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A neutron diffraction study of the magnetic ordering of HoMn₆Ge₆

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Abstract

The hexagonal compound HoMn₆Ge₆ of HfFe₆Ge₆-type of structure (P6/mmm) orders antiferromagnetically below \( T_N = 466 \) K and undergoes a second magnetic transition at \( T_t = 200 \) K. Neutron powder diffraction has shown that the low-temperature phase is a triple skewed spiral with wave vector \( q_1 = (0, 0, q_z) \), consisting of ferromagnetic Ho and Mn layers coupled almost antiparallel in a three-layer sequence: Mn(+)–Ho(−)–Mn(+). The plane of the moments is rotated about an axis in the hexagonal plane so that its normal makes a nonzero angle with \( q_1 \). 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 \( q_1 \). Above \( T_t = 200 \) 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 \( q_1 = (0, 0, q_z) \) and \( q_2 = (0, 0, 1/2) \) corresponding to a distorted spiral with fluctuating Mn moment values and directions. The \( H + q_3 \) satellites (skewed spiral) comprise Ho as well as Mn contributions, while the \( H + q_2 \) comprise only the Mn antiferromagnetic ordering along \( c \). Above 260 K the ordering consists exclusively of the \( H + q_2 \) Mn intensity contributions.

1. Introduction

The magnetic properties of several heavy rare earth (R) compounds of the type RMn₆Ge₆ were determined recently [1,2]. These compounds have the hexagonal HfFe₆Ge₆-type of structure, P6/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 DyMn₆Ge₆ [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 Mn(+), Dy(−), Mn(+) along \( c \).
Fig. 1. Observed, calculated and difference neutron diagrams of HoMn$_6$Ge$_6$ 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 \( T_l = 100 \text{ K} \) to \( T_N \). Below \( T_l \) this length remains constant and has the value \( 8/49 \). At this same temperature \( T_l \) one observes a second-order spin reorientation transition consisting of the development of a ferrimagnetic \( \mu_z \) component resulting from the antiferromagnetically coupled ferromagnetic sublattices: \( \text{Mn}(+), \text{Dy}(-), \text{Mn}(+) \) 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 isomorphic compounds of the \( \text{RMn}_6\text{Ge}_6 \) series having similar bulk properties.

In the present paper we report on the magnetic structure and phase transitions occurring in the compound \( \text{HoMn}_6\text{Ge}_6 \). In a previous investigation [2] it was shown that \( \text{HoMn}_6\text{Ge}_6 \) orders antiferromagnetically below \( T_N = 466 \text{ K} \) and shows non-Curie-Weiss behaviour above \( T_N \). Similarly to \( \text{DyMn}_6\text{Ge}_6 \), a second transition was observed below \( T_N \) (at \( T_l = 200 \text{ K} \) in \( \text{HoMn}_6\text{Ge}_6 \)) [1].

### 2. Neutron diffraction

The powder sample of \( \text{HoMn}_6\text{Ge}_6 \) 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 \( 9-293 \text{ K} \) in order to follow the phase transitions. In view of the expected reduced moment values the (l.t) data were collected with twice the counting rate as the (l.t) data. The data were collected using the ‘DMC’ (double-axis multicounter diffractometer) at the Reactor Saphir, Würenlingen, \( \lambda = 1.7037 \text{ Å} \), using the high-intensity mode. The step increment of the diffraction angle \( 2\theta \) was \( 0.1^\circ \).

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 \( \text{R}^{3+} \) and \( \text{Mn}^{2+} \) as given in Refs. [9] and [10], respectively.

#### Table 1

Refined parameters of \( \text{HoMn}_6\text{Ge}_6 \): (a) in the (l.t) region at \( 9 \text{ K} \), skewed spiral \( \tilde{\text{SS}} \) model \((q_1 = (0, 0, q_z))\), and (b) in the (h.t) region at 240 K, antiferromagnetic AF \((q_2 = 001/2) + \tilde{\text{SS}} \) model. \( \mu_1, (s = x, y, z) \), \( \mu_2, \) are the moment components for (i) the \( \tilde{\text{SS}} \) \((q_1)\) and (ii) the antiferromagnetic \((q_2)\) structures. The direction of \( \mu_z \) is perpendicular to the spiral axis \( \overrightarrow{\gamma} \), \( \theta \) is the tilting angle of the spiral axis with respect to \( c \). \( \phi_{\text{Ho-Mn}} = 2\pi(q_1 \cdot R_{ij} + \phi_i) \) is the phase angle between the Ho and Mn sublattice moments, with \( \phi_i \) as given in Eqs. (2)-(5). \( \phi_0 = 2\pi q_z \) is the spiral turn angle. \( R_{m1} \), \( R_{m2} \) are the reliability factors for the integrated magnetic intensities of the \( \tilde{\text{SS}} \) and the collinear AF structures, respectively.

<table>
<thead>
<tr>
<th>Compound, space group</th>
<th>( \text{HoMn}_6\text{Ge}_6 ) P6/mmm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 9 \text{ K}, \tilde{\text{SS}} ((q_1 = (0, 0, q_z)))</td>
<td>0.2506(4)</td>
</tr>
<tr>
<td>( 240 \text{ K}, \tilde{\text{SS}} + \text{AF} ((q_2 = (0, 0, 1/2)))</td>
<td>0.2506(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z_{\text{Ho}} ) at 1(b), (0, 0, 0)</td>
<td>0.3459(4)</td>
</tr>
<tr>
<td>( z_{\text{Ge}3} ) at 2(e), (0, 0, z)</td>
<td>0.0050(5)</td>
</tr>
<tr>
<td>( c ) (nm)</td>
<td>9.97(5)</td>
</tr>
<tr>
<td>( \text{Mn:} \mu_1, [\mu_B] \mu_2, [\mu_B] \phi_{\text{Mn}} )</td>
<td>-2.03(3), -27(1)</td>
</tr>
<tr>
<td>( \theta ) (deg), ( \phi_0 ) (deg), ( q_z ) in r.l.u.</td>
<td>60(1), 71.24, 0.1978(2)</td>
</tr>
<tr>
<td>( \frac{a}{b} ) (nm)</td>
<td>0.52024(2)</td>
</tr>
<tr>
<td>( c ) (nm)</td>
<td>0.81411(4)</td>
</tr>
<tr>
<td>( R_m(%), R_{w}(%), R_m(%), R_{m2}(%), R_{exp}(%), \chi^2 )</td>
<td>4.65, 7.94, 5.64, -1.88, 17.8, 9.0, 1.88, 13.4</td>
</tr>
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</table>
2.1. The \((l.t)\) magnetic structure: skewed spiral \(SS\) \((q_l = (0, 0, q_z))\)

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 \(q_l = (0, 0, q_z)\) as already observed in DyMn\(_6\)Ge\(_6\) [5]. Contrary to DyMn\(_6\)Ge\(_6\), 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 \(I_{001} \mp I_{hkl} \mp q_z\) is much larger for the Ho compound than for the Dy compound. This fact indicates a deviation from the SS model proposed for DyMn\(_6\)Ge\(_6\). We considered possible triangular structures in the basal plane allowed by the symmetry as given in the symmetry analysis [11] of the \(P6/\text{mmm}\) 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 (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 SS model the moments of the Mn and Ho sublattices are coupled almost antiferromagnetically and point in the same direction within the corre-

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**Table 2**

Some of the observed and calculated integrated neutron intensities of HoMn\(_6\)Ge\(_6\) at 9 K. The indexing of the magnetic satellites \((H \pm q_l)\) refers to \(q_z = 0.1979(2)\).

<table>
<thead>
<tr>
<th>(h)</th>
<th>(k)</th>
<th>(l)</th>
<th>(2\theta) (deg)</th>
<th>(I_{\text{calc}}) (nucl.)</th>
<th>(I_{\text{obs}}) (total)</th>
<th>(h)</th>
<th>(k)</th>
<th>(l)</th>
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<th>(I_{\text{calc}})</th>
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<td>590</td>
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Fig. 2. (a) The triple skewed spiral model. \( \Phi_s \) 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 \( q_l \). (b) the distorted skewed spiral with fluctuating Mn moments observed in the region 200–260 K in HoMn\(_6\)Ge\(_6\). (c) Coordinate system for a spin vector rotating in the plane \((u, v)\). \( q \) is the wave vector, \( w \) is the spiral axis and \( e \) is the scattering vector. \( \theta_s \) the spiral tilting angle with respect to the \( c \)-axis.

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

\[
m_q = m_0 \left( u + i v \right) e^{i \phi_q},
\]

where \( u \) and \( v \) are two orthogonal unit vectors, in the plane of the moment rotation, \( m_0 \) is the moment value, and \( \phi_q \) 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\(_6\)Ge\(_6\) [5], the angle \( (\theta_s) \) 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 \( i \)th cell is given by the expression:

\[
m_{ji}(R_i) = m_0 \left[ u \cos 2\pi(q_i \cdot R_{ij} + \phi_j) + v \sin 2\pi(q_i \cdot R_{ij} + \phi_j) \right]
\]

where \( R_i \) is the position of the \( i \)th unit cell. Referring to an orthogonal system with \( u \) and \( v \) parallel to the crystal axes, expression (2) may be rewritten:

\[
m_{ji}(R_i) = \mu_{is} \left[ x \cos 2\pi(q_i \cdot R_{ij} + \phi_j) + y \cos \theta_s + z \sin \theta_s \right] \times \sin 2\pi(q_i \cdot R_{ij} + \phi_j),
\]

where \( \mu_{is} \) 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 \( |F|^2 \):

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

where \( \omega \) 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 \( \phi_j \) 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 \( \theta_s \) 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 \( \mu_{1sHo} \) and \(-2.03(2)\mu_B \) for \( \mu_{1sMn} \). These values are very close to the saturation values of Ho\(^{3+}\) (\( g_I\mu_B = 10\mu_B \)) and Mn\(^{2+}\), respectively. The low values of \( R_n = 4.6% \) and \( R_{ml} = 5.64% \) 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 \((q_2 = (0, 0, 1/2)) + \text{skewed spiral } (SS) \ (q_1 = (0, 0, q_z)).\)

The magnetic measurements have indicated a phase transition around \(T_t = 200\) K. The 240 K neutron diffraction pattern (see Fig. 1, top part), has been collected well above \(T_t\) and therefore is expected to provide information on the (h.t) magnetically ordered state. The refined parameters given in Table 1 confirm the HfFe_{6}Ge_{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_{6}Ge_{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_{6}Ge_{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 \(q_1 = 0.238(2)\).

\[
\begin{array}{cccccccccccc}
\ h & k & l & 2\theta \text{ (deg)} & I_{\text{calc}} \text{ (nucl.)} & I_{\text{calc}} \text{ (mag.)} & I_{\text{obs}} \text{ (total)} & h & k & l & 2\theta \text{ (deg)} & I_{\text{calc}} & I_{\text{obs}} \\
\hline
0 & 0 & 1/2 & 5.96 & 0 & 0 & 0 & 0 & 1 & 0 & 9.138 & 769 & 840 \\
0 & 0 & 1 & 12.008 & 58 & - & 50 & 0 & 0 & 1 & 14.885 & 184 & 58 \\
1 & 0 & 0 & 21.720 & 9344 & - & 9340 & 0 & 0 & 2 & 21.235 & 587 & 815 \\
1 & 0 & 1/2 & 2406 & 2440 & (1 & 0 & 0 & (0) & 21.912 & 1350 & 1328 \\
0 & 0 & 2 & 24.150 & 34585 & - & 37901 & (1 & 0 & 0 & -1 & 1) & 23.607 & 498 & 426 \\
1 & 0 & 1 & 24.889 & 96 & - & 189 & (1 & 0 & 0 & -1) & 26.434 & 430 & 420 \\
1 & 0 & 3/2 & 28.385 & 684 & 732 & 0 & 0 & 2 & 27.080 & 327 & 319 \\
1 & 0 & 2 & 32.703 & 16411 & - & 16897 & (0 & 0 & 1 & -2) & 30.559 & 92 & 928 \\
0 & 0 & 3 & 36.575 & 2655 & - & 3497 & (0 & 0 & 1 & -2) & 34.488 & 72 & 116 \\
1 & 0 & 5/2 & 37.603 & 156 & 150 & 0 & 0 & 3 & 33.578 & 30 & 239 \\
1 & 1 & 0 & 38.093 & 54940 & - & 50646 & (1 & 0 & 0 & -1) & 38.209 & 350 & 327 \\
1 & 1 & 1/2 & 38.598 & 558 & 846 & (1 & 0 & 0 & -1) & 39.257 & 28 & 221 \\
1 & 1 & 1 & 40.082 & 39 & - & 82 & (0 & 0 & 1 & -3) & 40.847 & 156 & 120 \\
1 & 1 & 3/2 & 42.458 & 264 & 264 & (1 & 0 & 0 & -3) & 41.110 & 156 & 1050 \\
1 & 1 & 5/2 & 42.939 & 12186 & - & 12707 & (1 & 0 & 0 & -3) & 42.419 & 48 & 39 \\
2 & 0 & 0 & 44.274 & 2074 & - & 2037 & (1 & 0 & 0 & -3) & 44.019 & 48 & 39 \\
2 & 0 & 1/2 & 44.721 & 2556 & 2556 & (1 & 0 & 0 & -3) & 44.376 & 0 & 0 \\
1 & 1 & 2 & 45.614 & 14278 & - & 13792 & (1 & 0 & 0 & -3) & 45.306 & 136 & 124 \\
2 & 0 & 1 & 46.042 & 25 & - & 26 & (1 & 0 & 0 & -3) & 45.610 & 104 & 102 \\
2 & 0 & 3/2 & 48.181 & 1914 & 1656 & (1 & 0 & 0 & -3) & 46.964 & 110 & 214 \\
0 & 0 & 4 & 49.446 & 102 & - & 99 & (1 & 0 & 0 & -3) & 47.361 & 43 & 66 \\
1 & 1 & 5/2 & 49.439 & 108 & 96 & (1 & 0 & 0 & -3) & 49.601 & 384 & 438 \\
2 & 0 & 2 & 51.069 & 1068 & - & 1689 & (1 & 0 & 0 & -3) & 51.674 & 85 & 38 \\
1 & 1 & 3 & 53.837 & 8193 & - & 8986 & (1 & 0 & 0 & -3) & 52.631 & 312 & 412 \\
2 & 0 & 5/2 & 882 & 978 & (1 & 0 & 0 & -3) & 56.114 & 61 & 33 \\
1 & 0 & 4 & 54.625 & 2357 & - & 2617 & (1 & 0 & 0 & -3) & 56.114 & 61 & 33
\end{array}
\]
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 \( \mu_2 \) value for Ho (\( \mu_2 \) 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.t.) incommensurate structure of DyMn\(_6\)Ge\(_6\) led to the rather high value of 49\% for the reliability factor \( R_{\text{m}} \). A refinement using the skewed spiral SS model (see Table 1) lowered the \( R_{\text{m}} \) 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\(_6\)Ge\(_6\). 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 (\( \mu_{1s} \)) perpendicular to \( w \), while the collinear antiferromagnetic structure comprises exclusively Mn contributions. Because the latter Mn moment components (\( \mu_{2z} \)) 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 \( \mu_{1s} \) (SS) component, an antiferromagnetic \( (+ -- +) \) \( \mu_{2z} \) component when referring to the \( c \)-doubled magnetic cell and can be given as a superposition of the observed Fourier coefficients/atom \( m(q_{1s}) \) and \( m(q_{2z}) \) 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):

\[
m_{ji}(R_l) = \mu_{1s}[x \cos 2 \pi(q_{1s} \cdot R_l) + \phi_{1s}] + (y \cos \theta_{1s} + z \sin \theta_{1s}) \times \sin 2 \pi(q_{1s} \cdot R_l + \phi_{1s})] + \mu_{2z\text{Mn}}(-1)^l.
\]

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

\[
\mu_{1s} \pm \mu_{2z} = \sqrt{\mu_{1s}^2 + \mu_{2z}^2} \pm \sqrt{2 \mu_{1s} \mu_{2z} \cos \alpha} = \sqrt{\mu_{1s}^2 + \mu_{2z}^2} \pm \sqrt{\mu_{1s} \mu_{2z}} \cos \alpha
\]

(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 \( \mu_{\text{TMn}} \) are 1.29\( \mu_B \) and 0.5\( \mu_B \). The corresponding angle limits between \( \mu_{\text{TMn}} \) and the \( c \)-axis are 10 and 28°.
The essential difference between the (l,t) skewed spiral (SS) and the AF 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 SS structure, which consists of (a) a triple SS unit of three ferromagnetic Mn–Ho–Mn layers (at \( z = -1/4, 0, \text{and} 1/4 \)) which changes its orientation collectively (within the tilted spiral planes) by \( \Phi_z = 2\pi q_z = 85.3^\circ \) when going from one cell to the other along the direction of the wave vector \( q_z \); and (b) collinear antiferromagnetic \( \mu_{z\gamma} \) 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
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 (I.t) region characterised by the presence of only the SS phase. Between 9–55 K the wave vector and consequently the spiral angle \( \Phi_s \) 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 \( \theta_s = 60° \) 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-
cients of $\mu_{15\text{Ho}}$ and $\mu_{15\text{Mn}}$ 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 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 $\mu_{15\text{Ho}}$ and $\mu_{15\text{Mn}}$, both residing in the tilted planes of the SS structure (see Fig. 2). The $\mu_{15\text{Ho}}$ 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 $\mu_{15\text{Mn}}$ 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 $\mu_{2z}$ component of the collinear structure starts to evolve. At 260 K the
spiral plane component $\mu_{1s,Mn}$ of Mn has vanished within experimental error while the $\mu_z$ 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 $\Phi_q < \pi/2$, $\theta_q = 60^\circ$ ($T < T_t$) to an antiferromagnetic one ($T > T_t$) (with $\Phi_q = \pi$ and $\theta_q = \pi/2$). 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 $T_t$, the former decreasing and the latter increasing with temperature. On the other hand, the very low moment value of $\mu_{1s,Mn}$ above $T_t$ 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$_6$Ge$_6$ 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$_6$Ge$_6$ 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 $z = -\frac{1}{4}$ and Mn at $z = \frac{1}{4}$). 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$_6$Ge$_6$ is a new type of structure, although it bears some resemblance to the double-cone simple spiral structure observed for YMn$_6$Ge$_6$ [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 ± 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 (1.0) magnetic spiral unit varies within the series. The angle of 54(2)° found for HoMn$_6$Ge$_6$ is similar to the value reported YMn$_6$Ge$_6$ of 56(15)° in Ref. [14] but the latter with a larger error.

Contrary to the conical spiral (FSS) observed for DyMn$_6$Ge$_6$, in the novel AFSS structure observed in HoMn$_6$Ge$_6$ 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 $(0, 0, q_{zz})$, as given by (7):

$$m_{nx} = A \cos 2\pi(q \cdot R_{nj} + \alpha),$$

$$m_{ny} = B \cos 2\pi(q \cdot R_{nj} + \beta),$$

$$m_{nz} = C \cos 2\pi(q \cdot R_{nj} + \gamma).$$
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 $m_0 = \mu_0$ and $\theta_s$ values can be found in Table 1 and Fig. 4).

The distorted spiral found for Mn gives rise to two distinct Fourier coefficients associated with 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 Mn(+)–Dy–Mn(+) (with $z = -\frac{1}{4}, 0, \frac{1}{4}$) where $\phi_{Mn} = 0$. This angle has to be corrected to $\phi_{Mn} = 20(2)\degree$ for the DyMn$_6$Ge$_8$ compound.

**References**

[13] P. Schobinger-Papamantellos et al., to be published.