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L.V.B. Diop, O. Isnard. A magnetic study of the HoCo12-xFexB6 ferrimagnetic compounds. Journal of Alloys and Compounds, 2019, 804, pp.392-395. 10.1016/j.jallcom.2019.07.030 . hal-02380844

HAL Id: hal-02380844
https://hal.science/hal-02380844

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Manuscript_29b251dbe2b112cd0a063d8edde6d0da

A magnetic study of the $HoCo_{12-x}Fe_xB_6$ ferrimagnetic compounds

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Abstract

The effects of Fe substitution on the structural and magnetic properties of the $HoCo_{12-x}Fe_xB_6$ ($0 \leq x \leq 2$) series of intermetallic compounds have been studied. All of the compounds form in the rhombohedral $SrNi_{12}B_6$-type structure, the lattice constants increasing linearly with x. These compounds are ferrimagnets with a small transition metal magnetic moment and exhibit a spin reorientation transition. The Curie temperature decreases from 147 K for x =0 to 105 K for x = 2. The Fe for Co substitution leads also to a progressive decrease of the spontaneous magnetization. The spin reorientation transition temperature is significantly reduced upon Fe for Co substitution whereas the compensation temperature is much less sensitive to the Fe composition.

1. Introduction

Intermetallic compounds based on rare-earth elements (R) and 3*d* transition metals (TM) form an important class of materials with various applications such as permanent magnets, magnetostrictive devices, or magneto-optical recording. The outstanding magnetic properties of these materials result from the combination of the different magnetic features of the itinerant 3*d* states of the transition metal and the localized 4*f* electronic states of the rare-earth. Some intermetallic compounds present a compensation point at which the partial magnetizations of the R and the TM sublattices have the same magnitude but opposite orientation. The temperature of the compensation point can be adjusted by controlling the rare-earth and the *3d* transition metal chemical composition. Such a remarkable feature of some ferrimagnetic materials like the solid solution $HoCo_{12-x}Fe_xB_6$ is a useful property wanted in the context of intense research for magneto-optical recording and magneto-transport in spintronics [1-2]. Moreover, R–TM alloys with heavy rare-earth elements are also investigated by means of optical switching experiments [2], in the context of ultrafast magnetization reversal of magnetic memories.

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The ternary system $RTM_{12}B_6$ adopts the rhombohedral $SrNi_{12}B_6$ prototype crystal structure, space group $R\bar{3}m$ [3-5]. The 3*d* transition metal atoms reside on two inequivalent Wyckoff positions (18g and 18h), whereas the rare-earth element occupies only one crystal site (3a). The boron atoms are located on another 18h crystallographic position. Earlier reported studies reveal that the $RCo_{12}B_6$ compounds are stable for essentially all of the rare-earths (with the exception of europium). The evolution of the unit-cell parameters among these compounds reflects the conventional lanthanide contraction. $RCo_{12}B_6$ systems order magnetically, they are ferro– (R =Y, La–Sm) or ferri– (R = Gd–Tm) magnets with a rather small mean Co moment – 0.42 μ_B/Co in $YCo_{12}B_6$ – and low Curie temperature T_C =134–162 K [6]. These weak intrinsic magnetic properties are ascribed to the relatively small number of Co with respect to B (factor of 2) and to the hybridization of B(p) and Co(d) electron states as a consequence of small distances between Co and B atoms (2.05 Å) [6-9]. The Co magnetic behavior has been studied in detail in both paramagnetic and magnetically ordered state. The itinerant character of the magnetism of these compounds has been established [6,] and the role of volume has been investigated by means of magnetization measurements under hydrostatic pressure up to 1 GPa [10-13]. Rather moderate pressure effect on the intrinsic magnetic properties has been observed. NMR studies [14-16] suggest that the Co moments on the two inequivalent crystallographic positions are different, with the Co(18h) moment being significantly larger than the Co(18g) moment. Neutron powder diffraction analyses confirmed different values of Co magnetic moments on the 18(g) and 18(h) crystal sites [12, 17]. This observed difference in the Co magnetic moments is driven by the different nearest-neighbour configurations: the 18g site has 7 Co neighbours and 4 B neighbours whereas the 18h site has 9 Co and 3 B neighbours, resulting in a larger moment at the 18h site.

Following earlier reports of the presence of a spin reorientation phenomenon in $HoCo_{12}B_6$ [17-18], the present work is devoted to the investigation of the ferrimagnetic $HoCo_{12-x}Fe_xB_6$ intermetallic compounds with Fe substitution in the range x = 0 – 2 to probe the effect of Fe on the remarkable magnetic properties of such pseudo-ternary system. Moreover, this study is motivated by the recent discovery of extreme sensitivity of the ordering direction to Fe concentration in $GdCo_{12-x}Fe_xB_6$ compounds [19-20].

2. Experimental techniques

Polycrystalline samples of $HoCo_{12-x}Fe_xB_6$ have been synthesized by melting starting elements of at least 99.9% purity in a high frequency induction furnace under a protective argon atmosphere. In order to ensure good homogeneity, the alloy buttons were turned and

remelted several times. Then, small pieces of the obtained ingots were wrapped in tantalum foil, sealed in evacuated quartz tubes and subsequently annealed at 1173 K for 21 days. The synthesized samples were characterized by chemical analysis, as well as by X-ray powder diffraction. The phase purity and the elemental composition were checked by scanning electron microscopy (SEM) in back scattered electron (BSE) contrast and energy-dispersive X-ray spectroscopy (EDS) analysis. Room temperature X-ray powder diffraction was performed on a Siemens D5000 diffractometer in reflection mode with the Bragg–Brentano geometry, using Co-Kα radiation. Least-squares refinement including all the observed Bragg reflections was applied to determine precisely the unit-cell parameters. Following the X-ray diffraction analysis, magnetic susceptibility and magnetization measurements were performed. The magnetic measurements were carried out on free powder samples in steady magnetic fields up to 10 T at temperatures ranging from 1.7 to 300 K using an extraction magnetometer. A detailed description of the extraction magnetometer can be found in Ref. 21. The ac magnetic susceptibility was measured at a frequency of 10 kHz down to 4.2 K in a magnetic field of 3 mT.

3. Results and discussion

SEM and EDS microanalysis performed on the as-cast and annealed samples reveals their high chemical purity. These alloys contain a main phase $HoCo_{12-x}Fe_xB_6$ with some amount of the pseudo-binary system $(Co,Fe)_2B$. In order to minimize the quantity of this spurious phase, a slight excess of Ho was used, after which the $HoCo_{12-x}Fe_xB_6$ synthesized materials were found to be mainly single phase according to the analysis of the X-ray diffraction patterns.The diffraction patterns were indexed on the basis of the rhombohedral $SrNi_{12}B_6$ structure; the $R\bar{3}m$ space group symmetry is retained for all the investigated compounds. A careful look at the diffraction patterns indicates the presence of residual traces of the $(Co,Fe)_2B$ compound as minority impurity phase. The lattice parameters of the parent compound $HoCo_{12}B_6$ at room temperature are a = 9.451(2) Å and c = 7.454(3) Å, in good agreement with previous results on polycrystalline samples [6, 18]. The lattice constants for the entire series of samples studied here are plotted as a function of concentration in figure 1, confirming the presence of a solid solution over the entire composition range studied. The corresponding values are summarized in table 1. It can be seen that both lattice parameters increases linearly versus Fe content. Partial substitution of Fe for Co induces a continuous increase of the unit cell volume (figure 2). The Fe ion radius is larger than Co one, that results in the observed lattice parameters and volume change. Samples with higher Fe concentration were prepared,

however, they were found to contain much larger amounts of the additional $(Co,Fe)_2B$ phase. Consequently, those samples with $x > 2$ were not considered further in the present study.

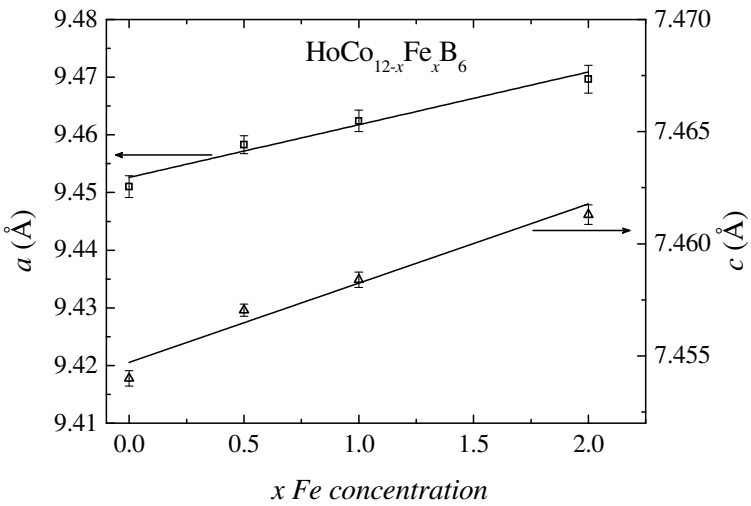

Figure 1: Lattice parameters of $HoCo_{12-x}Fe_xB_6$ obtained from refinement of room temperature X-ray diffraction data.

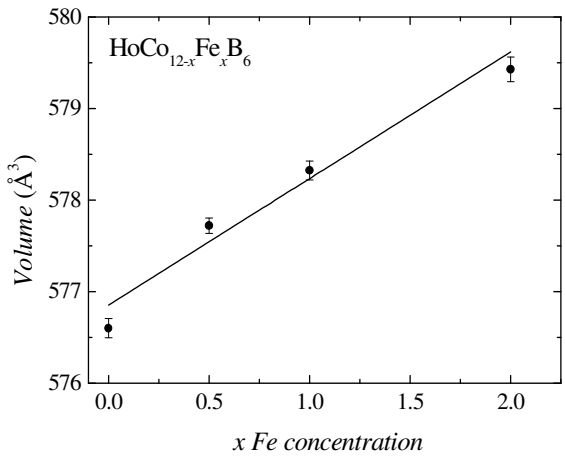

Figure 2: Room temperature cell volume as a function of Fe content in $HoCo_{12-x}Fe_xB_6$ series of compounds.

$HoCo_{12-x}Fe_xB_6$	a (Å)	c (Å)	V (Å^3)
$x = 0$	9.451(2)	7.454(3)	576.6(4)
$x = 0.5$	9.458(2)	7.457(1)	577.7(2)
$x = 1$	9.462(3)	7.458(2)	578.3(3)
$x = 2$	9.469(4)	7.461(3)	579.4(5)

Table 1: Lattice parameters and unit cell volume for the $HoCo_{12-x}Fe_xB_6$ series of compounds.

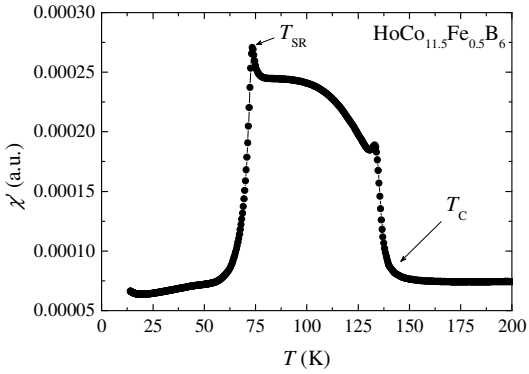

Figure 3: AC magnetic susceptibility (χ') for $HoCo_{11.}Fe_{0.5}B_6$ compound.

Figure 3 shows the measurement of the ac magnetic susceptibility (χ') of $HoCo_{11.5}Fe_{0.5}B_6$. Two magnetic anomalies are observed at about 73.5 K and 133 K. The latter is similar to the peak observed in $YCo_{12}B_6$ [22-23] and $HoCo_{12}B_6$ [13, 17] just below the Curie temperature. This peak, also known as Hopkinson effect, is often very sharp [24]. The former indicates a magnetic phase transition of the order-order, spin reorientation type, in which a rotation of the magnetization vector with respect to the crystallographic axes occurs upon change of temperature. The values of the Curie (T_C) and spin reorientation (T_{SR}) temperatures were determined from the analysis of the temperature dependence of the ac magnetic susceptibility (χ'). T_C was taken as the onset of the strong increase seen on cooling, while T_{SR} was defined as the maximum on the $\chi'(T)$ plots observed well below T_C (see figure 3). The spin reorientation transition is characterized by a change of the easy magnetization direction with temperature. The spin reorientation transition is caused by the temperature induced competition between the Ho and (Co, Fe) sublattice magnetocrystalline anisotropies which have different preferred direction. In the $RCo_{12}B_6$ crystal structure the Co sublattice anisotropy favors the basal plane as it has been reported for non magnetic rare-earth isotype compounds R = Y, La [12, 25]. On the contrary, Ho and Nd atoms having negative second-order Stevens coefficient have been proved to favor alignment of the magnetic moments along the crystallographic *c*-axis in the $RCo_{12}B_6$ crystal structure [17, 18]. This originates from the sign of the second order crystal-electric field parameter A_2^0 which is positive and amounts to 254 K a_0^{-2} in the $RCo_{12}B_6$ crystal structure [17]. This positive sign of A_2^0 is in agreement with the magnetic structure derived from neutron powder diffraction studies showing that the Ho sublattice anisotropy prefers the *c*-axis in $HoCo_{12}B_6$ compound. $HoCo_{12}B_6$ orders its magnetic moments close to the crystallographic *c*-axis at 1.5 K and undergoes an axial to basal plane spin reorientation upon heating.

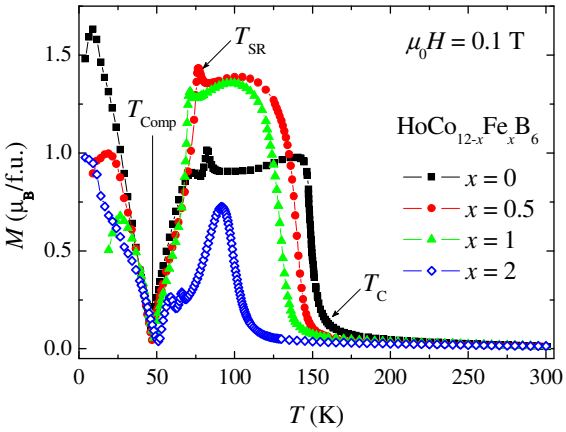

Figure 4: Temperature dependence of the magnetization of $HoCo_{12-x}Fe_xB_6$ measured in a magnetic field of 0.1 T.

The temperature dependence of the magnetization, measured during heating of the zero-field cooled $HoCo_{12-x}Fe_xB_6$ samples, is shown in figure 4. These thermomagnetic curves exhibit a compensation point of the magnetization of the Ho and (Co, Fe) sublattices. The compensation temperature (T_{Comp}) is characterized by the deep minimum on the magnetization versus temperature curves. The observed behavior is related to the ferrimagnetic structure of the compounds with the antiparallel coupling of the Ho and (Co, Fe) sublattices. The magnetization data were corrected for the presence of the $(Co,Fe)_2B$ impurity phase noted above. The amount of impurity present in the various samples can be readily determined by performing magnetization measurements just above T_C of each compound. The extra phase was consequently considered as carrying a saturated magnetic moment simplifying the correction for its ferromagnetic contribution. The impurity concentration increases from about 3 wt% up to 7 wt% for $x = 0$ and $x = 2$, respectively. The amount of impurity estimated in this manner corresponds closely to that found from X-ray diffraction analysis. The transition temperature, T_C, decreases nearly linearly with the Fe concentration at a rate of -4 K/at. % Fe, as illustrated in figure 5. Figure 6 presents the compensation, T_{Comp}, and spin reorientation, T_{SR}, temperatures versus the Fe content in $HoCo_{12-x}Fe_xB_6$ alloys. T_{Comp} increases slightly as iron is added, while T_{SR} exhibits a more pronounced decrease with Fe content. The decrease of T_{SR} reflects a modification of the magnetocrystalline anisotropy of these compounds upon Fe for Co substitution.

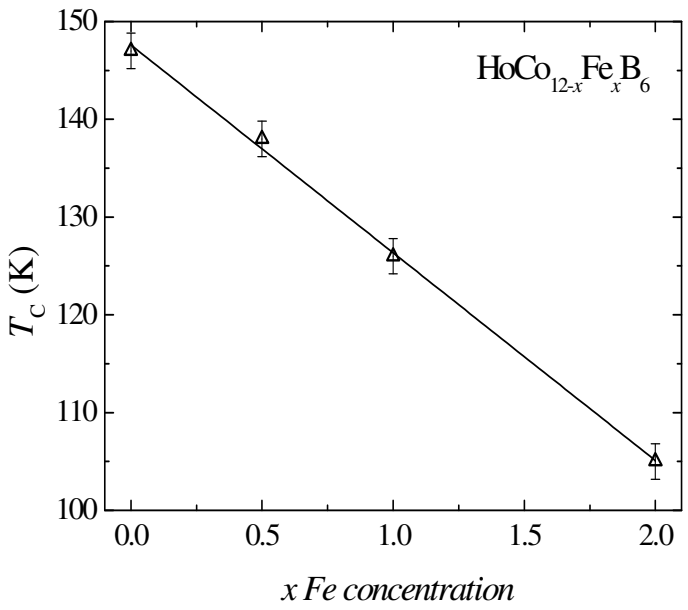

Figure 5: Curie temperature T_C versus x for $HoCo_{12-x}Fe_xB_6$, showing the linear decline with increasing iron concentration.

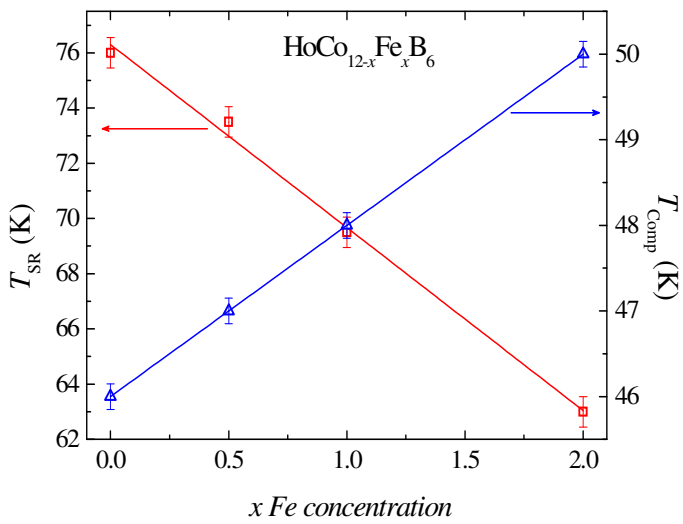

Figure 6: Spin reorientation temperature T_{SR} and compensation temperature T_{Comp} versus x for $HoCo_{12-x}Fe_xB_6$.

$HoCo_{12-x}Fe_xB_6$	T_C (K)	T_{Comp} (K)	T_{SR} (K)	M_S (μ_B/f.u.) @4K	μ_{TM} (μ_B/TM)	μ_{Fe} (μ_B/Fe)
$x = 0$	147	46	76	3.69	0.53	—
$x = 0.5$	138	47	73.5	3.19	0.57	1.43
$x = 1$	126	48	69.5	2.84	0.60	1.33
$x = 2$	105	50	63	2.62	0.62	1.04

Table 2: Magnetic parameters: Curie temperature, compensation temperature, spin reorientation temperature and spontaneous magnetization for the $HoCo_{12-x}Fe_xB_6$ series of compounds.

Magnetization isotherms recorded at 4 K for $HoCo_{12-x}Fe_xB_6$ intermetallics are reported in figure 7. The spontaneous magnetization M_S for each compound was determined as the ordinate of the crossing point of the linearly extrapolated low- and high- field portions of the isothermal magnetization curves. As can be seen from figure 7, the spontaneous magnetization is strongly dependent on Fe content. M_S at 4 K exhibits a monotonic decrease with increasing Fe concentration from 3.69 μ_B/f.u. to 2.62 μ_B/f.u. as x increases from 0 to 2. The corresponding values are given in table 2. Assuming that the Ho atom carries its free-ion moment of 10 μ_B oriented antiparallel to the transition metal magnetization, the average transition metal magnetic moment μ_{TM} can be derived by using $M_S = |\mu_{Ho} - 12\mu_{TM}|$. For $HoCo_{12}B_6$ compound the obtained value of $\mu_{TM} = 0.53$ μ_B is typical of that found in the $RCo_{12}B_6$ ternary system [6]. If we then write μ_{TM} as $\mu_{TM} = ((12-x)/12)\mu_{Co} + (x/12)\mu_{Fe}$ and further assume that the Co magnetic moment μ_{Co} can be considered fixed, then we can calculate the Fe magnetic moments μ_{Fe} in these compounds. The fact that the estimated Fe moment decreases with increasing Fe concentration, as shown in table 2, suggests that the *a priori* assumption of a constant Co magnetic moment is probably invalid. Nevertheless, it is clear that both μ_{Co} and μ_{Fe} are very low in these compounds when compared to the metallic cobalt and iron.

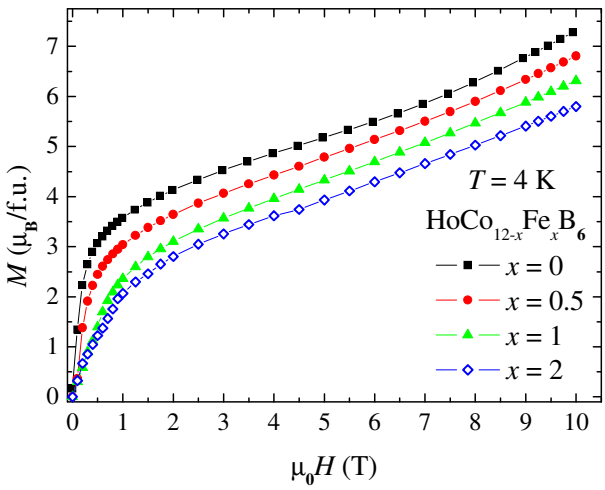

Figure 7: Isothermal magnetization of $HoCo_{12-x}Fe_xB_6$ series of compounds measured at 4 K.

The magnetization of $HoCo_{11.5}Fe_{0.5}B_6$, measured in the isothermal regime in the temperature range between 4 and 175 K, is shown in figure 8. One can first observe a decrease of the spontaneous magnetization when increasing the temperature from 4 to 50 K,

then the spontaneous magnetization increases with increasing temperature before decreasing again when approaching the Curie point. At 50 K, the magnetization increases nearly linearly with the applied magnetic field. This behavior is typical of a ferrimagnet exhibiting a compensation point near 50 K. The interpretation of the magnetization isotherms is confirmed by the analysis of the thermomagnetic curves as shown in figure 4, the magnetization of the Ho atoms being dominant below T_{comp} whereas at higher temperature and up to the Curie temperature the (Co, Fe) sublattice magnetization dominates.

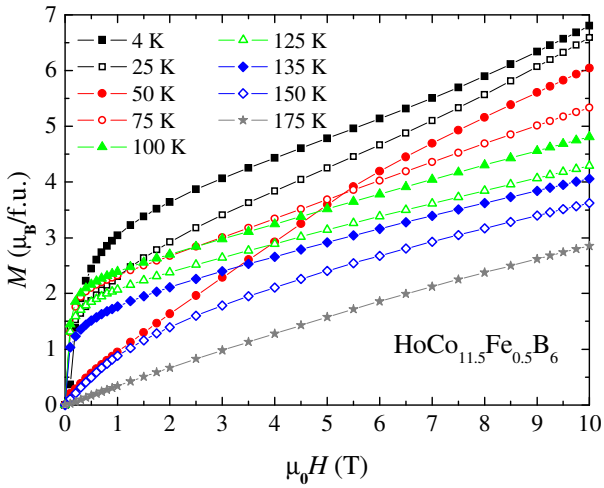

Figure 8: Isothermal magnetization of $HoCo_{11.5}Fe_{0.5}B_6$ measured between 4 and 175 K.

4. Conclusions

The rhombohedral crystal structure of the $HoCo_{12-x}Fe_xB_6$ intermetallic compounds is preserved at least as far as $x = 2$. The substitution of Fe for Co leads to a lattice expansion and a progressive decrease in the Curie and spin reorientation temperatures. On the contrary, the compensation temperature is barely sensitive to the Fe content and the magnetization of the Ho and (Co, Fe) sublattices cancel out at about 50 K for all x. The spin reorientation phenomenon is interpreted as resulting from the competition between the magnetocrystalline anisotropy terms of the Ho and the transition metal sublattices.

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