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High-field magnetization of RMn_6Sn_6 compounds with R = Gd, Tb, Dy and Ho

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Abstract

We have measured the temperature dependence of the magnetization on single crystals of the RMn_6Sn_6 compounds with R = Gd, Tb, Dy and Ho. The observed magnetic-ordering temperatures and the anisotropy types agree well with earlier results from literature. Measurements of the magnetization with the field applied along the main crystallographic directions have been made at 4.2 K in magnetic fields up to 55 T. Field-induced transitions are observed that are interpreted in terms of the interplay between the antiferromagnetic intersublattice R–Mn coupling and the magnetocrystalline anisotropy.

Keywords: RMn_6Sn_6; High-field magnetization; Field-induced transition; Spin reorientation

1. Introduction

The hexagonal $HfFe_6Ge_6$-type (P6/mmm) RMn_6Sn_6 compounds with R = Gd, Tb, Dy and Ho order ferrimagnetically below the Curie temperatures (T_C) that range from 375 to 450 K. $GdMn_6Sn_6$ exhibits easy-plane anisotropy in the whole ordered temperature range, but the others display spin-reorientation temperatures (T_{sr}) due to the dominance of the magnetocrystalline anisotropy of the rare-earth sublattice at low temperatures [1]. $TbMn_6Sn_6$ has been found to change from easy-plane to easy-axis anisotropy below 310 K [2], while for $DyMn_6Sn_6$ and $HoMn_6Sn_6$ transitions from easy plane to easy cone have been reported below 320 [3] and 175 K [2], respectively. For $TbMn_6Sn_6$ and $HoMn_6Sn_6$, the magnetic properties have been studied on single crystals in magnetic fields up to 9 T [2]. Free-powder-magnetization studies have been performed in fields up to 38 T [4] in which field-induced transitions from the ferrimagnetic to the canted-moment phase have been observed for $DyMn_6Sn_6$ and $HoMn_6Sn_6$ at 22 and 17 T, respectively, enabling a determination of the exchange-coupling constants $J_{DyMn}/k_B = -11.3$ K and $J_{HoMn}/k_B = -8.7$ K. A value for $GdMn_6Sn_6$ has been obtained from inelastic-neutron-scattering experiments ($J_{GdMn}/k = -10.7$ K) [5].

The temperature dependence of the magnetization of single crystals of the RMn_6Sn_6 compounds with R = Gd, Tb, Dy and Ho was measured and compared with earlier results. Magnetization measurements in high fields were performed on the single crystals to study the magnetic interactions.

2. Experimental methods

The thermal variation of the magnetization of the compounds has been measured in a MANICS magnetosusceptometer in a field of 0.1 T at temperatures between 5 and 450 K. The transition temperatures (T_C and T_{sr}) have been taken at the maximum of the first derivative dM/dT. The high-field magnetization has been measured at KYOKUGEN, Osaka University in pulsed fields up to 55 T with pulse duration of 20 ms. The fields were applied along the a-axis

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(the [1 0 0] direction), the *b*-axis (the [1 2 0] direction) and the *c*-axis (the [0 0 1] direction). The high-field measurements were performed on single crystals with mass of 7.2 mg for Gd, 13.8 mg for Tb, 12.8 mg for Dy and 19.1 mg for Ho compound. The results are plotted as *M*–*B* curves as shown in Figs. 2–5, where *B* represents the magnetic induction in the empty coil, i.e. $B = \mu_0 H$.

3. Sample preparation and characterization

RMn_6Sn_6 single crystals with R = Gd, Tb, Dy and Ho have been synthesized in a flux method similar to the method previously reported by Clatterbuck and Gschneidner [2]. A mixture of the RMn_6Sn_6 compound and pure Sn metal, with an overall atomic ratio RMn_6Sn_{30}, is compacted into pellets and put into a silica tube with a quartz-wool stopper. The silica tube is sealed under argon (267 mbar) and heated to 1273 K (at 50 K/h) for 24 h. Then it is 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 in 65 h. The tube is quickly removed from the furnace, inverted and centrifuged manually using a David's sling device. The Sn flux lies at the bottom of the tube and the large hexagonal crystal prisms with masses up to 100 mg remain on the quartz-wool stopper. Some of them were ground and analyzed by X-ray diffraction Guinier patterns with Cu Kα radiation and Si calibration. The prepared RMn_6Sn_6 crystals are isotypic with the $HfFe_6Ge_6$ structure. The lattice parameters, the unit-cell volumes and the *c*/*a* ratios are presented in Table 1.

Table 1
Unit-cell parameters of RMn_6Sn_6 single crystals with R = Gd, Tb, Dy and Ho

	a (Å)	*c* (Å)	*V* (Å^3)	*c*/*a*
Gd	5.537(2)	9.026(5)	239.6(3)	1.6303
Tb	5.531(4)	9.017(8)	238.9(6)	1.6304
Dy	5.222(2)	9.008(5)	237.9(3)	1.6313
Ho	5.521(3)	9.005(8)	237.7(5)	1.6311

4. Results and discussion

The thermal variation of the magnetization in a field of 0.1 T, applied along and perpendicular to the *c*-axis, has been examined to obtain the T_C and T_{sr} values (Fig. 1 and Table 2). Above T_{sr}, it is observed that an easy plane prevails for

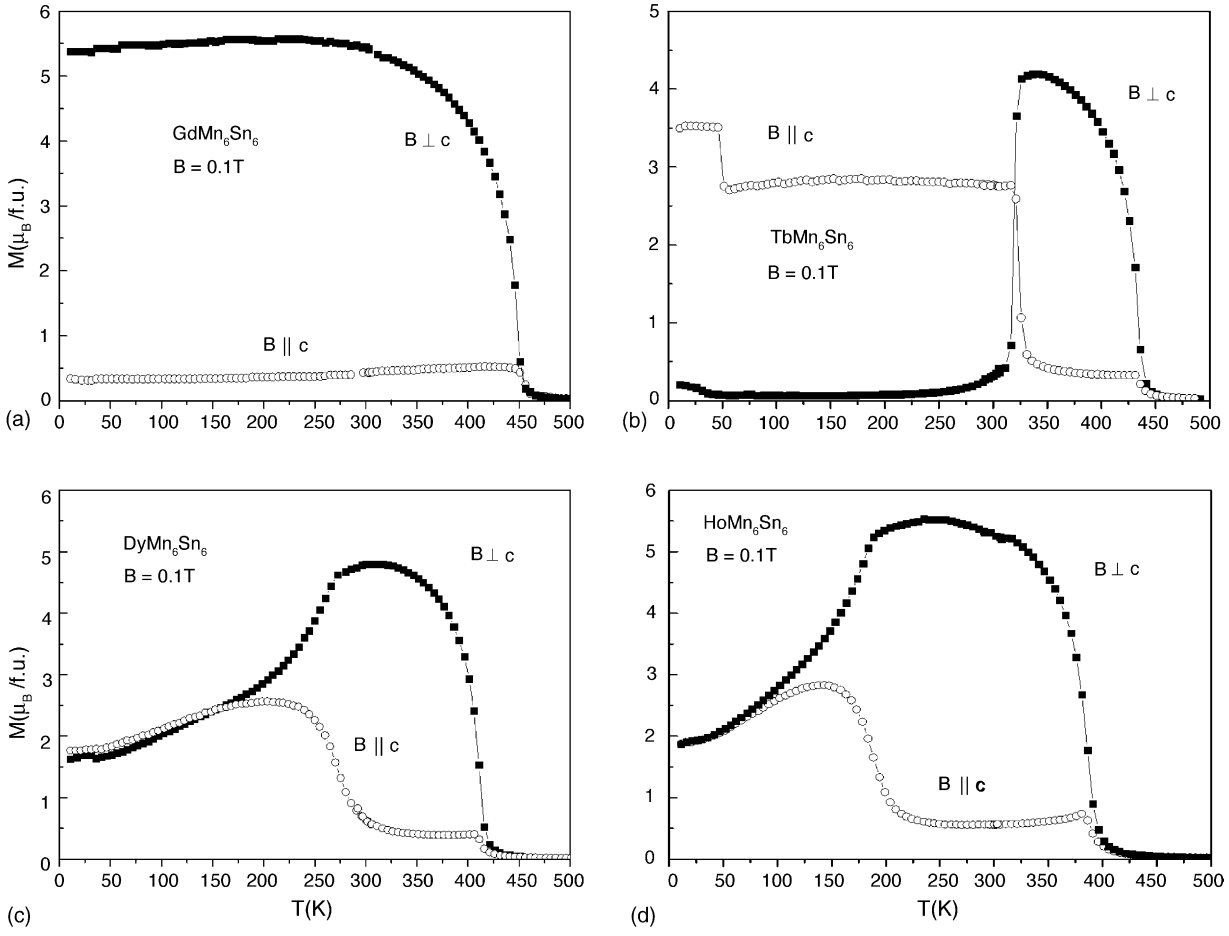

Fig. 1. Temperature dependence of the magnetization in an applied field of 0.1 T of RMn_6Sn_6 crystals with (a) R = Gd; (b) Tb; (c) Dy; and (d) Ho.

Table 2
Magnetic-ordering temperatures and spin-reorientation temperatures of RMn_6Sn_6 single crystals with R = Gd, Tb, Dy and Ho

	T_C (K)	T_{sr} (K)
Gd	445	–
	435 [1]	
Tb	430	320
	423 [1]	330 [1]
	450 [2]	310 [2]
Dy	410	270
	393 [1]	320 [3]
Ho	385	185
	376 [1]	200 [1]
	410 [2]	175 [2]

the four compounds. Below T_{sr}, a complete rotation of the moments towards the *c*-axis is observed for $TbMn_6Sn_6$. For $DyMn_6Sn_6$ and $HoMn_6Sn_6$, the occurrence of spontaneous magnetization along both main directions below T_{sr} indicates a conical arrangement of the moment, in good accordance with previous neutron-diffraction results [3]. It can be seen in Table 2 that the observed values for T_C and T_{sr} are in fair agreement with results from literature.

Measurements of the magnetization with the field applied along the main crystallographic directions have been made at 4.2 K in magnetic fields up to 55 T. In Fig. 2 the magnetization curves for $GdMn_6Sn_6$ are shown. Because Gd is an S-state ion, the magnetic anisotropy in this compound is determined by the Mn sublattice. As has been found for the RMn_6Sn_6 compounds with the non-magnetic elements Sc, Y and Lu, the Mn sublattice has easy-plane anisotropy [1,2,6]. The compound displays spontaneous magnetization with the field applied perpendicular to the *c*-axis. The magnetization saturates at a value of about 5 μ_B/f.u. in agreement with ferrimagnetic order, the Gd-sublattice moment being antiparallel to the Mn-sublattice moment. There is no appreciable difference between the isotherms measured along the *a*- and the *b*-axis, indicating that the in-plane anisotropy is small.

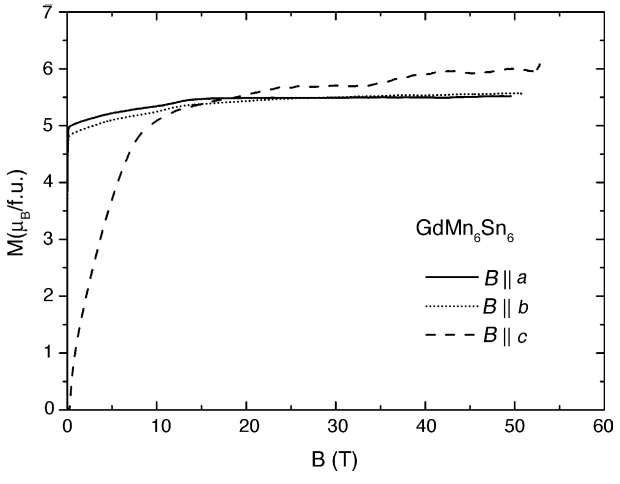

Fig. 2. Magnetization at 4.2 K of $GdMn_6Sn_6$.

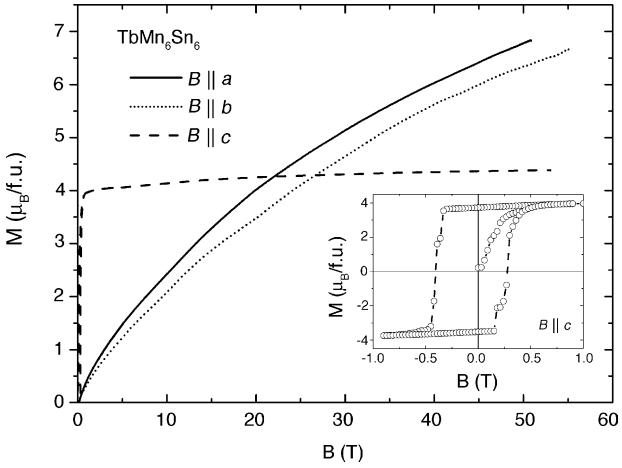

Fig. 3. Magnetization at 4.2 K of $TbMn_6Sn_6$.

Due to the strong Gd–Mn exchange coupling [4], the Gd- and Mn-sublattice moments remain strictly antiparallel in the applied fields up to 55 T and neither bending of the moments nor a field-induced transition is observed. The magnetization measured with the field applied along the *c*-axis increases non-linearly with the applied field, indicating that the rotation of the antiparallel Gd- and Mn-sublattice is accompanied by a small amount of simultaneous bending. The further sluggish increase of magnetization can be attributed to the further bending of the canted moments towards the field direction. The canted-moment structure is the consequence of the interplay among Zeeman energy, easy-plane anisotropy energy of the Mn-sublattice and antiparellel coupling energy of the Gd- and Mn-sublattice.

$TbMn_6Sn_6$ compound (Fig. 3) displays spontaneous magnetization parallel to the *c*-axis and exhibits hysteresis around $B = 0$. The saturation magnetization is about 4 μ_B/f.u., corresponding to ferrimagnetic order of the Tb- and Mn-sublattice moments. Analogous to the case of the Gd compound, the Tb and Mn exchange coupling is strong enough [4] to preserve a strict antiparallel alignment of the Tb and Mn moments in the whole investigated field range. The magnetic isotherms measured with the field applied in the *a*- and in the *b*-direction do not saturate in whole applied-field range. They are very similar, indicating the anisotropy within the basal plane to be small. The observed continuous increase of the magnetization corresponds with an increasing bending of the two sublattice moments.

$DyMn_6Sn_6$ compound (Fig. 4) displays spontaneous magnetization along all three crystallographic directions. The values of the magnetization obtained for the field along the *c*-axis and the field in the basal plane are very similar, in agreement with a cone angle of about 45° obtained in neutron-diffraction experiments [3]. The magnetization along the *c*-axis gradually increases in the applied fields up to 56 T. Starting in zero field from the moment configuration in diagram (a) in which the sublattice moments are strictly antiparallel on a cone, the moment gradually rotates into the field direction

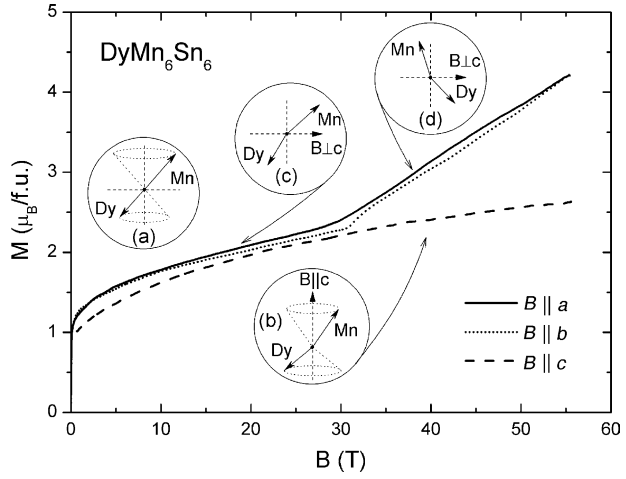

Fig. 4. Magnetization at 4.2 K of $DyMn_6Sn_6$.

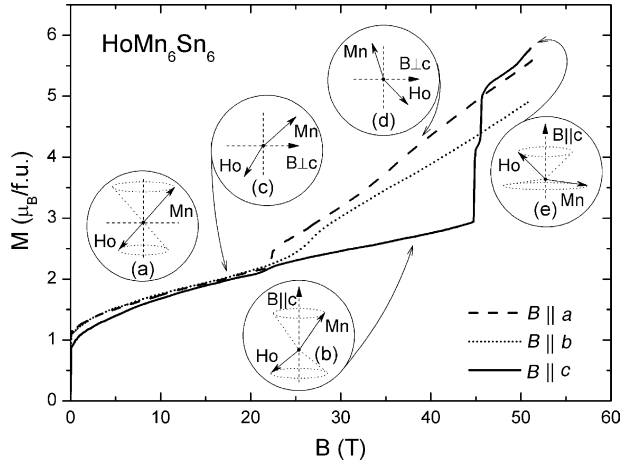

Fig. 5. Magnetization at 4.2 K of $HoMn_6Sn_6$.

with increasing field, accompanied by bending of the two sublattice moments, as shown in diagram (b) for B||c and diagram (c) for B⊥c. Both isotherms measured with the field perpendicular to the *c*-axis display a field-induced transition around 30 T, which is most likely from the moment configuration depicted in diagram (c) to that in (d) where the Dy moment returns to the initial easy cone but on the side of the field direction. The small change in magnetization for this transition indicates a small energy barrier, implying that the rotation of the Dy moment takes place on a cone. Both transitions occur at the same field value which indicates that the anisotropy within the basal plane is very small. Above 30 T, the magnetization in both directions shows stronger increase, corresponding to bending of the Dy- and Mn-sublattice moments into the field direction.

The high-field magnetization behavior of $HoMn_6Sn_6$ (Fig. 5) is very similar to that of $DyMn_6Sn_6$. Up to about 22 T, the isotherms measured with the field along and perpendicular to the *c*-axis are almost identical, indicating again a cone angle near 45°. Along the *c*-axis, the magnetization increases gradually up to about 44 T, from the zero-field configuration in diagram (a) to the canted-moment configuration shown in diagram (b). Around 45 T, a pronounced transition is found in which the Ho-sublattice moment jumps from a position on the cone where it has a component opposite to the field direction (diagram (b)) to a position on the cone where it has a component in the field direction (diagram (e)). Above this transition, in which the total anisotropy is preserved, the two sublattice moments are gradually bent into the direction of the field. Transitions occur along the *a*- and the *b*-direction at 22 and 26 T, respectively, from the moment configuration depicted in diagram (c) to that in (d), similar to the situation in $DyMn_6Sn_6$. The fact that both transitions occur at slightly different field values indicates that the anisotropy within the basal plane is not negligible. Above the transition, the magnetization measured in the *a*- and the *b*-direction both further increase, like in the *c*-direction, corresponding to further bending of the two sublattice moments into the field direction.

Acknowledgments

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References

[1] G. Venturini, B. Chafik El Idrissi, B. Malaman, J. Magn. Magn. Mater. 94 (1991) 35.
[2] D.M. Clatterbuck, K.A. Gschneidner Jr., J. Magn. Magn. Mater. 207 (1999) 78.
[3] B. Malaman, G. Venturini, R. Welter, J.P. Sanchez, P. Vulliet, E. Ressouche, J. Magn. Magn. Mater. 202 (1999) 519.
[4] J.H.V.J. Brabers, G.F. Zhou, J.H.P. Colpa, K.H.J. Buschow, F.R. de Boer, Physica B 202 (1994) 1.
[5] P. Tils, M. Loewenhaupt, K.H.J. Buschow, R.S. Eccleston, J. Alloys Compd. 279 (1998) 123.
[6] A. Matsuo, K. Suga, K. Kindo, L. Zhang, E. Brück, K.H.J. Buschow, F.R. de Boer, C. Lefèvre, G. Venturini, J. Alloys Compd.; doi:10.1016/j.jallcom.2005.04.080.