Orbital Magnetism: Pros and Cons for Enhancing the Cluster Magnetism

Antonis N. Andriotis*
Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, 71110 Heraklion, Crete, Greece

Madhu Menon†
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055, USA and Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045, USA

(Received 11 February 2004; published 9 July 2004)

The discrepancy seen in the experimental and theoretical results on the magnetic moment of a small magnetic cluster has been attributed to the contribution arising from orbital magnetism. In this Letter we show that the magnetic states with large orbital magnetic moment are not always energetically favorable; they could, however, be realizable by coating the cluster or deposing it on appropriate substrates. More importantly, our work shows that the crucial factors that determine the cluster magnetism are found to be the intrinsic, and consequently, the extrinsic properties of the constituent atoms of the cluster.

DOI: 10.1103/PhysRevLett.93.026402 PACS numbers: 36.40.Mr, 31.15.Ar, 61.46.+w, 82.30.Nr

The possibility of synthesizing magnetic clusters with enhanced magnetic moments is a topic of great current interest and has been the focus of both experimental and theoretical investigations. These clusters may appear either in isolation or deposited on various substrates. The recent experimental finding of enhanced magnetic performance of the Fe-Co alloy clusters and the follow-up work on magnetic multilayer systems [1–4] offer an intriguing possibility of improving the magnetic efficiency of clusters by employing binary bimetallic clusters of materials with naturally large magnetic moments [for example, transition metal atoms (TMAs) of the $3d$-series] as the starting material along with the exploitation of other factors that could contribute to the improvement of their performance. This has inspired both theoretical and experimental investigations along two major directions towards achieving enhancement of the magnetic properties of magnetic clusters.

The first direction involves efficient ways of exploiting the orbital magnetic moment (OMM), $\langle \mu_L \rangle$. Owing to the fact that the major factors controlling the OMM is the spin-orbit (SO) interaction, and the magnetic anisotropy energy (MAE) of the cluster, considerable efforts have been devoted to producing nanograins made of magnetic materials exhibiting large magnetic moments, large SO coupling and large MAE [1,5–13]. This has led to the speculation that the SO interaction H_{SO}, in small magnetic clusters consisting of $3d$ TMAs, can account for: (i) the major part of the observed discrepancy between calculated and experimentally observed magnetic moments and (ii) the enhancement of the magnetic moments of small binary magnetic clusters, either in a free state or when deposited on appropriately chosen substrates [14]. Our work, however, has shown that the inclusion of H_{SO} in the cluster Hamiltonian does not always lead to energetically stable states of large and collinear to the spin contribution, $\langle S_z \rangle$, OMM. In other words, while H_{SO} is a necessary prerequisite for obtaining a nonzero average value of the atomic angular momentum, $\langle L \rangle$ [15], it cannot constitute a major source of magnetic enhancement of either the single-species TMA clusters or the binary ones as collinearity of $\langle L_z \rangle$ and $\langle S_z \rangle$ is not always energetically favorable.

The second direction towards achieving enhanced magnetic moments involves exploiting the effect of the cluster symmetry and the ligand field effects on the magnetic properties of the clusters [16–20]. In particular, this approach relies on the inherent properties of the materials used (as, for example, their d-band filling factor) and the symmetry-induced rehybridization of the cluster-atom orbitals. As a result, the cluster geometry as well as the "interface" properties between atoms of different material become of central importance in tailoring the magnetic properties of the clusters produced [1–4]. In fact, our recent works [16–20] have revealed that the ligand field effects depend strongly on the d-band filling and, therefore, on the attainable symmetry of the cluster. Thus, it determines to a high degree the hybridization of the electron orbitals and, therefore, the spin multiplicity (and, in turn, the magnetic moment) of the cluster ground state.

It is clear that the formation of the cluster magnetic moment is a complex process resulting from a delicate interplay involving many factors. They include both the intrinsic properties (d-band filling, SO coupling) of the cluster material as well as the extrinsic cluster properties (attainable symmetry of the cluster, hybridization level of the atomic orbitals, magnetic anisotropy, OMM, and $\langle S_z \rangle$). A systematic theoretical study of these effects on prototype clusters to assess their contribution to the magnetic moment is, therefore, timely and will lead to a benchmark for the contribution of these parameters and

0031-9007/04/93(2)/026402(4)$22.50

could provide a guide towards realizing materials exhibiting large magnetic moments.

In this Letter we carry out theoretical investigation of magnetic moments in clusters containing Fe, Co, and Ni atoms. We also use a large graphene sheet to simulate the effects of substrate. All structures are fully relaxed without any symmetry constraints using our tight-binding molecular dynamics (TBMD) scheme which allows dynamic simulations of the magnetic properties [21]. The magnetic moments calculated for Ni_m clusters using this method have been found to be in best agreement with experimental determination of magnetic moment for these clusters [22,23]. We begin our study by exploring the effects of the orbital contribution, $\langle L\rangle$. In order for $\langle L\rangle$ to have a substantial nonzero contribution to the cluster magnetic moment it is necessary for the $\langle L_z\rangle \neq 0$ states to be energetically more favorable. This, however, is not always the case. In Fig. 1 we show that for the icosahedral Ni_{13} (shown at top) the states of large $\langle L_z\rangle$ are energetically not favorable [24]. This is reflected in the higher values of the MAE of the low $\langle L_z\rangle$ states [28].

At the same time it is observed that the spin contribution to the magnetic moment remains unaffected as the magnetization direction is varied. Our work, while supporting the conjecture that the enhanced orbital moments are aligned parallel to the spin moments in Ni clusters [14], also points to the possibility of these states being energetically unfavorable [29]. However, the effect of the SO interaction can be exploitable only if the energetically unfavorable (due to the H_{SO} effect) cluster states become realizable. This possibility is supported by the results of Fig. 1 which shows only small changes in the MAE. Similar conclusions were also obtained for the other systems studied in the present work (see next).

We next explore the effect of the intrinsic properties of the materials used on the magnetic performance of a binary cluster by a detailed consideration of the $\mathrm{Fe}_n\mathrm{Co}_m$ clusters ($n + m = 13$). Following Ref. [12], all of these clusters are taken to be in the icosahedral geometry exhibiting uniaxial symmetry as shown in the top portion of Fig. 2. In the same figure we also present the results of our investigation. The main graph of this figure and its upper inset show the dependence of the $\langle L_z\rangle$ on the strength of the SO interaction in the $\mathrm{Fe}_3\mathrm{Co}_{10}$ cluster. It is clear from these graphs that (as expected) $\langle L_z\rangle$ increases as the SO-coupling parameter (λ_{Fe} or λ_{Co}) increases. This appears more pronounced in the case where we vary the SO-coupling parameter of the majority component atoms (Co) and it is worth noting that $\langle L_z\rangle \to 0$ and MAE $\to 0$ as $\lambda_{\mathrm{Co}} \to 0$ (main graph) for $\lambda_{\mathrm{Fe}} =$ constant. By contrast, MAE saturates to a nonzero value as $\lambda_{\mathrm{Fe}} \to 0$ while λ_{Co} is kept constant (upper inset). At the same time it can be seen that the spin contribution, $\langle S_z\rangle$, to the magnetic moment remains almost constant. For comparison, results for the Fe_{13} and Co_{13} clusters are

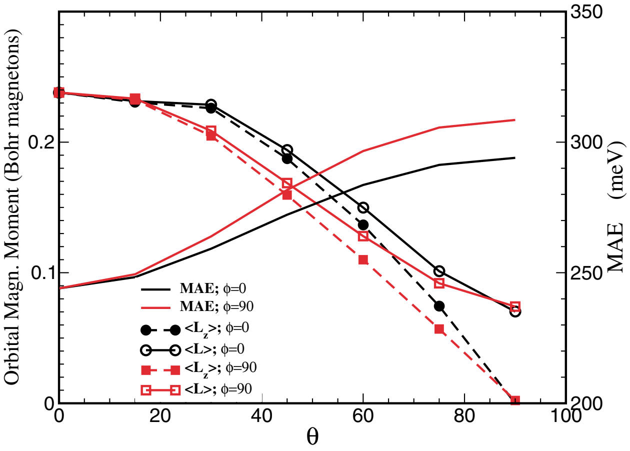

FIG. 1 (color online). Variation of the orbital magnetic moments (per atom) and the magnetic anisotropy energy (per atom) with the magnetization angle (i.e., angle between **L** and **S**) for the Ni_{13} cluster in icosahedral geometry (shown at top of Fig. 2).

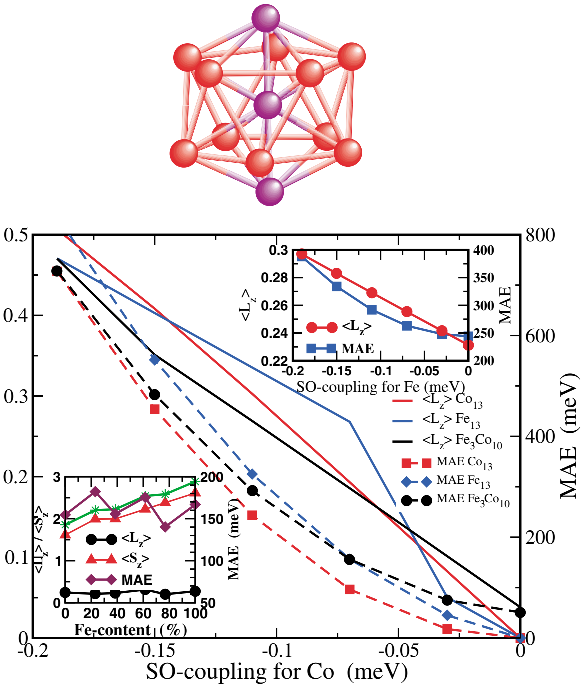

FIG. 2 (color online). (Top) X_{13}, $X =$ Ni, Fe, Co clusters. The $\mathrm{Fe}_3\mathrm{Co}_{10}$ cluster is obtained by setting atoms colored in dark gray (purple) to be Fe atoms and the atoms shown in light gray (red) to be Co atoms. $\mathrm{Fe}_{10}\mathrm{Co}_3$ cluster is obtained by switching Fe with Co. The clusters $\mathrm{Fe}_8\mathrm{Co}_5$ and $\mathrm{Fe}_5\mathrm{Co}_8$ are obtained by taking the dark gray (purple) atoms and one of the light gray (red)-ring atoms to be Fe atoms and the rest to be Co atoms and vice versa. (Bottom) As in Fig. 1 for the icosahedral $\mathrm{Fe}_3\mathrm{Co}_{10}$ cluster with uniaxial symmetry. (Upper inset) Variation of $\langle L_z\rangle$ and MAE of the $\mathrm{Fe}_3\mathrm{Co}_{10}$ as the SO-coupling constant of the Fe atoms is changed, while the SO-constant of the Coatoms is kept constant; $(\theta, \phi) = (0, 0)$. (Lower inset) Variation of $\langle L_z\rangle$, $\langle S_z\rangle$ and MAE corresponding to $(\theta, \phi) = (0, 0)$ for $\mathrm{Fe}_n\mathrm{Co}_m$, $n + m = 13$ icosahedral clusters exhibiting uniaxial symmetry (see top). The light gray (green) curve corresponds to the algebraic sum, $\langle S_z\rangle + \langle L_z\rangle$.

also presented. The interesting thing to note here is the linear variation of $\langle L_z \rangle$ with λ_{Co} for the Co_{13} cluster, while the variation for Fe_{13} is nonlinear. Finally, in the lower inset of Fig. 2 we observe that, in the Fe-Co clusters studied, the total magnetic moment per atom is dominated by the spin contribution $\langle S_z \rangle$ and increases almost linearly with the Fe content. Another point worth noting is the oscillatory behavior in both the MAE and $\langle L_z \rangle$ as a function of the Fe content.

The interface effects on the magnetic performance are investigated next. We do this by calculating the magnetic properties of a Ni_7 cluster adsorbed on a graphene sheet. The latter is simulated by a 275 atom carbon cluster (to be denoted as C_{275}). The system is fully relaxed without any symmetry constraints using the TBMD scheme. A portion of the relaxed geometry is shown at the top of Fig. 3. This includes the 42 carbon atoms in the neighborhood of Ni_7 (to be denoted as the $\mathrm{C}_{42}\mathrm{Ni}_7$ cluster). In Fig. 3 we also present the magnetic behavior of the $\mathrm{C}_{42}\mathrm{Ni}_7$ cluster. The values given in the figure correspond to results obtained using the relaxed structures of the 42 C and seven Ni atoms. The main graph of Fig. 3 shows the calculated variation of both $\langle L_z \rangle$ (dashed curves) and MAE (solid curves) with the magnetization directions (θ, ϕ) given by $(\theta, \phi) = (\theta, 0°)$ (circles); $(\theta, \phi) = (90°, \phi)$ (squares) and $(\theta, \phi) = (30°, \phi)$ (triangles). It is apparent from the figure that states of maximum $\langle L_z \rangle$ do not correspond to energetically more favorable states (as with Ni_{13} of Fig. 1); the Ni atoms closest to the graphitic layer exhibit much smaller $\langle L_z \rangle$ and $\langle S_z \rangle$ values as compared to those of the Ni atoms not in contact with the graphite surface; this is indicated in the right inset for $(\theta, \phi) = (0, 0)$ and in the left inset for $(\theta, \phi) = (\theta, 0)$.

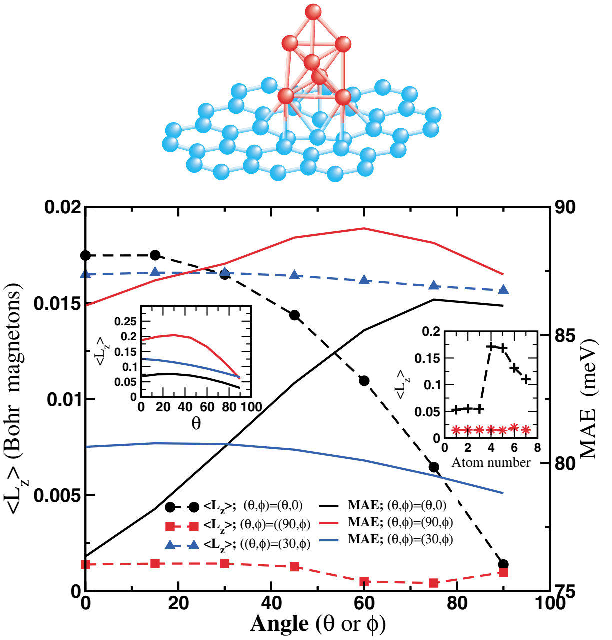

FIG. 3 (color online). (Top) A portion of the relaxed geometry of Ni_7 on a graphene layer. Atoms 1–3 form the closest layer to the graphene sheet, 4–6 form the next layer, and atom seven forms the cap. (Bottom) As in Fig. 1, results for the relaxed Ni_7 cluster interacting with graphite. Solid (dashed) curves correspond to MAE ($\langle L \rangle_z$) results, respectively, for magnetization directions: $(\theta, \phi) = (\theta, 0°)$ (circles); $(\theta, \phi) = (90°, \phi)$ (squares), and $(\theta, \phi) = (30°, \phi)$ (triangles). (Right inset) Contributions per cluster atom as these are assigned according to their distance from the graphene sheet; crosses (stars) denote contribution from minority (majority) spin-states for $(\theta, \phi) = (0, 0)$. (Left inset) Variation of $\langle L_z \rangle$ with the polar angle θ for $\phi = 0$ for first layer Ni atoms (lower curve) the second layer (top curve), and the third layer Ni atoms (middle curve).

From the discussion of results above it is evident that the OMM contribution to the magnetic moment of the cluster may not be taken for granted without also checking the stability of the corresponding structure as it could be energetically unfavorable. This, in fact, is expected to be the case in free clusters as shown in the present studies and may be attributed to the interplay between the crystal field which favors the alignment of **L** along the easy magnetization axis and the action of H_{SO} which favors the alignment of **L** along the direction of **S**. One must, therefore, consider other factors such as the d-band filling and ligand field effects, which can lead to significant magnetic enhancement by playing a much more important role [16,17]; they can also affect the effect of the SO interaction. However, the effect of the latter can only be exploitable if the energetically unfavorable cluster states become realizable. The results of Figs. 1–3 make it clear that this is indeed possible due to the small energy changes found in the MAE. Thus, the energetically unfavorable states (as the ones of large $\langle L_z \rangle$) or the metastable [30] states (due to a possible degree of noncollinearity of the atomic magnetic moments) can become realizable as *blocked magnetic states* by, for example, coating the elemental clusters with another material or by depositing the clusters on suitable substrates allowing, thus, the exploitation of the magnetic enhancement due to the SO interaction as well.

Furthermore it should be noted that both the MAE and the OMM are influenced by the inherent properties (i.e., the SO coupling, the d-band-filling, etc.) of the majority atoms in a binary TMA cluster. In these clusters the spin contribution varies linearly between the values attained in the corresponding single species clusters of each of the constituent materials. By contrast the $\langle L_z \rangle$ may not vary linearly with the content level of the cluster for a given magnetization direction. This may be understood as follows: The shift in the energy levels introduced by H_{SO} does not span the same number of spin-up and spin-down energy levels as the cluster content changes. Furthermore, it should be noted that contrary to the calculation of $\langle S_z \rangle$ as a function of the Fe content, the calculation of the $\langle L_z \rangle$ may be more influenced by the cluster configuration the calculation was based upon [31].

On the other hand, in the case of clusters deposited on a substrate, the $\langle L_z \rangle$ and the spin-derived magnetic moment are significantly affected by the substrate-cluster interaction, with main effect on the cluster atoms that are in direct interaction with the substrate. In this case, it is worth noting that the substrate interaction is effective only on the $\langle L_z \rangle$ contribution that is derived from the minority spin electrons. This is because the states of these electrons (being near the Fermi energy or the highest occupied molecular orbital (HOMO) energy level) are strongly affected by their hybridization with the substrate states because this process changes their character and occupancy and, therefore, their contribution to OMM. Hybridization and charge transfer expected in binary clusters and at interfaces switch on the ligand field effects and, as was shown earlier [3,16–20], may result in significant changes in both the spin and the orbital derived magnetic moments.

To summarize, the magnetic state of a magnetic cluster (free or deposited) is a result of a very complex process involving a delicate interplay among many factors. The most important ones appear to be the intrinsic properties of the cluster materials because these properties specify the extrinsic cluster properties which contribute to the magnetic performance of the cluster. The present Letter and our previously reported works [16–20] help in setting up a benchmark involving all these factors and specify a possible pathway towards the search for materials exhibiting large magnetic moments.

The present work is supported through grants by EU-GROWTH research project AMMARE (G5RD-CT-2001-00478), NSF (ITR-0221916), DOE (00-63857), NASA (00-463937), and the Kentucky Science & Technology Corporation (03-60214).

---

*Electronic address: andriot@iesl.forth.gr
†Electronic address: madhu@ccs.uky.edu

[1] B. Lazarovits, L. Szunyogh, and P. Weinberger, Phys. Rev. B **65**, 104441 (2002).
[2] B. Nonas, I. Carbia, R. Zeller, P. H. Dederichs, T. Huhne, and H. Ebert, Phys. Rev. Lett. **86**, 2146 (2001).
[3] Y. Huttel, G. van der Laan, T. K. Johal, N. D. Telling, and P. Bencok, Phys. Rev. B **68**, 174405 (2003).
[4] A. Scherz, P. Poulopoulos, R. Nunthel, J. Lindner, H. Wende, F. Wilhelm, and K. Baberschke, Phys. Rev. B **68**, 140401(R) (2003).
[5] S. H. Baker, C. Binns, K. W. Edmonds, M. J. Maher, S. C. Thornton, S. Louch, and S. S. Dhesi, J. Magn. Magn. Mater. **247**, 19 (2002).
[6] C. Binns, S. H. Baker, K. W. Edmonds, P. Finetti, M. J. Maher, S. C. Louch, S. S. Dhesi, and N. B. Brookes, Physica (Amsterdam) **B318**, 350 (2002).
[7] Y. Xie and J. A. Blackman, Phys. Rev. B **66**, 155417 (2002).
[8] Y. Xie and J. A. Blackman, Phys. Rev. B **66**, 085410 (2002).
[9] D. Zitoun, M. Respaud, M. C. Fromen, M. J. Casanove, P. Lecante, C. Amiens, and B. Chaudret, Phys. Rev. Lett. **89**, 037203 (2002).
[10] R. Felix-Medina, J. Dorantes-Davila, and G. M. Pastor, New J. Phys. **4**, 100 (2002).
[11] J. Tuailon-Combes, M. Negrier, B. Barbara, W. Werndorfer, M. Treilleux, P. Melinon, O. Boisron, and A. Perez, Int. J. Nanosci. **2**, 75 (2003).
[12] J. Kortus, T. Baruah, M. R. Pederson, C. Ashman, and S. N. Khanna, Appl. Phys. Lett. **80**, 4193 (2002).
[13] B. K. Rao, S. R. de Debbiaggi, and P. Jena, Phys. Rev. B **64**, 024418 (2001).
[14] R. A. Guirado-Lopez, J. Dorantes-Davila, and G. M. Pastor, Phys. Rev. Lett. **90**, 226402 (2003).
[15] Nonzero (and very large for Fe, Co, Ni) OMMs, even in the absence of the H_{SO}, have been obtained by introducing a m_L-dependent splitting of the energy bands by incorporating Brooks' heuristic self-consistent Orbital Polarization (OP) Hamiltonian term [2]. However, it is not clear if this term accounts for nonspherical corrections omitted by the $L \cdot S$ representation of the SO coupling or for correlation effects that have been omitted.
[16] G. Mpourmpakis, G. E. Froudakis, A. N. Andriotis, and M. Menon, Phys. Rev. B **68**, 125407 (2003).
[17] G. Mpourmpakis, G. E. Froudakis, A. N. Andriotis, and M. Menon, J. Chem. Phys. **119**, 7498 (2003).
[18] M. Menon, A. N. Andriotis, and G. E. Froudakis, Nanoletters **2**, 301 (2002).
[19] A. N. Andriotis, G. Mpourmpakis, G. Froudakis, and M. Menon, New J. Phys. **4**, 78 (2002).
[20] A. N. Andriotis, G. Mpourmpakis, G. E. Froudakis, and M. Menon, J. Chem. Phys. **120**, 11 901 (2004).
[21] A. N. Andriotis and M. Menon, Phys. Rev. B **57**, 10069 (1998).
[22] S. E. Apsel, J. W. Emmert, J. Deng, and L. A. Bloomfield, Phys. Rev. Lett. **76**, 1441 (1996).
[23] M. B. Knickelbein, J. Chem. Phys. **116**, 9703 (2002).
[24] The present results were obtained by a single iteration process using our TBMD scheme [21] with $H_{\mathrm{SO}} = -\lambda \sum \mathbf{L}_i \cdot \mathbf{S}_i$ and $\lambda = 110$, 73, 88 meV for Ni, Fe, and Co, respectively. However, no appreciable changes were found upon structural relaxation. Some changes (which do not affect the trends shown in Fig. 1) are also found when we used the various expressions for the matrix representation of the SO-interaction term [25–27].
[25] H. Brooks, Phys. Rev. **58**, 909 (1940).
[26] H. Takayama, K.-P. Bohnen, and P. Fulde, Phys. Rev. B **14**, 2287 (1976).
[27] P. Bruno, Phys. Rev. B **39**, 865 (1989).
[28] The MAE is defined as the energy change due to the SO interaction (MAE $= E_{\lambda=0} - E_{\lambda}$).
[29] Noncollinearity among the magnetic moments μ_a of the cluster atoms may also have dramatic effect on the results because it may lead to enhanced mixing of spin-up and spin-down states.
[30] T. Oda, A. Pasquarello, and R. Car, Phys. Rev. Lett. **80**, 3622 (1998).
[31] Because of the fact that $\lambda_{\mathrm{Fe}} \approx \lambda_{\mathrm{Co}}$, a major decline in the MAE results upon relaxation will be due to the changes in the spin contribution as this may be affected by geometry changes.