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Magnetization study on single-crystalline $TbMn_6Ge_6$

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Abstract

The compound $TbMn_6Ge_6$ exhibits unusual magnetic properties. Low-field magnetization measurements show that $TbMn_6Ge_6$ orders around 450 K. In the whole ordered range, metamagnetic behavior with appreciable hysteresis is observed, both for the field applied parallel and perpendicular to the crystallographic *c*-direction. The saturation moment of 5 μ_B/f.u. obtained at temperatures around 300–350 K after the metamagnetic transition that occurs below 1 T suggests collinear ferrimagnetic order of the magnetic Tb and Mn sublattices after the transition. The critical field of the metamagnetic transition increases with decreasing temperature. Also, measurements of the magnetization have been carried out in high magnetic fields up to around 50 T at various temperatures in the ordered region. The magnetic isotherms measured with the field applied along the main crystallographic directions exhibit a wealth of field-induced phase transitions that provide information on the competing interactions in this compound.

Keywords: $TbMn_6Ge_6$; High-field magnetization; Field-induced transition; Conical spin structure; Magnetocrystalline anisotropy

1. Introduction

The RMn_6Ge_6 compounds, crystallizing in the $HfFe_6Ge_6$-type of structure, have extensively been studied in polycrystalline form during the last decade [1–3]. They display a complicated magnetic behavior, characterized by the occurrence of various magnetic phase transitions below the magnetic-ordering temperature. The compound $TbMn_6Ge_6$ exhibits particularly unusual magnetic properties [4–8]. A not well defined magnetic ordering characterized by a strong spike-like peak in the temperature dependence of the magnetic susceptibility takes place around 427 K [1,2]. At lower temperature ($T < 85$ K), an additional transition has been reported by Brabers et al. [2]. This transition was also detected by a small kink in the temperature dependence of the electrical resistivity [3]. Neutron-diffraction studies have evidenced a main helimagnetic order in the whole temperature range (2–410 K), the spiral plane lying in the (0 0 1) plane. Moreover, Schobinger-Papamantellos et al. [6] found indications for an additional ferromagnetic component at low temperature ($T < 85$ K) and at high temperature ($T = 410$ K). According to this study, the ferromagnetic component is directed along the *c*-axis at low temperature, thus giving rise to a conical structure, and lies in the (0 0 1) plane at high temperature (fan-like structure). Magnetic isotherms measured above 190 K in fields up to 1.5 T exhibit a metamagnetic behavior with a critical field that increases upon cooling [1]. High-field free-powder magnetization measurements made at 4.2 K indicate a strong increase of the magnetization below 3 T, an almost-field-independent plateau in the 4–25 T range and a further increase of the magnetization at larger applied fields [5]. More recent magnetization measurements performed by Kelemen et al. [8] have enabled the construction of a *B*–*T* magnetic phase diagram. In order to obtain more insight, a high-field study on a single crystal of $TbMn_6Ge_6$ has been undertaken.

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2. Experimental methods

The temperature dependence of the magnetization was recorded on a magneto-susceptometer in a field of 0.8 T and in the temperature range 5–520 K. The magnetization was measured with the field applied parallel and perpendicular to the *c*-axis. The high-field magnetization has been measured in the Research Center for Materials Science at Extreme Conditions at Osaka University in pulsed fields up to 55 T with pulse duration of 20 ms. The high-field measurements were performed on a sample consisting of seven stacked platelets, all oriented in the same way. The total mass of this sample was 3.6 mg. The fields were applied along the *a*-axis (the [1 0 0] direction) and the *c*-axis (the [0 0 1] direction).

3. Sample preparation and characterization

$TbMn_6Ge_6$ single crystals were prepared by using an In flux. A mixture of the compounds $TbMn_6Ge_6$ and $TbGe_3$, obtained by induction melting and pure Ge is compacted into pellets and put into a silica tube with a large amount of In metal with a total atomic ratio of $Tb_2Mn_6Ge_{10}In_{60}$. A quartz-wool stopper is introduced into the silica tube, which is sealed under argon (267 mbar). The tube is placed in a furnace and quickly heated to 1273 K (50 K/h), where it is kept for 24 h. The furnace is then slowly cooled down to 1223 K (6 K/h), heated again up at the same rate to 1263 K, and finally slowly cooled down to 873 K in 65 h. The tube is quickly removed from the furnace, inverted and centrifuged manually 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 is dissolved in diluted hydrochloric acid. Most of the crystals display a thin hexagonal platelet-like shape (with mean diameter up to 1 mm), while some of them display a needle-like shape (with length up to 2.5 mm). The crystals have been characterized by means of Guinier patterns (with Co Kα radiation) with high-purity Si as standard ($a = 5.43082$ Å) and by Weissenberg photographs. One of them has been used to refine the crystallographic structure by X-ray diffraction and the results have been previously reported elsewhere [9]. The In content has been checked at the Service Commun d'Analyse par Microsondes Electroniques de l'Université de Nancy I-Henri Poincaré using the SX50 electron probe. It was found that the In concentration is smaller than the detection limit (<0.1%).

4. Results and discussion

The thermomagnetic curves recorded in an applied field of 0.8 T (Fig. 1) indicate a magnetic-ordering temperature of about 450 K. The thermal variation of the magnetization does not indicate any additional magnetic transition at lower temperature.

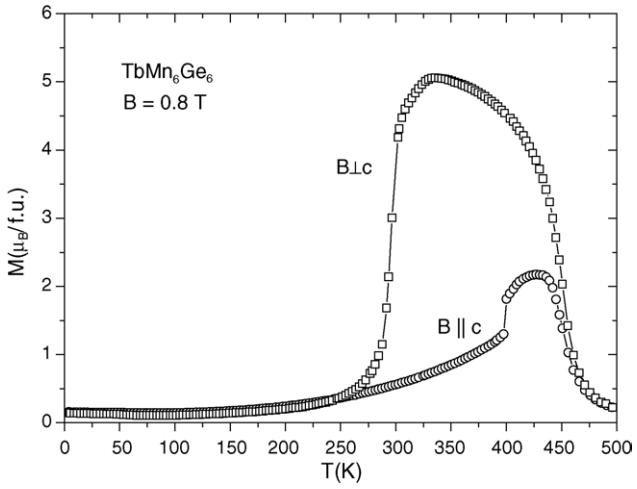

Fig. 1. Temperature dependence of the magnetization of $TbMn_6Ge_6$ in a field of 0.8 T, applied parallel and perpendicular to the [0 0 1] direction. No correction has been applied for the demagnetizing field.

The magnetic isotherms measured at various temperatures along (Fig. 2a) and perpendicular (Fig. 2b) to the [0 0 1] direction display significant differences. Metamagnetic behavior characterized by a first-order field-induced magnetic transition is observed when the field is applied perpendicular to the *c*-axis and above the critical field saturation is easily reached. The critical field of the metamagnetic transition strongly increases upon cooling, which may be related with the temperature dependence of the q_z component of the propagation vector of the magnetic structure, which varies from 0.09 r.l.u. at 410 K to 0.1307 r.l.u. at 1.8 K [6]. At the ordering temperature, the critical field reaches a zero value (Fig. 2c). The isotherms recorded with the field applied along the *c*-axis indicate that $TbMn_6Ge_6$ is an easy-plane system, in good agreement with the spiral plane obtained from neutron diffraction [4,6]. These inconsistencies with some of the previous results [2,6] suggest that the magnetic properties of $TbMn_6Ge_6$ may be strongly dependent on the sample preparation.

The high-field isotherms shown in Figs. 3 and 4 display complicated features and very different shapes depending on the orientation of the crystal and on the measuring temperature. We will start from the neutron-diffraction result [4] that in zero field the magnetic structure consists of a flat spiral with moments oriented perpendicular to the *c*-axis. In Fig. 3, at the lowest fields applied along the *c*-direction, there is some bending of the moments out of the basal plane leading to the initial increase of the magnetization. At higher fields, there is a first-order field-induced phase transition (around 4 T at 4.2 K) leading to a field-independent plateau. According to the magnetization value ($M = 2.8\ \mu_B$/f.u.), this plateau most likely corresponds to a ferrimagnetic moment arrangement in which the Tb-sublattice magnetization is antiparallel to the Mn-sublattice magnetization.

As seen in Fig. 3, the plateau region of the magnetization measured at 4.2 K with the field applied along the [0 0 1] direction is surrounded by two large field-induced

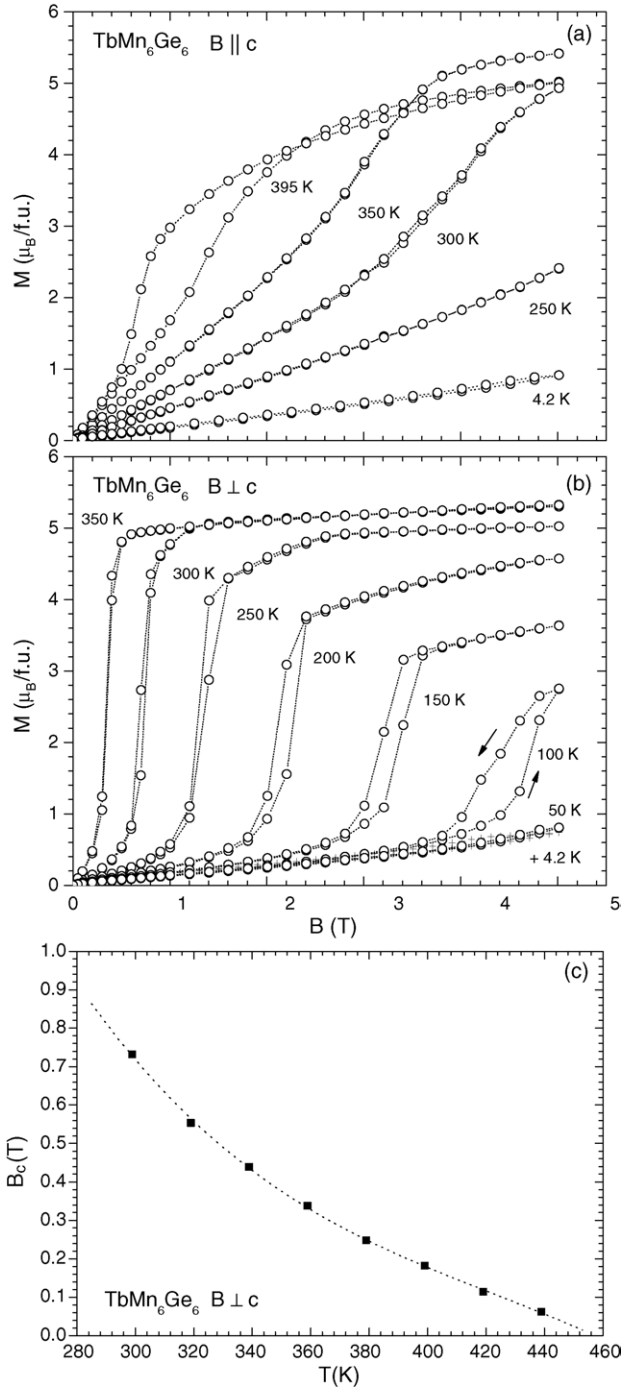

Fig. 2. Magnetic isotherms of $TbMn_6Ge_6$ at various temperatures in the magnetically ordered range in magnetic field up to 5 T applied: (a) parallel to the [0 0 1] direction and (b) perpendicular to the [0 0 1] direction. In (c), the temperature dependence of the critical field measured perpendicular to the [0 0 1] direction is presented.

magnetic transitions showing strong hysteretic behavior around $B_{c1} \approx 4$ T and $B_{c2} \approx 41$ T. Interestingly, it is observed that B_{c1} increases upon heating while B_{c2} decreases. Possible magnetic moment arrangements that could account for these transitions have been included in Fig. 3. The lower transition involves a change in moment orientation roughly from

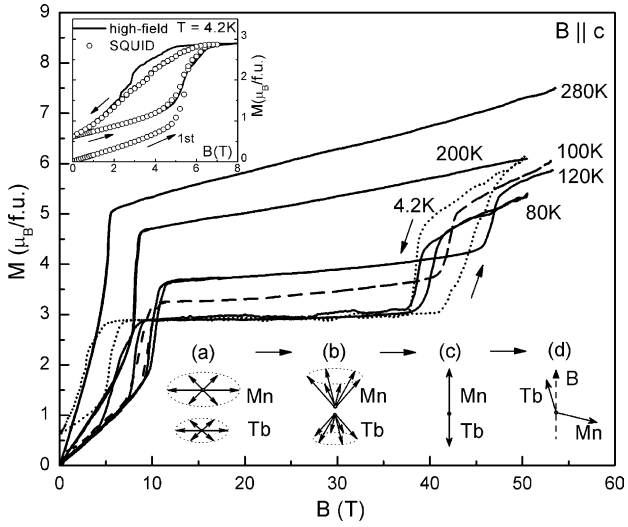

Fig. 3. Magnetization of $TbMn_6Ge_6$, measured at 4.2, 80, 100, 120, 200 and 280 K with the field applied along the [0 0 1] direction.

the easy-plane direction to the hard *c*-axis direction. Generally, the magnetic anisotropy increases with decreasing temperature. However, in the case of the competing Mn- and Tb-sublattice anisotropies with different temperature dependencies it may very well be that the easy-plane anisotropy decreases with decreasing temperature. Indications for this behavior are obtained from neutron diffraction showing that, below about 85 K, the moment moves somewhat out of the basal plane forming a cone structure [6], which accounts for the remanence observed in the magnetic isotherm at 4.2 K in Fig. 3 (inset). Given the fact that the easy-plane anisotropy increases with increasing temperature it is plausible that the transition from arrangement (b) to (c) involves higher fields at higher temperature. By the same token, one easily finds that the transition from (c) to (d) requires a lower field if the temperature is increased from 4.2 to 80 K. Likely, the collinear ferrimagnetic structure depicted in diagram (c) becomes a

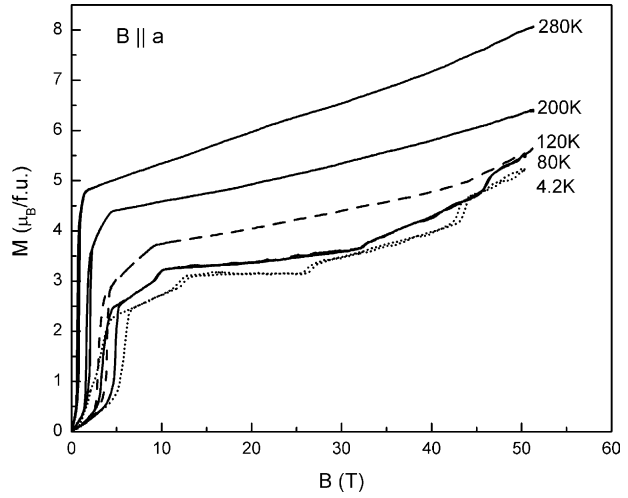

Fig. 4. Magnetization of $TbMn_6Ge_6$, measured at 4.2, 80, 120, 200 and 280 K with the field applied along the [1 0 0] direction.

canted structure at temperatures above 80 K due to the prominent easy-plane anisotropy. An increase of the moment value corresponding to the plateau region with increasing temperature is attributed to the reduction of the ordered Tb-sublattice moments, which also results in a reduction of the driving force from the Zeeman energy for the transition depicted in diagram (c) and (d). As a consequence, the B_{c2} increases when the temperature increases from 80 to 120 K. The decrease of B_{c1} above 120 K is primarily due to thermal expansion that weakens the antiferromagnetic coupling of the magnetic fan structure as depicted in Fig. 3a.

It can be seen in Fig. 4 that the isotherms recorded with the field applied perpendicularly to the *c*-axis display many field-induced transitions: a main one at low field characterized by a large hysteresis and a multi-step behavior which is more and more smoothed upon heating. Whatever the temperature, the plateau region seems to be reached after a two-step process. We ascribe the first transition to a change from flat spiral to ferrimagnet as in Fig. 3. The sloping behavior of the isotherm after this transition is probably due to a more perfect ferromagnetic alignment of the Mn moment in the sublattice. The moment values corresponding to the plateau region do not differ much from those obtained with the field in the [0 0 1] direction. The complex nature of the interplay between the various types of exchange interactions and anisotropies leads to three more field-induced phase transition in the isotherms of 4.2 and 80 K at about 11, 30 and 45 T. At present, we are not able to offer an adequate explanation for these transitions. However, it is interesting to note that theoretical studies for free-hexagonal crystals with non-zero basal-plane anisotropy have predicted such oscillating isotherms containing three minor transitions [10].

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