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Magnetic properties of Co2-xTMxC and Co3-xTMxC nanoparticles

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Magnetic properties of $Co_{2-x}TM_xC$ and $Co_{3-x}TM_xC$ nanoparticles

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Using synthetic chemical approaches, it is now possible to synthesize transition metal carbides nanoparticles with morphology, where the transition metal layers are embedded with intervening layers of carbon atoms. A composite material consisting of Co_2C and Co_3C nanoparticles has been found to exhibit unusually large coercivity and energy product. Here, we demonstrate that the magnetic moments and the anisotropy can be further enhanced by using a combination of Co and other transition metals (*TM*). Our studies are based on mixed nanoparticles $Co_{2-x}TM_xC$ and $Co_{3-x}TM_xC$, in which selected Co sites are replaced with 3d transition elements Cr, Mn, and Fe. The studies indicate that the replacement of Co by Fe results in an increase of both the magnetic moment and the magnetic anisotropy. In particular, $CoFe_2C$ is shown to have an average spin moment of 2.56 μ_B and a magnetic anisotropy of 0.353 meV/formula unit compared to 1.67 μ_B and 0.206 meV/formula unit for the Co_3C. Detailed examination of the electronic structure shows that the limited hybridization of carbon p-states with transition metal d-states drives the larger anisotropy. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4858391]

I. INTRODUCTION

Extensive research over the past two decades has shown that novel behaviors can emerge as the size of the system is reduced to a nanoscale.[1] The atomic arrangements, electronic structure, reactivity, are all found to be different from bulk and change non-monotonically with size. In the area of magnetism, small particles of ferromagnetic solids are found to exhibit superparamagnetic relaxations,[2,3] while those of non-magnetic solids can be magnetic.[4,5] The properties are found to evolve with size and composition offering the possibility of tailoring the behavior of individual particles. An important direction in nanoscale research is then to generate nanoscale materials, whereby selected nanoparticles serve as the elementary building blocks.[6] Unlike ordinary solids, the nanoassembled materials unify intra-atomic interactions in individual nanoparticles with inter-atomic interactions between assembled units, in a single material. The collective emergent behaviors in such solids can therefore offer unique possibilities.

In a recent paper, Carpenter and co-workers reported synthesizing a nano-composite material consisting of cobalt carbide nanoparticles using a wet chemical technique, known as the polyol process.[7] Basically, the process involves a reduction of the metal salt (cobalt chloride) using a polyol process. The resulting material contained a mixture of Co_2C and Co_3C nanoparticles of varying size. The atomic arrangements in the nanoparticles consisted of layers of cobalt atoms separated by those of carbon offering morphologies unavailable in bulk carbides. The material offered unusual magnetic properties with a maximum high energy product exceeding 20 kJm^{-3} and coercivity greater than 3.4 kOe. Further, the properties changed with size and ratio of the nanoparticles in the mixture. In a recent joint experimental/theory paper,[7,8] we examined the origin of some of the observed features. The magnetic properties were rather surprising since the composite nano-material did not contain any 5d transition or rare earth elements and bulk fcc Co is a soft magnetic material. Theoretical electronic structure studies on Co_2C and Co_3C structures derived from the x-ray diffraction data showed that the nanoparticles had high magnetic anisotropy and that the cobalt sites had large magnetic moments despite the presence of carbon atoms that generally quench magnetic moments. The studies also revealed that a minor mixing between the C *p*- and Co *d*- states leads to an enhancement of magnetic anisotropy, while maintaining appreciable magnetic moments of 1.04 μ_B per Co atom in Co_2C and 1.72 μ_B per Co atom in Co_3C. Preliminary macromagnetic simulations on a collection of nanoparticles indicated that the nanoassembly did offer a high coercivity. These findings raise the issue, if the magnetic properties could be further improved by mixing/replacing cobalt with other transition metal elements (*TM*). This optimism arises from the fact that Fe, Mn, and Cr all have higher magnetic moments per atom than Co. Further, it is known that the bulk Fe_xCo_{1-x} alloys offer the highest magnetic moment around 35% Co.[9] Could such an increase be realized in carbide nanoparticles?

The purpose of this paper is to present our findings based on theoretical investigations of the magnetic moment and magnetic anisotropy of $Co_{2-x}TM_xC$ and $Co_{3-x}TM_xC$ carbides, where the Co sites are replaced by other 3*d* transition elements. Our objective is to find how the substitution affects the overall magnetic moment and the magnetic anisotropy energy of the system. The theoretical studies are carried out using the atomic arrangements of the pure carbides, where a selected set of Co sites are substituted with Cr, Mn, or Fe atoms and the structures relaxed maintaining the overall shape. As we show, the magnetic moment as well as the magnetic anisotropy are sensitive to the composition of the system. Since the principal contribution to anisotropy comes from the magnetocrystalline anisotropy, we will primarily

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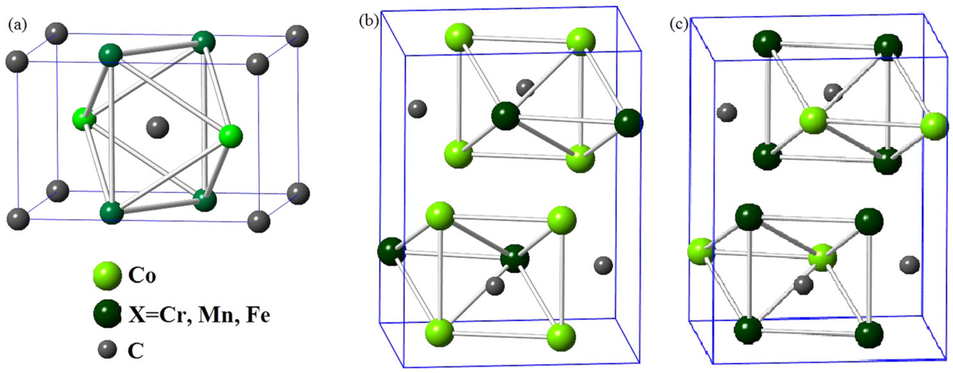

FIG. 1. The crystal structure of (a) $Co_{2-x}TM_xC$ and (b) and (c) $Co_{3-x}TM_xC$. The green spheres are cobalt atoms, the dark green spheres are other transition metal atoms, and the grey spheres are carbon atoms.

focus on this term. Through first principles calculations, we then provide an insight into how the interaction between C atoms and the transition metal atoms controls the anisotropy of individual phases.

II. THEORETICAL APPROACH

The theoretical studies were carried out using a first principles approach, where the exchange correlation effects are treated within a density functional framework.[10–14] In our previous work,[8] we had shown that an accurate description of the magnetic properties of the carbide requires a treatment of electron correlations beyond the generalized gradient approximation (GGA) level. As we showed, a GGA + U approach provides a computationally viable framework. Consequently, all the calculations have been carried out using a GGA functional proposed by Perdew, Burke, and Ernzerhof in a GGA + U approach with a U value of 4.0 eV. As we previously showed, such a combination yields results comparable to B3LYP hybrid functional. The actual calculations were carried out using the Vienna Ab initio Simulation Package (VASP) using a supercell containing 4 *TM* and 2 C atoms for $Co_{2-x}TM_xC$ and containing 12 *TM* and 4 C atoms for the case of $Co_{3-x}TM_xC$. These unit cells are depicted in Fig. 1. Note that for the case of $Co_{2-x}TM_xC$, (Fig. 1(a)), we replaced the interior Co sites in Co_2C with other *TM* atoms. For the case of $Co_{3-x}TM_xC$, however, one can replace 4 or 8 Co atoms by the *TM* atoms offering the effect of composition (Figs. 1(b) and 1(c)). Finally, we also examined structures, where all Co sites were replaced by other *TM* atoms. The electron ion interactions were modeled using a projector-augmented wave method to remove the core states. Further, the valence states of *TM* and C were described by [Ar] $3d^n4s^m$, and [He] $2s^22p^2$ electron configurations, respectively.[10] We have used a plane wave basis with an energy cutoff of 400 eV and a Mokhorst-Pack scheme of $9 \times 9 \times 9$ division was employed to generate the special k-points for constructing the electron charge density.[14] For determining the magneto-crystalline anisotropy energy (MAE), we calculated the contribution from spin-orbit coupling by constraining the moments along specific directions. For the case of pure Co_2C and Co_3C phases, the structures based on the x-ray diffraction were further optimized by relaxing internal bond lengths. These relaxed structures were used for the remaining calculations.

III. RESULTS AND DISCUSSION

The results of our investigations for the pure cobalt phases were described in an earlier publication and are included here only for reference. For pure α-Co, the present calculations yielded a moment of 1.63 μ_B, close to the experimental value of 1.75 μ_B. For the Co_2C and Co_3C, our calculations also yield magnetic moments close to experimental values as described in an earlier paper.[8] We start by first discussing the case of $Co_{2-x}TM_xC$ systems. In each case, the investigations of the magnetic state included ferromagnetic (parallel) and anti-ferromagnetic (anti-parallel) orientation of the atomic moments at the Co and *TM* sites. The ferromagnetic arrangements were found to be more stable in all the cases. Table I contains our results on the spin magnetic moment at the Co and *TM* sites for the Co*TM*C structures and the moment on *TM* atoms in the TM_2C structures. Note that the local spin magnetic moments at the Co sites of CoCrC compound are higher than those in the Co_2C structure. More importantly, the local magnetic moments at the Fe, Mn, and Cr sites are larger than that at the Co sites indicating that alloys have higher magnetization. The local magnetic moment of Cr, Mn, and Fe are, however, reduced from their free atom value. The other quantity of interest is the MAE. In Table II, we list the MAE along various symmetry

TABLE I. Atomic magnetic moment (in unit of μ_B) for $Co_{2-x}TM_xC$ bulk compounds obtained by GGA + U (U = 4 eV) calculations.

	Co_2C	CoCrC	Cr_2C	CoMnC	Mn_2C	CoFeC	Fe_2C
Co	1.04	1.46		0.70		0.82	
TM		3.54	2.91	3.66	2.89	2.42	2.21

TABLE II. Magnetic anisotropy energies (MAE) of bulk $Co_{2-x}TM_xC$ in unit of meV per formula unit obtained by GGA + U (U = 4 eV) calculations. The zero energy is set as the reference and the corresponding direction is the easy axis.

	[100]	[010]	[001]	[110]	[111]
Co_2C	0.156	**0.203**	0	0.180	0.120
CoCrC	0	0.090	0.032	**0.045**	0.042
Cr_2C	0	**0.061**	0.055	0.030	0.037
CoMnC	0.046	0.035	0	**0.158**	0.104
Mn_2C	0.047	0	**0.130**	0.023	0.059
CoFeC	0.003	0.007	0	**0.061**	0.042
Fe_2C	**0.571**	0.212	0	0.390	0.260

TABLE III. Atomic magnetic moment (in unit of μ_B) for $Co_{3-x}TM_xC$ bulk compounds obtained by GGA + U (U = 4 eV) calculations.

	Co_3C	Co_2CrC	$CoCr_2C$	Cr_3C	Co_2MnC	$CoMn_2C$	Mn_3C	Co_2FeC	$CoFe_2C$	Fe_3C
Co	1.67	1.83	1.85		1.64	1.61		1.70	1.84	
TM		3.60	3.99	1.90	3.86	3.97	3.05	3.09	3.06	2.77

directions. In all cases, the easy axis is chosen as the zero of energy. The hard axis lies along different directions depending on the composition and the contribution is highlighted in bold as it indicates the anisotropy energy of the system. It is interesting to note that several alloys have a higher MAE compared to the pure carbides. In fact, the average magnetic moment in CoFeC is more than double of that of the pure carbide and is reminiscent of the increase of moment in bulk Fe_xCo_{1-x} alloys.[9] Before we probe the nanoscopic origin of these variations, let us present our results for $Co_{2TM}C$ and $CoTM_2C$ systems obtained by replacing 4 or 8 Co sites by TM atoms in the Co_3C structure shown in Figure 1(c). The variations in the magnetic moment are collected in Table III. It is surprising that the transition metal sites have significantly higher moments when alloyed with Co compared to the pure carbide phase. The increase is particularly impressive for $CoCr_2C$, where the Cr sites have a local spin magnetic moment of 3.99 μ_B per atom compared to the Cr_3C, where the sites have a moment of 1.90 μ_B per atom. The Co sites in alloys also have higher moments than in the pure phase. Amongst different transition metals, Co_2CrC and Co_2MnC have comparable average moments and $CoFe_2C$ has a smaller moment. For the bulk Fe_xCo_{1-x} alloys, the largest moment per/atom occurs around 35% Co.

Here, a similar increase is observed. The increase in moments is also accompanied by an increase in the MAE. Table IV lists our calculated MAE for various compositions. It is interesting to note that the alloying not only modifies the anisotropy energy but the direction of the easy axis is as well. The magnetic anisotropy in Co_2CrC is almost three times of that in Co_3C. This coupled with the large magnetic moment in alloys indicates that the energy product can be substantially increased over the pure carbides.

Before we discuss the nanoscopic mechanisms underlying these changes, it is desirable to briefly discuss the implications of such large anisotropies for individual nanoparticles and compare some of the current findings with experiments. It is well known that starting from the bulk material, the reduction to size less than the typical domain size leads to nanoparticles, where the local moments are exchange coupled and the nanoparticle behaves as a single magnet with a giant moment determined by the number of atoms in the particle and the localized moment at the individual sites.[2] The decrease in size, however, reduces the total magnetic anisotropy and total moment can undergo fluctuations in direction at temperatures above the so called, Blocking temperature T_B. These superparamagnetic relaxations above T_B limit the particle size that can be used for memory storage or transport. For Co/CoO core shell nanoparticles, the previous maximum T_B is around 290 K.[15] Using the present calculated anisotropies for Co_3C, a 8.1 nm nanoparticle would have a T_B of around 570 K.[16] It is gratifying to note that recent experiments on Co_3C nanoparticles of around 8.1 nm size, indeed find a blocking temperature of 576 K in good agreement with the calculated value.[17] Our work on alloy nanoparticles shows that this limit can be substantially enhanced, i.e., around 2 nm particles of the alloy carbides would offer blocking temperatures far higher than the room temperature. Such developments could play an important role in spin based molecular electronic devices using the nanoparticles.

To gain additional insight into the nature of anisotropy, we calculated the orbital angular momentum and the contribution to orbital angular momentum by various sites along the easy and hard axis for different compositions that exhibit high anisotropy (Tables V and VI). According to Bruno formula[18] based on second order perturbation model, the anisotropy is related to angular momentum by the relation

$$\mathrm{MAE} = \lambda |(L_{easy} - L_{hard})|/4,$$

where L_{easy} and L_{hard} are the orbital moments along easy and hard axis, respectively, and λ is the spin orbit coupling constant. As one notices, the qualitative trends in the calculated

TABLE IV. Magnetic anisotropy energies (MAE) of bulk $CoTM_2C$ in unit of meV per formula unit obtained by GGA + U (U = 4 eV) calculations. The zero energy is set as the reference and the corresponding direction is the easy axis.

	[100]	[010]	[001]	[110]	[111]
Co_3C	0.178	**0.206**	0	0.191	0.128
Co_2CrC	0.149	0	**0.579**	0.074	0.243
$CoCr_2C$	0.140	**0.140**	0	0.137	0.090
Cr_3C	0.041	0	**0.256**	0.021	0.100
Co_2MnC	0	0.265	**0.312**	0.131	0.192
$CoMn_2C$	0	**0.090**	0.032	0.045	0.042
Mn_3C	**0.180**	0.080	0	0.130	0.090
Co_2FeC	**0.236**	0.210	0	0.223	0.149
$CoFe_2C$	0	0.264	**0.373**	0.132	0.210
Fe_3C	0.164	**0.255**	0	0.211	0.142

TABLE V. Orbital magnetic moment (in unit of μ_B) on each atomic site and one formula unit of bulk Co_2TMC obtained by GGA + U (U = 4 eV) calculations.

	C	Co	TM	Total	Direction
Co_2CrC	0.001	0.056	−0.016	0.097	Easy[010]
Co_2CrC	0.002	0.039	−0.009	0.071	Hard[001]
Co_2MnC	0.001	0.052	0.007	0.112	Easy[100]
Co_2MnC	0.002	0.042	0.007	0.093	Hard[001]
Co_2FeC	0.002	0.046	0.051	0.145	Easy[001]
Co_2FeC	0.001	0.047	0.039	0.134	Hard[100]

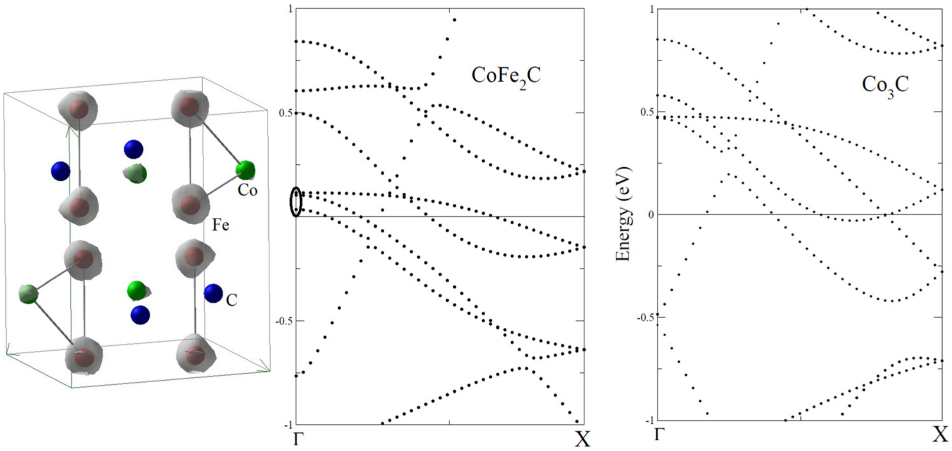

FIG. 2. The band structure of $CoFe_2C$ and Co_3C compounds without spin-orbit coupling in majority spin channel. The left one shows the distribution of wave function's square at Γ point for these three circled unoccupied states of $CoFe_2C$ compound.

MAE are in agreement with the above relation. For Co_2CrC and Co_2MnC that exhibit a large MAE, the above table shows that the main change in the orbital contribution is derived from the cobalt sites. For Co_2FeC, on the other hand, the major contribution is due to Fe sites. Hence, the mixing between the transition metal atoms and C is the principal source of enhanced anisotropy. To further quantify this effect, we proceeded to examine the effect of C on the electronic structure of the system. In particular, we wanted to examine how the *d*-states of the transition metal site are affected by the presence of the C sites. The MAE in transition metal systems is small and previous studies have shown that a second order perturbation calculation of the spin orbit interaction can provide the qualitative picture.[19,20] Within a second order model, the MAE is determined by the matrix element of the spin orbit interaction between the occupied and the unoccupied states. We therefore proceeded to examine the location of the occupied and unoccupied Co *d*-states close to Fermi energy for the various carbides. We first focus on $CoFe_2C$ and here we examined the case of pure cobalt carbide and the mixed carbide. Fig. 2 shows the energy bands along Γ to X for the pure cobalt carbide and $CoFe_2C$. The states with larger *d*-component are shown by the dark dots. In particular, the lowest unoccupied states (circled) are largely located on the Fe sites as seen from the distribution of the square of the wave functions. This is also seen from Fig. 3 that shows the total density of states and the projected density of states at the various sites. We also found that there is significant reduction in the spacing between the filled and unfilled *d*-states in going from the pure cobalt to the mixed carbide. To further quantify the change, we list in Table VII, the energy difference between the highest occupied and lowest unoccupied d-states at the Γ and X points for the $CoFe_2C$, Co_3C, and pure bulk Co (hcp). One notices that there is a decrease in spacing in going from pure Co to the cobalt carbide and a further decrease in going to mixed carbide.

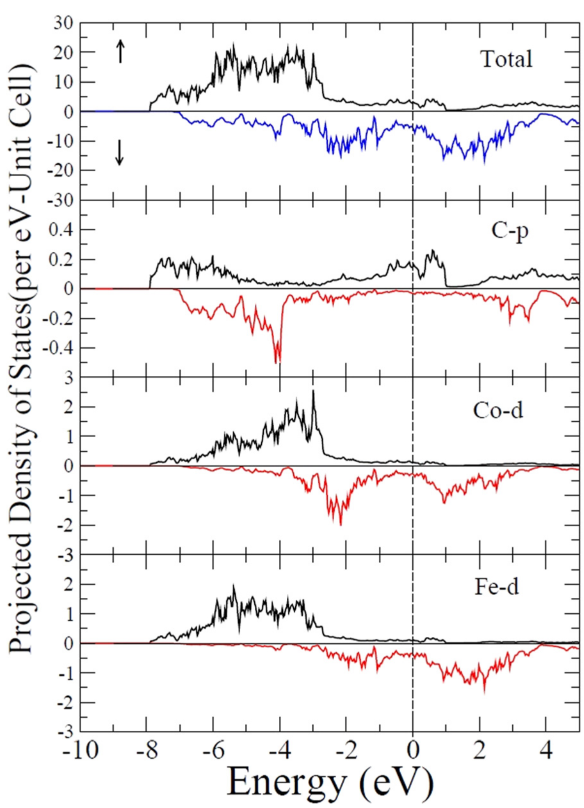

FIG. 3. The total and projected density of states for $CoFe_2C$ obtained in GGA + U (U = 4 eV) calculations.

TABLE VI. Orbital magnetic moment (in unit of μ_B) on each atomic site and one formula unit of bulk $CoTM_2C$ obtained by GGA + U (U = 4 eV) calculations.

	C	Co	TM	Total	Direction
$CoCr_2C$	0.001	0.048	−0.014	0.021	Easy[001]
$CoCr_2C$	0.002	0.053	−0.013	0.029	Hard[010]
$CoMn_2C$	0.002	0.052	0.002	0.056	Easy[100]
$CoMn_2C$	0.002	0.045	0.003	0.053	Hard[110]
$CoFe_2C$	0.002	0.057	0.044	0.147	Easy[100]
$CoFe_2C$	0.003	0.054	0.040	0.137	Hard[001]

TABLE VII. The energy difference of occupied and unoccupied states near Fermi level (in unit of eV) for $CoFe_2C$, Co_3C, and bulk Co without spin-orbit coupling, in majority spin channel.

	Γ	X
$CoFe_2C$	0.801	0.365
Co_3C	0.955	0.400
Co(hcp)	6.13	2.44

We also found that amongst carbides there are variations in the anisotropy that do not necessarily correlate with the separation. This is because, as we have shown above, the major contribution to the anisotropy can originate in Co or the other transition metal depending on the system.

IV. CONCLUSIONS

To summarize, the present studies indicate that the magnetic moment and the anisotropy can be significantly controlled by going from pure cobalt carbides to mixed transition metal carbides. In addition to the larger moments at the Fe, Mn, or Cr sites, the mixing enhances the local moment at the Co sites compared to that in pure cobalt carbide. An analysis of the orbital angular momentum indicates that depending on the alloy, the increase in orbital angular momentum can come from Co sites or from the other element. Examination of the electronic structure reveals that the enhancements in anisotropy are driven by the mixing between C *p*- and the transition metal *d*- states, and that the mixing reduces the gap between the occupied and unoccupied d-states. Since the nanoparticles are synthesized by reducing transition metal salts, we believe that the present work will motivate synthesis of the mixed transition metal composites that offer substantially better magnetic characteristics.

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