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# Structural and magnetic properties of hexagonal DyCo<sub>4</sub>M compounds (M = Al, Ga)

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## Abstract

The DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga compounds crystallize in the hexagonal CaCu<sub>5</sub>-type structure (space group  $P6/mmm$ ). Al atoms exclusively occupy the 3g crystallographic site of the structure, whereas most of the Ga atoms occupy the 3g site, the rest being located at the 2c site. Both compounds are ferrimagnetic, and remarkable changes in the magnetic properties are observed with respect to DyCo<sub>5</sub>. Al or Ga substitution for Co causes a drastic reduction of the Curie temperature, from ~970 K in DyCo<sub>5</sub> to 479(5) K (M = Al) and 475(5) K (M = Ga). This reduction is accompanied by an important increase of the saturation magnetization at 4 K: from 0.7  $\mu_B$ /fu for DyCo<sub>5</sub> up to 4.7 and 4.9  $\mu_B$ /fu for DyCo<sub>4</sub>Ga and DyCo<sub>4</sub>Al, respectively. The compensation temperatures  $T_{\text{comp}}$  are close to 300 K, while  $T_{\text{comp}}$  equals 124 K in DyCo<sub>5</sub>. These phenomena are clearly linked to a decrease of the mean Co magnetic moment. For these two materials, thermomagnetic measurements have evidenced a spin reorientation transition at  $T_{\text{SR}} \sim 400$  K. Powder neutron diffraction investigations were performed, and the Rietveld refinements led to the characterization of the magnetic phase diagrams of both compounds in the whole ordered temperature range. The Co magnetic moments are typically about 1.2  $\mu_B$ .

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The hexagonal RCo<sub>5</sub> intermetallic compounds have received a lot of attention in recent decades. These materials, which crystallize in the CaCu<sub>5</sub>-type structure (space group  $P6/mmm$ ), were

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studied from a fundamental viewpoint but also for their possible applications as permanent magnets [1]. Their interesting magnetic properties are due to the favourable combination of the complementary characteristics of 3d itinerant and 4f localized magnetism of the Co and R sublattices, respectively, resulting in high Curie temperatures ( $T_C$ ), large magnetocrystalline anisotropy (MCA) and important saturation magnetizations ( $M_s$ ).

Numerous attempts have been made to improve the overall properties of these materials by substituting various elements for R or Co [2–5]. More recent studies have evidenced the effects of Al or Ga substitutions for Co on the crystallographic and magnetic properties of some  $\text{RCo}_5$  compounds (R = Y, Pr, Tb, Ho) [6–9]. As a main result, a serious reduction of the uniaxial anisotropy of the Co sublattice upon Al or Ga substitution has been shown. For instance the magnetocrystalline anisotropy (MCA) stays planar over the whole magnetic ordering range of the  $\text{TbCo}_4\text{Al}$  and  $\text{TbCo}_4\text{Ga}$  compounds, whereas  $\text{TbCo}_5$  exhibits a spin reorientation transition (SRT).

In order to complete this systematic study of  $\text{RCo}_4\text{M}$  (M = Al, Ga) compounds, and to achieve a better understanding of the MCA in such compounds, we focused on the  $\text{DyCo}_4\text{M}$  compounds, especially by means of magnetic measurements and powder neutron diffraction.

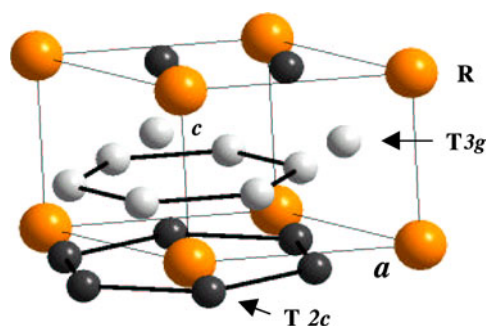
## 2. Experimental procedure

Two polycrystalline samples of  $\text{DyCo}_4\text{Al}$  and  $\text{DyCo}_4\text{Ga}$  were prepared by melting high purity starting elements (>99.9%) in a high frequency induction furnace under a purified Ar atmosphere. The resulting ingots were then annealed at 1173 K for a week in evacuated quartz tubes to achieve better homogeneity. The purity of the final phases was checked by x-ray diffraction (XRD) using a Siemens D5000 powder diffractometer ( $\text{Cu K}\alpha_1$ ,  $\lambda = 1.5406 \text{ \AA}$ ). Lattice parameters were refined by a least-squares procedure from the patterns recorded with Si as internal standard.

To determine the easy magnetization direction (EMD) at room temperature, XRD experiments (Philips PW1050  $\theta/2\theta$  diffractometer,  $\lambda = 1.5406 \text{ \AA}$ ) were performed on powders (grain size  $\leq 50 \mu\text{m}$ ) diluted in epoxy resin, the mixtures being solidified under an external magnetic field of about 1 T.

The Curie temperatures were measured using a ‘home-made’ Faraday-type balance from 300 up to 1000 K. Samples of about 50–100 mg were sealed under vacuum in small silica tubes to prevent oxidation during heating. The magnetization measurements were carried out on powder samples using an extraction method in fields up to 10 T. The  $M_s$ -values at 4 K were obtained by extrapolation to zero field of the magnetization curves in fields higher than 4 T. A detailed description of the experimental set-up can be found elsewhere [10].

The neutron powder diffraction patterns were recorded at the Institut Laue-Langevin (ILL, Grenoble, France), and analysed by the Rietveld method using the FULLPROF software [11]. The high-resolution D1A diffractometer ( $\lambda = 1.91 \text{ \AA}$ ) was used for the room temperature measurements, and the high-flux CRG-CNRS D1B diffractometer ( $\lambda = 2.52 \text{ \AA}$ ) for the low/high temperature experiments. A detailed description of these instruments can be found in [12]. Due to the huge neutron absorption cross section of Dy and Co (994 and 37 b, respectively, at  $v = 2200 \text{ m s}^{-1}$  [13]), small quantities of powder and long counting times were essential (each sample was placed in a cylindrical vanadium sample holder of 6 mm inner diameter). However, the patterns obtained display an important background. Correction for absorption has been performed according to [14]. The transmission factor  $A_{hkl}$  has been calculated according to the formula proposed by Hewat [15]. This led to adjustments of the isotropic Debye–Waller factors ( $B$ ), also often referred to as atomic displacement parameters.



**Figure 1.** Tridimensional view of the CaCu<sub>5</sub>-type structure (*P6/mmm*). R atoms occupy Ca (1a) positions, and T atoms are located on the two Cu sites (2c and 3g).

**Table 1.** Room temperature lattice parameters obtained from x-ray diffraction and main magnetic data of DyCo<sub>5</sub> [16, 17], DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga.

Compound	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>	<i>V</i> (Å <sup>3</sup> )	<i>T<sub>C</sub></i> (K)	<i>T<sub>SR</sub></i> (K)	<i>M<sub>s</sub></i> at 4 K (μ <sub>B</sub> /f.u)
DyCo <sub>5</sub>	4.926	3.988	0.809	83.81	970	325–367	0.7
DyCo <sub>4</sub> Al	4.990(1)	4.028(1)	0.807	86.87	479(5)	404(2)	4.9
DyCo <sub>4</sub> Ga	4.995(1)	4.017(1)	0.804	86.78	475(5)	400(5)	4.7

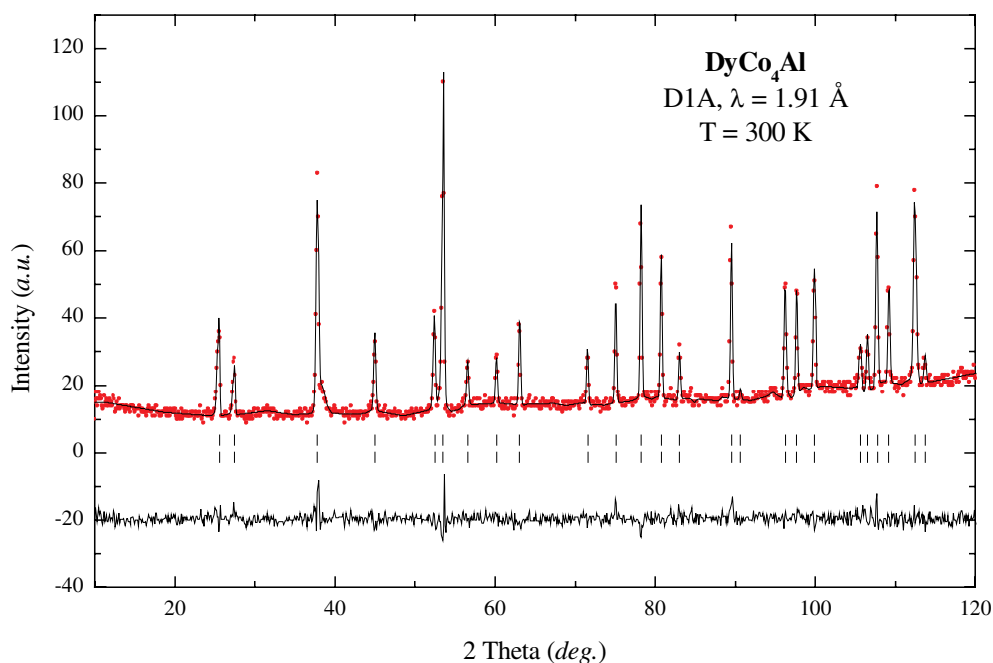
### 3. Results and discussion

#### 3.1. Crystal structure

The XRD analysis confirms that the two compounds are nearly single phase with the CaCu<sub>5</sub>-type structure. In isotypic RT<sub>5</sub> compounds, R atoms occupy the 1a crystallographic site, whereas the T atoms occupy both 2c and 3g sites (figure 1). The 2c site lies in the same plane as the 1a site, and the 3g position is situated between the layers containing the 2c and 1a sites. The fact that the DyCo<sub>4</sub>M compounds crystallize within the CaCu<sub>5</sub>-type structure implies that there is no ordering of M atoms but a random distribution on the Co sites.

Table 1 reports the main structural data of DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga in comparison with those of DyCo<sub>5</sub> [16, 17]. The increase of the *a* and *c* lattice parameters upon M (Al or Ga) substitution with respect to the DyCo<sub>5</sub> compound is due to the larger atomic size of M with respect to Co. Indeed, in a Co-rich environment, the corresponding atomic radii are:  $r_{\text{Al}} = 1.43 \text{ \AA} > r_{\text{Ga}} = 1.35 \text{ \AA} > r_{\text{Co}} = 1.25 \text{ \AA}$  [18]. Moreover, *a*-values are almost equal in DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga, whereas the *c*-parameter is larger in the Al compound. This results in a higher *c/a* ratio in DyCo<sub>4</sub>Al than in DyCo<sub>4</sub>Ga. But these values are both inferior to the *c/a*-value in DyCo<sub>5</sub>, thus indicating that the expansion of the unit cell upon Al or Ga substitution for Co is more pronounced in the basal plane.

From the neutron diffraction experiments carried out at room temperature on D1A diffractometer (figures 2 and 3, tables 2 and 3), it is found that the Al atoms exclusively occupy the 3g crystallographic site of the CaCu<sub>5</sub> structure, whereas most of the Ga atoms occupy the 3g site and a small fraction is located at the 2c site. This small Ga occupation at the 2c site is probably responsible of the more pronounced expansion of the unit cell in the basal plane observed for the DyCo<sub>4</sub>Ga compound than for the DyCo<sub>4</sub>Al compound. These results are in fair agreement with recent studies [7–9], in which the Al and Ga preferential occupations of the 3g site were explained by steric and enthalpy considerations. The ability of



**Figure 2.** Neutron powder diffraction pattern of  $\text{DyCo}_4\text{Al}$  obtained at room temperature on D1A diffractometer. The dots represent the experimental data, and the continuous curve is the calculated diffractogram. The small vertical lines are the calculated  $hkl$  positions for nuclear and magnetic cells, and the bottom trace is the difference plot.

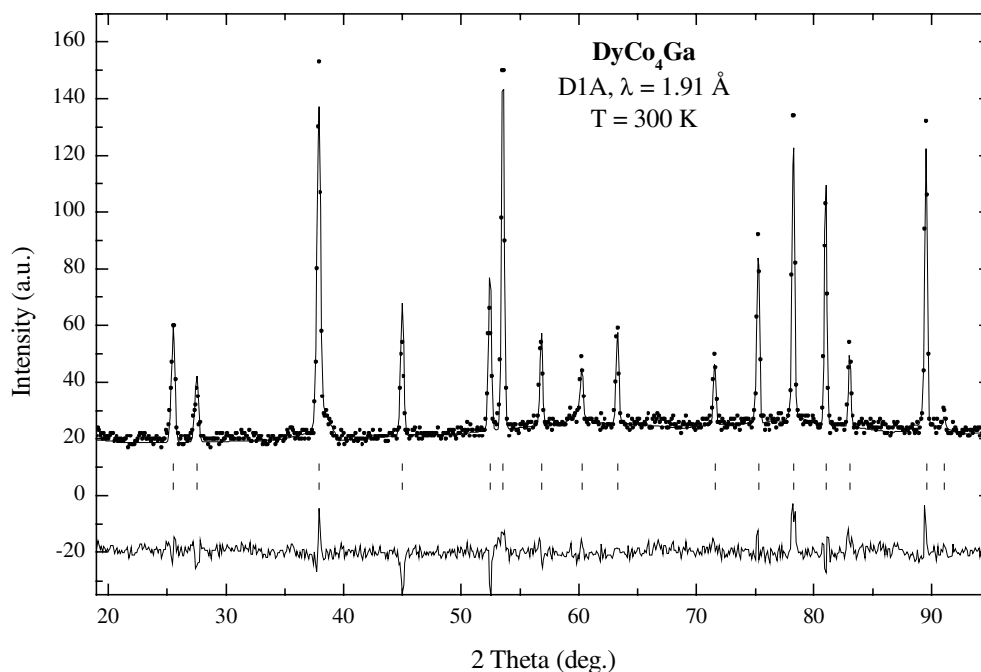
**Table 2.** Rietveld results of the neutron powder diffraction analysis of  $\text{DyCo}_4\text{Al}$  at 2, 300, 415 and 450 K (the site occupancy by Co was refined at 300 K and assumed constant for the other temperatures).

$T$ (K)	2	300	415	450
$\lambda$ (Å)	2.52 (D1B)	1.91 (D1A)	2.52 (D1B)	2.52 (D1B)
$a$ (Å)	4.974(1)	4.990(1)	4.996(1)	5.001(1)
$c$ (Å)	4.023(1)	4.028(1)	4.029(1)	4.032(1)
$\mu_{\text{R } 1a}$ ( $\mu_{\text{B}}$ )	7.5(6)	5.8(3)	4.6(4)	1.6(4)
$\mu_{\text{Co } 2c}$ ( $\mu_{\text{B}}$ )	1.2(1)	1.3(2)	1.0(1)	0.9(2)
$\mu_{\text{Co } 3g}$ ( $\mu_{\text{B}}$ )	1.1(2)	1.2(4)	1.0(1)	0.9(2)
2c site (% Co)			100(2)	
3g site (% Co)			65(4)	
$\theta$ (deg) <sup>a</sup>	90	90	53(3)	0
$\chi^2$ , $R_{\text{Bragg}}$	3.24, 4.7	1.63, 7.6	5.36, 15.2	7.29, 8.4
$R_{\text{mag}}$ , $R_{\text{wp}}$ (%)	5.1, 13.0	9.8, 22.8	16.8, 14.4	7.9, 17.1

<sup>a</sup> Angle between the magnetic moments direction and  $c$ -axis.

Ga to occupy both 2c and 3g sites is probably related to the fact that Ga atoms have an atomic radius closer to that of Co than Al.

It is noteworthy that the replacement of a fraction of R atoms by a pair of Co atoms (thus forming a so-called dumbbell) has been previously reported in  $\text{DyCo}_5$ , as in the other heavy rare earth  $\text{RCO}_5$  compounds [19], imposing us to consider  $\text{R}_{1-5}\text{Co}_{5+2s}$  formulae. The presence



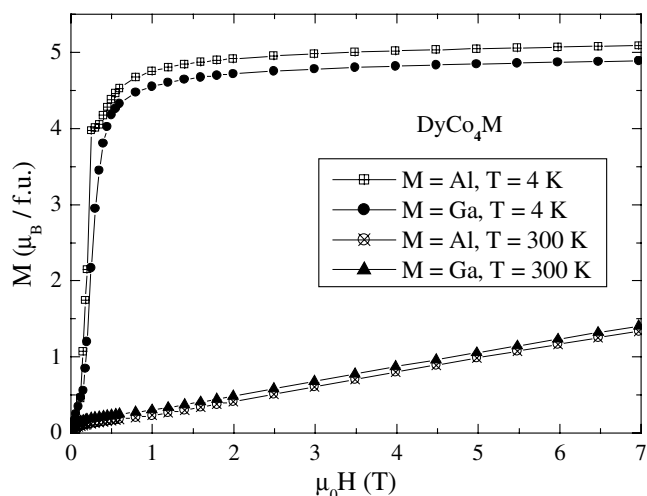
**Figure 3.** Neutron powder diffraction pattern of DyCo<sub>4</sub>Ga obtained at room temperature on D1A diffractometer.

**Table 3.** Rietveld results of the neutron powder diffraction analysis of DyCo<sub>4</sub>Ga at 2, 300 and 450 K (the site occupancy by Co was refined at 300 K and assumed constant for the other temperatures).

<i>T</i> (K)	2	300	450
$\lambda$ (Å)	2.52 (D1B)	1.91 (D1A)	2.52 (D1B)
<i>a</i> (Å)	4.986(1)	4.995(1)	5.005(1)
<i>c</i> (Å)	4.016(1)	4.017(1)	4.023(1)
$\mu_{R\ 1a}$ ( $\mu_B$ )	9.1(3)	5.2(3)	1.6(3)
$\mu_{Co\ 2c}$ ( $\mu_B$ )	1.3(3)	1.1(2)	0.9(2)
$\mu_{Co\ 3g}$ ( $\mu_B$ )	1.4(3)	1.0(2)	0.9(2)
2c site (% Co)		90(4)	
3g site (% Co)		75(4)	
$\theta$ (deg) <sup>a</sup>	90	90	0
$\chi^2, R_{Bragg}$	9.27, 10.5	1.63, 7.6	17.39, 12.7
$R_{mag}, R_{wp}$ (%)	13.6, 14.9	9.8, 22.8	7.6, 18.7

<sup>a</sup> Angle between the magnetic moment direction and the *c*-axis.

of such dumbbells is known to be accompanied by an increase in the *c/a* ratio. Their formation in some heavy rare earth RCo<sub>4</sub>Al compounds (R = Gd, Ho) has been also reported recently [5]. In contrast, our Rietveld refinements prove unambiguously the absence of such dumbbells in the DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga compounds, as in TbCo<sub>4</sub>Al and TbCo<sub>4</sub>Ga [9]. This result was already strongly suggested by the reduction of the *c/a* ratios for our two compounds.



**Figure 4.** First magnetization curves recorded at 4 and 300 K for the  $\text{DyCo}_4\text{M}$  compounds ( $\text{M} = \text{Al, Ga}$ ).

### 3.2. Magnetic properties

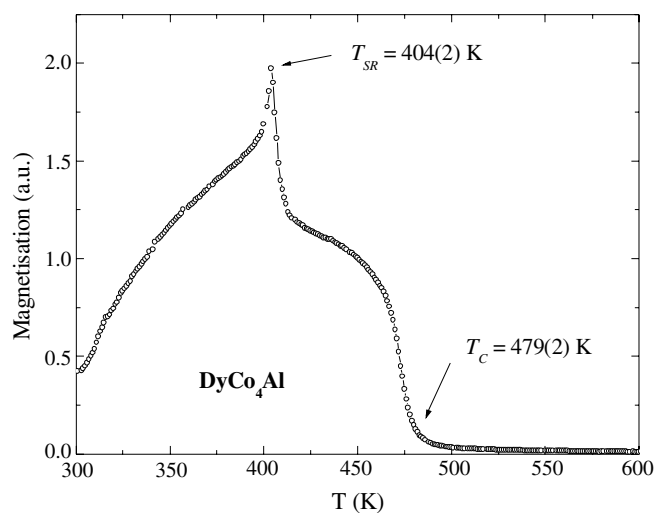
As a preliminary remark, it is important to keep in mind that the existence of different off-stoichiometric  $\text{Dy}_{1-s}\text{Co}_{5+2s}$  stable compounds induces variations of the magnetic properties (very sensitive to the chemical composition) reported for the ‘ $\text{DyCo}_5$ ’ phase. This explains why different values of  $T_C$ ,  $M_s$ , of the compensation temperature or of the spin reorientation temperature can be found in the literature.

Like  $\text{DyCo}_5$ , the  $\text{DyCo}_4\text{M}$  ( $\text{M} = \text{Al, Ga}$ ) compounds are ferrimagnetic, in fair agreement with the antiparallel coupling assumed between a 3d moment and a heavy rare earth 4f moment. As can be seen from table 1, the substitution of Al or Ga for Co induces remarkable changes in the magnetic properties.

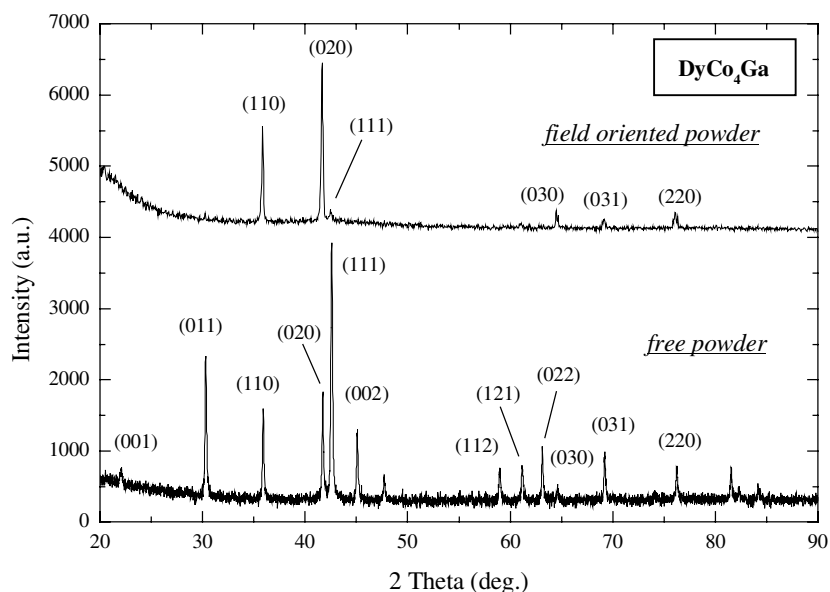
First, substitution leads to a drastic reduction of the Curie temperature  $T_C$ , from  $\sim 970$  K in  $\text{DyCo}_5$  [17, 20] down to 479(5) K in  $\text{DyCo}_4\text{Al}$  and 475(5) K in  $\text{DyCo}_4\text{Ga}$ . In such 3d–4f intermetallic compounds, the Curie temperature is mainly determined by the Co 3d–Co 3d exchange interactions. Here its reduction is due to the presence of nonmagnetic M atoms which induce a decrease of the Co–Co exchange interactions by reducing their number. The M p–Co 3d hybridization probably also causes a decrease in the strength of the Co–Co exchange interaction.

Secondly, this reduction of  $T_C$  is accompanied by an important increase of the saturation magnetization at 4 K: from  $0.7 \mu_B/\text{f.u.}$  for  $\text{DyCo}_5$  [17, 20, 21] up to  $4.7 \mu_B/\text{f.u.}$  for  $\text{DyCo}_4\text{Ga}$  and  $4.9 \mu_B/\text{f.u.}$  for  $\text{DyCo}_4\text{Al}$  (figure 4). The linear shape of the magnetization curves recorded at 300 K clearly indicates that, for both compounds, the compensation temperature  $T_{\text{comp}}$  is close to room temperature, whereas  $T_{\text{comp}} = 124$  K in  $\text{DyCo}_5$  [17]. Similar phenomena were already observed with the  $\text{TbCo}_4\text{Al}$  and  $\text{TbCo}_4\text{Ga}$  compounds [9] and are obviously linked to a decrease of the Co sublattice magnetization upon Al or Ga substitution. The neutron diffraction study will confirm this assumption.

The thermomagnetic curves recorded above 300 K (figure 5) exhibit a sharp discontinuity at 404(2) K ( $\text{DyCo}_4\text{Al}$ ) or 400(5) K ( $\text{DyCo}_4\text{Ga}$ ) that may indicate the occurrence of an SRT. In  $\text{DyCo}_5$ , such a conical-to-axial SRT occurs in the temperature range 325–370 K [17, 20–22].



**Figure 5.** Thermomagnetic measurement carried out above 300 K for  $\text{DyCo}_4\text{Al}$ .



**Figure 6.** Comparison between the XRD patterns recorded for a field oriented sample of  $\text{DyCo}_4\text{Ga}$  (top) and free  $\text{DyCo}_4\text{Ga}$  powder (bottom) at room temperature ( $\lambda = 1.5406 \text{ \AA}$ ). The Miller indices of the observed reflections are also indicated.

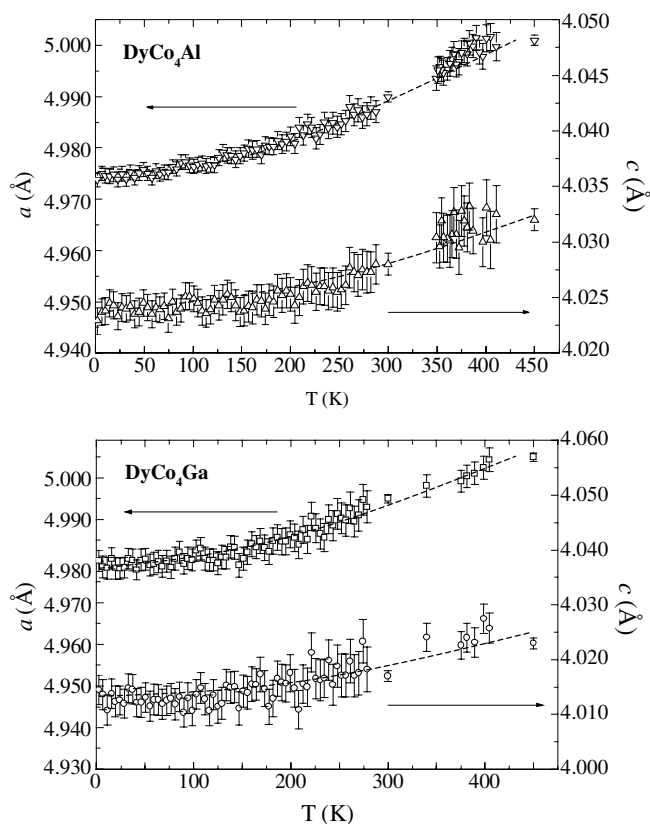
In order to determine the EMD of the compounds at room temperature, we first performed XRD experiments (reflection geometry) on samples oriented under an external magnetic field, the latter being applied perpendicularly to the plane of the samples. The XRD pattern obtained with  $\text{DyCo}_4\text{Ga}$  is represented in figure 6. For both compounds, the only observed Bragg peaks being indexed as  $(hk0)$ , we concluded that the EMD is within the  $(a, b)$  plane of the crystal structure at 300 K.



Neutron diffraction experiments were then carried out on D1B diffractometer between 2 and 450 K to determine the magnetic phase diagrams of DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga. The results of our refinements for DyCo<sub>4</sub>Al at 2, 415 and 450 K and for DyCo<sub>4</sub>Ga at 2 and 450 K are reported in tables 2 and 3, together with the results of the refinements from the D1A data at 300 K. At 2 K and at room temperature, for both compounds, the best fits were obtained by considering the Dy and Co magnetic moments aligned within the (*a*, *b*) plane, in fair agreement with the XRD results. Above ~350 K, we had to consider an orientation of the moments which is intermediate between the basal plane and the *c*-axis: for DyCo<sub>4</sub>Al at 415 K they make an angle of about 50° with the latter, thus confirming the proximity of an SRT. Finally, at 450 K the refinements led to an axial orientation of the magnetic moments along the *c*-axis of the crystal structure. Contrary to what was reported for DyCo<sub>5</sub> above ~325 K, no deviation in the colinearity between Co and Dy magnetic moments could be detected in DyCo<sub>4</sub>Ga and DyCo<sub>4</sub>Al. Hence, for both DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga compounds, the moments order axially (along the *c*-axis) at *T<sub>C</sub>*, and they undergo a reorientation toward the basal plane around *T<sub>SR</sub>* ~ 400 K. This phenomenon originates from the competition between Co (3d) and Dy (4f) magnetocrystalline anisotropies. Indeed, the anisotropy of the 3d sublattice is dominant at high temperature, and the Co anisotropy must be axial in the DyCo<sub>4</sub>M compounds, as in YCo<sub>4</sub>Al [7], YCo<sub>4</sub>Ga [8] and YCo<sub>5</sub> [23]. In contrast, the Dy sublattice anisotropy is planar in our materials, as already observed in DyCo<sub>5</sub> [24]. As a consequence, the competition between the two contributions to the magnetocrystalline anisotropy gives rise to an SRT, as the 4f anisotropy becomes preponderant at low temperature, and the Dy–Co exchange interaction is strong enough to retain colinearity between the magnetizations of the two sublattices. It is noteworthy that the slight enhancement of the SRT temperature in DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga with respect to DyCo<sub>5</sub> should reflect a weakening of the Co uniaxial anisotropy upon Al or Ga substitution, as previously reported for the isotypic YCo<sub>4</sub>M compounds (M = Al, Ga) [4, 7, 8].

The SRT appears to occur over a quite wide range in temperature. Indeed the magnetization curves exhibit a discontinuity attributed to the SRT at *T<sub>SR</sub>* ~ 400 K, but at 415 K the Rietveld refinements lead us to consider an angle (*θ*) of about 50° between the magnetization direction and the *c*-axis in DyCo<sub>4</sub>Al. This result indicates that the magnetic moments do not tilt brutally from an axial orientation to a planar one at *T<sub>SR</sub>*, but that they rotate continuously with temperature, as already reported for DyCo<sub>5</sub> [24]. Even if no accurate refinement of the *θ* angle could be performed for DyCo<sub>4</sub>Ga around *T<sub>SR</sub>*, this continuous rotation process is very probably also true for the latter compound. The SRT in DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga thus appears to be a second order transition. The thermal evolutions of the lattice parameters of both compounds, deduced from the Rietveld refinements of the neutron diffraction patterns (extrapolated in the ~300–350 K and ~420–450 K ranges), are plotted in figure 7. Contrary to what was previously observed with the PrCo<sub>4</sub>M compounds (M = Al, Ga) [7, 8], no step-like increase of the *c*-parameter around *T<sub>SR</sub>* could be evidenced. The apparent monotonous increase of the lattice parameters with temperature in the vicinity of *T<sub>SR</sub>* seems to agree with the continuous rotation of the moments during the reorientation process.

At low temperature, the mean Co magnetic moment was refined to ~1.2–1.3  $\mu_B$  (tables 2 and 3). No significant difference in the moment values between the 2c and 3g sites could be detected, due to the neutron absorption and to the low intensity of magnetic diffraction. As previously inferred from magnetic measurements, the  $\langle\mu_{Co}\rangle$  value is strongly reduced in comparison with the value of about 1.6–1.7  $\mu_B$  deduced from macroscopic measurements in DyCo<sub>5</sub> [17, 20, 21]. As a result, the Co sublattice magnetization decreases from ~8.1  $\mu_B$  in DyCo<sub>5</sub> down to ~4.8  $\mu_B$  in DyCo<sub>4</sub>Al and ~5.5  $\mu_B$  in DyCo<sub>4</sub>Ga. This phenomenon is probably related to an electronic transfer occurring from the Al 3s and 3p or Ga 4s and 4p bands to the Co 3d band. Electronic structure calculations will have to be performed to confirm

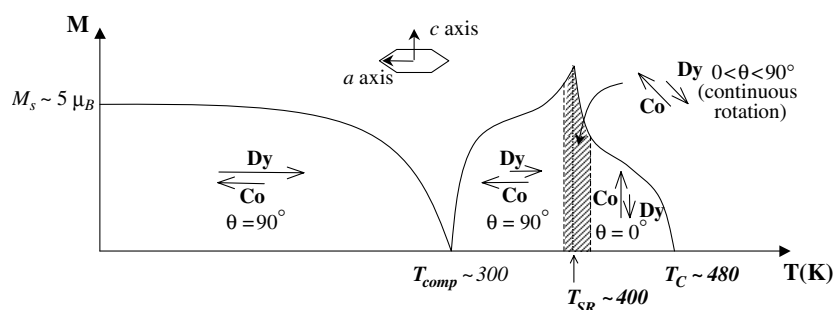


**Figure 7.** Temperature dependence of  $a$  and  $c$  lattice parameters of DyCo<sub>4</sub>Al (upper part) and DyCo<sub>4</sub>Ga (lower part) determined by neutron thermodiffraction. The dashed curves are guides for the eye.

this point. The Dy magnetic moment is also quite strongly decreased from about  $9.7 \mu_B$  in DyCo<sub>5</sub> [17, 20, 21] down to about  $7.5 \mu_B$  in DyCo<sub>4</sub>Al, whereas it is almost unmodified in DyCo<sub>4</sub>Ga ( $\mu_{Dy} \sim 9.1 \mu_B$ ). The Dy moment value in DyCo<sub>4</sub>Al is thus significantly reduced with respect to the expected theoretical value for the free Dy<sup>3+</sup> ion ( $gJ = 10 \mu_B$ ), indicating a larger crystal electric field effect on the rare earth moment amplitude in the Al-containing compound than in the Ga-containing one. This is probably linked to the slightly different locations of Al and Ga atoms in the unit cell, Al being exclusively located at the 3g sites whereas some Ga atoms also occupy the 2c positions. Therefore, the Dy environment is not completely similar in DyCo<sub>4</sub>Al and DyCo<sub>4</sub>Ga, so neither is the crystal electric field.

*Remark.* The Co magnetic moments are overestimated by powder neutron diffraction since this technique is weakly sensitive to the negative polarization of the conduction electrons. This can explain the difference between bulk magnetic measurements and neutron diffraction results. Another origin of this difference could be the method used to correct for neutron absorption. Indeed, our calculation is not free of systematic errors such as the incorrect estimation of the powder density or the gradient of the latter along the container length.

The Dy magnetic moment appears to be much more temperature dependent than  $\mu_{Co}$ . Indeed the two inequivalent Co magnetic moments are found to be nearly constant up to 450 K,



**Figure 8.** Schematic representation of the thermal evolution of the total magnetization of the  $\text{DyCo}_4\text{M}$  compounds ( $\text{M} = \text{Al}, \text{Ga}$ ), with the corresponding moments' orientation and relative amplitudes for the Dy and Co sublattices. The hatched region corresponds to the continuous rotation of the moments.

whereas the Dy moment amplitude strongly decreases with temperature. As a result one can observe for both compounds that there is almost cancellation of the Dy and Co sublattice magnetizations at room temperature:  $|\mu_{\text{Dy}}| \approx |\Sigma(\mu_{\text{Co}})|$ . This result confirms the proximity of the compensation temperature, as deduced from the magnetization measurements. In fact, from the previous remark, one can deduce that  $T_{\text{comp}}$  is probably slightly above 300 K for both compounds.

To summarize, this magnetic study has led us to characterize the magnetic phase diagrams of  $\text{DyCo}_4\text{Al}$  and  $\text{DyCo}_4\text{Ga}$  in the whole ordered temperature range. They are very similar for both compounds, and a sketch of the thermal evolution of the moments' orientation and of the total magnetization is given in figure 8.

#### 4. Conclusions

The  $\text{DyCo}_4\text{Al}$  and  $\text{DyCo}_4\text{Ga}$  compounds were investigated by means of XRD, magnetic measurements and neutron diffraction. As previously observed with  $\text{R} = \text{Y}, \text{Pr}$  and  $\text{Tb}$ , the  $\text{CaCu}_5$ -type structure is retained upon substitution of Al or Ga for Co, and M atoms preferentially occupy the 3g site of the structure. Unlike for the  $\text{DyCo}_5$  phase, no overstoichiometry related to the formation of Co–Co (*dumbbells*) pairs has been observed for  $\text{DyCo}_4\text{Al}$  and  $\text{DyCo}_4\text{Ga}$ . On passing from  $\text{DyCo}_5$  to  $\text{DyCo}_4\text{Al}$  and  $\text{DyCo}_4\text{Ga}$ , an important decrease of the mean Co magnetic moment and of the Curie temperature were evidenced. Moreover, the compensation temperature and the SRT temperature increase upon Al or Ga substitution for Co. The latter phenomenon evidences a weakening of the uniaxial anisotropy of the Co sublattice.

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