5]. These nanoparticles have layers of Co atoms separated by carbon layers and our studies have shown that the large MAE is driven by the reduced mixing between C and Co states. In fact, our calculated anisotropies were within a few percent of the experimental values.

In this work, we examine Co clusters supported on graphene. Graphene is an ideal substrate as it is strong and non-reactive. In addition, it is conducting so that the deposited species can be accessed in experiment [7, 8]. In general, the bonding with C in metal carbides quenches the magnetic moment of transition metal (TM) atoms [9]. However, since the C atoms in graphene are strongly bonded, the deposited clusters are expected to bind weakly preventing substantial reduction of the moment. The mild interaction, however, could affect MAE as the binding with C-p electrons could provide directionality to the d-states of the TM clusters. Co\textsubscript{5} and Co\textsubscript{13} clusters were selected as prototype systems to demonstrate the observed effect, since the free clusters have low MAE. We show that the deposited species not only exhibit enhanced anisotropy, the interaction between the deposited species can be modified by separation and by creating defects in the support.

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2. Computational method

The magnetic and electronic properties were probed using density functional theory (DFT) within generalized gradient approximation (GGA) using the parameterizations by Perdew et al [10]. We have used the Vienna *ab initio* simulation package [11, 12] for our calculations which uses the plane wave basis set. For the case of strong correlations, we used a GGA + U approach [13] with a U value of 4.0 eV for Co 3d-states. The projector-augmented wave method [14] was used to represent the electron–ion interaction and the valence states of Co and C were described by [Ar] 3d⁴⁴s¹, and [He] 2s²2p², respectively. The energy cutoff for the plane-wave basis was set to be 400 eV. The calculations for free Co₅ and Co₁₃ clusters are done using simulation box of size (12x12x12) Å³ and (15x15x15) Å³, respectively, which is sufficiently large to minimize the interaction between the periodic images.

In order to calculate the MAE, we have performed non-self consistent calculation with the SOI included where the charge density is kept fixed as obtained from the self-consistent scalar relativistic calculation. The details of the calculational procedure of MAE has been published elsewhere [21]. In order to calculate MAE and the distance-dependent exchange energies for deposited clusters, we have used (5 × 3) and (14 × 6) supercells of graphene sheets constructed from an orthorhombic primitive cell consisting of 60 and 336 carbon atoms, respectively. The length of the supercell along the direction perpendicular to graphene plane is set to 23 Å. While the free cluster calculations are performed using only one k-point, i.e., at the Γ-point, a k-mesh of (3 × 3 ×1) was used for graphene-supported clusters within the Mokhorst–Pack scheme to generate the special k-points for constructing the charge density. The structural optimization is done using the conjugate gradient method. The tolerance for the total energy change for structural optimization was set to 10⁻⁶ eV. The electronic density of states (DOS) are calculated with Gaussian broadening parameter of 0.05 eV. The local magnetic moments are calculated by the integration of the spin-density over atom-centered spheres with radius 1.302 and 0.863 Å for Co and C atoms, respectively.

Previous studies have shown that gradient corrected functionals [10] used in this work can provide quantitative estimates for several properties of free clusters or their assemblies including nanomagnets where the magnetic clusters are linked by organic linkers [15]. One such example is a Mn₁₂O₁₂ acetate nanomagnet where Pederson and Khanna obtained a MAE of 56 K, close to the experimental value of 55.6 K. The functionals also lead to electronic band gaps in cluster assembled materials within few percent of the experimentally measured values [16]. The success of the functionals in describing cluster properties could be due to the localization of charge in clusters that reduces the delocalization errors known to be one of the principal sources of failure of DFT in extended systems [17]. For supported clusters, Co₅ and Co₁₃ were placed on the graphene sheet at various locations and with different orientations, to determine the most stable configuration.

3. Results and discussions

The lowest energy structures for the graphene-supported clusters as well as the free ones along with their magnetic moments are shown in figure 1. Previous studies on free clusters have indicated that Co₅ has a triangular bipyramidal structure while the Co₁₃ has an icosahedral shape marked by high symmetry and stability [18].

For a Co₅ cluster, two geometries are examined, namely, the trigonal bipyramid and a square pyramid. A distorted-triangular bipyramid structure for a free Co₅ is found to be 0.14 eV lower in energy than the square pyramidal structure which is in agreement with previous studies [19]. Assuming a perfect triangular bipyramid with bulk Co lattice spacing that corresponds to a Co–Co distance (d_Co–Co₅) of 2.50 Å, the two apex atoms with three-fold coordination in the trigonal bipyramid structure contracted to a separation from 3.80 Å in the ideal structure to 3.11 Å with an average nearest neighbor d_Co–Co of 2.18 Å. The remaining three sites (atoms in the basal plane) with four-fold coordination exhibit an expansion d_Co–Co from 2.50 to 2.64 Å. Two d_Co–Co in the basal plane are of length 2.64 Å, while the other d_Co–Co is of length 2.67 Å, which is reminiscent of Jahn–Teller distortion in clusters [20]. The geometry optimization of free Co₁₃ cluster results in a slightly distorted icosahedral structure compared to its ideal structure [21] where the average radial and outer-shell bond lengths increase by 0.43% and 0.81% compared to the corresponding bond lengths of the ideal icosahedron. The key issue is the change in atomic structure as the clusters are supported on graphene. For Co₅, the optimized structure is reminiscent of a square pyramid, where the apex Co atom is bonded to the six-fold hollow site of graphene with the average d_Co–C of 2.25 Å. While the d_Co–Co for atoms in the square plane is 2.16 Å, the d_Co–Co from apex to basal plane is elongated to 2.40 Å. For supported Co₁₃, the icosahedral symmetry of the cluster is substantially reduced. The most stable structure has two of the Co atoms of cluster bonded to the bridge site of the graphene sheet. The radial d_Co–Co in the adsorbed Co₁₃ vary from (2.30 to 2.50) Å whereas the outer shell
shows a variation from (2.31 to 2.78) Å. Such large variations in $d_{\text{Co-Co}}$ w.r.t. the free Co$_{13}$ cluster indicate a strong structural distortion.

The strength of the interaction between the cluster and graphene determines the stability of cluster. Therefore, we calculated the binding energy (BE) via the energy difference:

$$BE = E_{\text{(graphene)}} - E_{\text{Co$_n$}} - E_{\text{Co$_n$ on graphene}},$$

where, $n$ is the number of Co atoms in the cluster. $E_{\text{(graphene)}}$, $E_{\text{Co$_n$}}$, and $E_{\text{Co$_n$ on graphene}}$ are the total energies of the graphene sheet, free Co$_n$ cluster, and that of the supported species, respectively. We find that Co$_5$ and Co$_{13}$ are bound to graphene with a BE of 1.02 and 2.24 eV, respectively, which are lower than the BE of a free Co–C dimer (3.20 eV). This indicates that the clusters are only moderately bound to graphene but enough to prevent the detachment and migration of clusters on the surface under ambient temperature. The binding reduces the spin moments from 13 $\mu_B$ (free Co$_5$) to 11 $\mu_B$ and from 31 $\mu_B$ (free Co$_{13}$) to 21 $\mu_B$ for the deposited species. The reduction in the magnetic moment is non-uniform across the cluster and the maximum reduction occurs at sites linked to graphene as the bonding of the Co-d states with C-sp states reduces the magnetic moment. Figures 1(c) and (d) quantifies this reduction for various sites in Co$_5$ and Co$_{13}$, respectively.

The change in geometry due to binding affects the electronic structure that determines the MAE. In small clusters, the main contribution to MAE comes from the SOI which can be calculated by perturbation approach using the charge density obtained from scalar-relativistic treatment. The MAE was obtained by using the magnetic force theorem [23], where we calculated the difference between the maximum and minimum values of the $\theta$-dependent total energy, i.e., $\text{MAE} = |E_{\text{max}}(\theta, \phi) - E_{\text{min}}(\theta, \phi)|$ [21]. The SO contribution to energy was calculated by constraining the magnetic moment along different directions of azimuthal angle $\phi$ in steps of 15°. For each $\phi$, the polar angle $\theta$ was varied in steps of 10°. For free Co$_5$ and Co$_{13}$, we obtain MAE values of 0.9 and 0.12 meV, respectively. The calculated value of Co$_{13}$ is found to be larger compared to the previous study [21], as the clusters in the present work are fully optimized without any symmetry constraints, whereas in the previous work, the structure was transformed through a path characterized by two structural parameters and a series of single point calculations were performed. It is known that the presence of structural symmetry reduced the MAE due to cancellation of symmetry of the even order terms. When the symmetry is reduced due to the complete structural optimization associated with local distortions, the lower even order terms contribute to the MAE.

In the present calculations the MAE of supported Co$_5$ and Co$_{13}$ are found to be 2.31 meV (27 K) and 2.98 meV (35 K), respectively. These values translate into an increase by factors of 2.6 and 25 compared to the free clusters for Co$_5$ and Co$_{13}$, respectively. The change in MAE is accompanied by a change in the direction of easy ($E$) and hard ($H$) axes as shown in figure 1. We found that while the spin moments remain collinear for all cases, there exists a degree of non-collinearity in orbital moments. This is in agreement with a previous study [22]. The changes in the $E$ and $H$ axes as well as the increase in MAE are ultimately linked to the evolution of the electronic structure. One effect of adsorption is the charge exchange with the support. A Bader analysis [24] of the resulting charges indicates a net charge transfer from the cluster to the graphene of 0.38 e and 1.16 e for Co$_5$ and Co$_{13}$, respectively, where e is the electronic charge. The numerical values of the local charge on each atom are listed in table 1.

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**Figure 1.** Geometrically optimized structures of free (a) and (b) and graphene-supported (c) and (d) Co$_5$ and Co$_{13}$ showing the onsite spin moments (in $\mu_B$) $m_i$, where $i$ denotes the atom index. The light (orange) and dark (black) balls denote the Co and C atoms, respectively. The blue arrows represent the easy ($E$) and hard axis ($H$) for each case.
The significant charge transfer occurs from the Co atoms bonded to the C-atoms of graphene. This evoked the suspicion that the graphene–cluster interface might be playing an important role in determining the MAE. To gain a physical insight we used the perturbative approach as the change is small [15]. To a second order in perturbation, the change in energy, $\Delta_2$, with the quantization axis can be expressed as

$$\Delta_2 = \alpha + \sum_{ij} y_{ij} \langle S_i \rangle \langle S_j \rangle,$$

where,

$$\alpha = \sum_{ij} \left( M_{ij}^{12} + M_{ij}^{21} \right),$$

$$y_{ij} = \frac{1}{(\Delta N)^2} \sum_{ij} \left( M_{ij}^{11} + M_{ij}^{22} - M_{ij}^{12} - M_{ij}^{21} \right),$$

$$M_{ij}^{\sigma\sigma'} = \sum_{k=\text{occ.}} \sum_{k'=\text{unocc.}} \langle \psi_{k\sigma} | V_i | \psi_{k'\sigma'} \rangle \langle \psi_{k'\sigma'} | \psi_{k\sigma} \rangle.$$  

Here,

$$\langle \psi_{k\sigma} | V_i | \psi_{k'\sigma'} \rangle = \frac{1}{2\Delta^2} \left( \left( \frac{\partial \psi_{k\sigma}}{\partial z} \right)^2 - \left( \frac{\partial \psi_{k\sigma}}{\partial y} \right)^2 - \left( \frac{\partial \psi_{k\sigma}}{\partial x} \right)^2 \right).$$

$\Phi (r)$ is the Coulomb potential, $S_i$’s are the $i$th ($i = x, y, z$) component of the total spin of the system along the quantization axis, $\epsilon_{k\sigma}$ is the single particle energy of the $k$th state with spin $\sigma$ (assigned 1 and 2) and $\Delta N$ is the number of unpaired electrons. Since the tensor $y_{ij}$ (equation (4)) depends on the orbital character of the system, anisotropy depends on both orbital and spin character of the single particle levels. The matrix elements $M_{ij}$ involve a transition from occupied ($k$) to unoccupied states ($k'$) and hence the anisotropy is sensitive to the details of the electronic structure. There are four terms coupling the occupied and unoccupied states. Two of these couple spin-up (1) or -down (2) occupied states with unoccupied states of similar spin while the remaining terms involve a spin flip between occupied and unoccupied states. The denominator in these terms involves the energy difference between occupied and unoccupied states and it is reasonable to assume that the main contribution comes from levels close to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels. The minimum energy difference corresponds to the HOMO–LUMO gap which plays a significant role (the values are listed in table 2). In order to show these competing effects, we also show the spin-polarized DOS in figure 2 for the free and deposited Co$_5$ and Co$_{13}$, respectively. For free clusters, the discrete energy levels have been broadened to facilitate the comparison with the deposited
species. The electronic structures of free Co$_5$ and Co$_{13}$ clusters lead to a grouping of levels resulting in a larger HOMO–LUMO gap of 0.43 and 0.19 eV, respectively, and the lower values for MAE as 0.9 meV (10.44 K) for Co$_5$ and 0.12 meV (1.4 K) for Co$_{13}$ clusters. As the clusters are supported on graphene, the electronic states are spread out leading to a lowering of the HOMO–LUMO gap of 0.1 eV (deposited Co$_5$), 0.04 eV (deposited Co$_{13}$) and a larger number of states close to the Fermi level.

We observed that the HOMO and LUMO for free and deposited clusters are primarily composed of Co-d states. For deposited Co$_5$, the HOMO and LUMO are composed of the states from the Co atom close to the graphene whereas, for deposited Co$_{13}$, the HOMO is occupied by d-states of Co atoms that are away from graphene and the LUMO is occupied by the d states of the Co atoms close to the graphene. Such difference in the occupancies of the energy levels are probably responsible for the strong enhancement of MAE for the deposited Co$_{13}$ relative to its free cluster by a factor of 25 unlike that of the adsorbed Co$_5$ which is enhanced by a factor of 3. In addition, the levels around HOMO or LUMO have both spin-up and spin-down character and all four terms contribute to the anisotropy. For Co$_{13}$ that shows the larger increase in MAE compared to free cluster, the levels in the spin-down for the supported cluster are densely populated around the HOMO and LUMO and contribute to the enhancement of MAE.

Within a second order perturbation theory, anisotropy of a system can be related to the orbital moments by the Bruno formula [25]

Table 2. The MAE (meV), total spin moment ($\mu_B$) and the HOMO–LUMO gap (eV) for free and graphene-supported Co clusters based on GGA and GGA + $U$ calculations with $U = 4$ eV for Co-d orbitals.

| System                | MAE (meV) | Magnetic moment ($\mu_B$) | HOMO–LUMO gap (eV) |
|-----------------------|-----------|---------------------------|--------------------|
|                       | GGA       | GGA + $U$                 |                     |
| Co$_5$                | 0.90      | 1.54                      | 0.43               |
| Co$_{13}$             | 0.12      | 0.23                      | 0.19               |
| Co$_5$ on graphene    | 2.31      | 0.48                      | 0.10               |
| Co$_{13}$ on graphene | 2.98      | 2.14                      | 0.04               |

Figure 2. The spin–polarized scalar–relativistic density of states (DOS) for free Co$_5$ and Co$_{13}$ clusters shown in (a) and (b) and deposited Co$_5$ and Co$_{13}$, clusters (c) and (d). The dashed vertical line indicates the Fermi level which is set to zero.
where, $|\mathbf{L}_{\text{easy}}|$ and $|\mathbf{L}_{\text{hard}}|$ are the orbital moments along the $E$ and $H$ axes, respectively, and $\lambda$ is the SO coupling constant, which for 3d elements is about 50 meV [26]. We have calculated the projected orbital angular momentum at the various sites along the $E$ and $H$ axes and these are listed in table 2. For Co$_5$, the maximum difference between $|\mathbf{L}_{\text{easy}}|$ and $|\mathbf{L}_{\text{hard}}|$ comes from the site 1 that is coupled to the graphene sheet. A similar scenario occurs for Co$_{13}$ that has multiple sites close to graphene. This would suggest that the coupling of the d-states of the cluster to the p-states of the graphene does stabilize orientation of the orbital moments along the easy axis.

As mentioned earlier, previous studies on Mn$_{12}$O$_{12}$-acetate and other nanomagnets indicate that the gradient corrected functionals can provide a reasonably accurate values for the MAE. However, we did investigate the change in MAE if an additional Hubbard term $U$ were included in the functionals. We used a GGA + $U$ functional with a $U$ = 4.0 eV typical for TM systems. The effect of $U$ is generally to shift the energy of occupied orbitals by $-U/2$ and those of the unoccupied orbitals by $U/2$. This is the reason that the inclusion of $U$ leads to better values for the band gaps. For MAE that is governed by the transitions from occupied to unoccupied states, the opening of the gaps might be expected to generally reduce MAE. Such a trend has been observed for the free clusters where inclusion of $U$ leads to increase of HOMO–LUMO gap of Co$_5$ and Co$_{13}$ clusters from 0.43 eV and 0.19 eV to 0.52 eV and 0.42 eV, respectively (refer table 2). Further, the effect of $U$ is to make the d-states more localized that can be expected to reduce the amount of quenching of the moments by the substrate and could enhance the anisotropy. For free clusters, the magnetic moment was the same as in GGA calculations, i.e., 13 $\mu_B$ for Co$_5$ and 31 $\mu_B$ for Co$_{13}$, whereas the anisotropy are calculated as 1.54 and 0.23 meV for Co$_5$ and Co$_{13}$, respectively. The reduced interaction to the substrate leads to a triangular bipyramid structure for Co$_5$ upon deposition as in a free cluster. Furthermore, the magnetic moment of the deposited Co$_5$ and Co$_{13}$ are found to be 11 $\mu_B$ and 26 $\mu_B$, respectively, indicating that the magnetic moment of Co$_{13}$ is closer to the free cluster value than in the absence of $U$. The MAE for deposited Co$_5$ and Co$_{13}$ were calculated to be 0.48 and 2.14 meV, respectively. Table 2 shows a comparison of the above quantities obtained from GGA and GGA + $U$ calculations. The MAE of Co$_{13}$ is still enhanced by approximately a factor of 9 from the free cluster but the MAE of Co$_5$ is slightly reduced indicating that the reduced interaction of the cluster from the substrate and the stabilization of the more symmetric geometry adversely affects its MAE.

While a graphene surface can stabilize orientation of moments, can it also mediate interaction between the supported species? In particular, the possibility of RKKY exchange coupling between magnetic moments of defects has attracted considerable attention. It has been suggested that while the Fermi momentum in a graphene plane is zero and excitations are gapless, the inclusion of spin orbit interactions opens an energy gap at the Fermi level leading to an absence of electrons at the Fermi level. Here we consider a different situation where the cobalt clusters that interact reasonably with the graphene substrate have d-states at the Fermi energy. A Co$_5$ cluster was positioned on the surface and a Co atom was placed on the hollow site of the sheet at increasing separations from Co$_5$ cluster. The position of Co adatom is marked as 1–5 in figure 3(a). At each separation, we examined the stability of magnetic order by calculating the total energy difference between the ferromagnetic (FM) state and the antiferromagnetic (AFM) state where the magnetic moment of the adatom was aligned opposite to that of the magnetic moment on the Co$_5$ cluster as

$$\Delta E_{\text{ex}} = E_{\text{AFM}} - E_{\text{FM}}.$$  \hfill (8)

Regions where the exchange energy $\Delta E_{\text{ex}}$ is positive (negative) correspond to the situation where the FM (AFM) alignment is more stable. Figure 3(a) shows $\Delta E_{\text{ex}}$ as a function of separation between the center of mass of the Co$_5$ cluster and Co adatom. It is observed that $\Delta E_{\text{ex}}$ changes as a function of separation, and become AFM at $\approx$12 Å. Thereafter it reverts back to FM.

To further probe the origin of such interaction, figure 4 shows the DOS of the system with a cluster supported on graphene. It is interesting to note that there is appreciable mixing between the C p-states and the Co d-states. In fact the C p-states are polarized and mediate the magnetic interaction by coupling to d-states.

Although pristine graphene is nonmagnetic it is well known that the presence of vacancy makes graphene magnetic [27]. Therefore, we have examined if these vacancies could magnetically interact the deposited species and if the nature of interaction and its strength could be altered by the position of vacancy. To examine this, for Co$_5$ and Co, we introduced a carbon monovacancy at four different locations marked as A–D in figure 3(b). After relaxing the structures in each case, $\Delta E_{\text{ex}}$ was calculated using equation (8) and the resulting values are shown in figure 3(b). The interaction at 12 Å is AFM without vacancy. The presence of vacancy alters the ground state from AFM to FM for most cases. For the FM case, while the presence of vacancy enhances the total magnetic moment of the system by 1 $\mu_B$ compared to the pristine case (12 $\mu_B$), the total magnetic moment, however, remains unaffected for the AFM case (10 $\mu_B$). The magnitude of onsite magnetic moment around the vacancy is calculated to be about 1 $\mu_B$ where one of the C atoms close to the vacancy exhibits the largest
contribution of 0.5 μB. This is in agreement with previous studies [27]. Since the nature of interaction and its strength can be changed by just changing the position of vacancy, therefore for an assembly of clusters the choice of separation and vacancies can be used to enhance the overall ΔE\text{ex}, which could help to stabilize the magnetic order against thermal fluctuation.

4. Summary

The present work emphasizes how a nonmagnetic support having no significant SOI can enhance the MAE in supported clusters and also allow a magnetic interaction that varies with the separation between species as well as can be controlled by defects and their location. The great advantage of graphene is that it is conducting and hence allows easy access to the deposited species. The physical origin of the observed effects is the mild hybridization between the C p-states with the Co d-states that orients the magnetization as well as acts to mediate the interaction between the supported clusters. It will be interesting to see if these effects could be also observed on similar supports including BN sheets and could be extended to other TM clusters.

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