Magnetism of ErMn₆Ge₆

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Abstract. The magnetic properties of ErMn₆Ge₆ have been investigated on single crystals that have been prepared in an In flux. The compound orders antiferromagnetically at 475 K and undergoes a second magnetic-ordering transition at 120 K. The evolution of the magnetization in the ordered state as a function of temperature and the magnetization processes have been investigated in fields up to 14 T. At 4.2 K, the magnetization process has been studied in pulsed fields up to around 50 T.

1. Introduction
The RMn₆Ge₆ (R = rare-earth element) compounds, that crystallize in the hexagonal HfFe₆Ge₆-type of structure (P6/mmm), are of particular interest because they exhibit a wealth of magnetic phase transitions and a wide variety of complex spiral magnetic structures, as pointed out by neutron diffraction studies [1]. The crystal structure of these compounds consists of Mn-(R,Ge)-Mn and Mn-Ge-Ge-Ge-Mn slabs that are alternately (Mn-(R,Ge)-Mn-Ge-Ge-Ge-Mn-) stacked along the c-axis. The first studies of the magnetic properties have been carried out more than one decade ago on polycrystalline material [2, 3]. ErMn₆Ge₆ orders antiferromagnetically at T_N = 475 K [2]. At about 100 K, the compound has been reported to undergo a second transition [3].

In this paper, we investigate the magnetization behaviour of single-crystalline ErMn₆Ge₆ in the temperature range from 2 K up to 600 K.

2. Experimental
ErMn₆Ge₆ single crystals were obtained by using an In flux. A mixture of ErMn₆Ge₆ and ErGe₆ alloys, obtained before by induction melting, and Ge were compacted into pellets and put into an alumina crucible with a large amount of In metal, giving rise to the total atomic composition ErMn₆Ge₆In₃₀. The crucible was put into silica tube and sealed under protective argon atmosphere. The tube was placed in a furnace and quickly heated up to 1273 K (50 K/h) where it remained for 24 h. The furnace was then slowly cooled down to 1223 K (6 K/h), heated again up to 1263 K at the same rate and finally slowly cooled down to 873 K for 65 h. After this thermal process, the alumina crucible was put
into another silica tube with quartz-wool stopper and sealed under argon (100 mm Hg). The tube was quickly removed from the furnace, inverted and centrifuged manually by using a David's sling device. After this treatment, the single crystals remain on the quartz-wool stopper and the In flux lies at the bottom of the tube. The remaining flux was dissolved in diluted hydrochloric acid. The crystals display a thin hexagonal platelet-like shape and have masses up to 2 mg. The crystals have been characterized by Guinier patterns (Co-Kα) with high purity Si as internal standard (a = 5.43082 Å) and by Weissenberg photographs and found to possess the HfFe6Ge6 structure (P6/mmm) with lattice parameters \(a = 5.219(4) \text{ Å}\) and \(c = 8.153(7) \text{ Å}\). The In content was checked at the Service Commun d'Analyse par Microsondes Electroniques de l'Université de Nancy I-Henri Poincaré, by using the SX50 electron probe and was found to be below the detection limit (\(C_{\text{In}} < 0.1 \%\)). Some presence of Si (0.1 %) was observed.

Magnetization measurements in the temperature range from 2 K to 600 K and in magnetic fields up to 14 T, applied along the \(a\)-axis and along the \(c\)-axis, were carried out at the Joint Laboratory for Magnetic Studies in Prague by using a PPMS Vibrating Sample Magnetometer. The high-field magnetization has been measured in the Center for Quantum Science and Technology under Extreme Conditions (KYOKUGEN) at Osaka University, in pulsed fields up to 52 T with pulse duration of 20 ms, applied along the \(a\)-axis and along the \(c\)-axis.

3. Results and discussion

The temperature dependences of the magnetization measured on an ErMn6Ge6 single crystal with needle-like shape of about 1.9 mg in a magnetic field of 0.8 T, applied parallel and perpendicular to the \(c\)-axis, are shown in Fig. 1. The investigated crystal is found to order magnetically at about 475 K, which is in perfect agreement with the value reported in literature [2]. The second magnetic-order transition, reported earlier to occur around 100 K [3], is found around 115 K. It is likely that this difference should be attributed to a difference in composition.

Neutron diffraction carried out on ErMn6Ge6 has pointed out that the magnetic structure at 1.5 K is a triple skew spiral structure with wave vector \(q = (0,0,q_z)\) with the commensurate value \(q_z = 0.25\) [4]. The magnetic structural units of the spiral are the magnetic moments of Mn-(Er,Ge)-Mn slabs which consist of two Mn layers, in which the moments are ferromagnetically ordered, and an Er layer in which the moments are ferromagnetically ordered as well. The ferromagnetic moments of two neighbouring Mn-layers of neighbouring slabs, constituting the Mn-Ge-Ge-Mn slabs, are almost parallel (20°). Within the magnetic structural unit, the Mn-(Er,Ge)-Mn slab, the angle between the two
Mn-sublattice moments equals 70° and the Er-sublattice moment is directed in the opposite direction of the bisectrix of the two Mn-sublattice moments, i.e. the angle between the Er-sublattice moment and each of the Mn-sublattice moments equals 145°. Using the magnetic moments $\mu_{\text{Er}} = 8.34 \mu_B$ and $\mu_{\text{Mn}} = 1.81 \mu_B$, as obtained in the neutron-diffraction experiment, one can derive that the resultant moment in the spiral plane is very small. In the skew spiral structure of ErMn$_6$Ge$_6$, the axes of the spirals (being perpendicular to the spiral plane) make a 60° angle with the $c$-axis. Upon going from one spiral to a neighbouring one, the direction of the moment changes by an angle of 90° ($q_z = 0.25$).

![Figure 2. Magnetization of ErMn$_6$Ge$_6$ at 4.2 K, measured with the field applied along the $a$-axis and along the $c$-axis.](image)

The magnetic isotherms of ErMn$_6$Ge$_6$ measured at 4.2 K in magnetic fields up to 50 T applied along the $a$- and the $c$-axis are presented in Fig. 2. The magnetization along the $a$-direction increases almost linearly up to the highest field. The magnetization with $B \parallel c$ exhibits a very pronounced hysteretic transition, followed by a plateau region between 25 and 35 T with a saturation value close to the value of the Er moment. In this plateau region, the Er moments may be arranged parallel to the $c$-axis with one of the two neighbouring Mn-sublattices moments having its moment oriented parallel to the Er-sublattice moment and the other one antiparallel so that, effectively, there is no Er-Mn coupling. Energetically, the antiferromagnetic arrangement of the moments of the two Mn sublattices is a favourable situation. Above 35 T, with increasing field, there will be a departure from this antiferromagnetic arrangement and the two Mn-sublattice moments will gradually rotate in the field direction. However, the increase of the magnetization is only modest because the field has to counteract the antiferromagnetic Er-Mn and Mn-Mn interactions. A discussion of the high-field magnetization of ErMn$_6$Ge$_6$ in conjunction with that of RMn$_6$Ge$_6$ compounds with R = Dy, Ho, Tm and Yb, will be presented elsewhere [5].

In low-field magnetization measurements, carried out at various temperatures in fields up to 14 T and displayed in Figure 3a, the onset of a transition is visible in the 100 K isotherm. Presumably, this transition is the same as the one observed at 4.2 K (Fig. 2). The value of the transition field and the size of the magnetization change decrease with increasing temperature, and the transition vanishes around 125 K, indicating that the transition is connected with the low-temperature magnetic phase. For a better insight into the magnetization behaviour of ErMn$_6$Ge$_6$ in the low-temperature magnetic state, the magnetization measurements will be extended to higher fields.

Neutron-diffraction experiments in the 80-160 K temperature region have shown that, at these temperatures, the low-temperature magnetic structure has developed to a complex distorted skew spiral [4]. The moments are strongly reduced and fluctuating Mn moments and directions are found. In the 160-200 K region, a collinear antiferromagnetic arrangement of the Mn moments along the $c$-axis was established with an ordered-moment value for the Er moments close to zero.
Figure 3. Magnetization of ErMn₆Ge₆ as a function of applied field at temperatures ranging (a) from 90 to 125 K and (b) from 300 to 500 K, measured with the field applied parallel and perpendicular to the c-axis

In accordance with the neutron-diffraction results, the magnetic isotherms in Fig. 3b exhibit typical behaviour of an antiferromagnet. At 300 K, a magnetic spin-flop type transition is observed around 7 T. In the limited temperature interval studied, the transition field and the magnetization change at the transition are observed to decrease with increasing temperature, vanishing at the Néel temperature. The development of the magnetization behaviour below 300 K, down to the temperature range of the distorted skew spiral structure, is presently subject of investigation.

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