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A neutron diffraction study of the magnetic ordering of HoMn_6Ge_6

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Abstract

The hexagonal compound HoMn_6Ge_6 of HfFe_6Ge_6 -type of structure ($P6_3/mmm$) orders antiferromagnetically below $T_N = 466$ K and undergoes a second magnetic transition at $T_i = 200$ K. Neutron powder diffraction has shown that the low-temperature phase is a triple skewed spiral with wave vector $\mathbf{q}_1 = (0, 0, q_z)$, consisting of ferromagnetic Ho and Mn layers coupled almost antiparallel in a three-layer sequence: $\text{Mn}(+) - \text{Ho}(-) - \text{Mn}(+)$. The plane of the moments is rotated about an axis in the hexagonal plane so that its normal makes a nonzero angle with $\mathbf{q}_1$. This structure may be regarded as a combination of an elliptic helix with a longitudinal wave with the same wave vector. The wave vector length is incommensurate with the crystal lattice and is temperature dependent, at 9 K $q_z = 0.1979(2)$ r.l.u., which corresponds to an interplanar turn angle of $\Phi_S = 71.24^\circ$ in the direction of $\mathbf{q}_1$. Above $T_i = 200$ K a spin reorientation transition, associated with a decoupling of the Mn and Ho sublattices sets in, and the skewed spiral structure gets destabilised. In the transition region 200–260 K the magnetic ordering is described as a superposition of two Fourier coefficients/atom, associated with the wave vectors $\mathbf{q}_1 = (0, 0, q_z)$ and $\mathbf{q}_2 = (0, 0, 1/2)$ corresponding to a distorted spiral with fluctuating Mn moment values and directions. The $\mathbf{H} \pm \mathbf{q}_1$ satellites (skewed spiral) comprise Ho as well as Mn contributions, while the $\mathbf{H} + \mathbf{q}_2$ comprise only the Mn antiferromagnetic ordering along c . Above 260 K the ordering consists exclusively of the $\mathbf{H} + \mathbf{q}_2$ Mn intensity contributions.

1. Introduction

The magnetic properties of several heavy rare earth (R) compounds of the type RMn_6Ge_6 were determined recently [1,2]. These compounds have the hexagonal HfFe_6Ge_6 -type of structure, $P6_3/mmm$ space group $a = 0.52$ nm, $c = 0.81$ nm, $Z = 1$ [3,4]. The particular interest in this family of compounds

arises from the fact that both the rare earth and the Mn atoms are carriers of magnetic moments that interact in a complex way, their bulk magnetic properties presenting at least two ordering temperatures.

A neutron diffraction study of the magnetic structure and phase transitions in the DyMn_6Ge_6 [5,6] compound over the temperature region 10–400 K has shown that at high temperatures (h.t) the magnetic structure is a triple flat spiral consisting of two ferromagnetic Mn layers and one ferromagnetic Dy layer (001) which are antiferromagnetically coupled in the sequence $\text{Mn}(+)$, $\text{Dy}(-)$, $\text{Mn}(+)$ along c .

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Fig. 1. Observed, calculated and difference neutron diagrams of HoMn₆Ge₆ measured at 240 K (top part) and 9 K (bottom part). The indexing $hkl \pm$ refers to the magnetic satellites of the skewed spiral present in both patterns while the $hkl/2$ reflections are only present in the 240 K data.

The wave vector length of the spiral is temperature dependent and remains incommensurate with the crystal lattice over the interval $T_i = 100$ K to T_N . Below T_i this length remains constant and has the value $8/49$. At this same temperature T_i one observes a second-order spin reorientation transition consisting of the development of a ferrimagnetic μ_z component resulting from the antiferromagnetically coupled ferromagnetic sublattices: Mn(+), Dy(−), Mn(+) along c . Thus the low-temperature (l.t) phase is a ferrimagnetic triple conical spiral. The origin of the spin reorientation transition is the temperature-dependent competition between the anisotropies of the two sublattices which was described by us recently using an expansion of the anisotropy energy up to fourth-order terms. It was of interest to extend this study to other isomorphous compounds of the RMn_6Ge_6 series having similar bulk properties.

In the present paper we report on the magnetic structure and phase transitions occurring in the compound HoMn_6Ge_6 . In a previous investigation [2] it was shown that HoMn_6Ge_6 orders antiferromagnetically below $T_N = 466$ K and shows non-Curie–Weiss behaviour above T_N . Similarly to DyMn_6Ge_6 , a

second transition was observed below T_N (at $T_i = 200$ K in HoMn_6Ge_6) [1].

2. Neutron diffraction

The powder sample of HoMn_6Ge_6 used for the neutron diffraction was prepared using the same methods as reported before [5]. Several neutron patterns were collected and analysed in the magnetically ordered region 9–293 K in order to follow the phase transitions. In view of the expected reduced moment values the (h.t) data were collected with twice the counting rate as the (l.t) data. The data were collected with the ‘DMC’ (double-axis multicounter diffractometer) at the Reactor Saphir, Würenlingen, $\lambda = 1.7037$ Å, using the high-intensity mode. The step increment of the diffraction angle 2θ was 0.1° . The data were corrected for absorption and evaluated by the Fullprof program [7] using scattering lengths for Ho, Mn, and Ge as reported in Ref. [8] and a magnetic form factor for R^{3+} and Mn^{2+} as given in Refs. [9] and [10], respectively.

Table 1

Refined parameters of HoMn_6Ge_6 : (a) in the (l.t) region at 9 K, skewed spiral $\widetilde{\text{SS}}$ model ($q_1 = (0, 0, q_z)$), and (b) in the (h.t) region at 240 K, antiferromagnetic AF ($q_2 = 001/2$) + $\widetilde{\text{SS}}$ model. μ_{1s} ($s = x, y, z$), μ_{2z} are the moment components for (i) the $\widetilde{\text{SS}}$ (q_1) and (ii) the antiferromagnetic (q_2) structures. The direction of μ_{1s} is perpendicular to the spiral axis $\bar{w}$. θ_s is the tilting angle of the spiral axis with respect to c . $\phi_{\text{Mn}} = 2\pi(\mathbf{q} \cdot \mathbf{R}_{ij} + \phi_j)$ is the phase angle between the Ho and Mn sublattice moments, with ϕ_j as given in Eqs. (2)–(5). $\Phi_s = 2\pi q_z$ is the spiral turn angle. R_{m1} , R_{m2} are the reliability factors for the integrated magnetic intensities of the $\widetilde{\text{SS}}$ and the collinear AF structures, respectively

Compound, space group temperature, model parameter	HoMn ₆ Ge ₆ P6/mmm	
	9 K, $\widetilde{\text{SS}}$ ($q_1 = (0, 0, q_z)$)	240 K, $\widetilde{\text{SS}}$ + AF ($q_2 = (0, 0, 1/2)$)
Ho at 1(b), (0, 0, 0)		
z_{Mn} at 6(i), (1/2, 0, z)	0.2506(5)	0.2506(4)
Ge1 at 2(d), (1/3, 2/3, 1/2)		
Ge2 at 2c, (1/3, 2/3, 0)		
z_{Ge3} at 2e (0, 0, z)	0.3459(4)	0.3460(4)
B_{of} (nm ²)	0.0050(5)	0.0030(3)
Ho: $\mu_{1s}[\mu_B]$	8.97(5)	−1.91(12)
Mn: $\mu_{1s}[\mu_B]$, $\mu_{2z}[\mu_B]$, ϕ_{Mn}	−2.03(3), −, 27(1)	0.48(6), −0.86(1), 25(1)
θ_s (deg), Φ_s (deg), q_z in r.l.u.	60 (1), 71.24, 0.1978(2)	60 (1), 85.3(2), 0.238(2)
a (nm)	0.52024(2)	0.52206(3)
c (nm)	0.81411(4)	0.8144(5)
$R_a(\%)$, $R_{\text{wp}}(\%)$, $R_{m1}(\%)$,	4.65, 7.94, 5.64	4.13, 7.32, 37
$R_{m2}(\%)$, $R_{\text{exp}}(\%)$, χ^2	−, 1.88, 17.8	9.0, 1.88, 13.4

2.1. The (l.t) magnetic structure: skewed spiral $\widetilde{SS}$ ($q_1 = (0, 0, q_z)$)

The (l.t) neutron pattern at 9 K shown in Fig. 1 comprises, next to the nuclear reflections, a set of magnetic satellites associated with a wave vector along the c -axis $q_1 = (0, 0, q_z)$ as already observed in DyMn_6Ge_6 [5]. Contrary to DyMn_6Ge_6 , no net ferromagnetic contributions were observed (zero field) as could have been assumed from the (l.t) magnetic data collected at a field of 0.5 T [1]. The refined wave vector value $q_z = 0.1979(3)$ corresponds to a spiral angle of 71.24° . However, the relative intensities of the observed magnetic satellites $I_{001\pm}/I_{hkl\pm}$ is much larger for the Ho compound than

for the Dy compound. This fact indicates a deviation from the SS model proposed for DyMn_6Ge_6 . We considered possible triangular structures in the basal plane allowed by the symmetry as given in the symmetry analysis [11] of the $P6/mmm$ space group with the wave vector $q = (0, 0, q_z)$. However, no convergence was found. The best agreement was achieved for a triple skewed spiral ($\widetilde{SS}$) model. The refined parameters are summarised in Table 1. The calculated and observed intensities are compared in Table 2 and the triple skewed spiral structure is displayed in Fig. 2(a).

In the $\widetilde{SS}$ model the moments of the Mn and Ho sublattices are coupled almost antiferromagnetically and point in the same direction within the corre-

Table 2

Some of the observed and calculated integrated neutron intensities of HoMn_6Ge_6 at 9 K. The indexing of the magnetic satellites ($H \pm q_1$) refers to $q_z = 0.1978(2)$

h	k	l	2θ (deg)	I_{calc} (nucl.)	I_{obs} (total)	h $\pm q_z$	k	l	2θ (deg)	I_{calc}	I_{obs}
0	0	1	12.014	31	16	0	0	1 -	9.631	9705	9772
1	0	0	21.800	5030	5104	0	0	1 +	14.402	1766	1782
0	0	2	24.162	18705	20168	0	0	2 -	21.742	5819	5939
1	0	1	24.963	51	196	{1	0	0} $\pm$	21.932	15018	15416
						{1	-1	-1} $\pm$	23.881	5370	5900
						{1	0	-1} $\pm$	26.226	5546	5878
						0	0	2 +	26.594	3594	3648
						{0	1	-2} $\pm$	30.980	1282	1610
1	0	2	32.767	8861	8959	0	0	3 -	34.104	277	293
0	0	3	36.594	1433	1804	{0	1	-2} $\pm$	34.645	1020	968
1	1	0	38.237	29423	27222	{1	-2	0} $\pm$	38.316	4428	4128
						{1	-2	-1} $\pm$	39.524	1736	1821
						0	0	3 +	39.598	158	123
1	1	1	40.222	20	42	{0	1	-3} $\pm$	40.843	1904	2032
						{1	-2	1} $\pm$	41.059	1965	2256
1	0	3	42.999	6537	6640	{1	-2	2} $\pm$	44.413	650	566
2	0	0	44.444	1105	987	{2	-2	0} $\pm$	44.514	0	0
1	1	2	45.746	7604	7389	{0	1	-3} $\pm$	45.210	1184	1214
2	0	1	46.208	13	15	{0	2	-1} $\pm$	45.585	1850	1790
						0	0	4 -	46.893	0	0
						{2	-2	-1} -	46.959	910	950
0	0	4	49.494	55	52	{1	1	-2} +	47.183	572	632
						{2	0	2} $\pm$	49.999	3914	4038
2	0	2	51.220	564	597	{2	1	-3} $\pm$	52.159	1030	958
						{1	0	4} $\pm$	52.277	1502	1436
1	1	3	53.961	4347	4605	{2	0	-2} $\pm$	52.544	3316	3186
1	0	4	54.687	1248	1238	{1	-2	3} $\pm$	55.841	706	590

Fig. 2. (a) The triple skewed spiral model. Φ_s is the interplanar spiral turn angle measured in the spiral plane. The structural unit consists of the three Mn–Ho–Mn layers which change their moment direction collectively along the direction of the wave vector q_1 . (b) the distorted skewed spiral with fluctuating Mn moments observed in the region 200–260 K in HoMn_6Ge_6 . (c) Coordinate system for a spin vector rotating in the plane (u, v) . q is the wave vector, w is the spiral axis and ε is the scattering vector. θ_s the spiral tilting angle with respect to the c -axis.

sponding (001) layers. The phase angle between the Mn and Ho sublattices is $\pi \pm \phi_{\text{Mn}}$ ($\phi_{\text{Mn}} = \pm 27(1)^\circ$), and the phase angle is $2\phi_{\text{Mn}}$ between Mn adjacent layers at $z = -1/4, 1/4$. Since no higher-order satellites have been observed this triple spiral unit of Mn–Ho–Mn moments (at $z = -1/4, 0, 1/4$) changes its direction collectively along the direction of the wave vector by a constant angle of $\Phi_s = 71.24^\circ$ (see Fig. 2a) [12].

The Fourier coefficients for a spiral structure can be expressed as a complex vector:

$$m_q = \frac{m_0}{2} (u + iv) e^{i\phi_q}, \quad (1)$$

where u and v are two orthogonal unit vectors, in the plane of the moment rotation, m_0 is the moment value, and ϕ_q is the phase factor associated with the wave vector q .

The normal of the plane of rotation w or the spiral axis may have any orientation relative to q and the crystal axis. For a flat spiral SS model, as found in DyMn_6Ge_6 [5], the angle (θ_s) of the spiral axis with c is zero, while in the SS type of structure the plane

of the moments is rotated about an axis in the hexagonal plane so that $\theta_s \neq 0$ (see Fig. 2c).

The moment distribution in the l th cell is given by the expression:

$$m_{ji}(R_l) = m_{0j} [u \cos 2\pi(q_i \cdot R_{lj} + \phi_j) + v \sin 2\pi(q_i \cdot R_{lj} + \phi_j)] \quad (2)$$

where R_l is the position of the l th unit cell. Referring to an orthogonal system with x and z parallel to the crystal axes, expression (2) may be rewritten:

$$m_{ji}(R_l) = \mu_{1s} [x \cos 2\pi(q_i \cdot R_{lj} + \phi_j) + (y \cos \theta_s + z \sin \theta_s) \times \sin 2\pi(q_i \cdot R_{lj} + \phi_j)], \quad (3)$$

where μ_{1s} ($s = x, y, z$) is the spiral moment value associated with the wave vector $q_1 = (0, 0, q_z)$. For $\theta_s = 0$ the moments rotate in the (a, b) plane for $\theta_s = \pi/2$ in the (a, c) plane (cycloidal spiral).

The scattered neutron intensity for the satellite reflections is proportional to the square of the scattered amplitude $|F|^2$:

$$F_{H \pm q} = p \left(\frac{1 + \cos^2 \omega}{4} \right)^{1/2} \times \sum_j f_{j(H \pm q)} m_{0j} \exp(2\pi i H \cdot r_j \mp \phi_j), \quad (4)$$

where ω is the angle between the spiral axis and the scattering vector, f_j is the magnetic form factor, H is a reciprocal lattice vector, and r_j and ϕ_j are the positional vector and the phase angle of the j th atom in the cell, respectively. The quantities that have to be derived from the refinement are the moment value, the phase angles and the angle θ_s of the spiral axis with c .

The refined tilting angle at 9 K is $\theta_s = 60^\circ$. The ordered moments are rotating in the plane perpendicular to w and have the values $8.97(5)\mu_B$ for $\mu_{1s\text{Ho}}$ and $-2.03(2)\mu_B$ for $\mu_{1s\text{Mn}}$. These values are very close to the saturation values of Ho^{3+} ($gJ\mu_B = 10\mu_B$) and Mn^{2+} , respectively. The low values of $R_n = 4.6\%$ and $R_{m1} = 5.64\%$ reliability factors lend credence to the correctness of the proposed model. The rather high value $\chi^2 = 17.8$ may be due to the presence of small amounts of an impurity phase

giving rise to reflections at 2θ positions 30, 41, 50.5 and 50.9° (not excluded from the refinement) that also persist at higher temperatures.

2.2. The (h.t) magnetic structure: AF ($q_2 = (0, 0, 1/2)$) + skewed spiral ($\widetilde{SS}$) ($q_1 = (0, 0, q_z)$).

The magnetic measurements have indicated a phase transition around $T_i = 200$ K. The 240 K neutron diffraction pattern (see Fig. 1, top part), has been collected well above T_i and therefore is ex-

pected to provide information on the (h.t) magnetically ordered state. The refined parameters given in Table 1 confirm the HfFe_6Ge_6 type of structure [2–4]. The value $R_n = 4.13\%$ is satisfactory and indicates no significant deviation of the crystal structure of HoMn_6Ge_6 from the basic structure. In addition to the nuclear reflections, one observes at least two sets of weak magnetic reflections that do not overlap with the nuclear reflections in the neutron pattern. Their indexing has been possible by using two wave vectors $q_1 = (0, 0, q_z)$ with $q_z = 0.237(2)$ r.l.u. and $q_2 = (0, 0, 1/2)$.

Table 3

A part of the observed and calculated integrated neutron intensities of HoMn_6Ge_6 at 240 K. The left part of the table comprises the nuclear and the antiferromagnetic contributions associated with $q_2 = (0, 0, 1/2)$. The right part refers to the magnetic ($H \pm q_1$) satellites associated with $q_{1z} = 0.238(2)$

h	k	l	2θ (deg)	I_{calc} (nucl.)	I_{calc} (mag.)	I_{obs} (total)	h $\pm q_{1z}$	k	l	2θ (deg)	I_{calc}	I_{obs}
0	0	1/2	5.96		0	0	0	0	1 –	9.138	769	840
0	0	1	12.008	58	–	50						
1	0	0	21.720	9344	–	9340	0	0	1 +	14.885	184	58
1	0	1/2			2406	2440	0	0	2 –	21.235	587	815
0	0	2	24.150	34585	–	37901	{1	0	0} $\pm$	21.912	1350	1378
1	0	1	24.889	96	–	189	{1	–1	–1} $\pm$	23.607	498	426
1	0	3/2	28.385		684	732	{1	0	–1} $\pm$	26.434	430	420
1	0	2	32.703	16411	–	16897	0	0	2 +	27.080	327	319
0	0	3	36.575	2655	–	3497	{0	1	–2} $\pm$	30.559	92	928
1	0	5/2	37.603		156	150						
1	1	0	38.093	54940	–	50646	0	0	3 –	33.578	30	239
1	1	1/2	38.598		558	846	{0	1	–2} $\pm$	34.488	72	116
1	1	1	40.082	39	–	82	{1	–2	0} $\pm$	38.209	350	327
1	1	3/2	42.458		264	264	{1	–2	–1} $\pm$	39.257	28	221
1	0	3	42.939	12186	–	12707	0	0	3 +	39.598	158	123
2	0	0	44.274	2074	–	2037	{0	1	–3} $\pm$	40.847	156	120
2	0	1/2	44.721		2556	2556	{1	–2	1} $\pm$	41.110	156	1050
1	1	2	45.614	14278	–	13792	{1	–2	2} $\pm$	44.019	48	39
2	0	1	46.042	25	–	26	{2	–2	0} $\pm$	44.376	0	0
2	0	3/2	48.181		1914	1656	{0	2	–1} $\pm$	45.306	136	124
0	0	4	49.446	102	–	99	{0	1	–3} $\pm$	45.610	104	102
1	1	5/2	49.439		108	96	0	0	4 –	46.338	0	0
2	0	2	51.069	1068	–	1689	{2	–2	–1} –	46.964	110	214
1	1	3	53.837	8193	–	8986	{1	1	–2} +	47.361	43	66
2	0	5/2			882	978	{2	0	2} $\pm$	49.601	384	438
1	0	4	54.625	2357	–	2617	{2	1	–3} $\pm$	51.674	85	38
							{1	–2	3} $\pm$	51.727	140	58
							{2	0	–2} $\pm$	52.631	312	412
							{1	–2	3} $\pm$	56.114	61	33

From the observation that all $0, 0, l/2$ peaks have zero intensity it can be concluded that the magnetic moments have a collinear antiferromagnetic arrangement and point along the c direction. The best agreement between observed and calculated values was achieved for a zero moment μ_2 value for Ho (μ_2 are the moment components giving rise to the Fourier coefficients $m(q_2)$ with $q_2 = (0, 0, 1/2)$). Mn has an antiparallel arrangement of the moments at $z \approx 1/4$ and $3/4$ (referring to the chemical cell with Ho in $(0, 0, 0)$) and a change in sign when going to the next cell along c : $(+ - - +)$. The ordered moment value is $\mu_{2z} = 0.86(3)\mu_B/\text{Mn}$. Here we would like to note that an alternative arrangement along c $(+ + - -)$ does not affect the R -factors and the refined parameters, so that a choice between these models can only be made on the basis of physical arguments.

On the other hand, the intensity of the satellites of the IC structure have strongly decreased. The first observable weak magnetic reflection at $2\theta = 9.2^\circ$ is the strongest resolved satellite (001) – pertaining to the spiral wave vector $q_1 = (0, 0, q_z)$, as was also found in the data obtained at 9 K. A refinement based on the simple spiral (SS) model used for the (h.i) incommensurate structure of DyMn_6Ge_6 led to the rather high value of 49% for the reliability factor R_{ml} . A refinement using the skewed spiral SS model (see Table 1) lowered the R_{ml} factor by 12%. The ordered moment values/ion of the skewed spiral, $-1.9(1)\mu_B/\text{Ho}$ and $0.47(6)\mu_B/\text{Mn}$, are lower by almost a factor of three than those found for DyMn_6Ge_6 . The refined phase factors between the Mn and Ho sublattices in adjacent layers Mn–(RE – x)–Mn are around $\pi \pm \phi_{\text{Mn}}$ ($\phi_{\text{Mn}} = 25(1)^\circ$) and $2\phi_{\text{Mn}}$ between adjacent Mn layers at $z = -1/4, 1/4$. This means that the two sublattice moments are almost antiferromagnetically coupled, as was observed also at 9 K. Again a refinement based on triangular structures in the basal plane [11] did not converge. The rather poor agreement factor $R_{\text{ml}} = 37\%$ may partly be due to the possible presence of coinciding reflections of small amounts of the already mentioned impurity phase and to the fact that, in spite of the double rate used in the counting time, the magnetic satellites of the spiral are very weak. A part of the calculated intensities are compared with the observed ones in Table 3.

The distorted spiral model

It was mentioned above that the relative orientation of the two magnetic sublattices is found to be almost antiferromagnetic for the skewed spiral components (μ_{1s}) perpendicular to w , while the collinear antiferromagnetic structure comprises exclusively Mn contributions. Because the latter Mn moment components (μ_{2z}) are along c , the two sublattices have different preferred directions of antiferromagnetism.

Thus the Ho moment arrangement participates only in the (SS) model which consists of $\mu_{1s\text{Mn}}$ and $-\mu_{1s\text{Ho}}$ (001) layers coupled antiparallel. These point in about the same direction perpendicular to w , the spiral axis, which makes an angle of $\theta_s = 60(1)^\circ$ with the c -axis.

The ordering of Mn comprises, in addition to the μ_{1s} (SS) component, an antiferromagnetic $(+ - - +)$ μ_{2z} component when referring to the c -doubled magnetic cell and can be given as a superposition of the observed Fourier coefficients/atom $m(\pm q_1)$ and $m(q_2)$ associated with the wave vectors $\pm q_1$ and q_2 which are not related by symmetry. The moment of the j th Mn atom in the l th cell is given for this model by (5):

$$\begin{aligned} m_{jl}(R_l) = & \mu_{1s} [x \cos 2\pi(q_i \cdot R_{lj} + \phi_j) \\ & + (y \cos \theta_s + z \sin \theta_s) \\ & \times \sin 2\pi(q_i \cdot R_{lj} + \phi_j)] \\ & + \mu_{2z\text{Mn}}(-1)^l. \end{aligned} \quad (5)$$

The resulting structure for Mn is therefore a distorted helical structure with *fluctuating* Mn moment values and directions. The limits of the μ_{TMn} (total moment) fluctuation are $\mu_{1s} + \mu_{2z}$ and $\mu_{1s} - \mu_{2z}$. For the refined skewed spiral angle $\theta_s = 60(1)^\circ$ the minimum and maximum angles $(\pi/2 \pm \theta_s)$ between the vectors μ_{1s} and μ_{2z} are $\alpha_{\text{min}} = 30^\circ$ and $\alpha_{\text{max}} = 150^\circ$, respectively, one finds:

$$\begin{aligned} \mu_{1s} \pm \mu_{2z} = & \sqrt{\mu_{1s}^2 + \mu_{2z}^2 \mp 2\mu_{1s}\mu_{2z} \cos \alpha} \\ = & \sqrt{\mu_{1s}^2 + \mu_{2z}^2 \mp \sqrt{3}\mu_{1s}\mu_{2z}} \end{aligned} \quad (6)$$

For the refined values at 240 K $\mu_{1s} = 0.48\mu_B$, and $\mu_{2z} = 0.86\mu_B$, the resulting fluctuation limits of μ_{TMn} are $1.29\mu_B$ and $0.5\mu_B$. The corresponding angle limits between μ_{TMn} and the c -axis are 10 and 28° .

The essential difference between the (l.t) skewed spiral ($\widetilde{\text{SS}}$) and the AF $\widetilde{\text{SS}}$ (h.t) structure is that in the latter structure at 240 K the two magnetic sublattices have different orientations and seem to be only weakly coupled.

Fig. 2(b) displays the schematic representation of the AF $\widetilde{\text{SS}}$ structure, which consists of (a) a triple $\widetilde{\text{SS}}$ unit of three ferromagnetic Mn–Ho–Mn layers (at $z = -1/4, 0$, and $1/4$) which changes its orientation collectively (within the tilted spiral planes) by $\Phi_s = 2\pi q_z = 85.3^\circ$ when going from one cell to the

other along the direction of the wave vector q_1 ; and (b) collinear antiferromagnetic μ_{zz} Mn components.

Three-dimensional models for the moment arrangements given in Table 1 for the Mn sublattice are displayed in Fig. 3. These models are calculated on the basis of (5).

2.3. The evolution of the skewed spiral and the Mn spin reorientation

The analysis of the 9 and 240 K neutron data has shown that the magnetic sublattice moments are

Fig. 3. (a) Three-dimensional schematic representation and two dimensional projection (below): of the skewed spiral model observed for Mn at 9 K stable for $T < 200$ K (right part) and of the distorted skewed spiral observed for Mn in the region 200–260 K (left part) for the compound HoMn_6Ge_6 .

Fig. 4. (a) Thermal variation of the neutron intensity of the magnetic satellite 001⁻ q_1 (and the antiferromagnetic peak 101/2. Also shown is the temperature dependence of the spiral turn angle Φ_s for the compound HoMn₆Ge₆. (b) Thermal variation of the diffraction angle 2θ (deg) of the strongest resolved satellite of the skewed spiral and thermal variation of the spiral wave vector length for the compound HoMn₆Ge₆.

strongly coupled and point to the same direction only at 9 K. The increase of the spiral angle from 71.24° at 9 K to 85.3° at 240 K indicates a change in the nature of the exchange interaction between the moments in adjacent cells along c . This is true particularly for the Mn moments for which a second wave vector ($q_2 = (0, 0, 1/2)$) associated with a collinear antiferromagnetic ordering along c has been observed at 240 K. On the basis of line profile analysis of 20 neutron patterns collected in the temperature region 9–293 K the evolution of the skewed spiral and the Mn spin reorientation and their relation to the magnetic measurements [1] could be more closely followed.

From the results displayed in Figs. 4–6 one may distinguish three distinct regions of a different magnetic behaviour with respect to the number of Fourier coefficients/atom present in the neutron patterns at various temperature intervals. This distinction also becomes evident in the bulk magnetic properties reported in Ref. [1] which are reproduced here in Fig. 7 for completeness.

(i) The 9–200 K (l.t) region characterised by the presence of only the SS phase. Between 9–55 K the wave vector and consequently the spiral angle Φ_s have their smallest values and remain unchanged with temperature see Figs. 4(a) and (b). Between 55–200 K the wavevector length and therefore the

spiral angle increase monotonously with temperature. This behaviour continues even at higher temperatures up to 260 K, where the magnetic intensities become negligible and the errors in the wave vector value too large. The angle $\theta_s = 60^\circ$ of the spiral axis with c remains constant and increases to about 87° near 260 K. The temperature dependence of the intensity of the magnetic satellite 001⁻ proportional to $(\mu_{1sHo} + 6\mu_{1sMn})^2$ shows that the Fourier coeffi-

Fig. 5. Temperature dependence of the rotating moment components μ_{1s} of the triple skewed spiral structure of HoMn₆Ge₆. Also shown is the collinear μ_{2zMn} moment component along c which is associated with $q_2 = (0, 0, 1/2)$.

Fig. 6. Thermal variation of the lattice constants, the volume and the ratio a/c , for the compound HoMn_6Ge_6 .

coefficients of $\mu_{1\text{S}\text{Ho}}$ and $\mu_{1\text{S}\text{Mn}}$ display different temperature dependences, at least below 100 K where a change in slope can be seen.

(ii) The 200–260 K region. Just above $T_t = 200$ K one observes a destabilisation of the $\widetilde{\text{SS}}$ spiral which is coupled with the Mn spin reorientation. One observes two coexisting Fourier coefficients/atom in the neutron data associated with the wave vectors $q_1 = (0, 0, q_z)$ and $q_2 = (0, 0, 1/2)$; the appearance of the latter one marks the set-in of the Mn spin reorientation. The temperature dependence of the intensity of the 001^- satellite shows a change in slope above T_t and falls to zero at 260 K, while the

intensities of the $hkl/2$ reflections associated with q_2 continue to increase up to 293 K.

(iii) The 260–293 K region, where one mainly observes magnetic reflections associated with the wave vector q_2 and most likely at higher temperatures the magnetic ordering is restricted to the Mn atoms.

2.4. The thermal evolution of the magnetic moment components

A complete set of refined data over the 9–293 K region has allowed us to make a precise determination of all magnetic components. These results are displayed in Fig. 4. We will first discuss the behaviour of the components $\mu_{1\text{S}\text{Ho}}$ and $\mu_{1\text{S}\text{Mn}}$, both residing in the tilted planes of the $\widetilde{\text{SS}}$ structure (see Fig. 2). The $\mu_{1\text{S}\text{Ho}}$ component, which shows a strong decrease between 9–100 K (from $8.9\mu_B$ to $6\mu_B$) and a smaller one between 100–195 K (from 6 to $4.2\mu_B$), falls more abruptly between 195–220 K to $2\mu_B$. Above 220 K it continues to decrease more smoothly up to 293 K where its value is $1.6(3)\mu_B$. Contrary to Ho, the $\mu_{1\text{S}\text{Mn}}$ spiral component decreases only weakly and almost linearly between 9 and 200 K, and falls abruptly above $T_t \approx 200$ K where the skewed spiral gets destabilised and the μ_{2z} component of the collinear structure starts to evolve. At 260 K the

Fig. 7. Magnetization versus temperature for HoMn_6Ge_6 in a field of 0.5 T (reproduced from Ref. [1]).

spiral plane component μ_{1sMn} of Mn has vanished within experimental error while the μ_z component slowly increases and most probably will decrease at even higher temperatures.

The spin reorientation observed for the Mn sublattice is associated with a change in the nature of the exchange interaction between the Mn moments in adjacent cells from a canted one with $\Phi_s < \pi/2$, $\theta_s = 60^\circ$ ($T < T_l$) to an antiferromagnetic one ($T > T_l$) (with $\Phi_s = \pi$ and $\theta_s = \pi/2$). This effect may be accompanied by magnetostriction effects and therefore changes in the lattice parameters. This is displayed in Figs. 6(a) and 6(b), where the values of the c and a parameters show a discontinuity at T_l , the former decreasing and the latter increasing with temperature. On the other hand, the very low moment value of μ_{1sHo} above T_l does not allow an accurate structure determination. Apparently the tilting angle of the spiral axis increases at 293 K so that the skewed spiral goes towards a cycloidal structure. It is difficult to exclude other kinds of ordering for Ho, like a longitudinal amplitude modulation above 260 K.

3. Concluding remarks

The magnetic ordering of RMn_6Ge_6 compounds, as already assumed from the bulk properties in Ref. [1], is complex and comprises commensurate and incommensurate structures and phase transitions related to spin reorientation phenomena. For all the presently known RMn_6Ge_6 compounds studied by us ($R = Dy, Ho, Er$ [5,13] and [14]) the incommensurate wave vectors are pointing along the hexagonal axis and their length decreases with decreasing temperature. It is interesting to note that one observes a systematic decrease of the wave vector length with increasing lattice constants or rare earth ionic radius. The structural magnetic unit in all observed incommensurate phases for ($R = Dy, Ho, Er$) is the same and consists of the triple-layered unit of Mn–R–Mn (at $z \approx 1/4, 0, -1/4$) with the R moments pointing in the opposite direction to the line bysecting the angle $2\phi_{Mn}$ (between Mn at $z = -1/4$ and Mn at $z = 1/4$). This unit changes its direction collectively in the SS and FS types of structures found for Dy and the SS phase observed for $R = Ho$.

The complex distorted spiral (AFSS) with fluctuating Mn moments and angles, found in the (h.t) region 200–260 K of $HoMn_6Ge_6$ is a new type of structure, although it bears some resemblance to the double-cone simple spiral structure observed for YMn_6Ge_6 [14]. Both structures need for their description three Fourier coefficients $m(\pm q_1)$ and $m(q_2)$ pertaining to the wave vectors $q_1 = (0, 0, q_z)$ and $q_2 = (0, 0, 1/2)$, the former corresponding to a spiral structure and the latter to a collinear antiferromagnetic structure for Mn. The main difference is that for the Ho compound the plane of the moment rotation makes an angle of 60° with the c -axis while for the Y compound this angle is zero. In addition, the total moment component of Mn is fluctuating in value and direction while for Y it maintains a constant value and describes a $\pm$ cone. It is also interesting that the phase factor found between the Mn atoms layers at $z = -1/4, 1/4$ related by the centre of symmetry in the (l.t) magnetic spiral unit varies within the series. The angle of $54(2)^\circ$ found for $HoMn_6Ge_6$ is similar to the value reported YMn_6Ge_6 of $56(15)^\circ$ in Ref. [14] but the latter with a larger error.

Contrary to the conical spiral (FSS) observed for $DyMn_6Ge_6$, in the novel AFSS structure observed in $HoMn_6Ge_6$ and the isomorphic Er and the Tm compounds [13] the R and Mn sublattices are less strongly coupled and therefore the two sublattices point in different space directions. Thus it can be concluded that in the (h.t) region the ordering is dominated by the Mn sublattice and that the magnetisation of Ho can be seen as an induced magnetisation originating from the Ho–Mn intersublattice interaction which becomes more important at lower temperatures.

An alternative description of the skewed spiral relative to an orthogonal axial system with x and z parallel to the crystal axes would need three modulation functions, two transversal and one longitudinal with the same wave vector $(0, 0, q_{2z})$, as given by (7):

$$\begin{aligned} m_{nx} &= A \cos 2\pi(q \cdot R_{nj} + \alpha), \\ m_{ny} &= B \cos 2\pi(q \cdot R_{nj} + \beta), \\ m_{nz} &= C \cos 2\pi(q \cdot R_{nj} + \gamma). \end{aligned} \quad (7)$$

In the most general case [16] of an elliptical motion, the spins may be described by six free parameters per atom (three amplitudes and three phases). In our case the transversal components m_{nx} and m_{ny} combine to an elliptical spiral in the hexagonal plane (see Fig. 3, bottom part) with a long axis A and a short axis B and the m_{nz} component corresponds to a longitudinal sine wave. $\alpha + \beta = \pi/2$, $B = m_0 \cos \theta_s$ and $C = m_0 \sin \theta_s$ (the $m_0 = \mu_s$ and θ_s values can be found in Table 1 and Fig. 4). The distorted spiral found for Mn gives rise to two symmetry-independent wave vectors. A case of a distorted flat spiral with fluctuating moments has been reported in Ref. [7] for the compound CsMnF_4 .

The different structures and spin reorientation transitions observed in this family of compounds are the result of the interplay between the long-range and oscillatory indirect exchange interaction and the crystal field induced anisotropy as also observed in other rare earth compounds [16,17]. The existence of a skewed spiral structure as a mode of transition has already been predicted by Sherrington [18] and Elliot [19] for pure Ho metal, but finally it has not been verified according to the more recent investigations discussed extensively in Ref. [20]. A double cone cycloidal structure has been reported in MnSO_4 [21]. We would like to note that powder diffraction does not allow the determination of the phase factors between different Fourier coefficients; thus the models proposed for the SS double cone structure and the AF SS distorted helix cannot rule out the possibility that the two Fourier coefficients originate from different domains corresponding to two distinct structures.

Note added in proof

Recently Prof. B. Malaman brought to our attention a deviation of the collinear model reported by us [5] for the magnetic structural unit $\text{Mn}(+) - \text{Dy} -$

$\text{Mn}(+)$ (with $z = -\frac{1}{4}, 0, \frac{1}{4}$) where $\phi_{\text{Mn}} = 0$. This angle has to be corrected to $\phi_{\text{Mn}} = 20(2)^\circ$ for the DyMn_6Ge_6 compound.

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