Magnetocrystalline anisotropy in Gd(Co,Fe)_{12}B_6: A first-principles study

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Abstract

The electronic structure, preferential site occupancy for Fe, and magnetocrystalline anisotropy (MCA) have been investigated in Gd(Co_{12-x}Fe_x)_{12}B_6 via a DFT (density functional theory) plus Hubbard U approach (DFT + U). For Gd atoms, the spin-up 4f bands are fully occupied while the spin-down 4f hole levels are completely empty. The d-like states dominate at the Fermi Level, mainly contributed by Co(Fe) 3d electrons. Co atoms in GdCo_{12}B_6 carry magnetic moments of –0.3 μ_B and –0.7 μ_B at the 18g and 18h sites respectively, while the 7.3 μ_B Gd moments are ordered antiparallel to the Co(Fe) sublattice. The DFT total energy calculations show that the Fe atoms prefer to replace Co at the 18h site rather than the 18g site, with an energy gain of 0.16 eV/f.u. and they carry a magnetic moment of 1.5 μ_B/Fe. GdCo_{12}B_6 shows a weak easy c– axis MCA (E_mca = 90 μ_eV/f.u.) while GdCo_{12}Fe_{0.5}B_6 displays a moderate easy ab– plane MCA (E_mca = –2690 μ_eV/f.u.). The spin reorientation induced by Fe doping is related to the electronic structure change near Fermi Level and the different contributions of Co and Fe to the MCA in GdCo_{12-x}Fe_xB_6.

1. Introduction

Since the discovery of the Nd_{2}Fe_{14}B permanent magnet [1–3], significant research effort has been devoted to R-Co-B and R-Fe-B based magnetic systems. In addition to their important technological performance, their intrinsic magnetic properties such as exchange interactions, magnetic anisotropy and ordering behavior, have been intensively investigated. The ternary boride system, RCo_{12}B_6, was first identified by Niihara and Yajima [4] and later found to form with iron by Buschow et al. during a survey of the Nd–Fe–B ternary phase diagram [5]. RTM_{12}B_6 adopts the trigonal SrNi_{12}B_6 structure (space group R3m #166) with the transition metal (TM) occupying the 18g and 18h sites, the rare earth (R) occupying the 3a and the boron atom at the 18h site [6–13].

The RCo_{12}B_6 compounds exist for the entire rare earth series with lattice parameters that follow the conventional lanthanide contraction [7]. They are all collinear ferro- (La-Sm) or ferri- (Gd-Tm) magnets with rather small cobalt moments of 0.4 μ_B and modest ordering temperatures T_C of about 150 K [7]. Mössbauer measurements on 57Fe-doped materials suggested that for R = Y, La, Sm, Gd, Tb, and Er, the ordering was in the basal plane [10,14,15]. However, compounds with R = Nd appeared to exhibit axial ordering at 4.2 K, but reoriented into the basal plane on heating [10]. Recently however, both 155Gd Mössbauer spectroscopy [16] and neutron diffraction [17] showed that the magnetic ordering direction of GdCo_{12}B_6 was in fact axial (i.e. parallel to the c– axis) and that basal plane ordering only developed when the system was doped with iron. As little as 4% Fe (0.5 Fe/f.u.) was sufficient to drive the axial to basal plane transition [16,17]. As the ordering directions for the other RCo_{12}B_6 compounds have all been derived from 57Fe-doped samples, a re-evaluation of these compounds may be necessary.

As part of our endeavor is to understand the magnetocrystalline anisotropy (MCA) in RCo_{12}B_6, we have investigated the MCA by a first-principles DFT calculation. In this paper, we report on the electronic structure, Fe preferential site occupancy, and the MCA effects of both the structural distortion and electronic changes induced by Fe doping in GdCo_{12-x}Fe_xB_6.

2. Methodology and computational details

The first-principles electronic structure calculations were performed in the framework of density functional theory (DFT). The QUANTUM ESPRESSO package [18], in the projector augmented wave (PAW) framework [19], was employed to perform DFT...
calculations using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof for solids (PBEsol) [20] for the exchange correlation functional. The atomic PAW potentials were adopted from the PSlibrary.1.0 generated by A Dal Corso [21]. The wave functions were expanded in plane-wave basis sets truncated at a cutoff energy of 50 Ry and the charge densities were truncated at 200 Ry. Brillouin zone integrations were performed on a 8 × 8 × 8 k-point grid, and the Marzari-Vanderbilt broadening [22] was applied with a smearing width of 5 mRy. The structural degrees of freedom were fully relaxed to obtain the optimized structural parameters.

The optimized structures from PAW calculation were used as the input for the MCA calculation. The MCA energy is defined as \( E_{\text{MCA}} = E_{100} - E_{001} \), where \( E_{001} \) and \( E_{100} \) are the total energies for the magnetization oriented along the [001] and [100] directions, respectively. Positive (negative) \( E_{\text{MCA}} \) corresponds to easy c– axis (easy ab– plane) MCA.

The MCA energies were calculated using a full potential plane wave plus muffin-tin orbital (PMTO) approach, a fusion of the linear augmented plane waves (LAPW) and muffin-tin orbital (MTO) method [23–25]. The relativistic effects were treated by solving a scalar relativistic wave equation. Spin-orbit coupling (SOC) are included to attain the orbital moments and evaluate MCA. The method has been used to calculate the MCA energy in FeP\(_2\)N\(_2\) [26]. Brillouin zone integrations were performed on a 24 × 24 × 24 k-point grid. The k-space integrations have been performed using the tetrahedron method [27,28]. Considering the strong correlation effect, the Gd 4\( f \) electrons were treated in a framework of DFT plus Hubbard U (DFT + U) [29–31]. In the DFT + U approach, the screened Coulomb and exchange energies of a chosen set of localized orbital (Gd 4\( f \) states) were added to the usual DFT functional and their orbital independent average was subtracted to avoid double counting. In the DFT + U calculations, we have used the Hubbard U = 6.7 eV and exchange parameter J = 0.7 eV for the Gd 4\( f \) electrons [32].

### 3. Results and discussion

#### 3.1. Fe preferential site occupancy in Gd(Co,Fe)\(_{12}\)B\(_6\)

GdCo\(_{12}\)B\(_6\) crystallizes with the trigonal SrNi\(_{12}\)B\(_6\) structure (space group \( R3m \)). In the primitive unit cell, there is one formula unit of GdCo\(_{12}\)B\(_6\) with two inequivalent crystallographic sites for the Co atoms (18g and 18h). To evaluate the effects of Co substitution by Fe, one Fe atom was placed on each of the two Co sites in turn. As all single-Fe replacements on a given site (18g or 18h) are equivalent, only a single substitutional configuration needed to be checked for each cobalt site.

The structural parameters of GdCo\(_{12}\)\(_x\)Fe\(_x\)B\(_6\) with \( x = 0 \) and 1 have been fully relaxed using the PAW method and are shown in Table 1. The experimental data are also listed in the table. As shown in the table, the lattice constants are underestimated by about 1%. The cohesion energy, \( E_c \), for \( x = 0 \) is smaller than that for \( x = 1 \) by about 0.42 eV/f.u., indicating Fe doping reduces the structural stability of GdCo\(_{12}\)B\(_6\). This is consistent with the fact that GdCo\(_{12}\)B\(_6\) is a stable compound while GdFe\(_{12}\)B\(_6\) does not exist. Indeed, GdCo\(_{12}\)\(_x\)Fe\(_x\)B\(_6\) can only be prepared as far as \( x = 3 \) [17].

The calculated cohesive energies \( E_c \) for Fe at the 18g and 18h sites are –128.00 eV/f.u and –128.16 eV/f.u. in GdCo\(_{11}\)Fe\(_1\)B\(_6\), respectively. The results indicate that Fe prefers to substitute for Co at the 18h site. The different substitution energies are the result of the different structural and chemical environments of the substituted sites. The Wigner-Seitz volumes (WSV) have been calculated for the two Co sites in Gd(Co,Fe)\(_{12}\)B\(_6\) with DFT optimized structural parameters using a DIDO code [33]. The 18h site has a larger site volume (11.6 Å\(^3\)) than the 18g (11.2 Å\(^3\)) site. The metallic atomic radii are 1.26 Å and 1.25 Å for Fe and Co, respectively [34]. The replacement of Co by Fe will induce local strains due to the atomic size mismatch. To reduce the local strain, the larger Fe atoms favor the larger volume 18h site. This has been observed to be the dominant factor in Fe(Co) substitutions in a wide variety of rare-earth iron intermetallic compounds [35].

The substitution energy of Co by Fe can be defined as

\[
E_{\text{sub}} = E_c(GdCo_{11}Fe_B_6) - E_c(GdCo_{12}B_6)
\]

Based on the Maxwell-Boltzmann distribution [36], the occupation probability of Fe at each Co site in Gd(Co,Fe)\(_{12}\)B\(_6\) can be expressed as

\[
P_i = \frac{g_i \exp(-\Delta E_i/k_BT)}{\sum_i g_i \exp(-\Delta E_i/k_BT)}
\]

Where \( g_i, \Delta E_i, T \) and \( k \) are the multiplicity of the crystallographic site \( i \), internal energy change (i.e. \( E_{\text{sub}} \)), temperature, and Boltzmann’s constant, respectively. The calculation details have been reported previously [37].

Fig. 1 displays the temperature dependence of the site occupancy of Fe in GdCo\(_{12}\)\(_x\)Fe\(_x\)B\(_6\). As expected, Fe prefers the 18h site and the occupation bias decreases with increasing temperature. The results are in good agreement with the experimental results [16,17].

#### 3.2. Electronic structure and magnetic moments in Gd(Co,Fe)\(_{12}\)B\(_6\)

The electronic structure of GdCo\(_{12}\)B\(_6\) has been calculated using DFT + U. As shown in Fig. 2, the spin-projected total density of states (DOS) are mainly distributed between –8.5 eV and the Fermi

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**Table 1** Calculated and experimental lattice constants, magnetic moments and cohesion energy (eV/f.u.) in GdCo\(_{12-x}\)Fe\(_x\)B\(_6\) (\( x = 0, 1 \)).

<table>
<thead>
<tr>
<th></th>
<th>x = 0</th>
<th></th>
<th>x = 1</th>
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<td></td>
<td>PAW</td>
<td>MTO exp.</td>
<td>PAW</td>
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<td>c (Å)</td>
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<td>M(_{\text{Co}}) (µB)</td>
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<td>–0.74</td>
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<tr>
<td>M(_{\text{Fe}}) (µB)</td>
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<td>–</td>
<td>–1.40</td>
</tr>
<tr>
<td>M(_{\text{Fe}}) (µB/u.r.)</td>
<td>0.30</td>
<td>1.56</td>
<td>1.68</td>
</tr>
<tr>
<td>( E_c ) (eV/f.u.)</td>
<td>–128.58</td>
<td>–</td>
<td>–128.16</td>
</tr>
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</table>

**Fig. 1.** Temperature dependence of the site occupation probability of Fe in GdCo\(_{11}\)Fe\(_1\)B\(_6\).
It is clear that undoped GdCo12B6 shows a very weak easy c–axis MCA, and this is consistent with the suggestion from the neutron diffraction study that while the order is essentially axial in nature, the moments are canted by at least 15° from the c–axis at 4 K in GdCo12B6 [17]. By contrast, GdCo11FeB6 clearly has a moderate easy ab–plane MCA. The MCA energies \( E_{\text{mca}} \) for \( x = 0 \) and \( x = 1 \) are 90 \( \mu \text{eV/\text{f.u.}} \) and –2690 \( \mu \text{eV/\text{f.u.}} \), respectively. This factor of 30 change in MCA associated with replacing a one (of twelve) cobalt atoms by an iron atom (a doping level of ~8%) is consistent with the observation that even a doping level of 0.5% is sufficient to lead to planar ordering [9,38].

Iron doping will distort the crystal structure in addition to causing changes in the electronic and magnetic behavior in Gd(Co,Fe)12B6. To understand the change of MCA induced by doping with Fe, the MCA energy has been calculated as a function of the relative lattice constant ratio \( \delta \) in GdCo12B6, where \( \delta = (c/a)/(c_0/a_0) \) and \( a \) and \( c \) are the lattice constants while \( a_0 \) and \( c_0 \) are the optimized lattice constants of GdCo12B6. As shown in Fig. 4, the lattice distortion has very little effect on the MCA in GdCo12B6. These results imply that the change of MCA comes mainly from electronic and magnetic factors.

The microscopic origin of MCA is from spin-orbital coupling (SOC). The SOC of 3d electrons can be considered as perturbation. The first order perturbation terms are zero due to the angular moment quenching in the solid. The SOC energy can be expressed,
Based on second order perturbation theory [39–41], as

$$E_{\text{SOC}} = \frac{\hbar^2}{2m} \sum_{n \neq k} \left| \langle n|L \cdot S|k \rangle \right|^2 \left( E_n - E_k \right)^2$$

(3)

where \( |n\rangle \) and \( |k\rangle \) denote eigenvectors of the unperturbed Hamiltonian and \( E_n \) and \( E_k \) are the associated energy eigenvalues. For the case with both \( |n\rangle \) and \( |k\rangle \) states are occupied or unoccupied, there is a cancellation of these terms in the sum. The remained terms are those coupled occupied \( \langle n| \) and unoccupied \( \langle k| \) states. Since the SOC is inversely proportional to the energy difference between unoccupied and occupied states, the most important contributions are from the states just below and above the Fermi level.

The orbital magnetic moment \( M_{\text{orb}} \) is related to SOC and MCA. In case the spin-flip contribution can be neglected, MCA is proportional to the orbital moments [42]. However, the simple corresponding relation will be invalid when spin-flip is important [41,43]. It is interesting that the site/atom resolved \( M_{\text{orb}} \) show almost linear variation as the spin quantization axis rotates from \([001]\) to \([100]\) direction in GdCo12-xFe2B6 with \( x = 0 \) and \( x = 1 \) (Fig. 5).

For \( x = 0 \), \( M_{\text{orb}} \) for the Gd site becomes slightly more negative while that of Co sites (18g and 18h) become more positive by approximately the same amount as the spin axis rotates from \([001]\) to \([100]\). On the other hand, for \( x = 1 \), while \( M_{\text{orb}} \) for Gd and the Co 18g sites show moderate negative tendency on rotating from \([001]\) to \([100]\), \( M_{\text{orb}} \) for Fe(18h) exhibits a very rapid change. The doped Fe greatly changes the dependence of the orbital moment of the Co(Fe) sublattice on the spin rotation angle in the compound with \( x = 1 \). The Fe orbital moment seems almost quenched along \([001]\) direction for \( x = 1 \). Here, a supercell approximation is employed to mimic alloying behavior so the more physical parameter is the average \( M_{\text{orb}} \) at the 18h site. The average \( M_{\text{orb}} \) at the 18h site for \( x = 1 \) is almost triple as that for \( x = 0 \), and changes by about 20–30% as the spin quantization axis changes from \([001]\) to \([100]\) direction.

As shown in Fig. 5, the absolute value of \( M_{\text{orb}} \) for Gd and Co increases and decreases almost linearly, respectively, for \( x = 0 \) as the spin quantization axis rotates from \([001]\) to \([100]\). However, all the \( M_{\text{orb}} \) absolute value for Gd, Co and Fe increases almost linearly for \( x = 1 \) upon rotating spin axis from \([001]\) to \([100]\). The spin axis dependence of \( M_{\text{orb}} \) for \( x = 0 \) is clearly opposite to that for \( x = 1 \), indicating a Fe-doping induced change of the orbital moment anisotropy. Fe-doping causes abrupt changes of both the anisotropy of orbital moment and the magneto-crystalline anisotropy (MCA). Although there is no quantitative relationship between \( \partial M_{\text{orb}} / \partial \theta \) and \( M_{\text{cma}} \) due to the spin-flip contribution to \( E_{\text{SOC}} \), we believe that both of them are related to changes in the electronic structure near Fermi level upon Fe-doping. One possible explanation is that the electron band filling near the Fermi level is changed upon partially replacing Co (3d) by Fe (3d) with fewer 3d electrons. This is responsible for the changes of the \( M_{\text{orb}} \), anisotropy and MCA in the compound with \( x = 1 \). The sensitive behavior of MCA to band filling has been reported in Li2(Li1-xTx)N with \( T = \text{Mn}, \text{Fe}, \text{Co} \) and Ni by Ke and van Schilfgaarde [41].

4. Summary

GdCo12-xFe2B6 has been investigated by DFT + U. The total energy calculations show that the Fe atoms prefer to substitute for Co at the 18h rather than the 18g site. However, an energy gain of 0.16 eV/f.u. Gd has a magnetic moment of 7.3 \( \mu_B \) that is ordered antiparallel to the Co(Fe) sublattice. The Co atoms in GdCo12-xFe2B6 carry magnetic moments of \(-0.3 \mu_B \) and \(-0.7 \mu_B \) at the 18g and 18h sites respectively. The doped Fe atoms at the 18h site have a magnetic moment of \( 1.5 \mu_B \). The MCA energy calculations indicate that GdCo12-xFe2B6 has a weak easy \( c \)-axis MCA with \( M_{\text{cma}} = 90 \mu_eV/\mu\text{u} \). However, GdCo12Fe2B6 displays an easy \( ab \)-plane MCA with \( M_{\text{cma}} = -2690 \mu_eV/\mu\text{u} \). The spin reorientation induced by doping Fe is related to the electronic structure change near Fermi Level and the different contributions of Co and Fe to the MCA in GdCo12-xFe2B6. As the ordering directions for the other RCo12B6 compounds have all been derived from \(^{57}\text{Fe}\)-doped samples, a re-evaluation of these compounds may be necessary due to the strong effect of Fe on the MCA in this system.

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References
