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Extreme doping sensitivity of the ordering direction in $GdCo_{12-x}Fe_xB_6$

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^{155}Gd Mössbauer spectroscopy has been used to investigate the magnetic ordering direction of $GdCo_{12-x}Fe_xB_6$ ($0 \le x \le 3$) at 5 K. The moment orientation was found to be extremely sensitive to doping with as little as ∼4% Fe doping (0.5 Fe/f.u.) causing the moment orientation to change from the *c*-axis to the basal plane. Including results from earlier ^{57}Fe-doping work suggests that the axial–basal boundary may lie below 0.5% Fe doping (∼0.06 Fe/f.u.). As the ordering directions for the other $RCo_{12}B_6$ compounds have all been derived from ^{57}Fe-doped samples, a re-evaluation of these compounds may be necessary. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4794373]

I. INTRODUCTION

The ternary boride system $RCo_{12}B_6$ was first identified by Niihara and Yajima[1] and later found to form with iron by Buschow *et al.* during a survey of the Nd–Fe–B ternary phase diagram.[2] $RTM_{12}B_6$ adopts the trigonal $SrNi_{12}B_6$ structure (space group $R\bar{3}m$, No. 166)[3] with the transition metal (TM) occupying the 18*g* and 18*h* sites, and the rare earth (R) occupying the 3*a* site.

While the cobalt compounds exist for the entire rare-earth series, only $LaFe_{12}B_6$ is stable for iron. Magnetization measurements of $LaFe_{12}B_6$ show a sudden jump at an applied field of about 8.6 T as the iron moment increases by more than a factor of three.[4] This low-moment → high-moment transition can also be driven by adding a magnetic rare earth such as neodymium[2] or gadolinium.[4] Recent tight-binding calculations have confirmed this moment instability, and have further shown that iron on the 18*h* site shows the greater sensitivity to its environment.[5,6] Mössbauer studies done by doping small amounts of iron (typically 0.5% as ^{57}Fe) into the cobalt compounds have also shown that iron has a larger moment in, and very strong preference for, the 18*h* site. The Mössbauer measurements on these ^{57}Fe-doped materials also show that in most cases (Y,[7] La,[8] Sm,[9] Gd,[10] Tb,[9] and Er[11]) the ordering is in the basal plane. However, two systems (Nd[7] and Ho[12]) exhibit axial ordering at 4.2 K but reorient into the basal plane on heating.

In this paper, we use ^{155}Gd Mössbauer spectroscopy as a direct measure of the ordering direction in both pure and Fe-doped samples of $GdCo_{12-x}Fe_xB_6$ ($0 \le x \le 3$). The moment ordering direction was found to be extremely sensitive to iron doping, with as little as ∼4% (0.5 Fe/f.u) causing an axial to basal plane re-orientation.

II. EXPERIMENTAL METHODS

Polycrystalline samples with composition $GdCo_{12-x}Fe_xB_6$ ($0 \le x \le 3$) were prepared by melting high purity starting elements in an induction furnace under a purified argon gas atmosphere. To promote homogeneity, the samples were wrapped in Ta foil and annealed at 900 °C for 3 weeks in an evacuated quartz tube. The crystallographic (phase) purity was checked by x-ray diffraction and confirmed that the $R\bar{3}m$ space group symmetry is retained for all the studied compounds and that $x = 3$ appeared to be the formation limit. The samples were mounted in a helium flow cryostat for the ^{155}Gd Mössbauer measurements,[13] and the spectra were fitted using an exact solution to the full hamiltonian.[14]

III. RESULTS

The Néel temperatures (T_N) and the compensation temperatures (T_{comp}) were determined from the temperature dependence of the a.c. susceptibility measured in a magnetic field of 3 mT, and are shown in Figure 1. T_{comp} was defined as the minimum on the magnetization vs. temperature curves. The magnetization curves are unremarkable: T_N decreases monotonically from 158 K to 93 K as iron is added, and there is a shallow minimum in the compensation temperature ($T_{comp} = 45$ K at x = 1). The basic bulk characterization does not hint at any abrupt changes in structure or magnetic properties.

It is, however, immediately apparent from a visual inspection of the 5 K ^{155}Gd Mössbauer spectra in Figure 2 that there is a large difference between the spectrum of the undoped $GdCo_{12}B_6$ sample and that of $GdCo_{11}FeB_6$. The $GdCo_{12}B_6$ spectrum was acquired a second time on a separately made sample to confirm the difference between the spectral shapes of the undoped and doped samples.

The $\bar{3}m$ point symmetry of the 3*a* site occupied by Gd guarantees an axially symmetric electric field gradient (efg) tensor ($\eta = 0$) with the principal axis aligned with the

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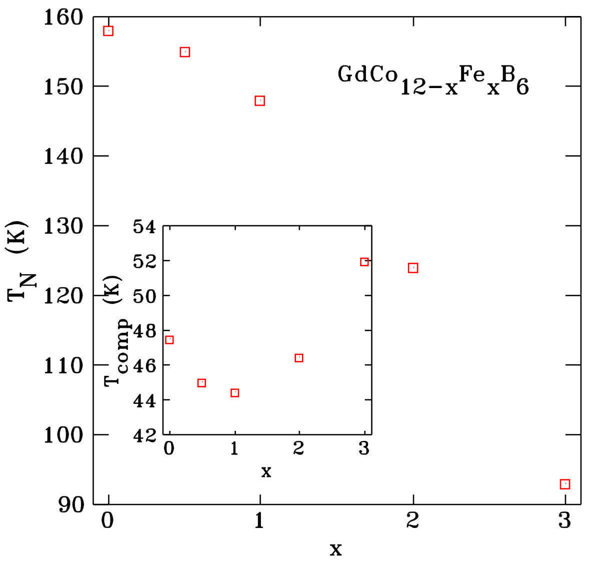

FIG. 1. The Néel temperature and the compensation temperature (inset) are smooth functions of iron content (x).

crystallographic *c*–axis.[15] Since the hyperfine field (B_{hf}) at the Gd site derives almost entirely from the local contribution of the Gd moment, B_{hf} will be parallel to the Gd moment and so the angle (θ) between the principal axis of the efg and B_{hf} is a direct measurement of the angle between the Gd moments and the crystallographic *c*-axis.

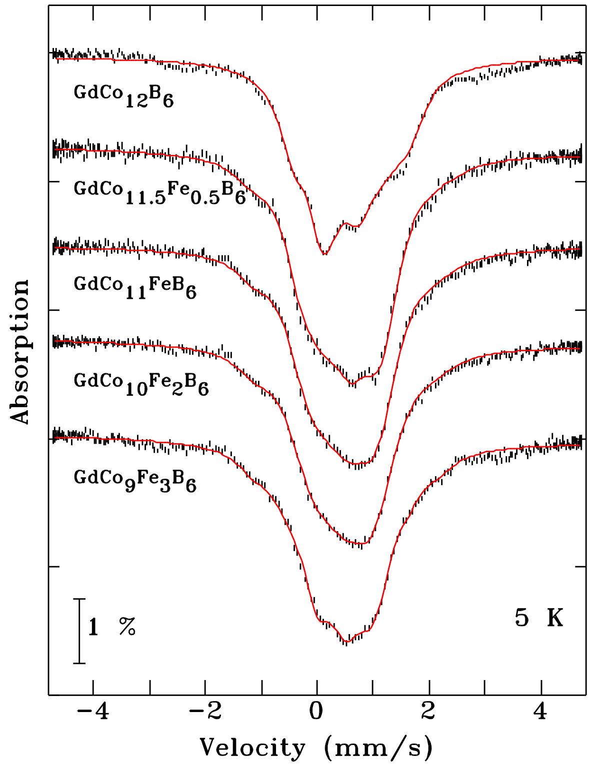

FIG. 2. ^{155}Gd Mössbauer spectra of $GdCo_{12-x}Fe_xB_6$ at 5 K showing the change in spectral shape between the undoped $GdCo_{12}B_6$ and doped samples.

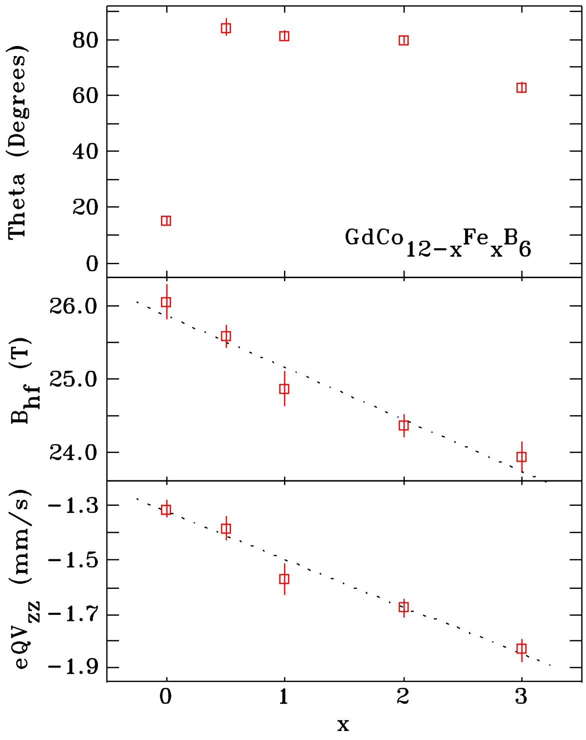

FIG. 3. The derived change in the moment direction is shown in the top panel. The hyperfine field (mid panel) and eQV_{zz} (bottom panel) are smooth functions of dopant amount (x). Dotted lines are guides for the eye.

X-ray diffraction rules out a major structural distortion as the origin of the changes in Figure 2 and the fitted Mössbauer parameters shown in Figure 3 reveal that the change in spectral shape arises from a change in the orientation of the Gd moments, and not from a change in the hyperfine field or in the quadrupole coupling constant (eQV_{zz}). The Gd moments in the undoped sample order close to the *c*-axis ($\theta = 15° \pm 2°$), while they are almost perpendicular to the *c*-axis for the doped samples.

To further explore the sensitivity of the ordering direction to iron doping, a less doped sample of composition $GdCo_{11.5}Fe_{0.5}B_6$ (~4% doping) was added to the study. As seen in Figures 2 and 3, the ordering direction was once again in the basal plane, meaning that the axial–basal boundary is somewhere below 4% iron doping. Indeed, the sensitivity may be even greater than that implied here as Rosenberg *et al.*[10] replaced only 2% of the cobalt with iron in their earlier ^{57}Fe doping work, and interpreted their ^{57}Fe Mössbauer spectrum as showing basal-plane ordering. A later study of a sample doped with only 0.5% ^{57}Fe (~0.06 Fe/f.u.) also suggested planar ordering.[16] Thus, the $GdCo_{12-x}Fe_xB_6$ system is remarkably sensitive to iron doping with the axial–basal boundary lying somewhere below 0.5% Fe-doping (~0.06 Fe/f.u.).

To explain the extreme sensitivity of the ordering direction, we note that the ordering temperatures for the $RCo_{12}B_6$ series are largely independent of the rare earth, varying by as little as ~15 K over the whole series,[17] indicating that Co–Co exchange dominates the ordering behaviour. Furthermore, since any anisotropy associated with the gadolinium will be small, it is likely that the choice of ordering direction is also controlled by the cobalt. There is considerable experimental evidence to suggest that the anisotropy behaviour of the Co and Fe sublattices in transition-metal rich intermetallics have opposite signs. For example,[18] in the $R_2TM_{14}B$ series, $Y_2Fe_{14}B$ shows easy-axis order, whereas $Y_2Co_{14}B$ exhibits easy-plane order. Similar behaviour is observed in the $R(TM, X)_{12}$ compounds with X = V and Si. The reverse, i.e., axial order for Co and planar order for Fe, is observed in $Y_2TM_{17}N_x$.[18] Work on R-(Co,Fe) intermetallics shows that very little Fe substitution is needed to alter the magnetic anisotropy of Co-rich compounds when there are multiple Co sites with competing anisotropies. This is particularly the case when Fe shows a distinct site occupancy preference, as is the case here. For example, in the $Y(Co,Fe)_4B$ series, iron strongly prefers the $2c$ site over the $6i$ site,[19] and point charge calculations suggest that the anisotropies at the two sites have opposite signs.[20] Replacing as little as ∼4% of the Co by Fe is sufficient to eliminate easy axis ordering and suppress the axial→planar reorientation observed at low temperatures.[21]

Therefore, we suggest that the dramatic effect that Fe substitution has on the magnetic ordering in $GdCo_{12-x}Fe_xB_6$ is related to the strong preference Fe has to occupy the $18h$ TM site and may also involve a weakening of axial anisotropy from that Co–$18h$ site. It is also conceivable that the two Co sites have opposing anisotropies which would fit in well with the fact that only very small amounts of Fe are sufficient to flip the anisotropy.

IV. CONCLUSION

Contrary to earlier, indirect measurements, we find that $GdCo_{12}B_6$ exhibits axial ordering, and that the moments only rotate into the basal plane once iron is doped into the material. We have found that the moment direction is extremely sensitive to Fe doping and the axial-basal boundary may lie below 0.5% Fe doping (∼0.06 Fe/f.u.). As all current ordering directions for the undoped $RCo_{12}B_6$ materials have been assigned under the assumption that low Fe doping would not have a profound impact, a complete re-evaluation of the system is needed. Neutron diffraction studies on the Gd compound are in progress to obtain an independent assessment of the moment orientations in both undoped and doped samples.

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