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Magnetic properties of $TbMn_6Sn_{6-x}Ga_x$ (x=0.0–1.2) compounds*

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Effects of Ga substitution for Sn on the structure and magnetic properties of $TbMn_6Sn_{6-x}Ga_x$ (x=0.0–1.2) compounds have been investigated by means of x-ray diffraction, magnetization measurement and ^{119}Sn Mössbauer spectroscopy. The substitution of Ga for Sn results in a decrease in lattice constants and unit-cell volumes. The magnetic ordering temperature decreases monotonically with increasing Ga content from 423 K for x=0.0 to 390 K for x=1.2. At room temperature, the easy magnetization direction changes from the c-axis to the ab-plane. This variation implies that the substitution of Ga for Sn leads to a decrease in the c-axis anisotropy of the Tb sublattice. An increase in the non-magnetic Ga concentration results in a monotonic decrease of the spontaneous magnetization M_s at room temperature. Since there are three non-equivalent Sn sites, 2c (0.33, 0.67,0), 2d (0.33, 0.67,0.5) and 2e (0,0,0.34) in the $TbMn_6Sn_{6-x}Ga_x$ compounds, the ^{119}Sn Mössbauer spectra of the $TbMn_6Sn_6$ and $TbMn_6Sn_{5.4}Ga_{0.6}$ compounds can be fitted by three sextets. The hyperfine fields (HFs) decrease in the order of HF(2d)>HF(2e)>HF(2c), which is in agreement with the magnetic structure.

Keywords: $TbMn_6Sn_{6-x}Ga_x$ compounds, magnetic properties, structure
PACC: 7530, 7525, 7530G

1. Introduction

In the past ten years, the series of RMn_6X_6 (R=rare earth and X=Sn or Ge) compounds with $HfFe_6Ge_6$-type structure ($P6/mmm$) have attracted extensive attention due to their magnetic structures and magnetic properties.[1] These compounds have a perfect layered structure, which can be described as built of alternating (001) layers along the c-axis with the sequence of –R–Mn–R–R–Mn–R–. These compounds show various behaviours, which should be correlated to a complex interplay between the nearest interlayer R–Mn, Mn–Mn and the intralayer Mn–Mn exchange interactions, and these interactions are believed to be very sensitive to the interatomic distance.[2,3] Among them, the $TbMn_6Sn_6$ compound shows ferrimagnetic structure, resulting from the strong coupling between the Tb and Mn moments, which are arranged antiparallel to each other.[4,5] The intralayer Mn moments are always parallel, resulting in a relatively high ordering temperature of T_C=423 K. Because of the strong coupling between Tb and Mn mentioned above, the interlayer Mn–Mn coupling is also parallel in the $TbMn_6Sn_6$ compound. $TbMn_6Sn_6$ has a spin-reorientation transition at T_{SR}=330 K, corresponding to the atomic moments along the c-axis below T_{SR} and in the ab-plane between T_{SR} and T_C. This compound exhibits a high coercivity of 896 kA/m at 4.2 K because of the high anisotropy of the Tb element at low temperature.

In this paper, the effects of Ga substitution for Sn on the structure and magnetic properties in $TbMn_6Sn_{6-x}Ga_x$ ($0.0 \leq x \leq 1.2$) compounds are reported. By replacing non-magnetic Sn atoms, the Mn–Mn and R–Mn interatomic distances were changed. Because of keeping the number of magnetic Tb and Mn atoms unchanged, the magnetic behaviour of $TbMn_6Sn_6$ can be better studied without considering the dilution of the magnetic sublattices in the compound.

2. Experiments

$TbMn_6Sn_{6-x}Ga_x$ ($0.0 \leq x \leq 1.2$) polycrystalline samples were prepared by arc melting constituent elements in a highly purified Ar atmosphere. The purity

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of the elements was better than 99.9%. An excess of Tb, Mn and Ga over the stoichiometric amount was added to compensate for the mass loss during melting. Having been remelted at least three times to ensure homogeneity, the ingots were wrapped in a Ta foil, and then annealed in an evacuated quartz tube at 1043 K for ten days. To investigate the magnetocrystalline anisotropy, magnetically oriented samples were prepared by mixing powders with epoxy resin into a Teflon tube, and then magnetically aligned (MA) in a field of 800 kA/m at room temperature. In addition, samples with easy-plane anisotropy at room temperature were rotationally aligned to obtain the perpendicularly aligned samples. We carried out x-ray diffraction (XRD) studies at room temperature to investigate the crystal structure and easy magnetization direction (EMD) of these compounds, using a Rigaku Rint 1400 diffractometer with Cu$K\alpha$ radiation. Below 400 K the magnetic properties of all samples were measured with a superconducting quantum interference device (SQUID) magnetometer, while those above 400 K were measured by a vibrating sample magnetometer (VSM) in a field of 40 kA/m. We used ^{119}Sn Mössbauer spectroscopy to investigate the hyperfine fields (HFs) at the three non-equivalent Sn sites.

3. Results and discussion

XRD patterns show that each sample with $x \leq 1.2$ is single phase with a hexagonal $HfFe_6Ge_6$-type structure. More Ga substitution leads to the appearance of some impurity phases. So, in this paper, the results and discussion are presented for samples with $x \leq 1.2$, when the substitution of Ga for Sn does not change the crystal structure of this series of compounds. Because the covalent radius of Ga is smaller than that of the Sn atom, the substitution leads to a decrease in both the lattice constants a and c and the unit-cell volume v (Fig.1). This also means that the Mn–Mn interatomic distance within (001) Mn planes and the interplanar distance are both decreased, because they are proportional to the lattice constants a and c, respectively. There are three different Sn sites, 2c, 2d and 2e, in the $TbMn_6Sn_6$ compound. Our recent XRD Rietveld analysis for the sample of $TbMn_6Sn_{5.4}Ga_{0.6}$ indicated that Ga atoms preferably occupy the 2d sites. It is worthy mentioning that, for all samples, the ratio of c/a almost remains constant, indicating an isotropic contraction. Similar results have also been shown in $YMn_6Sn_{6-x}Ga_x$ compounds.[6]

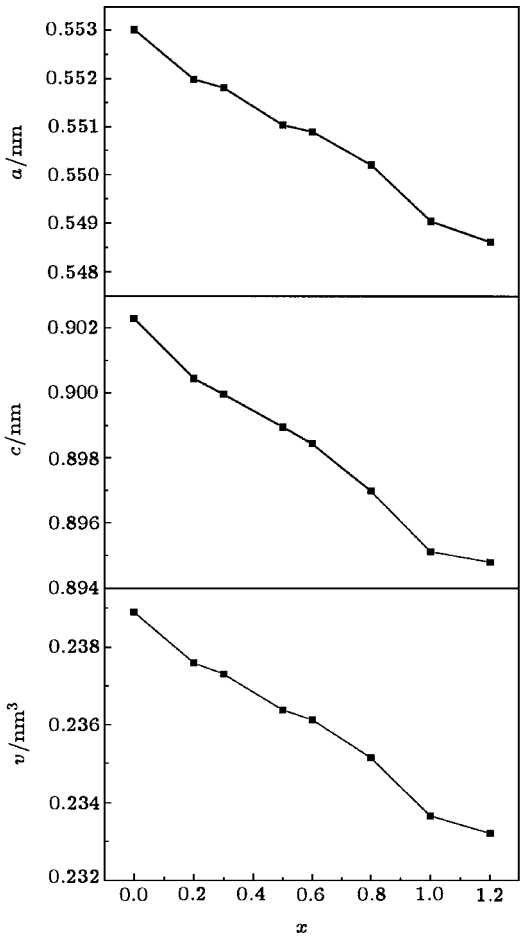


Fig.1. Dependence of the lattice constants a and c and the unit-cell volume v on Ga content in $TbMn_6Sn_{6-x}Ga_x$ compounds.

Figure 2 shows the temperature dependence of the magnetization of $TbMn_6Sn_{6-x}Ga_x$ compounds measured in a magnetic field of 40 kA/m. All the $TbMn_6Sn_{6-x}Ga_x$ compounds display a sharp Curie point above room temperature. At low temperatures, the magnetization of the compounds with low Ga concentration ($x \leq 0.8$) remains low, but when $x \geq 1.0$ the compounds show a significant increase in magnetization. From the thermomagnetic curves of all samples, the magnetic-ordering transition and the spin-reorientation transition can be observed and both transition temperatures decrease gradually by the substitution of Ga for Sn. The magnetic ordering temperature decreases slightly for the variation of Ga concentration from 423 K for x=0.0 to 390 K for x=1.2. The spin-reorientation transition becomes progressively less defined and decreases dramatically from T_C, that is, from 330 K for x=0.0 to 60 K for x=1.0.

For the sample with x=1.2, the spin-reorientation transition is difficult to identify. It seems that Ga concentration affects the spin-orientation transition more strongly than the transition from ferrimagnetic to paramagnetic in the compounds. According to our previous work, substitution of Sn by Ti enlarges the lattice volume, and also lowers the magnetic ordering temperature.[7] Although adding Ga into the compounds decreases the lattice volume, T_C and T_{SR} are both lowered, which indicates that there is no simple correlation between the size effect and the magnetic properties. The reasons for these variations need further investigation.

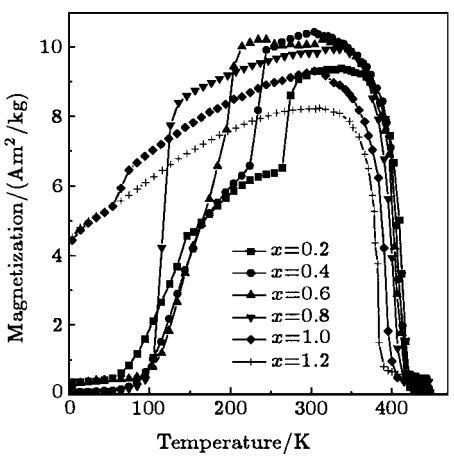


Fig.2. Thermomagnetic behaviour under a magnetic field of 40 kA/m for $TbMn_6Sn_{6-x}Ga_x$ compounds.

Figure 3 (a) displays the isothermal magnetization curves of $TbMn_6Sn_{6-x}Ga_x$ ($0.0 \leq x \leq 1.2$) compounds measured at 5 K. For x=0.0, the compound shows a large initial permeability, indicating that the domain walls are initially free to move and can be swept through the compound under low fields. While for x=0.2–0.4, the initial magnetization is marked by a low initial permeability, which then increases to a maximum and the magnetization increases sharply. For samples with x=1.0 and 1.2, the magnetization is high even at low fields, which is in agreement with the M–T curves shown in Fig.2. For $TbMn_6Sn_{6-x}Ga_x$ ($0.0 \leq x \leq 1.2$) compounds, the isothermal magnetization curves at room temperature have been measured and are shown in Fig.3(b). All samples display spontaneous magnetization, showing no evidence of significant magnetocrystalline anisotropy, and all the magnetization curves almost saturate in the applied field range. Because the samples do not saturate under a field of 4 MA/m at 5 K, the saturation magnetization is derived by extrapolating the linear parts of M–H curves at room temperature in the high field region to H=0. The spontaneous magnetization at room temperature decreases linearly with increasing non-magnetic Ga concentration. These results are in agreement with the decrease of T_C with increasing Ga content in $TbMn_6Sn_{6-x}Ga_x$. In order to gain a better understanding of the complicated behaviour of these compounds, a high-field study of these samples may be helpful.

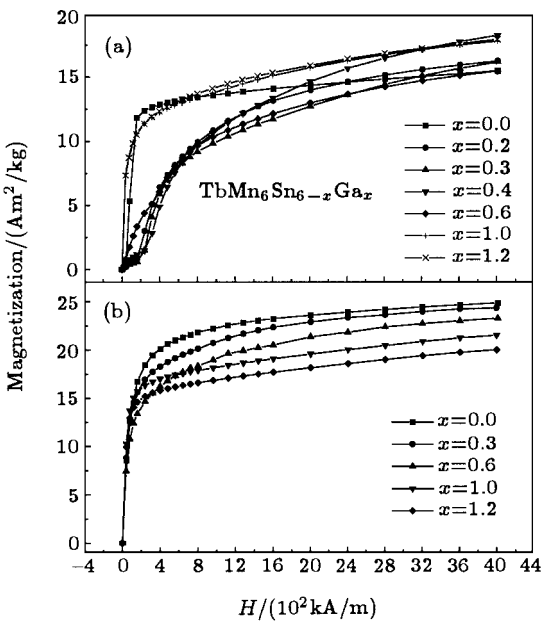


Fig.3. Isothermal magnetization curves of $TbMn_6Sn_{6-x}Ga_x$ compounds at 5 K (a) and 293 K (b).

Figure 4 shows the XRD patterns of magnetically oriented $TbMn_6Sn_{6-x}Ga_x$ samples at room temperature. The substitution of Ga for Sn causes the EMD to change directly from the c-axis to the ab-plane in the $TbMn_6Sn_{6-x}Ga_x$ compounds at room temperature. As shown in Fig.4, when x=0.2, the EMD of $TbMn_6Sn_{6-x}Ga_x$ has been changed to the ab-plane. According to Ref.[4], the Tb sublattice has an axial anisotropic contribution, while the Mn sublattice has a planar anisotropic contribution. A spin-reorientation transition occurs when the axial anisotropy of the heavy rare-earth element Tb and the planar anisotropy of the Mn sublattice cancel each other.[4] As discussed above, the Curie temperature of $TbMn_6Sn_{6-x}Ga_x$ compounds decreases with increasing substitution. Consequently, the anisotropy field H_A of these compounds also decreases with T/T_C.

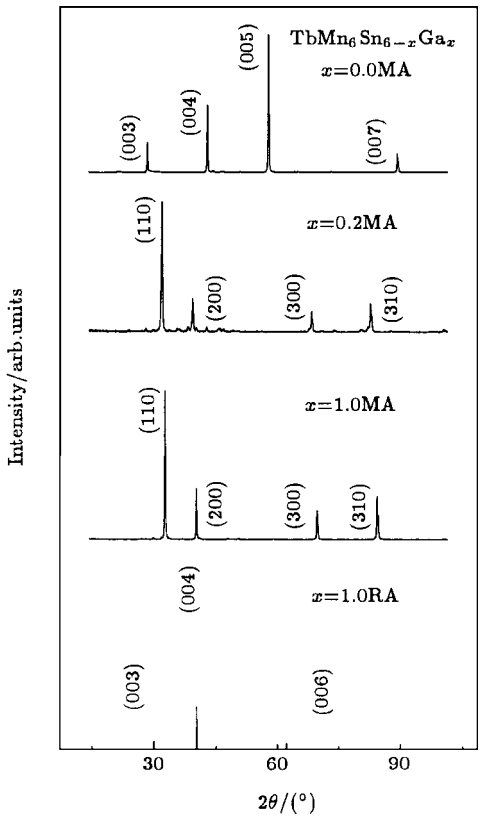


Fig.4. XRD patterns of the magnetically oriented Tb $Mn_6Sn_{6-x}Ga_x$ samples with x=0.0, 0.2 and 1.0 (MA, magnetically aligned; RA, rotationally aligned).

Especially, when T/T_C approaches 1, H_A decreases rapidly. Thus, the axial anisotropic contribution of the Tb sublattice at room temperature lowers by the decrease of the Curie temperature of these compounds. This results in a change of the EMD of $TbMn_6Sn_{6-x}Ga_x$ compounds from the c-axis to the ab-plane at room temperature. Rotationally aligned samples, as shown in Fig.4, also illustrate the conclusion made above. For example, for the sample with x=1.0, when its surface is perpendicular to the magnetic field, the XRD pattern shows an enhancement of the ($hk0$) peaks. When its surface is parallel to the magnetic field, the XRD pattern presents an enhancement of the (00l) peaks.

In order to verify the magnetic transition at low temperatures in $TbMn_6Sn_{6-x}Ga_x$ (x=1.0 and 1.2), we measured the isothermal magnetization curve of the magnetically oriented samples at various temperatures. The results are shown in Fig.5. It can be seen that, for the sample with x=1.0, the EMD has been changed gradually, from the ab-plane to the cone structure by decreasing the temperature to 5 K. For the sample with x=1.2, the magnetization curves indicate that its EMD is within the ab-plane throughout the magnetic ordering temperatures.

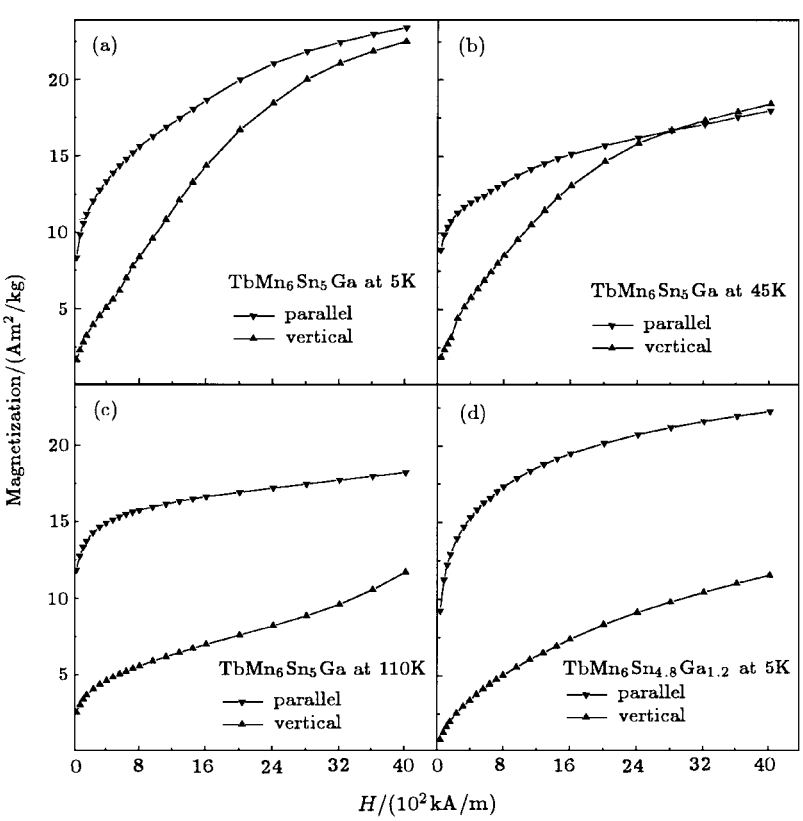


Fig.5. Isothermal magnetization curves of the magnetically oriented $TbMn_6Sn_{6-x}Ga_x$ compounds: (a) x=1.0 at 5 K, (b) x=1.0 at 45 K, (c) x=1.0 at 110 K, (d) x=1.2 at 5 K.

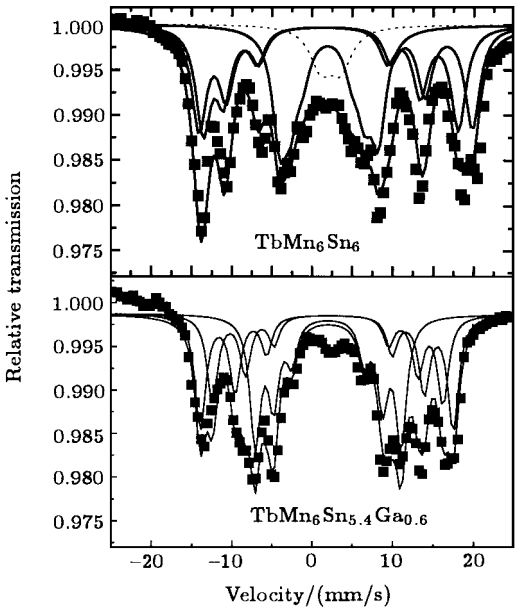


Fig.6. ^{119}Sn Mössbauer spectra of $TbMn_6Sn_6$ and $TbMn_6Sn_{5.4}Ga_{0.6}$ at room temperature: solid lines, the fitted results of the three subspectra and the sum of these subspectra; solid squares, the experimental data; dashed line, paramagnetic impurity.

Figure 6 illustrates the ^{119}Sn Mössbauer spectra of $TbMn_6Sn_6$ and $TbMn_6Sn_{5.4}Ga_{0.6}$ compounds. As mentioned above, there are three non-equivalent Sn sites, 2c (0.33, 0.67, 0), 2d (0.33, 0.67, 0.5) and 2e (0, 0, 0.34) in $TbMn_6Sn_{6-x}Ga_x$, supposing Tb (0, 0, 0) and Mn (0.5, 0, 0.245), and we fit the spectra with three subspectra. The HFs corresponding to these three subspectra are 20, 19 and 7.4 MA/m for $TbMn_6Sn_6$ and 19, 17.5 and 11 MA/m for $TbMn_6Sn_{5.4}Ga_{0.6}$, respectively. The addition of Ga leads to a decrease of the HFs due to the decrease of the saturation magnetization and the Curie temperature. Since Sn is a non-magnetic atom, the HFs at the Sn sites are transferred from neighbouring magnetic atoms and are proportional to the number of the neighbouring magnetic atoms and their magnetic moments. All three Sn sites have six nearest-neighbour Mn atoms, while the Sn atoms at 2c, 2d and 2e sites have three, zero and one Tb atoms as neighbours. Due to the anti-ferromagnetic coupling between Tb and Mn sublattices, the HFs decrease in the order HF(2d)>HF(2e)>HF(2c). The intensities of the three subspectra for $TbMn_6Sn_{5.4}Ga_{0.6}$ imply that the Ga atoms prefer the 2d sites, which is in agreement with the XRD results.

4. Summary

The substitution of Ga for Sn in $TbMn_6Sn_{6-x}Ga_x$ (x=0.0–1.2) leads to a decrease in the lattice parameters, the magnetic ordering temperature T_C and the spontaneous magnetization M_s at room temperature. The EMD at room temperature changes from the c-axis to the ab-plane, due to a decrease in the c-axis anisotropy of the Tb sublattice. ^{119}Sn Mössbauer spectroscopy and XRD Rietveld analysis of the $TbMn_6Sn_6$ and $TbMn_6Sn_{5.4}Ga_{0.6}$ compounds show that the Ga atoms prefer the Sn(2d) sites.

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