Magnetic enhancement and magnetic reduction in binary clusters of transition metal atoms

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Electronic and magnetic properties of small binary clusters containing one or two transition metal atoms are investigated using ab initio calculations with a view to explain the experimentally observed magnetic enhancement/reduction in these systems. As the present investigations do not rely on spin–orbit effects, our results reveal the enhancement or reduction in the magnetic moment to depend on two main factors; namely geometry and, most importantly, the d-band filling. The results can be used as a guide in the experimental synthesis of high density magnetic grains.

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The ability to continually miniaturize while at the same time increasing the recording density of hard disk drives requires the synthesis of new advanced magnetic materials which, while exhibiting large magnetization density values (even exceeding the present day limit of 2.45 μ₀), can push the existing technologies beyond the superparamagnetic (SPM) limit. With these in view, recent efforts have been concentrated on producing nano-grains made of magnetic materials with large magnetic moments, large spin–orbit (SO) coupling and large magnetic anisotropy energy. 1–15

Thus, magnetic nano-grains consisting of elemental or binary clusters based mainly on the transition metal (TM) atoms such as Co, Fe, Ni have been attempted. In the case of binary grains the second material can be a metal (TM, Cu, Ag, Au), a semiconductor (C, Si) or a rare earth (Sm). 12

An interesting result that emerged from these investigations is that by coating nano-grains of TMs one can achieve either an enhancement or a reduction in the average magnetic moment (per TM-atom) of the grain. 3–6,13 Thus, recent theoretical results have demonstrated that Cu coating of Fe clusters brings down the average magnetic moment per Fe atom to its bulk value. 6 By contrast, Co coating of Fe clusters allows the Fe atoms to maintain their magnetic moments at the free cluster value. 6 More interestingly, some alloying at the Fe–Co interface was found to lead to further enhancement. Similar calculations on Co clusters coated by Cu have shown that the Co moment is not affected by the coating or the alloying near the interface. 5 The enhancement of a magnetic moment with respect to the macroscopic Co–Rh alloy values was measured and theoretically justified in Co–Rh alloy-nanoparticles. 9 It is worth noting that there was no significant effect on the local moments of the Co atoms due to the presence of Rh atoms. Finally, magnetic enhancement was also found in computer simulations for Co-grains, Co–Pd clusters obtained in theoretical simulations was attributed to the magnetic polarizability of the Pd surface which leads to induced magnetic moments on the Pd interface atoms and the enhancement of the orbital contribution to the magnetic moment.

The enhancement (over the free atom value) of the magnetic moment per atom for small Fe, Fe–Co, Co–Rh and Co–Pd clusters obtained in theoretical simulations was attributed to the increased value of the surface to the bulk ratio (leading to an increased orbital contribution); it was attributed to the magneto-crystalline anisotropy energy and was related to the SO interactions. This led to the suggestion that clusters exhibiting a large surface to bulk ratio or consisting of 4d elements or binaries made of 3d and 4d elements are good candidates for producing magnetic materials with improved performance as discussed earlier because these features lead to enhanced orbital magnetism. The theoretical results were supported by recent experimental works showing an enhancement in the magnetic moment (10% over the corresponding bulk value in 180-atom Fe clusters) measured by an x-ray magnetic circular dichroism (XMCD) using synchrotron radiation in Fe clusters deposited on highly oriented pyrolytic graphite (HOPG). 1 The measurements traced half of the enhancement in the magnetic moment to an orbital contribution. In the case of Co-coated Fe clusters supported on HOPG, a further 10% enhancement in the spin contribution without any significant reduction in the orbital moment and total magnetic moments as in the corresponding free Fe clusters was found.

The significant technological implications for the magnetic moment of small clusters has generated a need for a systematic study of the trend of this contribution in binary
and/or ternary clusters consisting of various atomic species. Such a study is expected to lead to an optimal choice of materials that will exhibit enhanced magnetic moments in clusters, thereby providing a valuable guidance to experimentalists in their search for a new generation of materials with large magnetization density.

In this work we report results of our detailed systematic investigations of structural and magnetic properties of binary clusters of the form MnXn, M = V, Fe, Co; X = C, Si, V, Fe, Co; n + m ≤ 3 using ab initio calculations. Results for representative classes of larger clusters of the form MSi,n, n < 15, M = V, Fe, Ni, are also reported. Our calculations were performed using the density functional theory (DFT) at the B3LYP level of approximation and the LANL2DZ basis sets using the GAUSSIAN program package.16 All the clusters were fully relaxed with no symmetry constraints. No explicit SO interaction terms are considered. (SO effects may sometimes be incorporated implicitly in the construction of the basis functions.) The investigated clusters are assumed to be single domain particles in which the atomic spin-moments are strictly collinear.17 Under these assumptions, the present investigation is of great importance since it is expected to isolate and reveal those factors which play a critical role in the development and tailoring of the spin magnetic moments of the magnetic clusters. At present, a systematic study on this significant topic (especially in the case of bimetallic clusters) is lacking and the existing reports refer mainly to the enhancement/reduction of the cluster magnetic moments, mostly in connection with the SO interactions and the magnetic anisotropy. Marginally, the topic of the present work has recently been addressed by Lazarovits et al.15

Our results are shown in Fig. 1 in which we present the calculated spin magnetic moments of small binary clusters and compare them with the corresponding free atom values. The term “calculated sum of magnetic moments” (CSMM) of a cluster is defined as the sum of the absolute values of the calculated atomic magnetic moments of the cluster-constituent atoms, while the term “free-atom based sum of magnetic moments” (FASMM) is defined as the sum of the free-atom spin magnetic moments of the constituent cluster atoms. In Fig. 1, all points above the diagonal line denote enhancement, while all points below the diagonal line denote reduction. In the upper (lower) inset of Fig. 1 we present the magnetic moment of the V(Co) atom in VXn(CoXn) clusters, n = 1, 2 and X = C, Si, V, Fe, Co, Ni, Cu.

The results of Fig. 1 are in accordance with the experimentally observed enhancement or reduction of the magnetic moment observed for larger clusters and discussed above. Furthermore, it can be observed that other combinations of TMs with another metal or semiconductor leads to a significant reduction in the magnetic moment of the TM-atom, μTM. In particular, our results can be summarized as follows:

(i) In the case of V, it is found that V suffers a reduction in its magnetic moment, μV (with respect to its free atom value) when it forms clusters with semiconducting materials such as C and Si. By contrast, a significant increase in μV occurs when it forms clusters with any of the TMs Fe, Co, Ni. This increase leads to μV values greater than the corresponding atomic values, while at the same time μX; X = Fe, Co, Ni suffers a significant reduction. We attribute this to the electronic redistribution in the various molecular orbitals (MOs) in contradistinction to the atomic orbital (AO) distribution of free atoms.

A common feature seen in all the VX clusters studied is the antiferromagnetic (AF) alignment of the magnetic moments of the cluster atoms. As a result, the effective magnetic moment μeff, of each of the VX clusters is small. (μeff = 1.2, 3 μB for VF, VC, VNI, respectively.)18

(ii) In the case of Co, it is found that in CoXn clusters the Co magnetic moment, μCo, is in general not significantly affected by any choice of the element X (metal or semiconductor); its moment is significantly smaller than the free atom value, larger than the corresponding bulk value and aligns ferromagnetically (FM) with respect to μX. Additionally, it is worth noting that, in general, Co does not induce large magnetic moments on nonmagnetic materials; i.e., for X = C, Si, Cu.

(iii) Fe is found to exhibit an intermediate behavior between V and Co, when forming clusters with other elements. That is, Fe may undergo either a reduction or an enhancement in its magnetic moment; it may induce small or large magnetic moments on neighboring nonmagnetic materials and it may lead to FM or AF configurations of magnetic moments of the cluster atoms. It is worth noting that no systematic trend in the behavior of Fe (as a constituent cluster material) is seen and its behavior appears to depend strongly on the geometric configuration, i.e., on the coordination number and, interestingly, on the orientation of bonds.
TABLE I. Orientation and absolute value of atomic magnetic moments (in Bohr magnetons) of ground state (relaxed) FeSi$_{10}$ (C$_{5v}$ symmetry and 2S + 1 = 5) and FeSi$_{12}$ (C$_{6v}$ and 2S + 1 = 3) clusters.

<table>
<thead>
<tr>
<th>No.</th>
<th>Atom</th>
<th>$\mu$</th>
<th>Atom</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe</td>
<td>1.873</td>
<td>Fe</td>
<td>2.366</td>
</tr>
<tr>
<td>2</td>
<td>Si</td>
<td>0.231</td>
<td>Si</td>
<td>-0.002</td>
</tr>
<tr>
<td>3</td>
<td>Si</td>
<td>0.204</td>
<td>Si</td>
<td>-0.237</td>
</tr>
<tr>
<td>4</td>
<td>Si</td>
<td>0.212</td>
<td>Si</td>
<td>-0.008</td>
</tr>
<tr>
<td>5</td>
<td>Si</td>
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<td>+0.082</td>
</tr>
<tr>
<td>6</td>
<td>Si</td>
<td>0.191</td>
<td>Si</td>
<td>-0.085</td>
</tr>
<tr>
<td>7</td>
<td>Si</td>
<td>0.224</td>
<td>Si</td>
<td>+0.068</td>
</tr>
<tr>
<td>8</td>
<td>Si</td>
<td>0.214</td>
<td>Si</td>
<td>-0.008</td>
</tr>
<tr>
<td>9</td>
<td>Si</td>
<td>0.204</td>
<td>Si</td>
<td>-0.237</td>
</tr>
<tr>
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<td>Si</td>
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<td>Si</td>
<td>-0.002</td>
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<td></td>
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<tr>
<td>13</td>
<td>Si</td>
<td>+0.082</td>
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</tbody>
</table>

*The magnetic moment for the free Fe atom is 4 Bohr magnetons.

It is worth noting that in FeC$_2$, FeSi, CoC, CoFe, Fe$_2$Co and FeCo$_2$ clusters the atomic magnetic moments are found to be ferromagnetically aligned. These clusters exhibit $\mu_{\text{eff}}$ which is approximately equal to the FASMM value. All the other clusters (shown in Fig. 1) have their atomic magnetic moments antiferromagnetically aligned and therefore their $\mu_{\text{eff}}$ is much smaller than the FASMM value.

The enhancement/reduction of the cluster magnetism can be even better illustrated by studying the results for the TM encapsulated Si-cage clusters of the form $V_nSi_{6n+k}$, $k = 6, 8, n < 3$; Fe$_nSi_{6n+k}$, $k = 5, 6, 7, 8, n < 3$; and Ni$_nSi_{6n+k}$, $k = 5, 7, n < 3$ obtained using the same computational methods. A preliminary report has recently appeared in Ref. 19. In these larger clusters, the Si-contribution to the magnetic moment of the grain is more pronounced in systems exhibiting the C$_{5v}$ symmetry (i.e., for grains for which the TM is chosen from the early 3d-series). In these systems, the magnetic moments of the Si atoms are aligned ferromagnetically with respect to that of the TM. On the other hand, in systems with the C$_6$ symmetry (i.e., for grains for which the TM is chosen from the late 3d-series), the magnetic moments of the Si-atoms are arranged antiferromagnetically with respect to the magnetic moment of the TM and the Si-contribution is much smaller as compared to that of the C$_{5v}$ systems.\textsuperscript{19–21} In Table I we give an illustration of this effect by listing the magnetic moments of Fe and Si atoms in two Fe encapsulated Si-cage clusters, namely FeSi$_{10}$ with C$_{5v}$ symmetry and FeSi$_{12}$ of C$_6$ symmetry. The fully relaxed structures are shown in Fig. 2. We have also found AF-alignment in FeSi$_4$, FeSi$_{5}$ and FeSi$_{14}$ clusters for which $\mu_{\text{eff}}=2.4$ and 2 $\mu_B$, respectively. In the VSi$_{12}$ cluster, the magnetic moments induced on the surrounding Si atoms are very small and most of the contribution to the magnetic moment of the cluster ($\mu_{\text{eff}}=1.0 \mu_B$) comes from the magnetic moment of the V atom ($\mu_V=0.75 \mu_B$). Finally, in NiSi$_{10}$, the surrounding Si atoms exhibit relatively large magnetic moments ($\mu_{Si}=0.22 \mu_B$) making $\mu_{\text{eff}}=2.0 \mu_B$. The Si-magnetic moments, however, are AF-aligned to the magnetic moment of Ni ($\mu_{Ni}=-0.21 \mu_B$).

Our results for the small TM clusters of the 3d-series give evidence of an additional contribution to magnetic enhancement/reduction other than that attributed to the SO interaction terms. As is evident from Fig. 1, even in the absence of SO interaction, the values of the atomic magnetic moments may be enhanced (V-case) or reduced (Co-case) as compared to the corresponding free atom values. However, the effective magnetic moment of the cluster does not exceed the FASMM value. These suggest a strong need to look beyond the SO effects for additional factors necessary for justifying the magnetic behavior of the clusters studied. It may seem reasonable to associate the calculated enhancement/reduction of the cluster magnetism with a possible inter-atomic charge transfer that could take place among the cluster atoms leading to a considerable change in the number of atomic d-holes.\textsuperscript{22} Although such a contribution cannot be completely ruled out, the small interatomic charge transfers that we find do not support this association. Similarly, intratomic charge transfers cannot be of much help because the cluster electrons are assigned to MOs than to AOs with the MOs being usually of mixed character. On the other hand, our results demonstrate the dominant role played by the d-band filling factor in TM and TM-encapsulated Si-cage structures, affecting in a complicated (and one can say, in a self-consistent) way their stability, symmetry and the magnetic configuration. It supports the conjecture that any additional factors supporting magnetic enhancement or reduction found in small TM-clusters should, therefore, take into account d-band filling as one of the sources. These factors are associated with ligand field effects and include the available bonding orbitals, corresponding bond lengths and coordination number as well as the dependence of the correlation energy on these factors. For example, a detailed analysis of the differences in the bonding characteristics of the isoenergetic triplet and singlet states of the CoC dimer leads to the observation that the triplet state arises from the singlet one by the promotion of one electron from a nonbonding MO of character $Co(d_{z^2})$ to the bonding MO of character $Co(p_{x})Co(p_{x})$ in the triplet state. Such rearrangements lead to redistributions of the charge and spin density according to molecular Hund’s rules and, therefore, the stability and the properties (electronic and magnetic) of the cluster depend very sensitively on the d-filling factor of the TM. This is because the d-filling by influencing the point group symmetry of the TMA will specify the MOs which can be used in the redistribution of the electrons in the available electronic levels.
MOs can lead to atomic magnetic moments greater than the corresponding free-atom values. Then, for reasons not clear yet, they align ferromagnetically or antiferromagnetically leading, respectively, to enhanced or reduced values for $\mu_{\text{eff}}$. Thus, it is not surprising that although the atomic magnetic moments of cluster-atoms may be found enhanced, the effective magnetic moment of the corresponding cluster is relatively small and hardly surpassing the FASMM value. These observations lead us to the conclusion that the d-band filling factor in connection with molecular Hund’s laws may be the most prominent factors that dictate the magnetism in small magnetic clusters. The SO interaction and the interatomic charge transfer may provide additional contributions.

ACKNOWLEDGMENTS

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18 The term “antiferromagnetic” is used rather loosely here just to indicate the opposite alignment of magnetic moments. In the strict sense they also have to be equal in magnitude to cancel out the total magnetic moment.
23 Our results do not show a consistent correlation between bond lengths and type of alignment so as to assign the alignment of the magnetic moments to a Ruderman–Kittel–Kasuya–Yosida (RKKY) type of interaction; the magnetic alignment depends strongly on geometry and spin-multiplicity as well.