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Abstract
The structural and magnetic features of the TbCo$_4$M compounds (M = Al and
Ga) have been studied by means of neutron powder diffraction and magnetic
measurements. X-ray diffraction experiments show that the samples are
single phased, crystallizing in the CaCu$_5$-type structure. Neutron powder
diffraction measurements demonstrate a preferential substitution of Al and
Ga at the 3g crystallographic site of the CaCu$_5$-type structure. Together
with neutron powder diffraction investigations, magnetization measurements
and x-ray powder diffraction studies performed on field-oriented samples are
combined in order to clarify the effects of the Al and Ga substitutions on the
magnetic features of these compounds. The modifications of the magnetic
properties upon substitution are significant: a drastic decrease of the mean Co
magnetic moment and of the Curie temperature is observed. Unlike what was
found earlier for TbCo$_5$, no sign of a spin reorientation transition has been
observed in the present TbCo$_4$M compounds. Moreover, both compounds
present a planar magnetocrystalline anisotropy over the whole temperature
range. Finally, the thermal evolutions of the magnetization of terbium and
cobalt sublattices in TbCo$_4$Al and TbCo$_4$Ga are presented.

1. Introduction

The rare-earth (R)–3d transition metal (T) intermetallic compounds have received a lot of
attention in the past few years. This interest derives mainly from their possible applications
as permanent magnet materials [1, 2]. Among these intermetallics, the RCo$_5$ compounds,
crystallizing in the hexagonal CaCu$_5$-type structure ($P6/mmm$ space group), are especially

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interesting because of their high Curie temperature (T_C), large magnetocrystalline anisotropy (MCA), and important saturation magnetization (M_s). Their magnetic performances are due to the favourable combination of the complementary characteristics of 3d itinerant and 4f localized magnetism of the Co and R sublattices, respectively. The former mainly provides a high magnetization and a high magnetic ordering temperature and the latter offers a large MCA.

Numerous attempts have been made to improve the overall properties of these materials by substituting various elements in place of the rare earth or 3d metal [3–6]. Our recent studies have evidenced the effects of Al and Ga substitutions for Co on the crystallographic and magnetic properties of the YCo_5 and light-rare-earth $PrCo_5$ compounds [7, 8]. Like in other R–T intermetallics, the coupling between the two magnetic sublattices depends upon the nature of the rare-earth element. Light-rare-earth-containing compounds exhibit a ferromagnetic ordering whereas heavy-rare-earth-containing compounds are ferrimagnetic. Consequently, the study of heavy-rare-earth compounds is of interest since different magnetic behaviours are expected.

The $TbCo_5$ phase presents a spin reorientation transition, which occurs in the temperature range of 390–415 K [3, 9]. This phenomenon manifests itself by a change in the easy magnetization direction and is a consequence of the two opposite contributions to the MCA of the two magnetic sublattices (Tb and Co ones). That is to say, the Tb sublattice entails an alignment of the magnetic moments within the basal plane whereas the Co sublattice favours an orientation along the c-axis. Unlike what was observed earlier for $TbCo_5$, no spin reorientation transitions have been evidenced in the present $TbCo_4M$ compounds, when M is Al or Ga.

In this study we propose to investigate the structural and magnetic features of the heavy-rare-earth $TbCo_4M$ compounds (M = Al and Ga). Both compounds crystallize in the hexagonal $CaCu_5$-type structure as determined from x-ray powder diffraction and confirmed by neutron diffraction investigations. To our knowledge, no previous neutron powder diffraction investigations have been reported on the $TbCo_4Al$ and $TbCo_4Ga$ compounds. The use of the neutron powder diffraction technique is of great help in establishing both the location of Al and Ga in the crystal structure and the magnetic structure of these phases. This study reports also on magnetic measurements and x-ray diffraction (XRD) for field-oriented samples, which confirm the quality of our neutron diffraction results. Finally, combination of magnetic and neutron diffraction measurements will allow us to determine the thermal variations of the magnetic moments of both the terbium and the cobalt sublattices.

2. Experimental procedure

The polycrystalline samples of $TbCo_4M$ (M = Al and Ga) were prepared by melting high-purity starting elements (99.9% at least) in a high-frequency induction furnace under a purified argon gas atmosphere. To achieve better homogeneity, the samples were annealed at 1173 K for a week in an evacuated quartz tube. The purity of the phases was checked by means of XRD using a Guinier focusing camera with the Kα radiation of iron ($\lambda = 1.9373$ Å). The powder sample was mixed with silicon used as an internal standard. A precise determination of the lattice parameters was obtained by a least-squares refinement method for all the observed Bragg reflections.

The determination of the easy magnetization direction (EMD) at room temperature was performed by means of XRD investigations on powder samples oriented under an external magnetic field of about 1 T. The Curie temperatures were measured using a Faraday-type balance from 300 up to 1000 K with a heating and cooling rate of 5 K min^{-1}. The magnetization measurements were recorded using an extraction method in a field up to 7 T on a powder sample

Table 1. Structural and magnetic properties of TbCo$_4$M phases with M = Al and Ga compared with the TbCo$_5$ compound [9, 13]. The lattice parameters, volume and c/a ratio have been determined at room temperature. T_{comp} refers to the compensation temperature.

	a (Å)	c (Å)	V (Å^3)	c/a	T_C (K)	T_{comp} (K)	M_s (μ_B/fu) 4 K	M_s (μ_B/fu) 300 K
TbCo$_5$	4.946	3.980	84.31	0.804	980	90–110	0.6	1.7
TbCo$_4$Al	4.973(1)	4.000(1)	85.69	0.804	505(5)	351(5)	4.0(1)	0.5(1)
TbCo$_4$Ga	4.980(1)	3.990(1)	85.70	0.801	493(5)	338(5)	3.9(1)	0.4(1)

free to rotate in the sample holder. The M_s-values were obtained by extrapolation to zero field of the isothermal magnetization curves.

The neutron diffraction investigations were performed at the Institut Laue-Langevin (ILL, Grenoble, France). Two instruments were used: the high-resolution D1A diffractometer (operating at a wavelength of $\lambda = 1.91$ Å) and the high-neutron-flux CRG-CNRS D1B diffractometer (operating at a wavelength of $\lambda = 1.28$ Å at 300 K and $\lambda = 2.52$ Å at low temperature). A detailed description of these instruments can be found elsewhere [10]. The neutron powder diffraction data were analysed by the Rietveld method using the Fullprof software [11]. A full description of the Rietveld refinement and the agreement factors used in this article can be found in [12].

3. Results and discussion

3.1. Crystal structure

Combined inspection of the x-ray and neutron powder diffraction patterns reveals the formation of single-phase TbCo$_4$Ga and TbCo$_4$Al compounds adopting the CaCu$_5$-type structure ($P6/mmm$ space group). Table 1 presents the structural and magnetic properties of TbCo$_4$Ga and TbCo$_4$Al in comparison with those of the corresponding TbCo$_5$ compound [9, 13]. We observe an increase of the lattice parameters upon Al and Ga substitutions, which is due to the larger atomic size of the substituting elements. For TbCo$_4$Ga the expansion of the unit cell is more pronounced in the basal plane since the c/a ratio is decreasing. It is well established that heavy-rare-earth RCo$_5$ compounds are metastable at room temperature [14]. The stability range of these phases imposes the use of the off-stoichiometric compositions described by the formula R$_{1-s}$Co$_{5+2s}$. This corresponds to a random replacement of a fraction s of the R atoms by a pair of Co atoms (so-called dumb-bells). The presence of the Co dumb-bells is known to be accompanied by an increase of the c/a ratio. The formation of the Co dumb-bells in heavy-rare-earth RCo$_4$Al compounds (R = Gd and Ho) has been reported recently [6]. In contrast, our Rietveld refinement results listed in table 2 prove the absence of Co dumb-bells in both TbCo$_4$Ga and TbCo$_4$Al compounds. This is also suggested by the reduction of the c/a ratio for TbCo$_4$Ga.

A preferential occupation by Al and Ga atoms of the 3g crystallographic site of the CaCu$_5$ structure is seen from the neutron powder diffraction (see table 2). Most of the Ga atoms occupy the 3g site (0.8 Ga atom/fu) and only a small fraction are found to be located at the 2c site (0.2 Ga atom/fu). This small fraction of Ga atoms occupying the 2c site could possibly explain the more pronounced expansion of the unit cell in the basal plane observed for the TbCo$_4$Ga compound. In the homologous compounds TbCo$_4$Al, Al atoms are found to occupy exclusively the 3g site. No superstructure peaks are observed in the x-ray and neutron

Table 2. Rietveld analysis results of the neutron powder diffraction data recorded at 2 and 300 K for $TbCo_4Ga$ and $TbCo_4Al$. The investigations were performed on the D1A ($\lambda = 1.91$ Å) and D1B ($\lambda = 1.28$ and 2.52 Å) instruments at the Institut Laue-Langevin. The R-values of the agreement factors are given as percentages.

	$TbCo_4Ga$		$TbCo_4Al$	
T (K)	2	300	2	300
λ (Å)	1.911	1.911	2.520	1.287
a (Å)	4.983 (1)	4.990 (1)	4.959 (1)	4.973 (1)
c (Å)	3.998 (1)	4.001 (1)	3.997 (1)	4.000 (1)
2c site (% Co)	86 (2)		100 (2)	
3g site (% Co)	74 (2)		66 (2)	
$\mu_{Tb\,1a}$ (μ_B/Tb)	7.5 (5)	4.0 (3)	7.6 (5)	4.3 (3)
$\mu_{Co\,2c}$ (μ_B/Co)	1.0 (1)	1.0 (1)	1.2 (1)	0.8 (1)
$\mu_{Co\,3g}$ (μ_B/Co)	1.1 (1)	1.0 (1)	1.2 (1)	1.2 (1)
EMD	(a, b) plane			
R_{Bragg} (%)	5.4	5.0	5.2	8.9
R_{mag} (%)	4.9	6.4	3.2	7.5
R_{wp} (%)	12.3	12.2	12.2	10.7

diffraction patterns of the $TbCo_4M$ compounds. The $CaCu_5$ structure is kept after substitution, showing that there is no ordering but a random distribution of the Al and Ga atoms on the Co sites. The preferential occupations of the Al and Ga atoms of the 3g site are in good agreement with our recent studies on RCo_4M isotype compounds (R = Y and Pr; M = Al and Ga) based on neutron diffraction investigations [7, 8]. The Ga and Al preferential occupations of the 3g site have been explained by steric and enthalpy considerations [7, 8].

3.2. Magnetic structure

It is well known that all the heavy-rare-earth–3d transition metal compounds are ferrimagnetically ordered due to an antiparallel coupling of the 3d and 4f spin moments. This coupling can lead to a nil value of the magnetization at a certain temperature called the compensation point (T_{comp}).

The macroscopic magnetic properties of the $TbCo_4Ga$ and $TbCo_4Al$ compounds are summarized in table 1 and compared to those of the $TbCo_5$ compound as found in [9] and [13]. The existence of different off-stoichiometric $Tb_{1-s}Co_{5+2s}$ stable compounds induces slight variations of the magnetic properties. This can explain the different values of the magnetic properties such as the compensation point or the spin reorientation temperature found in the literature for $TbCo_5$.

We have performed neutron powder diffraction experiments in order to determine the magnitude and direction of each magnetic moment. The Rietveld refinements results for the neutron diffraction patterns are listed in table 2 for the $TbCo_4Ga$ and $TbCo_4Al$ compounds. Both magnetic measurements and neutron diffraction investigations confirm a ferrimagnetic ordering in these compounds. Figure 1 shows the magnetization curves recorded at 4 and 300 K for the present compounds. The $TbCo_4Al$ and $TbCo_4Ga$ neutron diffraction patterns recorded at 300 K are plotted in figures 2 and 3, respectively. Our neutron diffraction diagrams show a relatively large background. This feature might be a consequence of the random distribution of the Al and Ga atoms on the Co sites discussed above.

Our recent studies show that the Al and Ga substitutions in YCo_5 induce a dramatic decrease of the mean Co magnetic moment from 1.7 μ_B/Co to 1.1 μ_B/Co for YCo_5 and YCo_4M
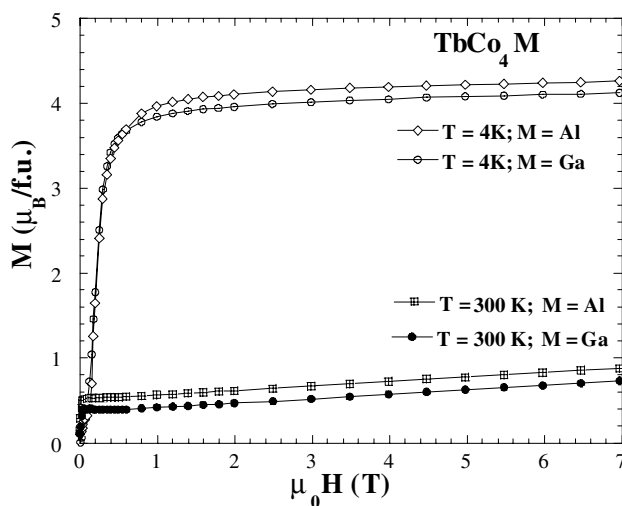
Figure 1. Magnetization curves recorded at 4 and 300 K for the TbCo₄M compounds (M = Al and Ga).

(M = Al and Ga), respectively [7, 8]. This is in agreement with the present Rietveld refinements for TbCo₄Ga and TbCo₄Al (table 2). A mean Co magnetic moment at low temperature of about 1 and 1.2 μ_B/Co is found for TbCo₄Ga and TbCo₄Al, respectively. This magnetic moment is dramatically reduced in comparison to about 1.7 μ_B/Co found for TbCo₅ [13]. Otherwise, the Co sublattice magnetization decreases from 8.5 μ_B to around 4 μ_B for TbCo₅ and TbCo₄M. This result can be explained in a band magnetism model by assuming that the three valence electrons of Al or Ga (s ^{2}p^1) are partially transferred into the Co 3d band, thus reducing the Co magnetic moment. The p–d hybridization might also influence the ordering temperature in the present compounds.

The Tb magnetic moments have similar magnitudes in the TbCo₄Al and TbCo₄Ga compounds. The rare-earth magnetic moment is also decreased from about 8.5 to about 7.5 μ_B for TbCo₅ [13] and TbCo₄M. It is worth noting that in these intermetallics the rare-earth sublattice presents a reduced magnetic moment compared to 9.7 μ_B expected for Tb^{3+} free ions. This feature has already been observed in the TbCo₄B compound [15, 16].

The two inequivalent Co magnetic moments (3g and 2c) are found to be weakly sensitive to the evolution of the temperature, whereas the Tb magnetic moment (1a) strongly decreases with temperature. Moreover, the magnetic moments carried by Co in TbCo₄Al and TbCo₄Ga are found to have about the same value.

The neutron diffraction technique is essentially sensitive to the localized magnetic moments and is less sensitive to the negative polarization of the valence electrons. Hence, the Co magnetic moments are overestimated by neutron diffraction and the overall magnetization resulting from the difference between the Tb and Co sublattice magnetizations is slightly smaller than the saturation magnetization as found by bulk measurements.

Both of the above-discussed reductions of the Co and Tb sublattice magnetizations influence the saturation magnetization of the present compounds. Thus, a comparison between M_s-values measured for TbCo₅ and TbCo₄M is of great help for understanding the changes of the magnetic characteristics upon substitution. The M_s-values of TbCo₄Al and TbCo₄Ga are about 4 and 0.5 μ_B/fu at 4 and 300 K, respectively. The relatively small values of the M_s observed at room temperature for the substituted compounds result from the cancellation of the
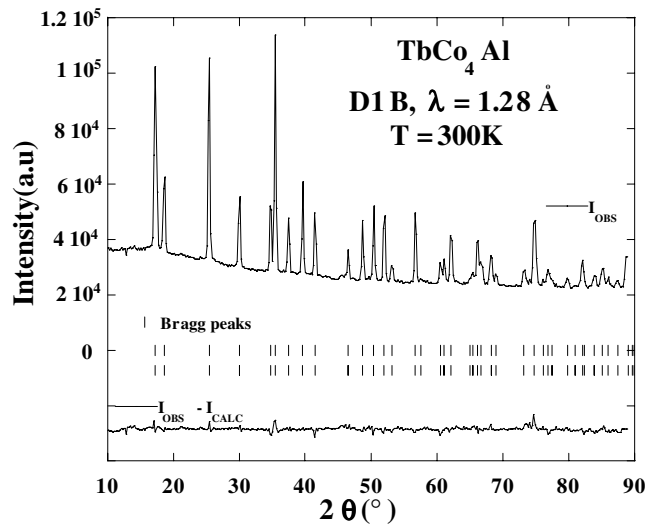
Figure 2. The neutron powder diffraction pattern of TbCo$_4$Al obtained at 300 K on the D1B instrument ($\lambda = 1.28$ Å). The pattern shown gives the experimental data. The difference between the experimental data and the calculated fit is plotted in the lower part of the figure. Vertical bars indicate calculated Bragg peak positions for both nuclear (first row) and magnetic structures (second row).

two sublattice magnetic moments just above room temperature (see figure 1). The M_s-values of TbCo$_5$ are 0.6 and 1.7 μ_B/fu at 4 and 300 K, respectively [9, 13]. The M_s-value observed at room temperature is larger than the value measured at 4 K, indicating that the compensation of the two magnetic sublattices (Tb and Co ones) takes place below 300 K for TbCo$_5$. Thus, the compensation temperature increases upon Al or Ga substitution for Co from 100 K for TbCo$_5$ [9] to 351 K and 338 K for TbCo$_4$Al and TbCo$_4$Ga respectively. The above-discussed drastic decrease of the Co sublattice magnetization upon substitution can be invoked to explain the increase of the compensation points for our phases (T_{comp} in table 1).

In addition to the saturation magnetization, another important intrinsic magnetic property studied here is the Curie temperature. The main contribution to T_C in this type of intermetallic arises from the Co–Co exchange interaction; this is followed in importance by the Tb–Co one. The Tb–Tb exchange interactions are generally negligible. Our measurements show a serious drop of the Curie temperature upon Al or Ga substitution for Co. This feature is due to the presence of a non-magnetic atom (Al or Ga), which induces a decrease of the exchange interactions upon substitution. The p–d hybridization, as discussed previously, might also go together with a decrease of the strength of the Co–Co exchange interactions. Hence, the drop of T_C can be explained by a reduction of both the number and the strength of the Co–Co exchange interactions.

In order to determine the easy magnetization direction at room temperature, we have performed XRD experiments on field-oriented samples under an external magnetic field. Figures 4 and 5 present the XRD diagrams recorded on field-oriented and free samples of TbCo$_4$Ga and TbCo$_4$Al, respectively. These measurements are performed at room temperature and confirm an alignment of the magnetic moments within the (a, b) basal plane since the reflection planes are perpendicular to the EMD. The neutron diffraction analysis confirms this EMD at 300 K. Moreover, our Rietveld analysis proves an alignment of the magnetic moments within the basal plane at 2 K. These results allow us to establish that the magnetic moments
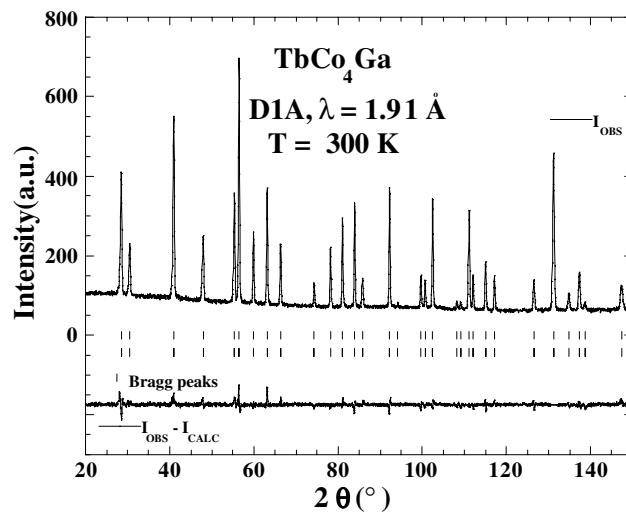
Figure 3. The neutron powder diffraction pattern of TbCo$_4$Ga obtained at 300 K on the D1A high-resolution instrument ($\lambda = 1.91$ Å). The pattern shown gives the experimental data. The difference between the experimental data and the calculated fit is plotted in the lower part of the figure. Vertical bars indicate calculated Bragg peak positions for both nuclear (first row) and magnetic structures (second row).
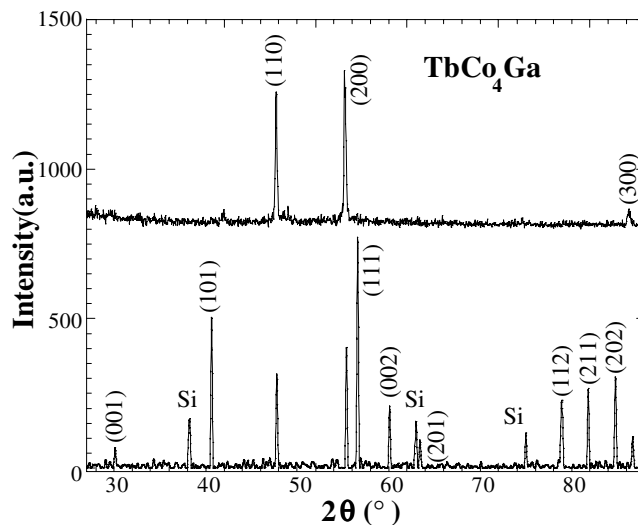
Figure 4. Comparison between the XRD patterns recorded for a field-oriented sample of TbCo$_4$Ga (top) and free TbCo$_4$Ga powder (bottom) at room temperature with $\lambda = 1.9373$ Å. The free powder sample was mixed with silicon used as an internal standard. The Miller indices of the reflection planes are also indicated.

of both compounds lie within the basal plane below 300 K. Furthermore, the thermomagnetic analysis performed between 300 and 1000 K for TbCo$_4$Al and TbCo$_4$Ga indicates only one transition from a ferrimagnetic order to a paramagnetic state. We thus conclude that TbCo$_4$Al and TbCo$_4$Ga exhibit a planar EMD whatever the temperature and up to the Curie temperature.
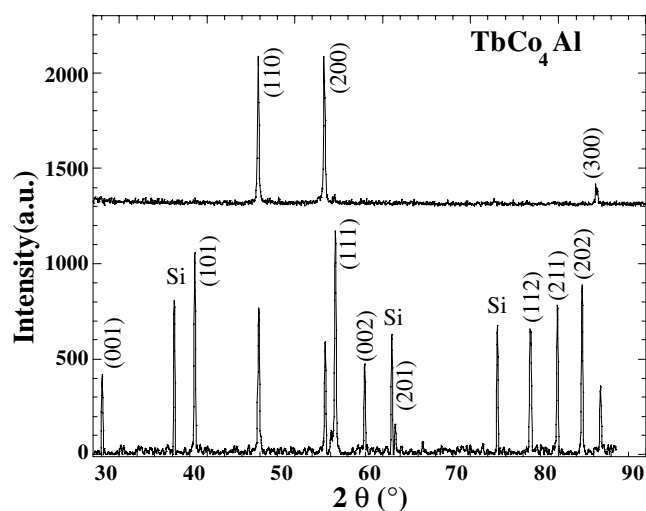
Figure 5. Comparison between the XRD patterns recorded for a field-oriented sample of TbCo$_4$Al (top) and free TbCo$_4$Al powder (bottom) at room temperature with $\lambda = 1.9373$ Å. The free powder sample was mixed with silicon used as an internal standard. The Miller indices of the reflection planes are also indicated.

It is well established that the Co anisotropy is axial in YCo$_5$ [17] and is considered generally unmodified upon substitution of a magnetic rare earth for yttrium. In contrast, the Tb sublattice anisotropy is planar in TbCo$_5$ [18]. This competition gives rise to a spin reorientation transition occurring in a temperature range of 390–415 K. Thus, we might expect a similar competition between the two sublattice anisotropies in our compounds. But no sign of a spin reorientation transition has been observed in the substituted compounds unlike what was reported earlier for TbCo$_5$ [3, 9, 18]. Hence, the main contribution to the MCA is due to the rare-earth sublattice, which imposes a planar EMD up to the ordering temperature. In TbCo$_5$ the Co sublattice contribution to the MCA is strong enough to overcome the planar anisotropy of the Tb sublattice and to entail an axial orientation of the magnetic moments at high temperature. The absence of spin reorientation transitions in both substituted compounds can be interpreted either as indicating a serious decrease of the Co axial anisotropy or a reinforcement of the Tb sublattice anisotropy due to a change in the crystal electric field (CEF) parameters experienced at the rare-earth site. The first hypothesis is in excellent agreement with earlier reported results on the YCo$_4$M (M = Al and Ga) isotype compounds [5, 7, 8] where the Co axial anisotropy has been found to decrease drastically upon Al or Ga substitution for Co. In the present compounds the Co anisotropy is probably too weak to overcome the stronger anisotropy of the rare-earth sublattice. Thus, we conclude that the Tb sublattice plays the major role in the MCA of the TbCo$_4$Al and TbCo$_4$Ga compounds.

Finally, we have deduced the thermal evolution of the Tb and Co sublattice magnetizations by combining neutron diffraction with magnetic and thermomagnetic measurements (see figure 6). A drastic decrease of the Tb moment with temperature is observed whereas the Co magnetic moment keeps a rather constant magnitude up to room temperature.

It is worth comparing these results with the effects of the substitution of B for Co in TbCo$_5$. This substitution changes the crystal structure, giving rise to a superstructure along the *c*-axis of the CaCu$_5$-type structure caused by an exclusive occupancy of the 2c site by the B atoms [19]. In spite of the different crystal structures, the effects of B, Al and Ga substitutions for Co on the magnetic properties exhibit similarities. A drastic decrease of the Curie temperature, a
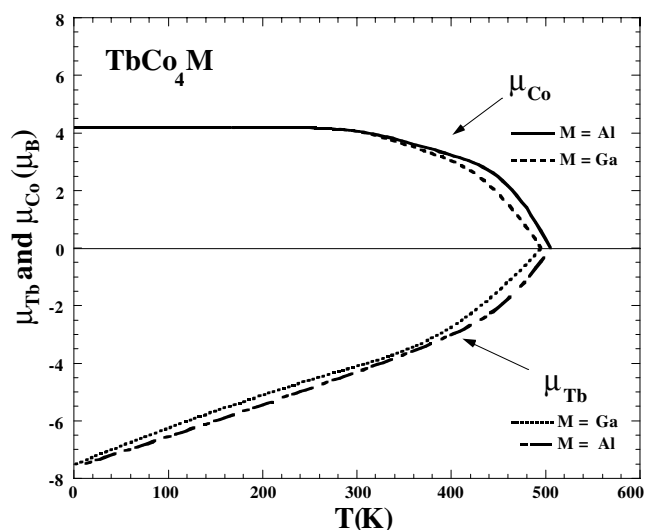
Figure 6. Thermal evolution of the terbium and cobalt sublattice magnetization as deduced by combining neutron diffraction, magnetic and thermomagnetic measurements on TbCo$_4$Ga and TbCo$_4$Al.

planar alignment of the magnetic moments over the whole ordered temperature range and the same evolution of the saturation magnetization were reported earlier for TbCo$_4$B [20].

4. Conclusions

In summary, the TbCo$_4$Ga and TbCo$_4$Al phases have been investigated by means of x-ray and neutron diffraction together with magnetic measurements in order to determine their crystal and magnetic features. The CaCu$_5$-type structure is retained upon substitution of Ga and Al for Co but with a significant unit-cell increase. A preferential occupation of Ga atoms of the 3g site is found by means of neutron powder diffraction investigations. Al atoms are found to exclusively occupy the 3g site. These characteristics have been explained recently for isotype compounds by size effect or mixing enthalpy considerations; these factors both favour the occupancy of the 3g site. The substitutions of Al and Ga for Co in the heavy-rare-earth TbCo$_5$ compound induce remarkable changes in the magnetic properties. We have evidenced a dramatic decrease of the mean Co magnetic moment and the Curie temperature. The compensation temperature increases upon Al or Ga substitution for Co. In these compounds no sign of spin reorientation has been observed, whichever the substituting element is (Al or Ga). Furthermore, the TbCo$_4$Al and TbCo$_4$Ga compounds show a planar MCA over the whole magnetic ordering range. The Co sublattice anisotropy in TbCo$_4$M phases is found to be too weak to overcome the planar contribution of the Tb sublattice, unlike what happens at high temperature in TbCo$_5$. This result proves that the main contribution to the MCA in the TbCo$_4$M (M = Al and Ga) compounds is played by the Tb sublattice. This can be understood on the basis of a serious reduction of the axial anisotropy of the Co sublattice upon substitution as reported recently in the YCo$_4$M (M = Al and Ga) isotype compounds. Nevertheless, a change of the Tb sublattice anisotropy upon Al or Ga substitution is expected via a modification of the CEF parameters acting at the rare-earth site. Finally, thermal variation of the magnetic moments of the two sublattices has been presented. A comparison of our results with the influence of the B substitution for Co in

TbCo$_5$ has shown that analogous effects on the magnetic properties are observed in spite of their different crystal structures.

Acknowledgments

References

[1] Buschow K H J 1997 *Handbook of Magnetic Materials* vol 10 (Amsterdam: North-Holland) p 463
[2] Strnat K J 1988 *Ferromagnetic Materials* vol 4 (Amsterdam: North-Holland) p 131
[3] Ma B M, Boltich E B, Sankar S G, Wallace W E, Malik S K and Tomy C V 1991 *J. Appl. Phys.* **69** 6061
[4] Thang C V, Thuy N P, Hein T D, Franse J J M, Colpa J H P, Brommer P E and Brück E 1996 *J. Magn. Magn. Mater.* **157–158** 643
[5] Ido H, Konno K, Ito T, Cheng S F, Sankar S G and Wallace W E 1991 *J. Appl. Phys.* **69** 5551
[6] Thang C V, Brommer P E, Colpa J H P, Brück E, Menovsky A A, Thuy N P and Franse J J M 1996 *J. Alloys Compounds* **245** 100
[7] Zlotea C and Isnard O 2002 *J. Magn. Magn. Mater.* **242–245** 832
[8] Zlotea C and Isnard O 2002 *J. Alloys Compounds* at press
[9] Franse J J M and Radwanski R J 1997 *Handbook of Magnetic Materials* vol 7 (Amsterdam: North-Holland) p 307
[10] www.ill.fr; Yellow Book
[11] Rodriguez Carjaval J 1993 *Physica* B **192** 55
[12] McCusker L B, Von Dreele R B, Cox D E, Louer D and Scardi P 1999 *J. Appl. Crystallogr.* **32** 36
[13] Burzo E, Chelkowski A and Kirchmayr H R 1990 *Landolt–Börnstein New Series* Group III, vol 19, subvol d2 (Berlin: Springer) p 248
[14] Velge W A J J and Buschow K H J 1968 *J. Appl. Phys.* **39** 1717
[15] Caspi E N, Pinto H and Melamud M 2000 *J. Appl. Phys.* **81** 416
[16] Chacon C 2000 *PhD Thesis* University of Grenoble
[17] Tasset F 1975 *PhD Thesis* University of Grenoble
        Schweizer J and Tasset F 1980 *J. Phys. F: Met. Phys.* **10** 2799
[18] Radwanski R J 1986 *J. Magn. Magn. Mater.* **62** 120
[19] Kuz'ma Y B and Bilonizhko N S 1974 *Sov. Phys.–Crystallogr.* **18** 447
[20] Chacon C and Isnard O 2000 *J. Solid State Chem.* **154** 242