ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 196–199

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Change of easy magnetization direction in $TmMn_6Sn_{6-x}Ga_x$ ($0.00 < x < 1.22$) studied in high magnetic fields

Y. Sawai [a,*], K. Kindo [a], L. Zhang [b], J.C.P. Klaasse [b], E. Brück [b], K.H.J. Buschow [b], F.R. de Boer [a,b], C. Lefèvre [c], G. Venturini [c]

[a] *Kyokugen, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[b] *Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, 1018 XE Amsterdam, The Netherlands*
[c] *Lab. Chim. Sol. Minéral, Université Henri Poincaré-Nancy 1, 54506 Vandoeuvre les Nancy Cedex, France*

Available online 13 June 2005

Abstract

Single crystals of $TmMn_6Sn_{6-x}Ga_x$ compounds ($0 \le x \le 1.22$) obtained in a tin flux have been studied by thermomagnetic and high-field magnetization measurements. A collinear-antiferro to heli-magnetic transition at 324 K has been observed in $TmMn_6Sn_6$. Spin-reorientation transitions at low temperature are found in the compounds with $x = 0.66$ and 1.22. The magnetization curves in high fields at 4.2 K are interpreted to result from the competition between the Tm–Mn exchange interaction and the magnetocrystalline anisotropy of the Tm and Mn sublattices. A strong easy-plane anisotropy is favored for the Ga-poor compounds and a strong easy-axis anisotropy for the Ga-rich compounds while the compounds of intermediate Ga content ($0.51 \le x \le 0.66$) display rather weak magnetocrystalline anisotropy.
© 2005 Elsevier B.V. All rights reserved.

Keywords: $TmMn_6(Sn,Ga)_6$; High-field magnetization; Field-induced transition

1. Introduction

Magnetization measurements performed on polycrystalline material of the hexagonal $HfFe_6Ge_6$-type ($P6/mmm$) compound $TmMn_6Sn_6$ have shown antiferromagnetic order to occur below $T_N = 347$ K and an anomaly at $T_t \approx 58$ K [1]. A single-crystal study undertaken in fields up to 9 T has led to the transition temperatures 355 and 40 K, and has enabled the construction of a B–T magnetic phase diagram [2]. A more recent neutron-diffraction study has pointed out collinear antiferromagnetic order above 330 K and helimagnetic order below 320 K. In the latter state, both magnetic sublattices have a non-zero magnetic moment and there is no evidence of an additional transition at low temperature [3].

The $TmMn_6Sn_{6-x}Ga_x$ solid solutions display an interesting evolution of the magnetic properties [4]. Magnetization measurements have shown that $TmMn_6Sn_{5.9}Ga_{0.1}$, like the compound without Ga substitution, still orders antiferromagnetically at $T_N = 343$ K and displays an antiferromagnetic to ferrimagnetic transition at $T_c = 55$ K. The compounds with $x \ge 0.4$ are characterized by ferrimagnetic order in the whole ordered range whereas the compounds of intermediate composition ($0.2 \le x \le 0.3$) display so-called re-entrant ferrimagnetic behavior. Moreover, the more Ga-rich compounds ($x \ge 1.0$) exhibit a considerable enhancement of the coercive field. A powder-neutron-diffraction study and thermomagnetic measurements on single crystals have shown that the increase of the magnetic hardness is correlated to a change of the easy magnetization direction from the basal plane towards the c-axis [3,5]. This evolution may be related to substitution of Ga at the Sn (2c) site close to the Tm (1a) site in the $HfFe_6Ge_6$ structure (see Fig. 1) [6]. The magnetic isotherms measured in fields up to 9 T indicate a strong interplay between the magnetocrystalline anisotropy and the Tm–Mn interaction [5]. In order to better understand these phenomena, a high-field magnetization study was undertaken.

* Corresponding author.
E-mail address: sawai@mag.rcem.osaka-u.ac.jp (Y. Sawai).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.04.038

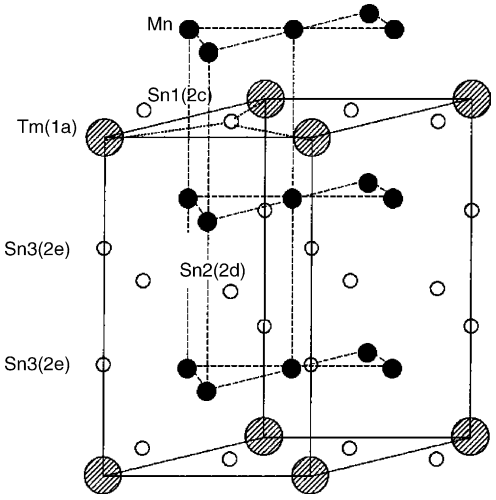

Fig. 1. Representation of the $TmMn_6Sn_6$ structure.

2. Experimental

The thermal variation of the magnetization of the compounds has been measured in a Manics magneto-susceptometer in a field of 0.5 T at temperatures between 5 and 450 K. The transition temperatures T_c and T_{sr} (spin-reorientation temperature) have been taken at the maximum value of the first derivative dM/dT. The high-field magnetization has been measured at 4.2 K in the high-field installation at the University of Amsterdam in quasi-stationary fields up to 40 T and in the Research Center for Materials Science at extreme conditions at Osaka University, in pulsed field up to 55 T with a pulse duration of 20 ms. The high-field measurements were performed on single crystals with masses between 3.5 and 5.9 mg. The fields were applied along the a-axis (the [1 0 0] direction), the b-axis (the [1 2 0] direction) and the c-axis (the [0 0 1] direction).

3. Sample preparation and characterization

$TmMn_6Sn_{6-x}Ga_x$ single crystals with $x = 0.00$, 0.15, 0.32, 0.51, 0.66 and 1.22 have been synthesized by a flux method similar to the one reported by Clatterbuck and Gschneidner [2]. A mixture of the $TmMn_6Sn_6$ compound, obtained by induction melting, and pure Sn and Ga metal, with an overall atomic ratio $TmMn_6Sn_{32-y}Ga_y$, was compacted into pellets and put into a silica tube with a quartz-wool stopper. The tube was sealed under argon (267 mbar) and quickly heated up to 1273 K (at 50 K/h) for 24 h. It was then slowly cooled down to 1223 K (6 K/h), heated up again to 1263 K at the same rate and finally slowly cooled down to 873 K in 65 h. The tube was quickly removed from the furnace, inverted and centrifuged manually using a David's sling device. After this treatment, the Sn flux was located at the bottom of the tube and hexagonal crystal prisms with masses up to 100 mg remained on the quartz-wool stopper. Some of them were ground and analyzed by X-ray diffraction Guinier patterns with Cu Kα radiation and high-purity Si as calibration ($a = 5.43082$ Å). The structure of the prepared $TmMn_6Sn_{6-x}Ga_x$ compounds is isotypic with the $HfFe_6Ge_6$ structure. The Ga contents, lattice parameters, unit-cell volumes and c/a ratios are presented in Table 1.

Table 1
Unit-cell parameters and Ga contents of the studied of $TmMn_6Sn_{6-x}Ga_x$ compounds

Starting composition	a (Å)	c (Å)	V (Å^3)	c/a	x
$TmMn_6Sn_{30}$	5.514 (2)	8.994 (3)	236.8 (2)	1.6311	0.00
$TmMn_6Sn_{31.5}Ga_{0.5}$	5.505 (2)	8.988 (5)	235.9 (3)	1.6324	0.15
$TmMn_6Sn_{31}Ga$	5.493 (2)	8.965 (5)	234.3 (3)	1.6319	0.32
$TmMn_6Sn_{30.5}Ga_{1.5}$	5.482 (2)	8.948 (2)	232.9 (3)	1.6320	0.51
$TmMn_6Sn_{30}Ga_2$	5.479 (2)	8.941 (5)	232.5 (3)	1.6317	0.66
$TmMn_6Sn_{28}Ga_4$	5.458 (3)	8.903 (6)	229.7 (4)	1.6311	1.22

4. Results and discussion

The thermomagnetic curves, measured in a field of 0.5 T applied parallel and perpendicular to the c-axis, are displayed in Fig. 2. All compounds show magnetic order below 350 K and the compounds with $x = 0.00$, 0.15, 0.66, 1.22 exhibit another magnetic transition at lower temperature. The transition observed at 324 K in $TmMn_6Sn_6$ is related to the transition from the collinear antiferromagnetic state to the helimagnetic state, recently established by neutron diffraction [3]. The large enhancement of the magnetization observed below 55 K for $TmMn_6Sn_{5.85}Ga_{0.15}$ corresponds to the transition from the heli- to the ferri-magnetic state with the moments lying in the basal plane. Finally, there is a clear spin-reorientation transition in the compounds with $x = 0.66$, and 1.22 from the basal plane at high temperature towards the c-axis at low temperature.

The high-field magnetic isotherms presented in Fig. 3 display interesting features. At about 2.5 T, the isotherms of $TmMn_6Sn_6$ measured with the field perpendicular to the c-axis display a metamagnetic transition from the helimagnetic state to the ferrimagnetic state. The strong field dependence of the magnetization above 25 T is most likely due to bending of the Tm- and Mn-sublattice magnetizations towards each other. No such metamagnetic transition is present in the isotherm measured with the field applied along the c-axis. The shape of this isotherm suggests that bending starts already in low fields. Most likely, there is a gradual closing of the cone angle of the Mn moments in the helimagnetic structure (the net Mn moment points into the field direction). Simultaneously, there is a gradual opening up of the cone angle associated with the Tm moments (the net Tm moment is opposite to the field direction). These results indicate an interplay between strong easy-plane anisotropy and the antiferromagnetic Tm–Tm, Mn–Mn, and Tm–Mn interactions.

The curves for the $x = 0.15$ compound display similar features, thus indicating that the Tm easy-plane anisotropy

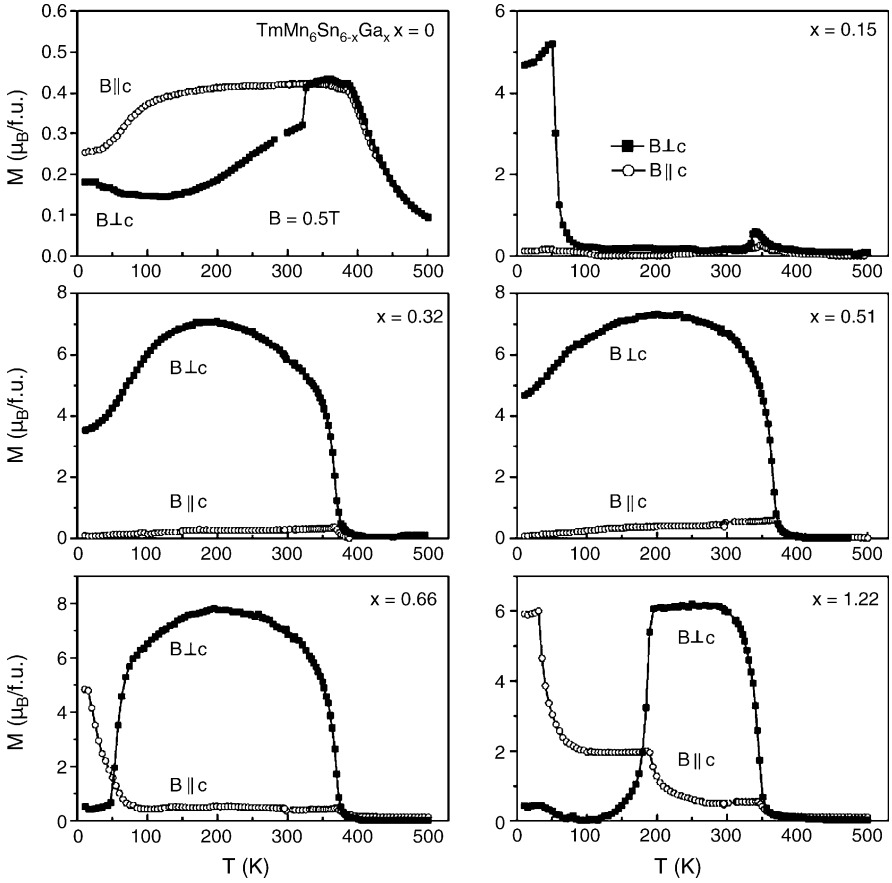

Fig. 2. Thermal variation of the magnetization of $TmMn_6Sn_{6-x}Ga_x$ crystals with $x = 0$, 0.15, 0.32, 0.51, 0.66 and 1.22 in a field of 0.5 T. No correction has been applied for the demagnetizing field.

remains strong. Also the curves for the $x = 1.22$ compound display similar features but the field directions in which these curves were measured have changed from $B \perp c$ to $B \,||\, c$ and vice versa. This indicates that the latter compound is characterized by a strong easy-axis anisotropy and gradual bending occurs when the field is applied perpendicular to the c-axis. The curves corresponding to the $x = 0.51$ and 0.66 compounds show a tendency to saturate whatever the orientation of the field. This suggests that the magnetocrystalline anisotropy is weak for these two compounds. These observations obviously indicate a continuous evolution of the anisotropy from strong easy-plane anisotropy for $x = 0$, 0.15 and 0.32 to weak easy-plane anisotropy for $x = 0.51$, weak easy-axis anisotropy for $x = 0.66$ and strong easy-axis anisotropy for $x = 1.22$. These results agree with the evolution of the magnetic hardness observed on powder samples [4].

Inspection of the magnetic isotherms displayed in Fig. 3 makes it clear that the continuous change from easy-axis anisotropy to easy-plane anisotropy with increasing Ga content nevertheless leads to complex magnetization curves in the intermediate Ga-concentration range. For the compound with $x = 0.32$, the anisotropy is still of the easy-plane type as can be derived from the low-field behavior of the isotherm measured with $B \,||\, c$. However, in contrast to the $B \,||\, c$ isotherms of the compounds with $x = 0$ and $x = 0.15$, the $B \,||\, c$ isotherm of the compound with $x = 0.32$ does no longer reflect a gradual bending of the net Mn and Tm moments towards each other. Instead, there are two field-induced transitions at $B_1 \approx 8$ T and $B_2 \approx 18$ T, both showing a pronounced hysteresis. Since the change in anisotropy implies a rearrangement of the crystal-field-split levels of the Tm ground-state multiplet, these field-induced transitions might reflect field-induced level crossings and concomitant changes in magnetostriction. The shifts of the two field-induced transitions to respective $B_1 \approx 1$ T and $B_2 \approx 24$ T in the compound with $x = 0.51$ point into this direction, but further studies are required to corroborate this hypothesis.

The curves recorded with the field perpendicular to the c axis for $0 < x \leq 0.66$ (i.e. for compounds with easy-plane or weak easy-axis anisotropy) display the same field-induced transition around $B_{cr1} = 24$ T. In this configuration, neglecting any possible anisotropy within the basal plane, the magnetization process can be considered to be the same as in free-powder experiments. In this case, the critical field is related to the Tm–Mn coupling through the relation $B_{cr1} = n_{Tm-Mn}|M_{Mn} - M_{Tm}|$. The absence of variation of B_{cr1}

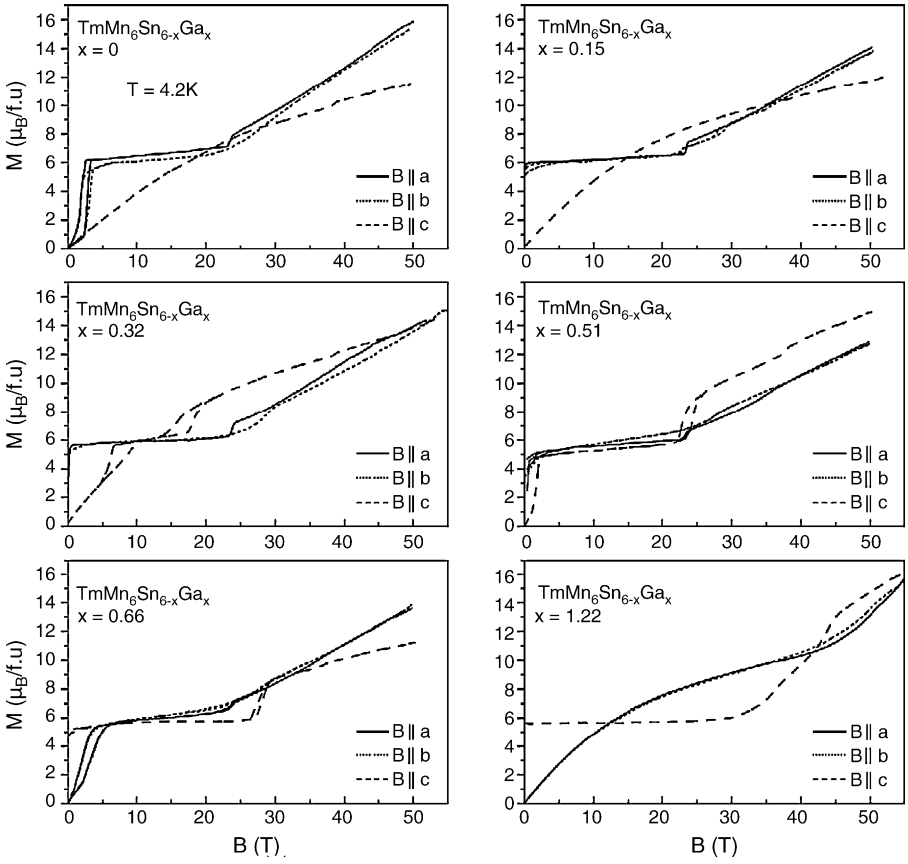

Fig. 3. Field dependence of the magnetization at 4.2 K of $TmMn_6Sn_{6-x}Ga_x$ crystals with $x = 0$, 0.15, 0.32, 0.51, 0.66 and 1.22.

indicates that the Mn–Tm coupling does not vary much upon Ga substitution.

Acknowledgments

This work was supported by the 21st Century COE Program named “Towards a new basic science: depth and synthesis”, and by a grant-in-aid for Science Research from the Japanese Ministry of Education, Science, Sports, Culture and Technology.

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] C. Lefèvre, G. Venturini, B. Malaman, J. Alloys Comp. 346 (2002) 84.
[4] C. Lefèvre, G. Venturini, J. Alloys Comp. 334 (2002) 45.
[5] F. Canepa, M. Napoletano, C. Lefèvre, G. Venturini, J. Magn. Magn. Mater. 285 (2005) 254.
[6] C. Lefèvre, G. Venturini, B. Malaman, J. Alloys Comp. 354 (2003) 47.