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Multi spin-reorientation process in $HfFe_6Ge_6$-type $HoMn_6Ge_{6-x}Ga_x$ compounds ($x=0.2$, 0.4, 1.0)

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Abstract

The $HoMn_6Ge_{6-x}Ga_x$ compounds ($x=0.2$, 0.4, 1.0) have been studied by magnetization measurements and neutron diffraction in the temperature range 2–300 K. The $HoMn_6Ge_{5.8}Ga_{0.2}$ compound orders antiferromagnetically at 415 K and displays a Curie point at 72 K. Neutron diffraction indicates a helimagnetic structure from 300 to 72 K and a cone structure at lower temperature ($\mu_{Mn}=2.23(6)$ μ_B and $\mu_{Ho}=9.46(12)$ μ_B at 2 K). The $HoMn_6Ge_{5.6}Ga_{0.4}$ compound orders antiferromagnetically at 395 K. Neutron diffraction study indicates a helimagnetic structure between 250 and 300 K, a ferrimagnetic structure with moments almost aligned along the *c*-axis between 225 and 180 K, a cone structure in the temperature range 180–70 K and finally a ferrimagnetic structure below 70 K. At 2 K, the moment direction is at 43(1)° from the *c*-axis ($\mu_{Mn}=2.18(6)$ μ_B and $\mu_{Ho}=9.59(9)$ μ_B. The $HoMn_6Ge_5Ga$ compound is ferrimagnetic in its whole ordered range ($T_C=378$ K). At room temperature, the moment direction is at 60(4)° from the *c*-axis and rotates continuously towards the *c*-axis on cooling. In the 250–150 K temperature range, the moments are almost aligned along the *c*-axis and rotate again towards the (001) plane at lower temperature. At 2 K, the moment direction is at 46(1)° from the *c*-axis ($\mu_{Mn}=2.28(5)$ μ_B and $\mu_{Ho}=9.81(9)$ μ_B at 2 K). The anomalous variation of the moment direction is discussed and related to the successive effect of the second and fourth order crystalline field parameters. The evolution of the magnetic order as a function of the Ga content is examined and comparisons are made with the $RMn_6Ge_{6-x}Ga_x$ compounds (R=Lu, Tm).

Keywords: Rare earth compounds; Transition metal compounds; Magnetically ordered materials; Neutron diffraction; Magnetic measurements

1. Introduction

Previous magnetization studies of pseudo-ternary $RMn_6Ge_{6-x}Ga_x$ compounds (R=Sc, Y, Tb–Tm, Lu; $x=2$) have evidenced many interesting phenomena [1–4]. One of the most interesting results is the modification of the interlayer Mn–Mn interactions which enables the stabilization of ferro- or ferrimagnetic structures for sufficiently high Ga concentration. Such a stabilization has allowed a macroscopic study of the magnetocrystalline anisotropy. It has been shown that the Tb, Er and Tm compounds were characterized by rather large coercive fields ($H_c=20$ kOe) whereas the Dy and Ho compounds displayed weaker magnetocrystalline anisotropy ($H_c\approx5$ kOe). As the Tb, Er and Tm elements are all characterized by positive Stevens' coefficient β_j, it has been suggested that the magnetocrystalline anisotropy was mainly driven by the fourth order crystal-field parameter in these compounds. Such an assumption well agrees with a recent neutron diffraction study of the $TmMn_6Ge_{6-x}Ga_x$ compounds ($0.2\leq x\leq1.0$) [5] which has shown that the moments direction was almost aligned along the *c*-axis in the ferrimagnetic representatives. Therefore, it is now necessary to examine the magnetic structures of compounds of R elements characterized by negative Stevens' coefficient β_j and it has been decided to firstly study the $HoMn_6Ge_{6-x}Ga_x$ series.

2. Experimental

The sample have been prepared from stoichiometric amounts of ternary $HoMn_6Ge_6$ and $HoMn_6Ga_6$ alloys previously prepared from the elements in an induction furnace. The mixtures are compacted into pellets, sealed in silica tube under argon and annealed at 1073 K during 2 weeks. The purity of the samples is checked by powder X-ray diffraction (Guinier Co Kα). The cell parameters

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have been refined from Guinier patterns recorded with high purity silicium (a=5.43082 Å) as internal standard.

Magnetic measurements have been undertaken on a MANICS magneto-susceptometer in the temperature range 10–600 K and in fields up to 1.5 T.

Neutron diffraction patterns have been recorded on the D1B apparatus at the Institut Laue Langevin (Grenoble) with the wavelength λ=2.526 Å. The parameters have been refined using the FULLPROF software [6].

3. Structure description and crystallographic data

The hexagonal $HfFe_6Ge_6$ type (S.G.: *P6/mmm*) may be described as a filled variant of the CoSn–B35 type. The insertion of the large metal Hf yields a doubling of the *c*-axis of the CoSn subcell and enables a description of the structure as a stacking along *c* of Fe–(Hf,Ge)–Fe and Fe–Ge–Ge–Ge–Fe slabs (Fig. 1). Such crystal chemistry view is of main interest since previous studies of helimagnetic RMn_6Sn_6 (R=Sc, Y, Lu) and $LuMn_6Ge_{6-x}Ga_x$ compounds have shown that the interlayer couplings within the Mn–(R,Sn[Ge])–Mn and the Mn–Sn[Ge]–Sn[Ge]–Sn[Ge]–Mn slabs were significantly different [7,8].

The atomic coordinates of the $HfFe_6Ge_6$ type structure are given in Table 1. The structure contains three Ge sites characterized by different environments. The Ge_1 and Ge_2 sites are located in trigonal Fe prisms while Ge_3 belongs to the corrugated hexagonal (Fe,Ge) plane. According to the different neutron scattering lengths of Ga and Ge atoms (7.288 and 8.185 fm, respectively), the site occupancies have been refined for the most substituted compound $HoMn_6Ge_5Ga$. Results of the refinements are given in Table 1. The Ga atoms seem to mainly occupy the Ge_3 site as previously observed for the $TmMn_6Ge_5Ga$ and $LuMn_6Ge_5Ga$ compounds studied by neutron diffraction [5,8]. Owing to this conclusion, the magnetic structure refinements of the other compounds have been done considering that Ga atoms are located in this site.

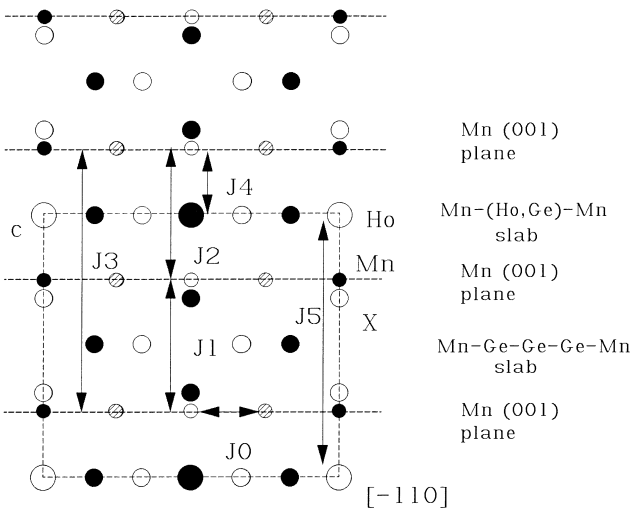

Fig. 1. Projection along [110] of the $HfFe_6Ge_6$-type $HoMn_6Ge_6$ structure (for the label J_i refer to Section 6).

Table 1
Crystallographic sites in $HfFe_6Ge_6$ and corresponding refined atomic parameters in $HoMn_6Ge_5Ga$ at 2 K

Atom	Position	x	y	z	m_j	
Hf	1(*a*)	0	0	0	1	Ho
Fe	6(*i*)	0	1/2	0.250(1)	1	Mn
Ge_1	2(*c*)	1/3	2/3	0	0.92(9)	Ge
					0.08(9)	Ga
Ge_2	2(*d*)	1/3	2/3	1/2	0.92(9)	Ge
					0.08(9)	Ga
Ge_3	2(*e*)	0	0	0.342(1)	0.66(9)	Ge
					0.34(9)	Ga

The cell parameters of the studied compounds are gathered in Table 2. The replacement of germanium by gallium is mainly characterized by a slight decrease of the *a* parameter and an increase of the *c* parameter. The substitution is therefore correlated to a significant increase of the c/a ratio.

4. Magnetic properties

The thermal variation of the magnetization is depicted in Fig. 2 and a summary of the magnetic properties is given in Table 2. The $HoMn_6Ge_{5.8}Ga_{0.2}$ compound displays a Néel point at 415 K and a sharp increase of the magnetization below 72 K. The $HoMn_6Ge_{5.6}Ga_{0.4}$ compound is characterized by a pronounced Néel point at 395 K, a small kink at 287 K and a large increase of the magnetization at 253 K. The $HoMn_6Ge_5Ga$ compound displays a Curie point at 378 K, a sharp maximum at 265 K and a second maximum around 140 K. The isotherm curves of $HoMn_6Ge_{5.8}Ga_{0.2}$ recorded at 100 and 290 K display a linear variation (Fig. 3). That recorded at 80 K exhibits a small curvature in the high field region indicating the onset of a metamagnetic transition. The curves recorded below 70 K display spontaneous magnetization and more or less large coercive fields. The isotherm curves of $HoMn_6Ge_{5.6}Ga_{0.4}$ display spontaneous magnetization below room temperature and a metamagnetic behaviour above room temperature. In spite of the magnetic structure change detected by neutron diffraction in the temperature range 70–180 K (see Section 5.2), additional curves recorded in the corresponding range do not exhibit significant differences (Fig. 4). The curves related to the $HoMn_6Ge_5Ga$ compound display spontaneous magnetization in the whole ordered range and more or less large coercive fields below 140 K. A plot of the thermal variation of the coercive fields is given in Fig. 5. In this connection we note that the characteristic transition temperatures are slightly different from those previously

Table 2
Cell parameters and magnetic properties of $HoMn_6Ge_{6-x}Ga_x$ compounds (transition temperatures in italic refer to previous magnetic measurements [4])

x_{Ga}	a (Å)	c (Å)	c/a	V (Å^3)	T_C (K)	T_N (K)	T_t (K)	M_{max} (10 K) μ_B/f.u.
0.2	5.220(2)	8.164(3)	1.5640	192.6(2)	72 (*68*)	415 (*420*)	–	1.2
0.4	5.221(1)	8.175(2)	1.5657	193.0(2)	253 (*206*)	395 (*402*)	287	2.1
1.0	5.219(2)	8.209(4)	1.5729	193.6(2)	378 (*384*)	–	265, 140	1.8

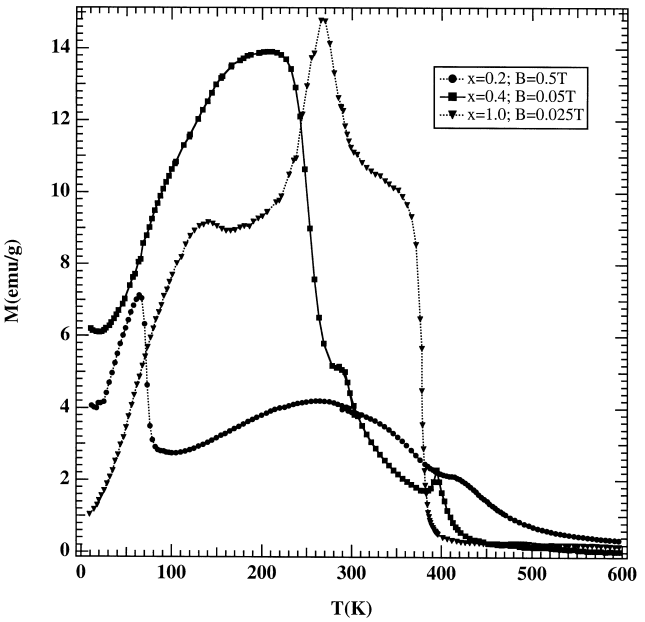

Fig. 2. Thermal variation of the magnetization of $HoMn_6Ge_{6-x}Ga_x$ compounds.

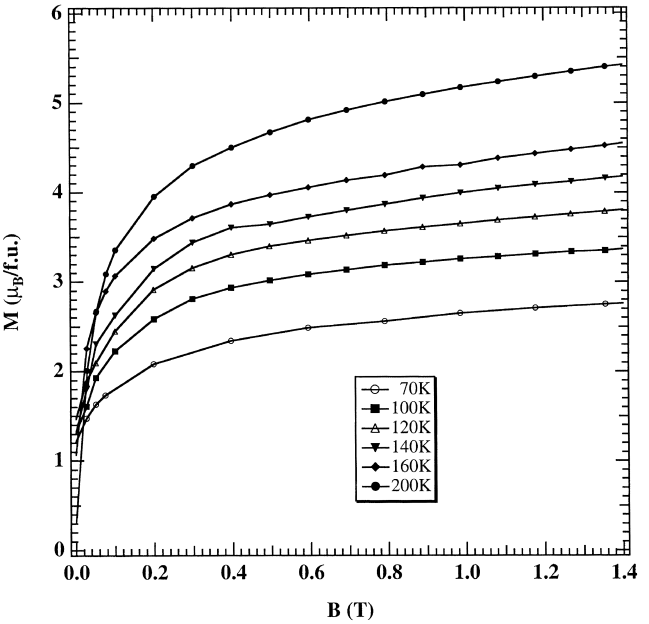

Fig. 4. Isotherm curves of the $HoMn_6Ge_{5.6}Ga_{0.4}$ compound at various temperatures.

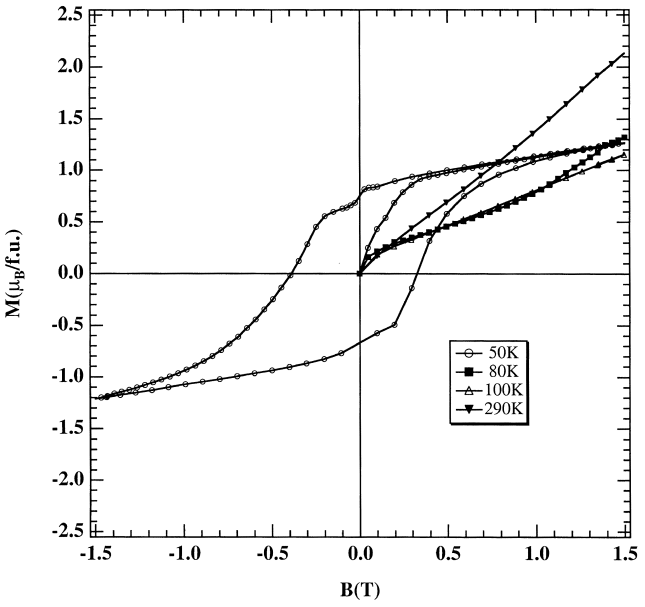

Fig. 3. Isotherm curves of the $HoMn_6Ge_{5.8}Ga_{0.2}$ compound at various temperatures.

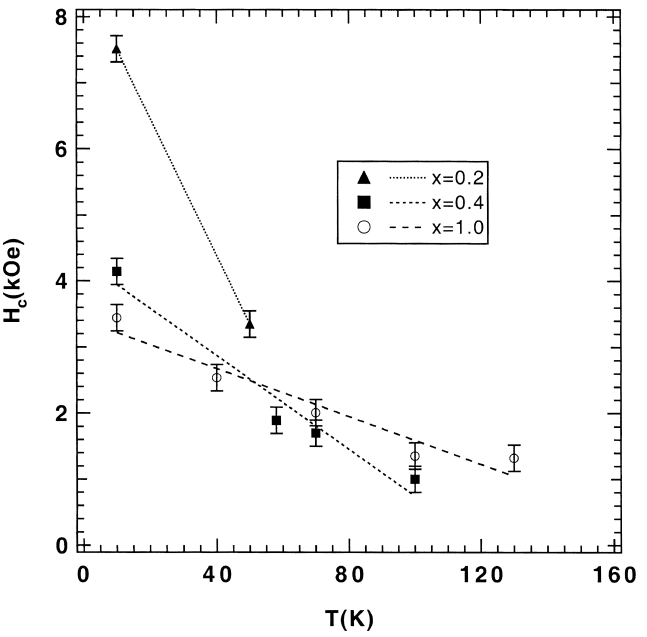

Fig. 5. Thermal variation of the coercive fields of the $HoMn_6Ge_{6-x}Ga_x$ compounds (x = 0.2, 0.4, 1.0).

measured [4]. As the magnetic properties of the $RMn_6Ge_{6-x}Ga_x$ solid solutions drastically vary with the Ga content, such discrepancies might arise from weak deviations of the stoichiometry.

5. Neutron diffraction study

5.1. $HoMn_6Ge_{5.8}Ga_{0.2}$

Three long duration patterns have been recorded at 300, 90 and 2 K and additional patterns have been quickly recorded in order to check the thermal variation of the intensities and Bragg angle variations of some magnetic peaks.

The 300 and 90 K patterns are characterized by additional lines well indexed considering the (0, 0, q_z) propagating vector (Fig. 6). The q_z value decreases from 0.2075(5) r.l.u. at 300 K to 0.1437(2) at 80 K. Refinements have been undertaken considering a helical structure and refining the Mn and Ho moment values, the tilt angle θ_t between the normal to the helical plane and the *c*-axis and the phase angles ϕ_{Mn} and $-\phi_{Mn}$ related to the Mn moments lying at $z_{Mn} \approx 1/4$ and $-z_{Mn} \approx 3/4$, respectively. The phase angle related to the Ho moments in position (0, 0, 0) is fixed at 0. The results of the refinements are gathered in Table 3. The θ_t value refines, within the standard deviations, to 90° and has been fixed at this value in the final step. Therefore, the spiral plane lies in the (101) plane. The magnetic structure is depicted in Fig. 7a.

The relative Ho and Mn moment directions corresponding to the helical arrangement are given by the following expressions:

$$\alpha\mathrm{Ho}(n) = 360 \cdot q_z(n)$$

$$\alpha\mathrm{Mn}(\approx 1/4 + n) = 360 \cdot q_z(\approx 1/4 + n) + \phi_{Mn}$$

$$\alpha\mathrm{Mn}(\approx 3/4 + n) = 360 \cdot q_z(\approx 3/4 + n) - \phi_{Mn}$$

where n is an integer corresponding to the successive chemical cells ($n = 0, 1 \ldots$).

The characteristic angles between the directions of the moments belonging to the successive (001) planes are given in Table 3. They are defined as follows:

$$\alpha_1 = \alpha\mathrm{Mn}(\approx 3/4) - \alpha\mathrm{Mn}(\approx 1/4) \text{ within Mn–Ge–Ge–Ge–Mn sheet}$$

$$\alpha_2 = \alpha\mathrm{Mn}(\approx 1/4) - \alpha\mathrm{Mn}(\approx -1/4) \text{ within Mn–(Ho,Ge)–Mn sheet}$$

$$\alpha_3 = \alpha\mathrm{Mn}(\approx 1/4) - \alpha\mathrm{Ho}(0) = (360 - \alpha_2)/2$$

Below 80 K, the (101) line intensity of which the nuclear contribution is very weak, increases considerably (Fig. 8) and except the (00l) lines, a growth of all the nuclear lines

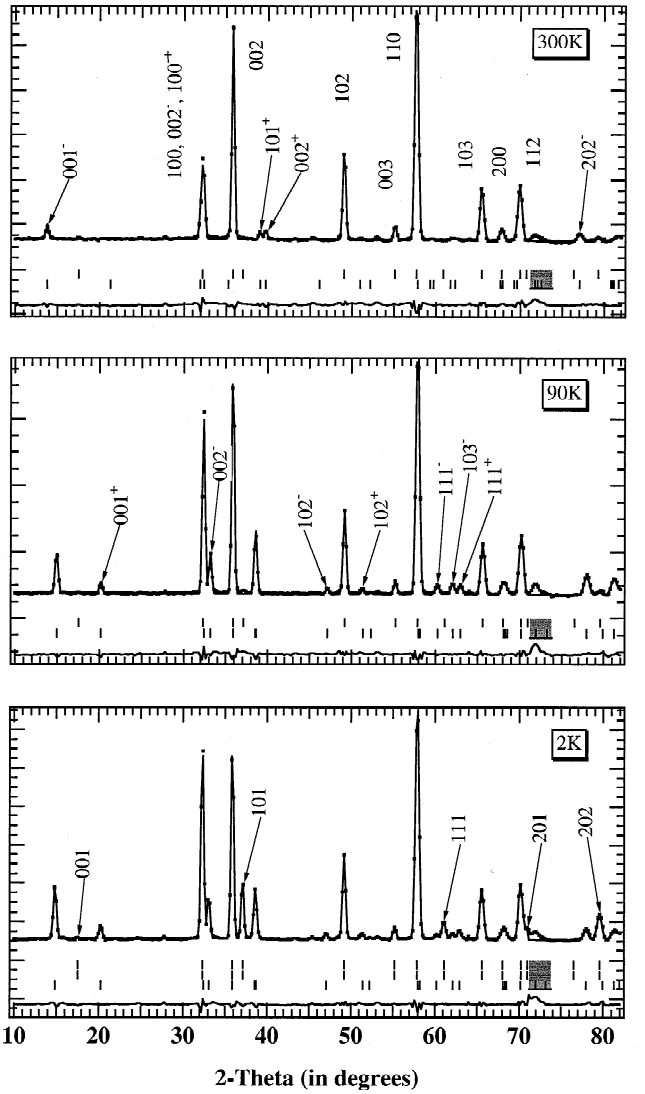

Fig. 6. Observed and calculated neutron diffraction patterns of $HoMn_6Ge_{5.8}Ga_{0.2}$ compound at 300, 90 and 2 K.

is observed. This phenomenon is in good agreement with the magnetic measurements indicating the occurrence of spontaneous magnetization below 72 K. The previous satellite lines remain but some change of their intensities are observed. The slight increase of the intensity of the (001^-) line and the correlated decrease of the intensity of the (111^-) line should be related to a change of the tilt angle θ_t (Fig. 8). Moreover, the refinement indicates a slight evolution of the q_z value. At 60 K, q_z increases to 0.1512(3) r.l.u. and decreases again down to 0.1493(2) r.l.u. at 2 K. The refinements have been undertaken considering a conical structure, refining besides the magnetic parameters belonging to the HT incommensurate structure, an additional collinear arrangement of ferromagnetic Mn and Ho components. The tilt angle of the helical plane θ_t has been fixed to be equal to the deviation of the ferromagnetic components from the *c*-axis (θ_c). Attempts

Table 3
Refined parameters of $HoMn_6Ge_{5.8}Ga_{0.2}$ and characteristic α_i angles of the helimagnetic component (see Section 5.1)

	300 K	90 K	2 K
a (Å)	5.2077(4)	5.1916(3)	5.1906(3)
c (Å)	8.1423(10)	8.1285(8)	8.1309(7)
$z_{Ge(Ga)}$	0.3435(8)	0.3437(11)	0.3436(9)
z_{Mn}	0.2501(14)	0.2519(5)	0.2530(12)
q_z (r.l.u.)	0.2075(5)	0.1451(3)	0.1493(2)
μ_{Ho} (μ_B)	3.14(12)	7.84(13)	6.68(10)
μ_{Ho} (μ_B)	1.69(6)	2.25(6)	1.63(4)
ϕ_{Mn} (°)	188(1)	186.1(7)	187.2(7)
θ_t (°)	90	90	11(1)
μ_{Ho}(F) (μ_B)	–	–	6.70(8)
μ_{Mn}(F) (μ_B)	–	–	1.52(6)
θ_c (°)	–	–	11(1)
μ_{Ho} (total) (μ_B)	3.14(12)	7.84(13)	9.46(12)
μ_{Mn} (total) (μ_B)	1.69(6)	2.25(6)	2.23(6)
R_n (%), R_{m1} (%), R_{m2} (%)	3.83, 13.3, –	4.68, 6.58, –	2.02, 5.57, 3.23
R_{wp} (%), R_{exp} (%), χ^2	9.2, 2.1, 19.8	9.8, 2.1, 22.0	7.1, 1.5, 20.9
α_1 (°)	21	14	12
α_2 (°)	54	38	42
α_3 (°)	153	161	159

to refine separately the two quantities do not lead to significant differences [16(2) against 10(3)°], respectively (Table 3). The semi-cone angles related to the Ho and Mn moments are close [45(1) against 43(2)°, respectively]. The total Ho moment (9.46(12) μ_B) is slightly reduced with respect to the free ion value. A structure representation is given in Fig. 7b.

5.2. $HoMn_6Ge_{5.6}Ga_{0.4}$

Four long duration patterns have been recorded at 2, 120, 200 and 300 K. This compound is characterized by several successive transitions. The 300 K pattern is characterized by the presence of additional lines well indexed considering a (0, 0, q_z) propagating vector (Fig. 9). There

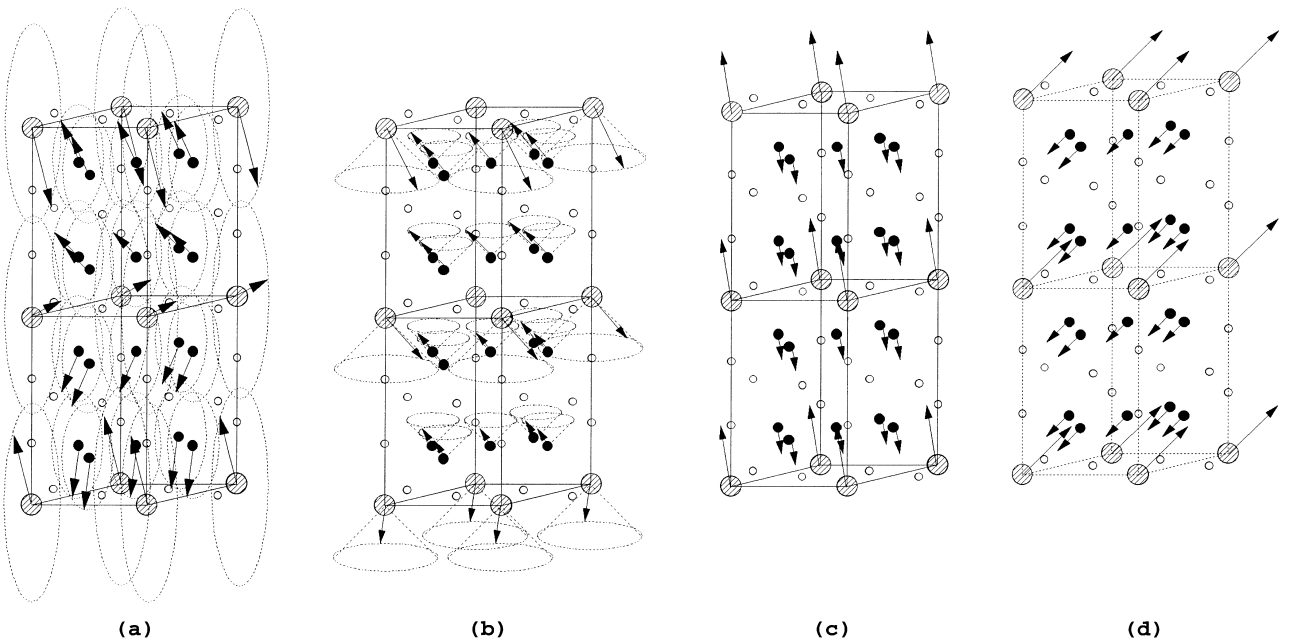

Fig. 7. Magnetic structures observed for $HoMn_6Ge_{6-x}Ga_x$ compounds ($x=0.2$, 0.4, 1.0). (a) Helimagnetic structure with tilt angle perpendicular to the c-axis ($\theta_t=90°$); (b) conical structure with the cone axis parallel to c ($\theta_t=0°$) and semi cone angle $\gamma=45°$; (c) ferrimagnetic structure with moment direction almost aligned along the c-axis ($\theta_c=10°$); (d) ferrimagnetic structure with moment direction halfway between the c-axis and the (001) plane ($\theta_c=45°$).

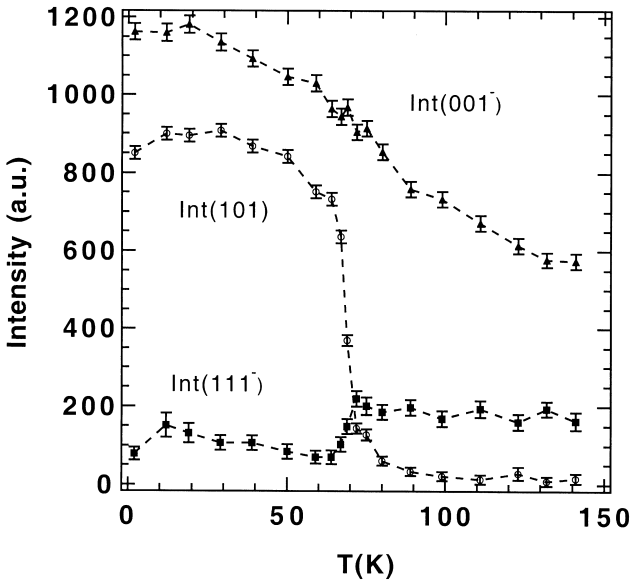

Fig. 8. Thermal variation of the (001$^-$), (111$^-$) and (101) line intensities for the $HoMn_6Ge_{5.8}Ga_{0.2}$ compound.

is no indication of any magnetic contribution on the nuclear peaks. Below $T_1 \approx 250$ K, the intensity of the previous magnetic lines begins to decrease and a growth of the nuclear peaks is observed (Fig. 10). The satellite peaks completely vanish around 225 K. Below $T_2 \approx 180$ K, they appear again, reach their maximum around 100 K and disappear around 70 K. Simultaneously, the intensity of the (101) peaks increases almost continuously from 250 to 2 K, whereas that of the (001) peak is negligible down to 150 K and increases considerably below 90 K.

These features suggest the following successive magnetic structures: a helimagnetic structure from room temperature down to $T_2 \approx 250$ K, a ferrimagnetic structure with moments almost aligned along the *c*-axis in the 225–180 K range, a conical structure in the 180–70 K range and finally a ferrimagnetic structure characterized by an easy direction not aligned along the *c*-axis.

The refinement of the variables corresponding to the 300 K pattern have been undertaken following the procedure given in Section 5.1. Results are gathered in Table 4. The refined parameters are comparable with those corresponding to the $HoMn_6Ge_{5.8}Ga_{0.2}$ compound except for the tilt angle which slightly deviates from 90°.

The refinements of the variables corresponding to the 200 and 2 K patterns have been done considering a collinear arrangement of ferromagnetic Mn and Ho sublattices and refining the moment amplitudes and their directions with respect to the *c*-axis (Table 4). The results indicate a ferrimagnetic structure with moment directions close to the *c*-axis ($\theta_c = 11(4)°$) at 200 K and half-way between the *c*-axis and the (001) plane at 2 K ($\theta_c = 43(1)°$). A representation of these ferrimagnetic structures is given in Fig. 7c and d.

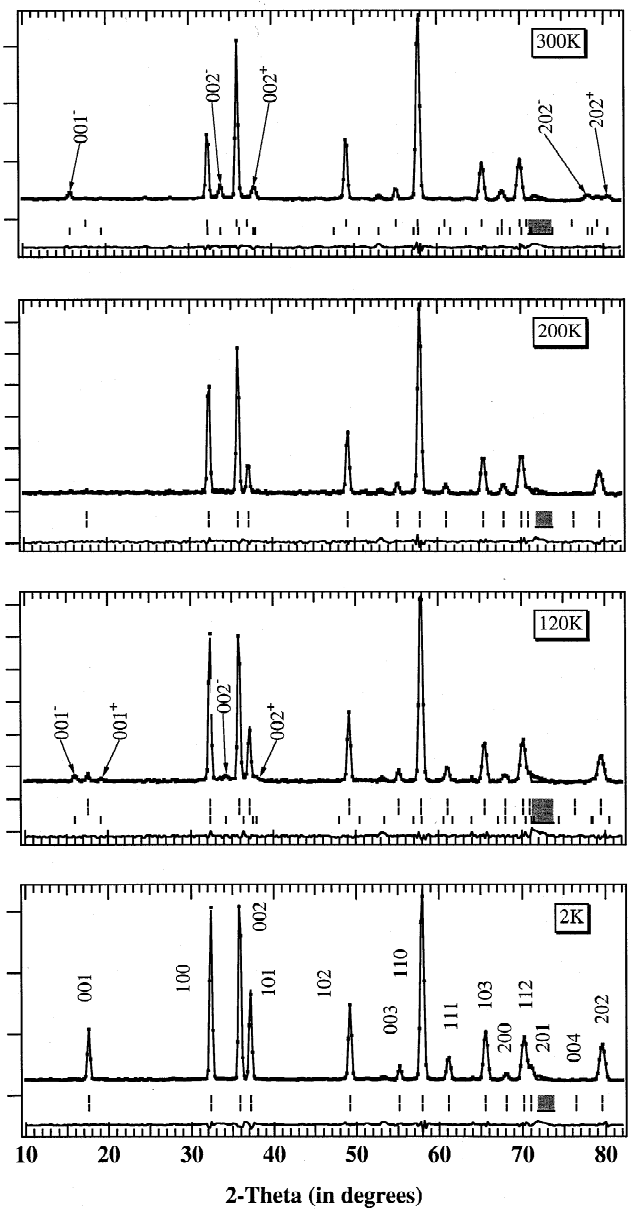

Fig. 9. Observed and calculated neutron diffraction patterns of $HoMn_6Ge_{5.6}Ga_{0.4}$ compound at 300, 200, 120 and 2 K.

The refinement of the variables corresponding to the 120 K pattern have been undertaken following the procedure used for the $HoMn_6Ge_{5.8}Ga_{0.2}$ compound at 2 K. Results are given in Table 4. The cone axis slightly deviates from the *c*-axis ($\theta_c = 21(1)°$). The semi-cone angles related to the Mn and Ho moments are weaker than those measured in $HoMn_6Ge_{5.8}Ga_{0.2}$ and close each to the other ($\gamma_{Mn} = 31(3)°$ and $\gamma_{Ho} = 27(2)°$).

5.3. $HoMn_6Ge_5Ga$

Three long duration patterns have been recorded at 312, 175 and 2 K and additional patterns have been quickly

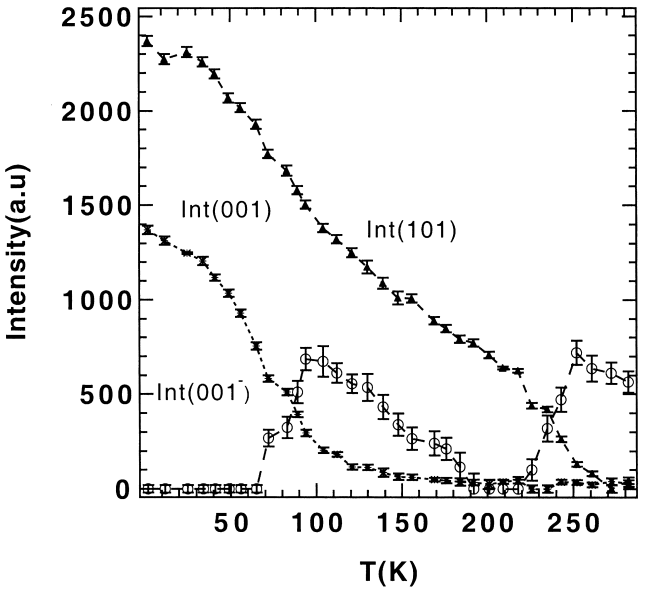

Fig. 10. Thermal variation of the (001¯), (001) and (101) line intensities for the $HoMn_6Ge_{5.6}Ga_{0.4}$ compound.

recorded in order to check the thermal evolution of the intensities. There is no indication of any magnetic contribution to the nuclear reflections. This is in good accordance with the results of the bulk magnetization measurements indicating spontaneous magnetization in the whole ordered range. The 312 and 2 K patterns are characterized by more or less large magnetic contributions on the (001) line whereas the corresponding contribution observed at 175 K is almost negligible (Fig. 11). The thermal variation of the (001) and (101) line intensities is depicted in Fig. 12. The (001) line intensity decreases below 290 K, becomes negligible around 250 K and then increases again below 150 K. The refinement of the variables have been done considering a collinear arrangement of ferromagnetic Mn and Ho sublattices and refining the moment amplitudes and their direction with respect to the *c*-axis. Results are gathered in Table 5. At 312 K, the moments are close to the (001) plane, whereas at 175 K their directions are close to the *c*-axis and an intermediate direction is observed at 2 K. At this temperature, the Ho moment is slightly higher than that measured in the other compounds and close to the free ion value ($gJ=10\ \mu_B$).

6. Discussion

The results of the present neutron diffraction study show that the $HoMn_6Ge_{6-x}Ga_x$ compounds globally behave as the previously studied $RMn_6Ge_{6-x}Ga_x$ compounds (R = Lu, Tm). However, this series displays some new particular features which will be discussed in this section.

Fig. 13 displays the measured Mn moments as a function of the Ga content in the three $RMn_6Ge_{6-x}Ga_x$ series (R = Ho, Tm, Lu) studied by neutron diffraction. It is worth noting that there are no large variations of the Mn moment amplitude as a function of the size of the R element. Moreover, one observes, whatever the involved R element, a slight increase of the moment amplitude with the Ga content.

The low temperature measurement of the Ho moment in the three studied compounds and in $HoMn_6Ge_6$ indicates a continuous increase of the corresponding amplitude with the Ga content from 8.97(5) μ_B in the ternary compound to 9.81(9) μ_B in $HoMn_6Ge_5Ga$. Such an evolution has been previously observed during the study of the $TmMn_6Ge_{6-x}Ga_x$ series [5]. Fig. 14 displays the variation of the reduced Ho moment as a function of the reduced temperature in the three studied compounds. For com-

Table 4
Refined parameters of $HoMn_6Ge_{5.8}Ga_{0.2}$ and characteristic α_i angles of the helimagnetic component (see Section 5.1)

	300 K	200 K	120 K	2 K
a (Å)	5.2102(3)	5.2024(5)	5.1980(4)	5.1938(4)
c (Å)	8.1594(7)	8.151(1)	8.1474(8)	8.1448(9)
$z_{Ge(Ga)}$	0.3451(7)	0.3450(14)	0.3435(9)	0.3435(13)
z_{Mn}	0.249(1)	0.251(2)	0.247(1)	0.251(1)
q_z (r.l.u.)	0.1054(5)	–	0.087(2)	–
μ_{Ho} (μ_B) (Heli)	3.20(13)	–	3.41(20)	–
μ_{Mn} (μ_B) (Heli)	1.83(6)	–	1.23(10)	–
ϕ_{Mn} (°)	186(1)	–	182(2)	–
θ_t (°)	74(1)	–	21(1)	–
μ_{Ho} (μ_B) (F)	–	5.23(10)	6.61(8)	9.59(9)
μ_{Mn} (μ_B) (F)	–	2.15(6)	2.05(5)	2.18(6)
θ_c (°) (F)	–	11(4)	21(1)	43(1)
μ_{Mn} (total) (μ_B)	3.20(13)	5.23(10)	7.43(10)	9.59(9)
μ_{Ho} (total) (μ_B)	1.83(6)	2.15(6)	2.39(10)	2.18(6)
R_n (%), R_{m1} (%), R_{m2} (%)	1.92, –, 12.2	1.32, 3.91, –	1.27, 1.97, 23.2	1.87, 2.29
R_{wp} (%), R_{exp} (%), χ^2	6.8, 1.5, 20.1	7.8, 5.0, 2.5	8.4, 5.5, 2.3	7.5, 1.8, 17.4
α_1 (°)	7	–	12	–
α_2 (°)	31	–	13	–
α_3 (°)	164	–	173	–

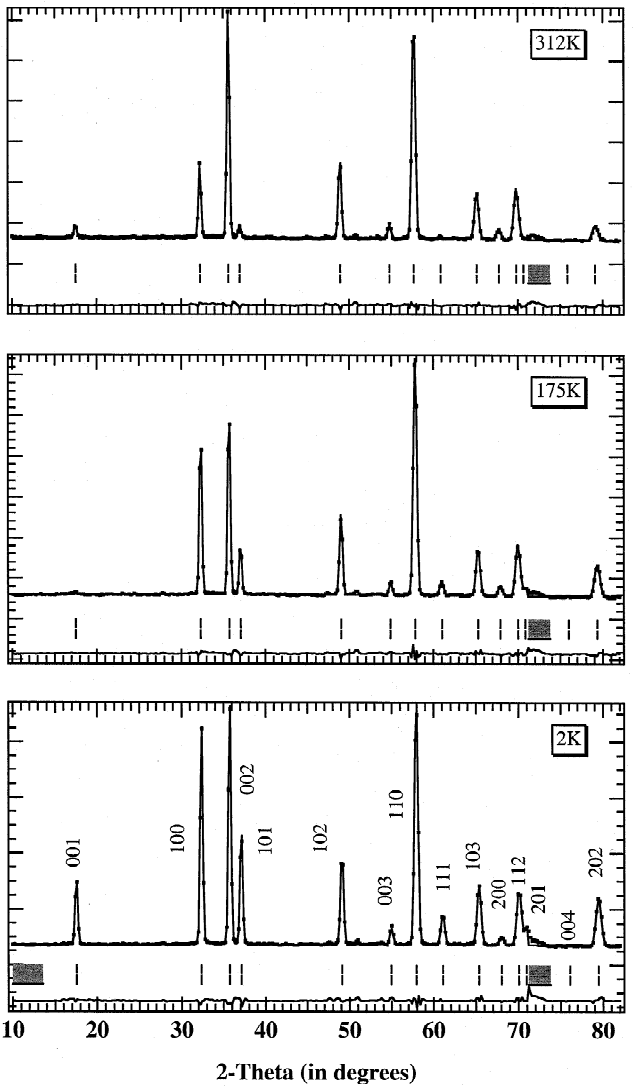

Fig. 11. Observed and calculated neutron diffraction patterns of $HoMn_6Ge_5Ga$ compound at 312, 175 and 2 K.

parison the corresponding variation observed in $TmMn_6Ge_5Ga$ [5] is also given. As previously observed in Tm compounds, in the high temperature region, the reduced Ho moment increases with the Ga content. This means that the polarization of the Ho moment by the Mn sublattice is stronger in the Ga rich compounds, i.e. in compounds characterized by a larger ferromagnetic character. The comparison of reduced moments of $HoMn_6Ge_5Ga$ and $TmMn_6Ge_5Ga$ is also interesting. In the high temperature region, the reduced Ho moment is about twice as large as the reduced Tm moment. Hence, the polarization of the Tm moment by the Mn sublattice is much weaker than that related to the Ho moment. This should be related to the different strengths of the Tm–Mn and Ho–Mn interactions.

The magnetocrystalline anisotropy related to the Mn sublattice may be checked in the high temperature region where the net moment of the Ho atoms remains weak.

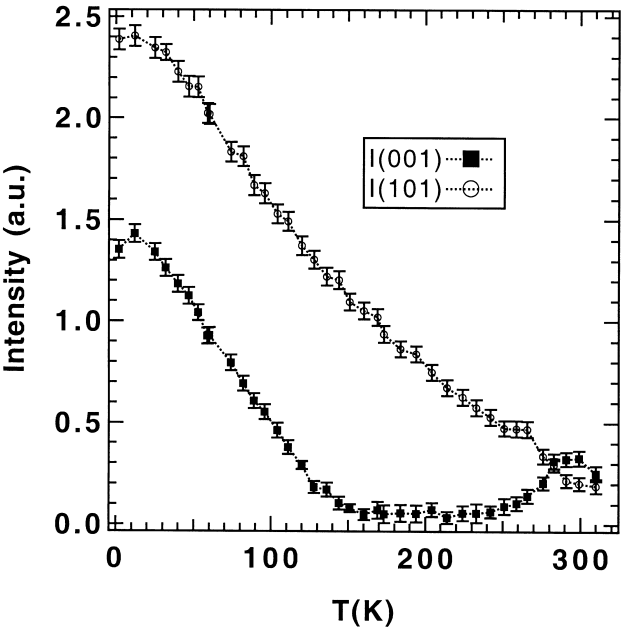

Fig. 12. Thermal variation of the (001) and (101) line intensities for the $HoMn_6Ge_5Ga$ compound.

Table 6 gives the tilt angle of the helical plane and the direction of the ferromagnetic components measured at 300 K, respectively, in the helimagnetic and ferrimagnetic $HoMn_6Ge_{6-x}Ga_x$ compounds and, for comparison, in the previously studied $TmMn_6Ge_{6-x}Ga_x$ compounds. It is worth noting that both series behave similarly. These results suggest that the easy direction related to the Mn sublattice rotates from the *c*-axis towards the (001) plane when the Ga content increases.

The effects of the holmium magnetocrystalline anisotropy leads to a rather original behaviour at lower temperature. This particularly appears in the neutron diffraction patterns of the ferrimagnetic $HoMn_6Ge_5Ga$ compound characterized by an intermediate temperature range where the (001) line disappears. This indicates that the moment direction changes two times as depicted in Fig. 15. At room temperature, the moment direction almost lies in the (001) plane. Between 300 and 250 K, the moment direction rotates towards the *c*-axis and below 150 K, turns back again towards the (001) plane. At low temperature,

Table 5
Refined parameters of $HoMn_6Ge_5Ga$

	312 K	175 K	2 K
a (Å)	5.2142(5)	5.2024(4)	5.1958(4)
c (Å)	8.199(1)	8.1822(9)	8.1761(8)
$z_{Ge(Ga)}$	0.344(1)	0.3440(9)	0.342(1)
z_{Mn}	0.249(1)	0.249(1)	0.251(1)
μ_{Ho} (μ_B) (F)	3.21(10)	5.96(8)	9.81(9)
μ_{Mn} (μ_B) (F)	1.60(8)	2.12(5)	2.28(5)
θ_c (°)	60(4)	12(2)	46(1)
R_n (%), R_m (%)	2.22, 6.30	1.65, 2.74	2.17, 2.41
R_{wp} (%), R_{exp} (%), χ^2	7.4, 2.4, 9.5	7.1, 2.2, 10.2	6.5, 1.6, 17.6

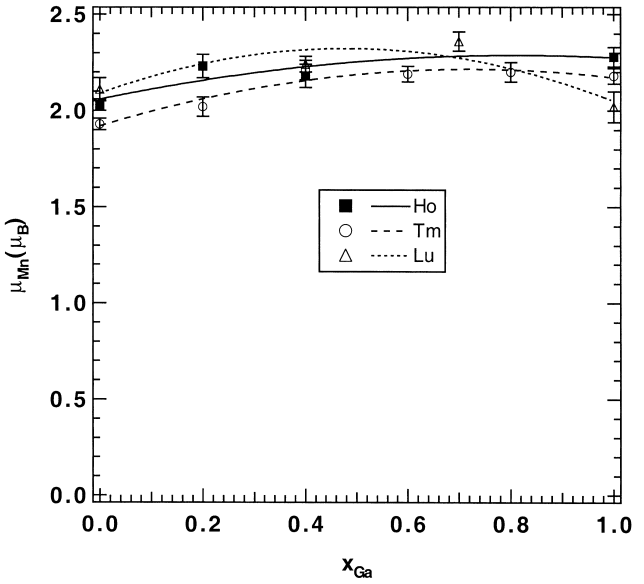

Fig. 13. Variation of the Mn moment magnitude as a function of the gallium content (x_{Ga}) in the $HoMn_6Ge_{6-x}Ga_x$, $TmMn_6Ge_{6-x}Ga_x$ and $LuMn_6Ge_{6-x}Ga_x$ compounds.

the moment direction is stabilized at 46(1)° from the *c*-axis. In the ferrimagnetic range of $HoMn_6Ge_{5.6}Ga_{0.4}$, a similar variation of the moment direction may be recognized. Finally, it is worth noting that, in the low temperature magnetic structure of $HoMn_6Ge_{5.8}Ga_{0.2}$, the moments rotate on a cone which makes an angle of almost 45° with the [001] direction. Therefore, it may be inferred that, whatever the Ga content, the stable easy direction of the Ho moments lies half-way between the *c*-axis and the (001) plane at 2 K whereas this direction is close to the

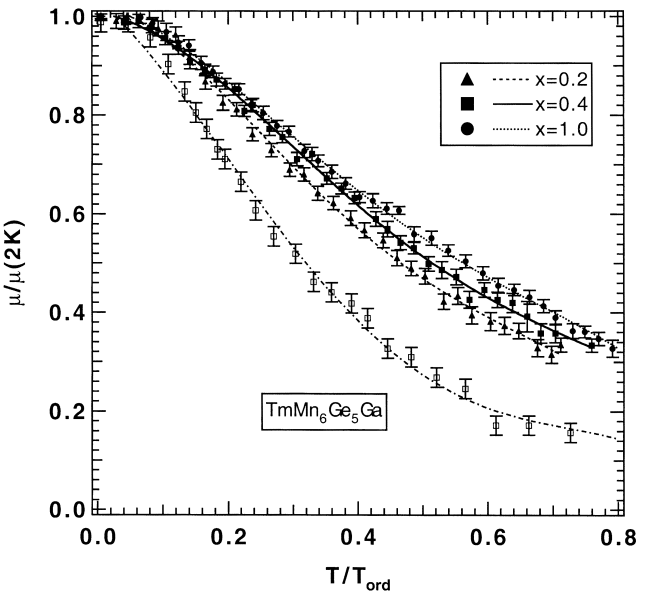

Fig. 14. Variation of the reduced Ho and Tm moments as a function of the reduced temperature in the $HoMn_6Ge_{6-x}Ga_x$ compounds ($x=0.2$, 0.4, 1.0) and in the $TmMn_6Ge_5Ga$ compound.

c-axis around 150 K. At room temperature, the moment direction is driven by the Mn sublattice and rotates continuously from the *c*-axis towards the (001) plane with the Ga content as discussed above. Quite a different behaviour has been observed in $TmMn_6Ge_5Ga$ since, in this compound, the moment direction remains close to the (001) plane from 300 to 100 K and is almost aligned along the *c*-axis below 56 K. As it may be assumed that the Mn anisotropy does not drastically vary between the $HoMn_6Ge_5Ga$ and $TmMn_6Ge_5Ga$ compounds, their different behaviours should be related to the different signs of the α_j and β_j Stevens' coefficients of the Ho and Tm elements.

Following the conclusions of Schobinger-Papamantellos et al. [9] concerning the study of $DyMn_{6-x}Cr_xSn_6$ compounds, it may be assumed that at room temperature the anisotropy of the Mn sublattice dominates and favours a direction close to the (001) plane. On cooling, the anisotropy of the Ho sublattice becomes non-negligible and competes with the anisotropy of the Mn sublattice. This latter one should not be very strong since a continuous change of the easy Mn direction with the Ga content is observed. Hence, the effect of the negative α_j Stevens' coefficient is able to almost align the moments along the *c*-axis. The behaviour observed at lower temperature should be related to the play of the second-order anisotropy constant which varies as high powers of the reduced Ho sublattice magnetization [9]. As β_j is negative, the effect of the second-order anisotropy constant tends to align the moments perpendicular to the *c*-axis and one observes a rotation from the *c*-axis towards the (001) plane. At 2 K, the competition between the various terms stabilizes an easy direction half-way between the (001) plane and the [1] direction.

The evolution of the magnetic order in the studied compounds may be discussed on the basis of the interactions scheme depicted in Fig. 1. The occurrence of helimagnetic structures in $LuMn_6Ge_{6-x}Ga_x$ compounds [8] suggests competing Mn–Mn interlayer J_1, J_2 and J_3 interactions. In a previous work [1], it has been suggested that J_1 and J_2 should be positive exchange interactions characterized by different strengths ($J_1 > J_2$) and J_3 a negative one mediated by the conduction electrons. In compounds of paramagnetic R elements, the R–Mn (J_4) interaction adds constructively with the J_2 one both favouring a parallel arrangement of the Mn moments belonging to the Mn–(R,Ge)–Mn slab. The replacement of the Ge atoms by the Ga atoms seems to reduce the strength of the negative J_3 interaction and yields the continuous transformation from collinear antiferromagnetic to helimagnetic and finally ferro- or ferrimagnetic structures as observed in $LuMn_6Ge_{6-x}Ga_x$ and $TmMn_6Ge_{6-x}Ga_x$ series ($0=x=1$) [5,8].

The evolution observed in the $HoMn_6Ge_{6-x}Ga_x$ series ($0 \leq x \leq 1$) follows the same trends. Fig. 16 depicts the thermal evolution of the corresponding propagating vec-

Table 6
Orientation of the moments and of the helical plane as a function of x_{Ga} in the $RMn_6Ge_{6-x}Ga_x$ (R=Ho, Tm, Lu) compounds at 300 K

x_{Ga}		0.2	0.4	0.6	0.7	0.8	1.0
Ho	(AF) angle of μ_{Mn} with *a*	–	–	–	–	–	–
	(Heli) angle of the normal with *c*	90°	74(1)°	–	–	–	–
	(Ferri) angle of μ_{Mn} with *a*	–	–	–	–	–	30(4)°
Tm	(AF) angle of μ_{Mn} with *a*	90°	–	–	–	–	–
	(Heli) angle of the normal with *c*	–	90°	41(1)°	–	–	–
	(Ferri) angle of μ_{Mn} with *a*	–	–	–	–	28(7)°	30(9)°
Lu	(AF) angle of μ_{Mn} with *a*	–	90°	–	–	–	–
	(Heli) angle of the normal with *c*	–	–	–	43(2)°	–	–
	(Ferro) angle of μ_{Mn} with *a*	–	–	–	–	–	39(12)°

tors. According to Schobinger-Papamantellos et al. [10], $HoMn_6Ge_6$ displays a helimagnetic structure up to 240 K, with propagating vector increasing from $q_z=0.1978(2)$ r.l.u. at 9 K to 0.238(2) r.l.u. at 240 K, and a coexistence of helimagnetic and colinear antiferromagnetic orders ($q_z=0.5$ r.l.u.) between 240 and 300 K. $HoMn_6Ge_{5.8}Ga_{0.2}$ is helimagnetic from 300 to 72 K ($q_z=0.1437$ r.l.u.) and displays a conical structure at lower temperature. $HoMn_6Ge_{5.6}Ga_{0.4}$ exhibits a complex behaviour characterized by still smaller values of the propagating vector ($q_z=0.1054$–0.087 r.l.u.) and by the stabilization of a ferrimagnetic structure at low temperature. Finally, $HoMn_6Ge_5Ga$ is ferrimagnetic ($q_z=0$) in the whole studied range. Therefore, the evolution of the propagating vectors and the stabilization of ferrimagnetic structure for $x=0.4$ and 1.0 well account for an enhancement of the ferromagnetic character of the Mn sublattice with the Ga content as previously deduced from magnetization measurements on $RMn_6Ge_{6-x}Ga_x$ compounds (R=Sc, Y, Tb–Tm, Lu) and from the neutron diffraction studies of $LuMn_6Ge_{6-x}Ga_x$ and $TmMn_6Ge_{6-x}Ga_x$ series [1–5,8].

The effect of the paramagnetic R element may be examined on the basis of Fig. 17 which displays the thermal evolution of the q_z values and magnetic orderings in the $RMn_6Ge_{5.6}Ga_{0.4}$ compounds (R=Lu, Tm, Ho). In these partially substituted compounds, the weakening of the J_3 interaction enables a drastic evolution as a function of the nature of the R element. In the temperature range where the three compounds display the helimagnetic structure (≈250 K), it is worthwhile to note that q_z decreases from 0.31 r.l.u. in the Lu compound to 0.21 r.l.u. in the Tm one and 0.10 r.l.u. in $HoMn_6Ge_{5.6}Ga_{0.4}$. Therefore, the turning angle decreases from 112 to 76° and finally 36°. This is mainly due to a large closing of the α_2 angle within the Mn–(R,Ge)–Mn slab in relation with stronger R–Mn interactions.

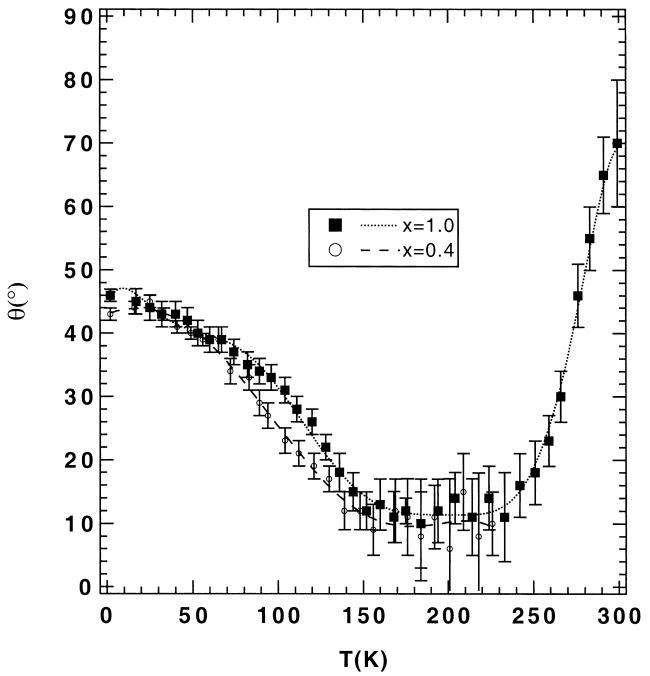

Fig. 15. Thermal variation of the moment direction in the $HoMn_6Ge_{5.6}Ga_{0.4}$ and $HoMn_6Ge_5Ga$ compounds.

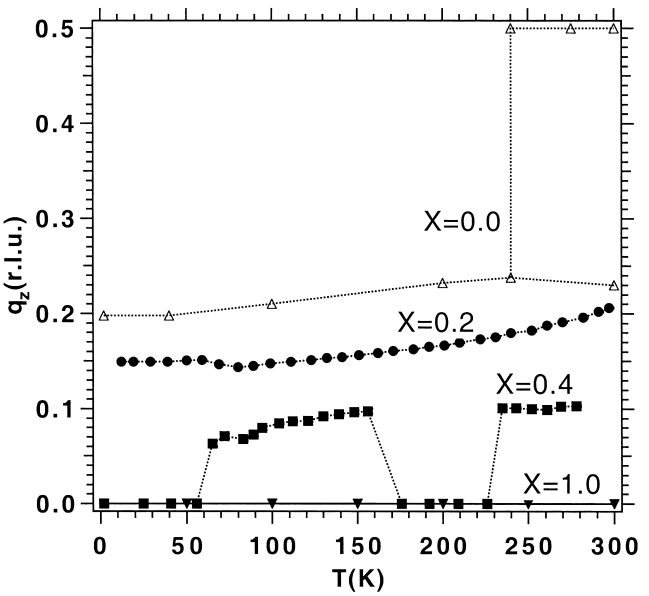

Fig. 16. Thermal variation of the q_z values measured in the $HoMn_6Ge_{6-x}Ga_x$ compounds ($x=0.2$, 0.4, 1.0) and in $HoMn_6Ge_6$ (after Ref. [10]).

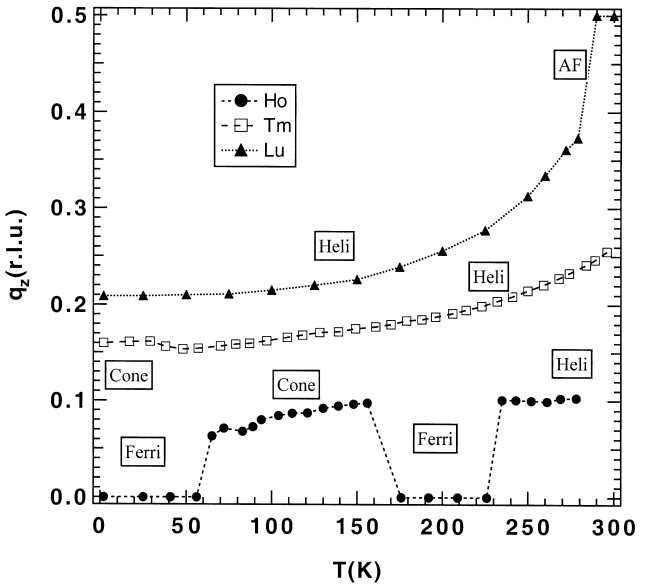

Fig. 17. Thermal variation of the q_z values measured in the $RMn_6Ge_{5.6}Ga_{0.4}$ compounds (R = Lu, Tm, Ho).

It is important to stress that in the Lu and Tm compounds, the q_z values decrease on cooling giving evidence that the global ferromagnetic character increases at the same time. This feature should be related to the stabilization of ferromagnetic structures at low temperature in compounds with non-magnetic R elements and to the decrease of the threshold fields with the temperature in the metamagnetic $RMn_6Ge_{6-x}Ga_x$ compounds (R = Sc, Y, Lu) [1,2].

In such a scheme, the behaviour of $HoMn_6Ge_{5.6}Ga_{0.4}$ is rather intriguing. Firstly, it can be seen that, in the pure helimagnetic state (230–300 K), the q_z value does not greatly vary. Secondly, a transition from the ferrimagnetic state to a cone structure is observed in the intermediate 60–160 K temperature range. These phenomena suggest that, in the holmium compounds, additional antiferromagnetic interactions take place on cooling and compete with the simultaneous decrease of the antiferromagnetic character of the Mn sublattice. These observations should be related to the behaviour of several ternary compounds. The $GdMn_6Ge_6$ compound displays spontaneous magnetization from the ordering temperature down to $\approx$200 K and an antiferromagnetic behaviour at lower temperature [11,12]. From NMR measurements it has been derived that a helimagnetic state takes place at low temperature [13]. A similar behaviour has been observed in $TbMn_6Ge_6$ which orders ferrimagnetically at 450 K and undergoes a transition to a helimagnetic structure at 410 K [14]. Moreover, it the helimagnetic state, an increase of the q_z value is measured on cooling [14,15]. All these observations suggest the presence of an antiferromagnetic J_5 (R–R) interlayer interaction in good accordance with the MFA model calculations reported by Rösch et al. [16] for the $GdMn_6Ge_6$ compound, attributing a negative value to the J_5 (Gd–Gd) exchange integral.

Therefore, the magnetic ordering in $RMn_6Ge_{6-x}Ga_x$ compounds might be described considering at least five interlayer interactions. The two nearest neighbour Mn–Mn interactions (J_1 and J_2) and the antiferromagnetic R–Mn (J_4) interaction tend to align the Mn moments and compete with the long range Mn–Mn (J_3) and R–R (J_5) antiferromagnetic interactions. Their relative thermal variations are probably different and for some critical Ga concentrations, complicated behaviour may be obtained.

This assumption should be related to the shape of the isotherm curve observed for the ferrimagnetic $ErMn_6Ge_{5.2}Ga_{0.8}$ in the temperature range 150–180 K [4]. The two-step magnetization process evidenced by these measurements might be also related to the occurrence of a cone structure.

7. Conclusion

The neutron diffraction study of the $HoMn_6Ge_{6-x}Ga_x$ compounds confirms the global evolution of the magnetic properties previously observed in the corresponding Lu and Tm compounds.

However, two results provide new informations concerning the role of the R element:

- The multi spin-reorientation process observed in the $HoMn_6Ge_{5.6}Ga_{0.4}$ and $HoMn_6Ge_5Ga$ compounds suggests the successive influence of the α_j and β_j Stevens' coefficients.
- The stabilization of a cone structure in an intermediate temperature range in $HoMn_6Ge_{5.6}Ga_{0.4}$ gives evidence of the presence of long range antiferromagnetic Ho–Ho interactions.

Further investigations need to study the $ErMn_6Ge_{6-x}Ga_x$ compounds also characterized by an intermediate magnetic state. The competition between the α_j and β_j Stevens' coefficients should be examined in the $DyMn_6Ge_{6-x}Ga_x$ solid solution.

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