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Skewed spiral magnetic structure in ErMn₆Ge₆

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Abstract

ErMn₆Ge₆ adopts the HfFe₆Ge₆-type structure and orders antiferromagnetically below \( T_N = 475 \) K. At \( T_i = 80 \) K it undergoes a first-order spin reorientation transition. Neutron powder diffraction has shown that the low temperature phase is a triple skewed spiral with wave vector \( q_i = (0, 0, q_z) \), consisting of three ferromagnetic Er and Mn layers \( \text{Mn}(z = -1/4) - \text{Er}(z = 0) - \text{Mn}(z = 1/4) \) with the Er moments orientated opposite to the line bisecting the Mn–Mn interplanar angle \( 2\phi_{Mn} = 70 \) deg. The spiral axis makes a non-zero angle with \( q_i \). The wavevector length is incommensurate with the crystal lattice and weakly temperature dependent. Below 70 K, \( q_i \) locks in to the commensurate value \( 1/4 \). Above \( T_i = 80 \) K a decoupling of the Mn and Er sublattices sets in, and the skewed spiral structure is destabilized. In the transition region 80–160 K the magnetic ordering is described as a superposition of two Fourier coefficients per atom, associated with the wave vectors \( q_1 = (0, 0, q_z) \) and \( q_2 = (0, 0, 1/2) \). The \( H + q_1 \) satellites (skewed spiral) comprise Er as well as Mn intensity contributions, while only the Mn antiferromagnetic ordering along \( c \) contributes to the \( H + q_2 \) satellites. Above 170 K one observes exclusively \( H + q_2 \) Mn intensity contributions.

Keywords: Skewed spiral; Magnetic structure; Neutron powder diffraction

1. Introduction

Ternary rare earth (R) compounds of the type RMn₆Ge₆ with HfFe₆Ge₆-type structure (space group \( P6/mmm \)) [1,2] are of particular interest because their magnetic properties present at least two ordering temperatures [3,4]. This behaviour is related to the fact that both the rare earth and the Mn atoms are carriers of magnetic moments that interact in a complex way giving rise to numerous magnetic phase transitions.

Neutron diffraction studies on the RMn₆Ge₆ (R = Y, Dy, Ho) [5–7] compounds have shown the existence of a large variety of complex spiral magnetic structures that require more than one Fourier coefficient per atom for their description, including the \( T \)-dependent phase transitions between them. The observed structures comprise simple (SS) and ferrimagnetic spirals (FSS) (R = Dy), double cone antiferromagnetic AFSS (Y), skewed (SS) and distorted skewed AFSSS spirals (R = Ho). A common feature of these structures is the triple magnetic structural unit consisting of two ferromagnetic Mn layers and one ferromagnetic R layer (001) \( \text{Mn}(z = -1/4) - \text{Er}(z = 0) - \text{Mn}(z = 1/4) \) with the R moments orientated opposite to the line bisecting the Mn–Mn interplanar angle \( 2\phi_{Mn} \). The atomic moments of this unit change direction by an amount \( \phi_z = 2\pi q_z \), collectively in the direction of the wavevector \( q_i = (0, 0, q_z) \) which has a temperature dependent length. The origin of the magnetic phase transition is the temperature dependent competition between the anisotropies of the two sublattices which leads to spin reorientation phenomena.

It is of interest to extend this study to the compound ErMn₆Ge₆ which orders antiferromagnetically below \( T_N = 475 \) K and shows non-Curie–Weiss behaviour above \( T_N \). Similar to other RMn₆Ge₆ isomorphs, a second transition was observed below about 100 K in ErMn₆Ge₆ [3].

2. Neutron diffraction

The ErMn₆Ge₆ sample used for neutron diffraction was prepared by the methods given in [6]. Data between 1.5 and 200 K were collected on the G4.1 diffractometer (800 cell multidetector) at the Orphéon reactor (LLB Saclay), \( \lambda = 2.427 \) Å. The step increment in \( 2\theta \) was 0.1°. The data were evaluated using the Fullprof program [8].
2.1. The low temperature (LT) magnetic skewed spiral structure SS \( (q_1=(0, 0, q_{1z})) \)

The LT neutron pattern at 1.5 K shown in Fig. 1 comprises, next to the nuclear reflections, a single set of magnetic satellites associated with a wavevector along the c-axis \( q_1=(0, 0, q_{1z}) \) as already observed in other RMn\(_6\)Ge\(_6\) compounds [5-7]. The refined wavevector value \( q_{1z}=0.2502(1) \) corresponds to a spiral angle of 90.08(1)°. The relative intensities of the observed magnetic satellites \( I_{001}/I_{001+} \) is similar to that found for the Ho compound at LT. This fact justifies the use of the triple skewed spiral (SS) model proposed for HoMn\(_6\)Ge\(_6\) in [7] displayed in Fig. 2. The refined parameters are summarized in Table 1.

In the SS structural unit Mn\((z=-1/4)\)-Er\((z=0)\)-Mn\((z=1/4)\) the phase angle \( \pi \pm \varphi_{\text{Mn}} \) between the moments of the Mn and Er sublattices is \( \pm 145(2)° \). The Er moments are opposite to the line bisecting the Mn-Mn interplanar angle \( (2\varphi_{\text{Mn}}=70°) \). This corresponds to an almost zero residual moment within the spiral plane. The moments of the magnetic structural unit change their direction collectively by a constant angle of 90.08(1)° when going from one cell to the other along c.

The moment distribution \( \mu_{nj} \) of atom \( j \) in cell \( n \) situated at \( R_{nj}=R_n+R_j \) is given by

\[
\mu_{nj}=\mu_0[\cos 2\pi(q_1\cdot R_{nj}+\varphi_j)\cdot u + \sin 2\pi(q_1\cdot R_{nj}+\varphi_j)\cdot v]
\]

(1)

\( \varphi_j \) is the \( j \) phase factor, \( u, v \) are two orthogonal unit vectors, in the spiral plane (see Fig. 2).

The normal to the spiral plane \( w \), or the spiral axis, may have any orientation relative to \( q \). The angle \( \theta_s \) of the spiral axis with \( q \) is zero for a flat spiral SS, as found in DyMn\(_6\)Ge\(_6\) [6], while in the SS spiral the plane of the moments is rotated about an axis in the hexagonal plane so that \( \theta_s \neq 0 \), see Fig. 2. The refined tilting angle at 1.5 K is \( \theta_s=60° \). The ordered moment

Fig. 1. Observed, calculated and difference neutron diagrams of ErMn\(_6\)Ge\(_6\) measured at 1.4 K and 130 K. 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 130 K data.
2.2. The AF (\(q_z = (0, 0, 1/2)\)) + skewed spiral (SS) high temperature (HT) magnetic structure

The 130 K neutron diffraction pattern (see Fig. 1), collected well above \(T_t = 80\) K [3] is expected to provide information on the HT state. The refined parameters (see Table 1) confirm the HfFe6Ge6-type structure [1,2]. In addition to the LT magnetic reflections \(q_i = (0, 0, q_z)\) with \(q_z = 0.246(1)\) rlu, one observes a second set of weak magnetic reflections associated with the wave-vector \(q = (0, 0, 1/2)\) corresponding to a cell doubling along \(c\).

The refined phase angle \(\phi_{Mn}\) and the refined tilting angle \(\theta_{Mn} = 54(4)^\circ\) of the skewed SS spiral model, are unchanged within 3\(\sigma\) limits. The moments are strongly reduced and take the values 1.55(1) \(\mu_B\) per Er and \(-0.62(4)\) \(\mu_B\) per Mn at 130 K. From the extinguished 0, 0, //2 peaks one may assume the same collinear antiferromagnetic arrangement as found in HoMn6Ge6 along the \(c\) direction. The refinement resulted in a zero moment \(\mu_{z2}\) value for Er and an antiparallel arrangement ((++++) or (---)) of the \(\mu_{z2Mn} = 1.04(23)\) \(\mu_B\). This means that above \(T_t\), the two sublattices have different preferred directions of antiferromagnetism and seem to be only weakly coupled. The resulting structure for Mn atoms obtained by superposition of the Fourier components \(\mu_{\pm q_i}\) and \(\mu_0(q_i)\) is a complex distorted skewed spiral structure AFSS as shown in Fig. 2. Referring to an orthogonal system with \(x, z\), parallel to the crystal axes \(a\) and \(c\), the moment of the \(j\)th Mn atom in the \(n\)th cell is given for this model by

\[
\mu_{n} = \mu_{z2Mn}[x \cos 2\pi(q_i \cdot R_m) + \phi_i] + (y \cos \theta + z \sin \theta_i) \sin 2\pi(q_i \cdot R_m + \phi_i)]
\]

\[
+ \mu_{z2Mn}(-1)^jz
\]

The resulting parameters of ErMn6Ge6 (P6/mmm)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1.4 K, SS ((q_i = (0, 0, q_z)))</th>
<th>130 K, SS+AF ((q_z = (0, 0, 1/2)))</th>
<th>190 K, AF ((q_i = (0, 0, 1/2)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er at ((b)， (0, 0, 0))</td>
<td>(0.2487(14))</td>
<td>(0.2522(15))</td>
<td>(0.2517(19))</td>
</tr>
<tr>
<td>(z_{Gc1}) at ((d)， (1/3, 2/3, 0))</td>
<td>(0.3482(9))</td>
<td>(0.3478(8))</td>
<td>(0.3464(9))</td>
</tr>
<tr>
<td>(B_{\mu2}) (nm)</td>
<td>(0.012)</td>
<td>(0.012)</td>
<td>(0.012)</td>
</tr>
<tr>
<td>Er, (\mu_{z2}) ((\mu_B))</td>
<td>(8.34(7))</td>
<td>(1.55(1))</td>
<td>(-0.62(4))</td>
</tr>
<tr>
<td>Mn, (\mu_{z2}) ((\mu_B)), (\phi_{Mn}) (deg)</td>
<td>(-1.81(1)), (-35(2))</td>
<td>(-0.62(4)), (1.04(3), 31(2))</td>
<td>(-1.02(2))</td>
</tr>
<tr>
<td>(a) (nm), (c) (nm)</td>
<td>(0.5207(3), 0.3464(7))</td>
<td>(0.5216(0), 0.8139(17))</td>
<td>(0.5220(7), 0.8144(16))</td>
</tr>
<tr>
<td>Ra (%), Rwp (%), Rml (%)</td>
<td>(6.22, 13.6, 6.5)</td>
<td>(8.4, 15.5, 22)</td>
<td>(7.8, 17.6, -)</td>
</tr>
<tr>
<td>Rml2 (%), Relp (%), (x^2)</td>
<td>(2.1, 16.1)</td>
<td>(17.6, 4.69, 14.7)</td>
<td>(22, 4.48, 15.4)</td>
</tr>
</tbody>
</table>

\(\mu_{z2}, \mu_{z2}\) are the moment components for (i) the SS, (ii) the antiferromagnetic structures. \(\theta_i\) is the tilting angle of the spiral axis with respect to \(c\). \(\phi_{Mn} = \pm 2\pi(q_i \cdot z_{Gc1} + \phi)\) is the phase angle of the Mn atoms at \(z = \pm 1/4\) and \(\phi\) as given in (1). \(\Phi_i = 2\pi \Phi_p\) is the spiral interplanar angle. Rml1, Rml2 are the reliability factors for the integrated magnetic intensities of the SS and the collinear AF structures respectively.

Fig. 2. (a) The triple skewed spiral model. \(\Phi_i\) is the interplanar spiral turn angle. The structural unit consists of the three \((+)Mn-(--)Er-(+)Mn\) layers which change their moment direction collectively along the direction of the wavevector \(q_i\) in the plane \((u, v)\). \(w\) is the spiral axis, \(\theta_i\) the spiral tilting angle with respect to the \(c\) axis. (b) The complex distorted skewed spiral observed in the region 80-160 K in ErMn6Ge6.

values 8.34(7) \(\mu_B\) for \(\mu_{z2Er}\) and \(-1.81(1)\) \(\mu_B\) for \(\mu_{z2Mn}\) are very close to the saturation values of Er\(^{3+}\) \((g\mu_B = 9/xB)\) and Mn\(^{2+}\) respectively. The low values of the reliability factors lend credence to the correctness of the model proposed. A small amount of an impurity magnetic phase denoted (i) in Fig. 1 was found to coexist with the main phase up to 5 K.
The resulting structure for Mn is therefore a distorted spiral structure with fluctuating Mn moment values and directions. The limits of the $\mu_{Tn}$ (total moment) fluctuation are $\mu_{1s} \pm \mu_{2s}$.

The refinement of the 190 K data also included in Table 1 shows that at this temperature the ordering is restricted exclusively to the Mn collinear antiferromagnetic moment arrangement.

2.3. Mn spin reorientation and thermal evolution of the magnetic moment components

Fig. 3(a) shows the temperature dependence of the intensity of the magnetic satellites 000$^\pm$ and 001$^-$ proportional to $(\mu_{1Er} \cos \phi)^2$ and $(\mu_{1Er} + 6 \sin \phi \mu_{2Mn})^2$, $\phi = 2\pi (q_{Er} - q_{Mn})^2$ respectively. The moment components of $\mu_{1Er}$ and $\mu_{1Mn}$ confined to the tilted SS planes are seen in Fig. 3(b) to display a different temperature dependence, at least below 80 K where a change in slope can be seen. The destabilization of the SS structure is clearly defined by the appearance of reflections associated with $q_2 = (0, 0, 1/2)$ which mark the transition occurring at $T_t = 80$ K.

Fig. 3(a) allows us to distinguish three regions of different magnetic behaviour with respect to the number of propagation vectors present in the neutron patterns at various temperature intervals. The thermal evolution of all magnetic moment components (Fig. 3(b)) derived by refining a set of neutron data taken at various temperatures provides some insight to the ordering mechanism and the phase transition at $T_t$, which consists in the decoupling of the two sublattices and/or the setting in of the Mn spin reorientation.

(i) The 1–80 K LT region is characterized by the presence of satellites of only the SS phase. The wavevector and consequently the spiral angle $\Phi$, remain unchanged with temperature up to 70 K. It is remarkable that the wavevector has, within experimental error, the commensurate value $q_{1s} = 1/4$ below 70 K as observed for Er metal [9]. Above 70 K (Fig. 3(c)) its value changes smoothly to smaller values. At $T_t = 80$ K the $\mu_{1sMn}$ sublattice moment maintains its saturation value while that of Er has decreased with temperature (Fig. 3(b)).

(ii) In the 80–160 K region one observes two sets of satellites associated with the wavevectors $\pm q_1$ and $q_2$. Just above $T_t = 80$ K the SS spiral is destabilized. Both sublattices display abrupt changes in their magnetic

![Fig. 3](image-url)

Fig. 3. (a) Thermal variation of the neutron intensity of the magnetic satellites 000$^\pm$ and 001$^-$, $q_1$, and of the antiferromagnetic peak 1, 0, 1/2. (b) Temperature dependence of the rotating moment components $\mu_z$, ($z = x, y, z$) of the triple skewed spiral structure of ErMn$_6$Ge$_6$. Also shown is the collinear $\mu_{2sMn}$ moment component associated with $q_2 = (0, 0, 1/2)$. (c) Thermal variation of the skewed spiral turn angle $\Phi$ and thermal variation of the spiral wavevector length. (d) Thermal variation of the lattice constants for the compound ErMn$_6$Ge$_6$. 
moment components. The $\mu_{1/2}$ spiral moment component drops to half its value while Mn exhibits a reorientation, its total value fluctuating between the limits $\mu_{1/2\text{Mn}} \pm \mu_{2\text{Mn}}$.

(iii) In the 160–200 K region, the magnetic ordering is mainly described by the wavevector $q_z$, and is most probably restricted to the collinear antiferromagnetic arrangement of the Mn atoms. The ordered moment value of $\mu_{1/2\text{Er}}$ is already close to zero at 170 K while a peak broadening can be observed in the low angle region, which concerns the propagation vector $q_1$, due to short-range effects.

The spin reorientation observed for the Mn sublattice is associated with a change in the Mn–Mn moment angles in adjacent cells, from a canted antiferromagnetic with $\phi_0 = \pi/2$, $\theta_0 = 60^\circ$ arrangement to a collinear arrangement $\phi_0 = \pi$, $\theta_0 = \pi/2$. This effect may be accompanied by magnetostriction effects and therefore changes in the lattice parameters. The values of the $c$ and $a$ parameters show (see Fig. 3(d)) a discontinuity at $T_1$, the former decreasing and the latter increasing with temperature.

3. Concluding remarks

The magnetic ordering of RMn$_6$Ge$_6$ compounds, as already assumed from the bulk properties in Refs. [3,4], is rather complex showing commensurate and incommensurate structures and phase transitions related to spin reorientation phenomena. For all the presently known RMn$_6$Ge$_6$ compounds (R = Y, Dy, Ho, Tm) [5–7] it seems that the high temperature ordering is dominated by Mn ordering and that the rare earth ordering is induced. The $T_N$ values increase with decreasing lattice constant. With the exception of the SS spiral in DyMn$_6$Ge$_6$, all isomorphs including Lu and Sc compounds display a collinear antiferromagnetic ordering of the Mn moments along c in the HT region associated with a doubling of the c-axis. The stability region of this structure increases with decreasing ionic rare earth radius, the spin reorientation transition temperatures $T_1$ decreasing when going from Ho to Er and Tm. For all reported SS structures appearing in the LT region one observes a systematic increase in the wavevector length with decreasing lattice constant or decreasing rare earth ionic radius, indicating a possible change in the strength or nature of the exchange interaction.

The complex distorted skewed spiral (AFSS) found in LT regions of RMn$_6$Ge$_6$ (R = Ho, Er, Tm) is a new type of structure. However, it bears some resemblance to the double cone simple spiral AFSS structure observed for YMn$_6$Ge$_6$ [5]. Both structures require two Fourier coefficients per atom for their description, pertaining to the wavevectors $q_1 = (0, 0, q_z)$ and $q_2 = (0, 0, 1/2)$. The main difference is the tilting angle the spiral axis makes with the c-axis and that in the (AFSS) structure the Mn total moment $\mu_{\text{TMn}}$ fluctuates within the limits $\mu_{1/2\text{Mn}} \pm \mu_{2\text{Mn}}$ as given by Eq. (2).

In the most general case of an elliptical arrangement, the spins may be described by six free parameters per atom (three amplitudes and three phases) corresponding to two transversal and one longitudinal modulation function with the same wave vector:

$$\mu_{\text{spin}} = A_{x,y} \cos 2\pi(q \cdot R + \varphi_x) = \alpha x, y, z$$

(3)

In the case of the skewed spiral the transversal components $A_{x,y}$ and $A_{x,y}$ combine to an elliptical spiral in the hexagonal plane with $A_x \neq A_y$ and $\varphi_x + \varphi_y = \pi/2$. $A_z = \mu_0 A_{x,y} = \mu_0 \cos \theta_0$, $A_z = \mu_0 \sin \theta_0$, while the ordering of the distorted skewed spiral requires for its description further Fourier coefficients. The existence of a skewed spiral structure has already been predicted by Sherrington [10] and Elliot [11] for pure Ho metal but it has not been verified according to [12]. A skewed spiral was found in the Tb$_{0.5}$Er$_{0.5}$ alloy [13] and a complex spiral with fluctuating moments has been observed in CsMnF$_4$ [8].

References


Note added in proofs

Owing to a misinterpretation of the results obtained for the compound DyMn$_6$Ge$_6$ by FULLPROF [8] the phase angle $\theta_{\text{TMn}}$ was taken by us in previous reports [6,7] to be equal to zero whereas it is equal to $\theta_{\text{TMn}} = 20(1)^\circ$, as pointed out by Venturini in Ref. [10].