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Structure and magnetic properties of $TbMn_{6-x}Ti_xSn_6$

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Abstract. $TbMn_{6-x}Ti_xSn_6$ compounds with $x = 0$, 0.5, 1.0, 1.5 and 2.0 have been studied in this paper. All compounds crystallize in the $HfFe_6Ge_6$-type structure (space group, $P6/mmm$). The substitution of Ti for Mn in $TbMn_6Sn_6$ results in a linear increase in the lattice constants and the unit-cell volume from $a = 5.531$ Å, $c = 9.025$ Å and $V = 239.10$ Å^3 at $x = 0$, to $a = 5.588$ Å, $c = 9.150$ Å and $V = 247.44$ Å^3 at $x = 2.0$. The ordering temperature and the reorientation temperature of the easy axis of these compounds decrease monotonically with Ti content from 423 K and 330 K at $x = 0$ to 362 K and 285 K at $x = 2.0$. In thermal magnetic curves a new transition was found at the temperature T_f at which the magnetization begin to increase and T_f increases from 37 K at $x = 0$ to 150 K at $x = 2.0$. The saturation magnetization at room temperature decreases linearly with increasing Ti content. The magnetization curves at 1.5 K in fields up to 70 kOe are given and the magnetization values at 1.5 K are derived from them.

1. Introduction

New ternary compounds RT_6X_6 (T = Fe or Mn; X = Ge or Sn) have attracted much attention recently [1–4]. In RMn_6Sn_6 (R = Gd, Tb, Dy or Ho), evidence of ferrimagnetism has been reported. Both the R and the Mn sublattices show ferromagnetic behaviour at high temperatures. The magnetic structure of $TbMn_6Sn_6$ at 300 K consists of a stacking of ferromagnetic (001) layers of rare earth and manganese with the coupling sequence Mn(+)R(−)Mn(+)Mn(+)R(−)Mn(+). The magnetic moments are $\mu(\mathrm{Mn}) = 2.0\mu_B$ and $\mu(\mathrm{Tb}) = 4.9\mu_B$, which deviate from the c axis with a deviation angle of 15°. At 2 K the magnetic moments are along [001] with $\mu(\mathrm{Mn}) = 2.4\mu_B$ and $\mu(\mathrm{Tb}) = 8.6\mu_B$ [2]. A second apparent transition was found to occur at 330 K, correlating to a change in the easy-axis magnetization direction [1]. The moments lie in the basal plane at high temperatures and are along or near c below the transition temperature. In the present paper, the structure and magnetic properties of pseudo-ternary $TbMn_{6-x}Ti_xSn_6$ compounds have been investigated in detail.

2. Experimental details

All compounds, each with a total mass of about 5 g, were prepared by argon arc melting from starting materials of at least 99.9% purity. The alloys were melted at least five times

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Table 1. Structural and magnetic data of the $TbMn_{6-x}Ti_xSn_6$ compounds.

x	a (Å)	c (Å)	V (Å)	T_c (K)	T_t (K)	T_f (K)	M_s^{exp} (RT) (μ_B FU^{-1})	M_s^{cal} (RT) (μ_B FU^{-1})	M (1.5 K) (μ_B FU^{-1})
0.0	5.531	9.025	239.10	423	330	37	7.03	7.10	3.32
0.5	5.541	9.050	240.63	381	293	114	5.95	6.10	0.05
1.0	5.559	9.085	243.14	371	288	118	4.85	5.10	0.04
1.5	5.577	9.117	245.57	369	283	135	3.74	4.10	0.04
2.0	5.588	9.150	247.44	362	285	150	3.18	3.10	0.04

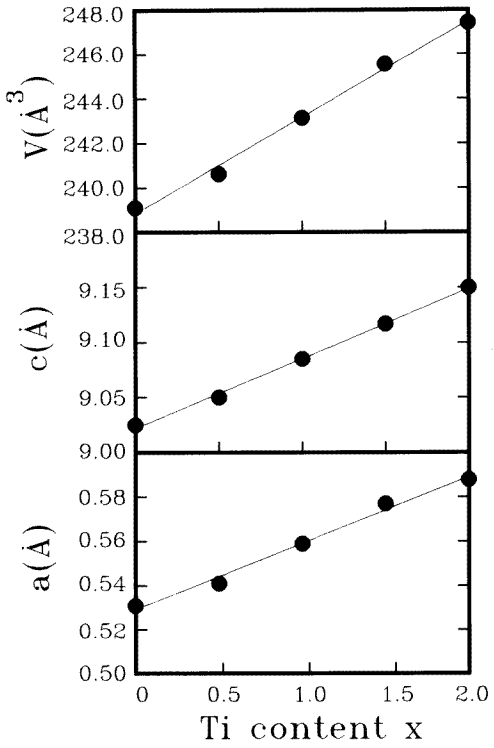

Figure 1. Dependence on Ti content of the lattice constants a and c and the unit-cell volume V of $TbMn_{6-x}Ti_xSn_6$.

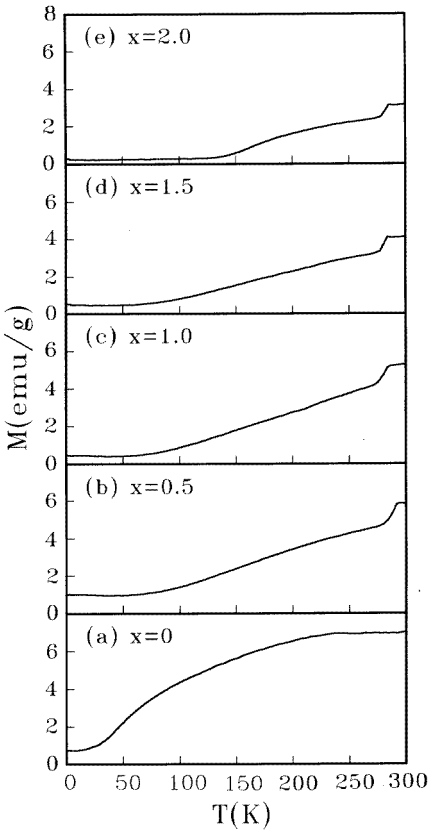

Figure 2. The thermal magnetic behaviour under a magnetic field of 400 Oe in the temperature range 1.5–300 K for $TbMn_{6-x}Ti_xSn_6$ compounds.

to ensure homogeneity. After arc melting, the polycrystalline specimens were sealed into evacuated quartz tubes and annealed at 1073 K for 2 weeks or more and then quenched into water. The crystal structure was analysed by x-ray powder diffraction using Cu Kα. The thermal magnetic behaviours from 1.5 to 300 K were measured on free powder with an extracting-sample magnetometer (ESM) in a field of 400 Oe. The temperature dependences of magnetization between 150 and 500 K at a magnetic field of 400 Oe were measured using a vibrating-sample magnetometer, and the ordering temperatures were derived from

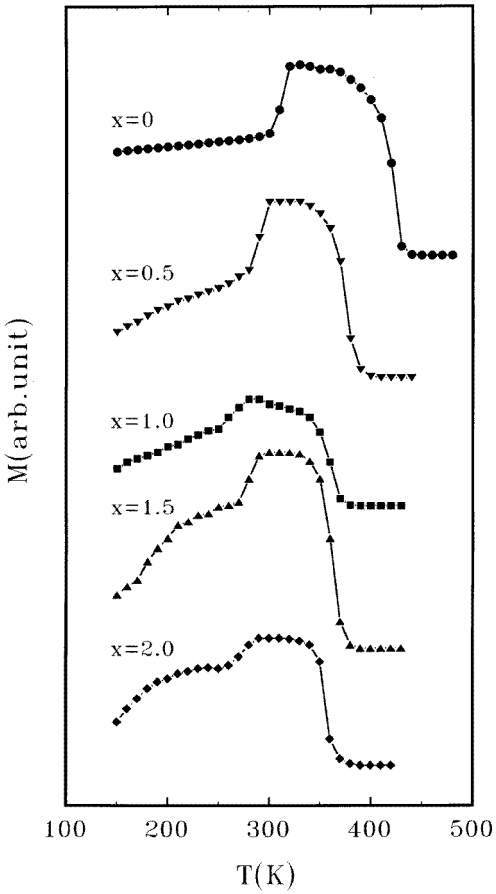

Figure 3. The thermal magnetic behaviour under a magnetic field of 400 Oe in the temperature range 150–500 K for $TbMn_{6-x}Ti_xSn_6$ compounds.

them. The specific magnetizations $\sigma(H)$ were measured in a high pulsed field up to 70 kOe at room temperature; the saturation magnetizations were found by fitting the experimental $\sigma(H)$-values plotted against 1/H using the law of approach to saturation. Data on the free-powder magnetization as a function of the applied magnetic field at 1.5 K were measured with an ESM up to 70 kOe. Due to the slope of the magnetization curves in the field up to 70 kOe, the magnetizations at 1.5 K are obtained by extrapolating H to zero.

3. Results and discussion

The crystal structures were analysed by x-ray diffraction using Cu Kα. The results indicate that all these compounds are single-phase materials, with $HfFe_6Ge_6$-type structure. The crystal structure of $HfFe_6Ge_6$ is a filled derivative of the CoSn B35-type structure (space group; $P6/mmm$). Neutron diffraction results have indicated that the Tb atom occupies the 1b site, the Mn atom occupies the 6i site, and the Sn atom occupies the 2e, 2d, 2c site [2]. In the substitution of Ti for Mn, the structure is not changed; therefore, the Ti atom also occupies the 6i site like Mn. The value of the lattice constants a and c and the unit-cell

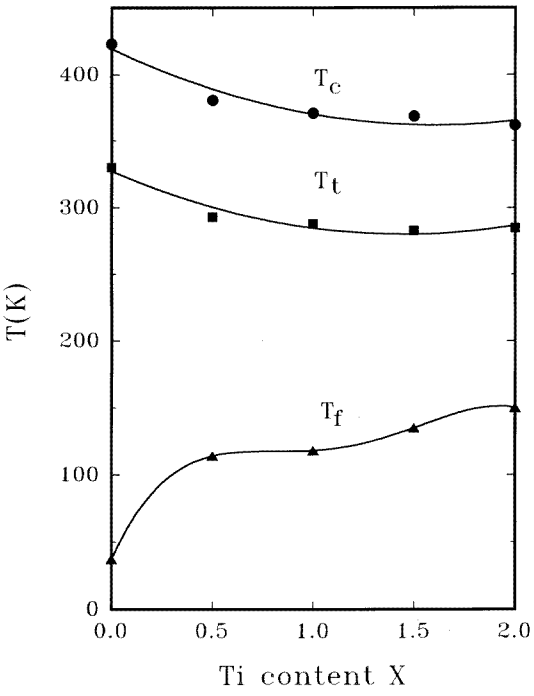

Figure 4. Dependence on Ti concentration of the ordering temperature, the reorientation transition temperature and the temperature of the newly found transition for $TbMn_{6-x}Ti_xSn_6$ compounds.

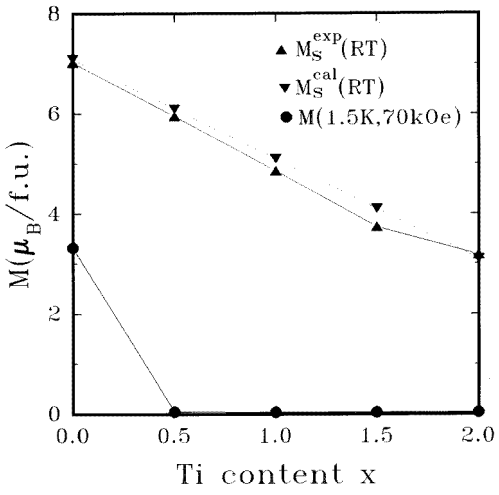

Figure 5. The Ti content dependence of magnetization in a field up to 70 kOe at 1.5 K and the experimental and calculated saturation magnetization at room temperature for $TbMn_{6-x}Ti_xSn_6$ compounds.

volume V are given in table 1. The lattice constants a and c and the unit-cell volume V as functions of the Ti concentration are also shown in figure 1. It can be seen that the

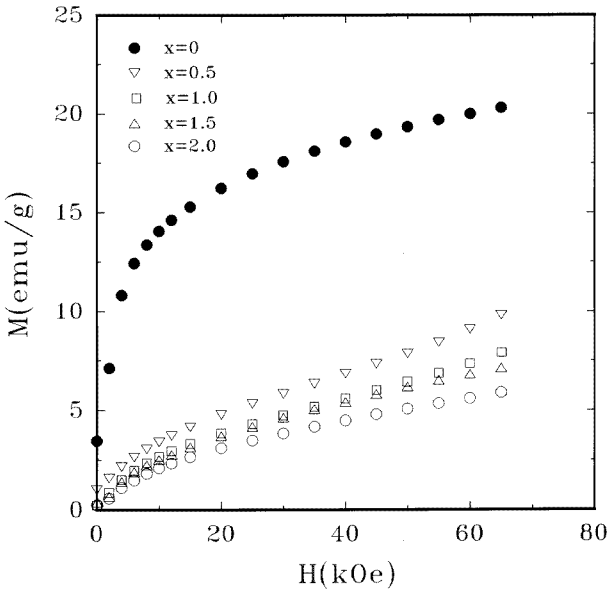

Figure 6. The magnetization curves for $TbMn_{6-x}Ti_xSn_6$ at 1.5 K.

substitution of Ti for Mn results in linear increases in the lattice constants a and c and the unit-cell volume V with increasing Ti concentration. This may be associated with the larger radius of the Ti atoms compared with the Mn atoms.

The temperature dependences of the magnetization of $TbMn_{6-x}Ti_xSn_6$ are shown in figures 2 and 3. Initially the magnetization values are almost independent of temperature and then begin to increase with increasing temperature at T_f. The mechanism of this transition is under investigation. It is also seen that the magnetization changes abruptly at T_t; the abrupt change could be related to a reorientation of the easy axis from the (001) plane to the c axis. The moments lie in the basal plane at high temperatures and are along or near c below the transition temperature. At the ordering temperature T_c the magnetization values decrease to nearly zero again. The values of T_f, T_t and T_c for these compounds are listed in table 1 and their changes as functions of Ti content are shown in figure 4. The Ti substitution not only makes the newly found transition indistinct but also delays it. The reorientation temperature decreases from 330 K at $x = 0$ to 285 K at $x = 2.0$. The ordering temperature decreases monotonically with increasing Ti content from 423 K at $x = 0$ to 362 K at $x = 2.0$. This may be caused by the decrease in magnetic moments.

The magnetization curves at room temperature are measured, and the saturation magnetizations are derived from them. Data on the saturation magnetization are listed in table 1 and its change as a function of Ti content are shown in figure 5. As has been shown in [2], at 300 K, the magnetic structure consists of a stacking of ferromagnetic (001) layers of rare earth and manganese with the coupling sequence Mn(+)R(−)Mn(+)Mn(+)R(−)Mn(+) with $\mu_{Mn} = 2.0\mu_B$ and $\mu_{Tb} = 4.9\mu_B$ and the magnetic moments deviate by $\Phi = 15^\circ$ from the c axis. The saturation magnetization at room temperature can be roughly calculated from $\mu_s = (6 - x)\mu_{Mn} - \mu_{Tb}$. The calculated values are also listed in table 1 and shown in figure 5. The experimental and calculated values coincide well.

The magnetization curves at 1.5 K are shown in figure 6. It can be found that none of these compounds saturate up to 70 kOe. This is consistent with the results of Brabers *et al* [5]. They have found that the magnetization of $TbMn_6Sn_6$ has a tendency towards saturation for higher fields in the H interval up to 350 kOe. The magnetizations at 1.5 K in fields up to 70 kOe derived from the M–H curves are listed in table 1 and shown in figure 5. It is found that the magnetization decreases drastically to nearly zero at $x = 0.5$. This may be related to the delay in the newly found transition on Ti substitution.

4. Conclusion

In this paper, a study of the structural and magnetic properties of $TbMn_{6-x}Ti_xSn_6$ compounds ($x = 0$–2.0) is reported. The main results are gathered in table 1. The $TbMn_{6-x}Ti_xSn_6$ compounds crystallize in the $HfFe_6Ge_6$-type structure. The substitution of Ti in $TbMn_6Sn_6$ increases the lattice constants and the unit-cell volume from $a = 5.531$ Å, $c = 9.025$ Å and $V = 239.10$ Å^3 at $x = 0$, to $a = 5.588$ Å, $c = 9.150$ Å and $V = 247.44$ Å^3 at $x = 2.0$. The ordering temperature is decreased from 423 K at $x = 0$ to 362 K at $x = 2.0$. The reorientation temperature also decreased from 330 K at $x = 0$ to 285 K at $x = 2.0$. In the $TbMn_{6-x}Ti_xSn_6$ compounds with $x = 0$–2.0, a new transition was found at low temperatures. The newly found transition becomes indistinct and is delayed on increase in the Ti content x. The saturation magnetization at room temperature decreases linearly with increasing Ti content from $7.03\mu_B$ FU^{-1} at $x = 0$ to $3.18\mu_B$ FU^{-1} at $x = 2.0$. It is also found that at 1.5 K the magnetization curves are still not saturated up to 70 kOe and the magnetization at 1.5 K in a field up to 70 kOe decreases to nearly zero at $x = 0.5$.

Acknowledgment

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