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Temperature-induced spin reorientation in $TbMn_6Sn_{6-x}Ga_x$

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The spin reorientation process in $TbMn_6Sn_{6-x}Ga_x$ has been investigated using ^{119}Sn Mössbauer spectroscopy. The Sn site hosting the substituting Ga atoms is identified as Sn-2*d*. The reorientation is confirmed to be a 90° rotation of the Mn moments from *ab* plane to *c* axis upon cooling through T_{sr}. The reorientation temperature T_{sr} is observed to decrease with increasing Ga doping at 255 ± 18 K/Ga. Finally, we evaluate the anisotropic contributions to the hyperfine field at the Sn sites as seen through the spin reorientation. © *2006 American Institute of Physics*.

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I. INTRODUCTION

The hexagonal $TbMn_6Sn_6$ system shows several interesting magnetic properties including two different magnetic transitions. It has a $HfFe_6Ge_6$-type crystal structure and crystallizes in the $P6/mmm$ space group ($n°$ 191). The magnetic structure is characterized by alternating ferromagnetic Mn and Tb layers, ordered in the *ab* plane and stacked along *c*.[1] Strong antiferromagnetic coupling between the Mn and Tb layers imposes simultaneous order and ferrimagnetism below T_N=423 K in $TbMn_6Sn_6$,[2] resulting in a stacking along *c* of Mn(←)Tb(→)Mn(←)Mn(←)Tb(→)Mn(←). Further cooling causes a spin reorientation of the Mn moments from the *ab* plane to the *c* axis at T_{sr}=330 K,[2] a process driven by the anisotropy of the Tb atoms along with their coupling to the 3*d*-Mn atoms. This is a strong function of the electron density at the Sn site so that doping with Ga in $TbMn_6Sn_{6-x}Ga_x$ will decrease T_{sr} as *x* is increased. Since the hyperfine field of the Sn atoms is a function of not only the magnetic structure but also of the chemical bonds of Sn with the magnetic atoms in the surrounding layers, ^{119}Sn Mössbauer spectroscopy is a reliable approach to the study of spin reorientation in $TbMn_6Sn_{6-x}Ga_x$.

There are three crystallographic Sn sites in $TbMn_6Sn_6$: Sn-2*c*, Sn-2*d*, and Sn-2*e*. Sn-2*c* lies in the plane of three rare-earth neighbors, and Sn-2*d* is out of plane. Work done on x-ray single-crystal refinement of $TmMn_6Sn_{6-x}Ga_x$ shows Ga atoms to be mostly located on the Sn-2*c* and Sn-2*d* sites, with a preference for Sn-2*c*.[3] In this study, we use ^{119}Sn Mössbauer spectroscopy to investigate these site occupations in $TbMn_6Sn_{6-x}Ga_x$ and evaluate the anisotropic contribution to the hyperfine fields at the three Sn sites, associating each site with an equivalent Mössbauer subspectrum. We also confirm the spin reorientation to be a rotation of the Mn moments by 90° and investigate the effect of Ga doping on the temperature of the spin reorientation.

II. EXPERIMENTAL METHODS

The four $TbMn_6Sn_{6-x}Ga_x$ compounds (x=0.2, 0.4, 0.6, and 0.8) were prepared by alloying stoichiometric amounts of Tb, Mn, Sn, and Ga (all of 99.9% purity) in an induction furnace.[4] The resulting ingots were sealed under argon in quartz tubes and annealed for 2 weeks at 973 K. Mössbauer spectra were collected using a 10 mCi ^{119m}Sn $CaSnO_3$ source and the spectrometer was calibrated with α-Fe and a ^{57}Co source. The temperature was varied from 12 to 300 K using a vibration-isolated closed-cycle refrigerator. Spectra were fitted using a conventional nonlinear least-squares minimization routine.

III. RESULTS AND DISCUSSION

An example of Mössbauer spectra for $TbMn_6Sn_{5.6}Ga_{0.4}$ is shown in Fig. 1. At 12 K, the patterns show relatively distinguishable lines and were fitted with three sextets and a central Sn impurity [isomer shift δ=2.69(5) relative to ^{57}Fe for x=0.4]. The fits were designed to permit the areas of the three sextets to be adjusted freely. The Mössbauer parameters given by Mazet *et al.*[5] for $TbMn_6Sn_6$ at T=4.2 K served as a guide in estimating the quadrupole splittings (Δ) of the 12 K patterns of all four alloys. The uniqueness of the hyperfine parameters given by these fits allows for the unambiguous assignment of each of the three Mössbauer sextets to a Sn site.

The rare-earth atoms sit in the Tb-1*a* site at the origin (0,0,0). The coordinates of the Sn sites relative to the origin are thus $(\frac{1}{3},\frac{2}{3},0)$, $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$, and (0,0,0.34) for Sn-2*c*, -2*d*, and -2*e*, respectively. The alternate choice of origin at $(0,0,\frac{1}{2})$, which assigns the rare-earth atoms to the Tb-1*b* site,

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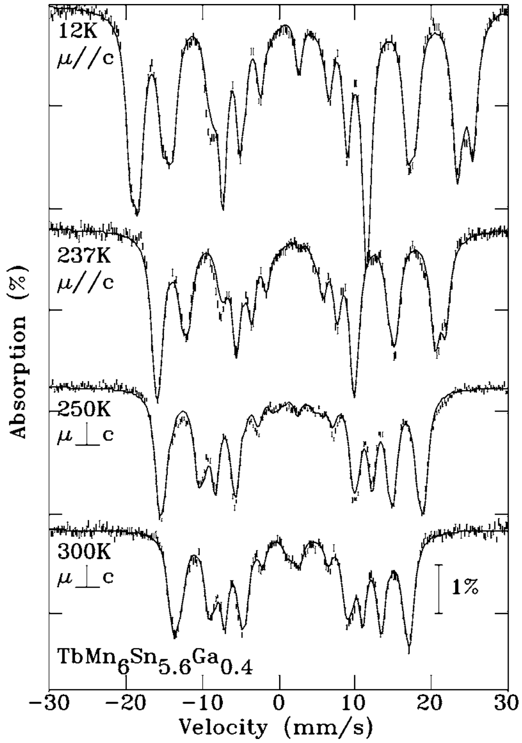

FIG. 1. Mössbauer spectra of $TbMn_6Sn_{6-x}Ga_x$ for $x=0.4$. The temperature of the spin reorientation is $T_{sr}=244(7)$ K.

moves Sn-2*d* into the plane of the rare earths and consequently leads to different labeling.[6] Of the three Sn sites, Sn-2*e* differs the most, lying in a hexagonal plane of Mn atoms with one Tb above and one Sn below. Sn-2*d* and Sn-2*c* both sit in Mn_6 hexagonal prisms, where Sn-2*d* has no rare-earth near neighbors and Sn-2*c* is in the plane of three Tb. This being the only difference between the two sites [considering the similar $Mn-Sn_i$ bond lengths of 2.75 and 2.78 Å for Sn-2*c* and -2*d* compared to the longer 2.88 Å for Sn-2*e* (Ref. 6)] suggests comparable prismatic environments. This assumption guides the assignment of Sn sites to Mössbauer sextets on the basis of their fitted quadrupole splittings at 12 K.

For example, the 12 K spectrum for $TbMn_6Sn_{5.8}Ga_{0.2}$ has quadrupole splittings $\Delta=1.57(3)$, 1.11(1), and 0.16(1) mm/s and hyperfine fields $B_{hf}=32.94(4)$, 30.44(4), and 13.81(2) T, respectively. The site assignments are based on previous studies of $HfMn_6Sn_6$ at 100 K, whose crystal structure is identical to that of $TbMn_6Sn_6$ but with antiferromagnetic order.[7] The ferromagnetic Mn layers above and below the nonmagnetic Hf layers are in this case antiparallel such that the Sn atoms in the plane of Hf (Sn-2*c*) see no net hyperfine field. The quadrupole splitting at Sn-2*c* is measured to be $\Delta=1.1$ mm/s, and assuming that the replacememt of nonmagnetic Hf with magnetic Tb has little or no effect on the crystalline electric field, we can assign $\Delta=1.11(1)$ mm/s to Sn-2*c* in $TbMn_6Sn_{5.8}Ga_{0.2}$. The field at Sn-2*c*, $B_{hf}=30.44(4)$ T, is due to the three neighboring Tb moments. We can then attribute the slightly larger $\Delta=1.57(3)$ mm/s [$B_{hf}=32.94(4)$ T] to the geometrically similar Sn−2*d*. This leaves Sn-2*e* with the smallest quadrupole splitting and field, $\Delta=0.16(1)$ mm/s and $B_{hf}=13.81(2)$ T.

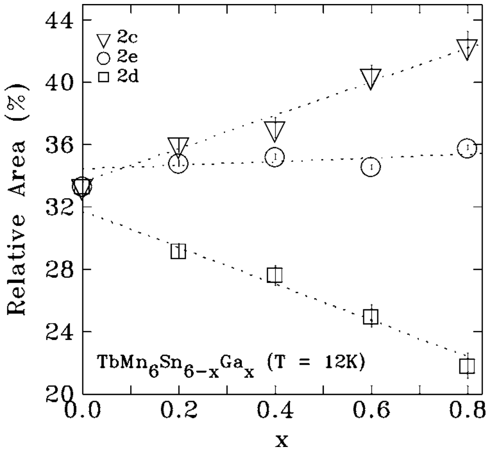

FIG. 2. Relative areas at 12 K of the three Sn sites with *x*.

Previous studies on x-ray single-crystal refinement of $TmMn_6Sn_{6-x}Ga_x$ have shown Ga atoms to substitute on both the Sn-2*c* and Sn-2*d* sites, with a preference for Sn-2*c*, while mostly avoiding Sn-2*e*.[3] The present Mössbauer study in contrast shows this substitution to occur *mostly* on Sn-2*d*. The area of the Mössbauer subspectrum associated with the Sn-2*d* site shows a strong relation to Ga concentration. The systematic reduction of the area of the Sn-2*d* component with increasing *x* indicates the depopulation of Sn atoms at the Sn-2*d* site caused by their replacement by Ga atoms (Fig. 2). There is also evidence of a slight bias for the Sn-2*e* site. After renormalizing to the Sn-2*c* area, the Sn-2*e* areas show a weak dependence on the level of Ga doping and decrease with *x* in the same manner as Sn-2*d*, though the effect is much smaller.

At 12 K, the Mössbauer lines are mostly distinct, but increasing temperature introduces dense overlapping of several of the Mössbauer lines, notably at $T > T_{sr}$. Thus the fitting of spectra for $12\text{ K} < T < 300\text{ K}$ involved a few carefully constructed constraints. The expectation that the reorientation involves a full 90° rotation of the Mn moments gives an estimate of quadrupole splittings for $T > T_{sr}$ according to those fitted at 12 K. The areas of the three Mössbauer sextets were constrained (allowing for the central Sn impurity area to vary and eventually become negligible) to the average values seen at $T \ll T_{sr}$. The removal of a few degrees of freedom in the fits allowed for a clearer picture of the evolution of the interesting phenomena manifested in the quadrupole splittings and hyperfine fields at the Sn sites.

The high point symmetries of the three Sn sites (6*mm* for Sn-2*e* and $\bar{6}m2$ for Sn-2*c* and Sn-2*d*) cause the crystallographic and electric-field gradient axes to coincide, guaranteeing that the principal axis of the electric-field gradient tensor V_{zz} lies along *a*, *b*, or *c*. V_{zz} is confirmed to be parallel to the *c* axis in a study by Perry *et al.* on $(Tb,Gd)Mn_6Sn_{5.5}In_{0.5}$ single crystals.[8] The local hexagonal point symmetries also impose axial symmetry ($\eta=0$), such that the quadrupole splitting Δ can be calculated as

$$\Delta = \frac{eQV_{zz}}{4}(3\cos^2\theta - 1), \tag{1}$$

where θ is defined as the angle between V_{zz} and the hyperfine field at the Sn sites due to the surrounding magnetic mo-

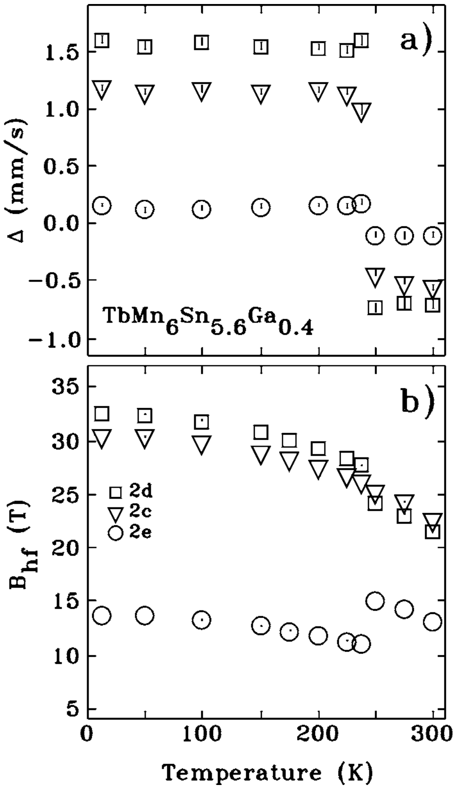

FIG. 3. (a) Quadrupole splittings of the three Sn sites as functions of temperature in $\mathrm{TbMn_6Sn_{5.6}Ga_{0.4}}$, which change by a factor of −2 (within error) when cooling through $T_{\mathrm{sr}}=244(7)$ K. (b) Hyperfine field variations with temperature for Sn-2*c*, Sn-2*d*, and Sn-2*e* in $\mathrm{TbMn_6Sn_{5.6}Ga_{0.4}}$.

ments. For $\theta=90°$ ($\mu\perp c$, i.e., *ab* plane), $\Delta=-\frac{1}{4}eQV_{zz}$ and for $\theta=0°$ ($\mu\parallel c$), $\Delta=\frac{1}{2}eQV_{zz}$. The factor of −2 between quadrupole splittings at 90° ($T>T_{\mathrm{sr}}$) and 0° ($T<T_{\mathrm{sr}}$) is seen in all of the $\mathrm{TbMn_6Sn_{6-x}Ga_x}$ alloys investigated [Fig. 3(a) shows an example for $x=0.4$]. This abrupt change by −2 confirms that the reorientation consists of a rotation of the Mn moments by 90°, from *ab* plane (001) at $T>T_{\mathrm{sr}}$ to *c* axis [001] at $T<T_{\mathrm{sr}}$, an effect independent of doping with the exception of the temperature at which the reorientation occurs. T_{sr} is a strong function of x, showing a significant decrease of 255 ± 18 K/Ga in T_{sr} as x increases from 0.2 to 0.8 (Fig. 4). The extrapolated reorientation temperature for $x=0$ is $T_{\mathrm{sr}}=332(19)$ K, in excellent agreement with the 330 K given by Venturini *et al.*[2] This variation in T_{sr} is an effect of the electron density at the Sn site, and a different choice of substituting atom will give a different spin reorientation temperature. For example, $\mathrm{TbMn_6Sn_{5.2}Ga_{0.8}}$ has $T_{\mathrm{sr}}=116(8)$ K, whereas $\mathrm{TbMn_6Sn_{5.2}Ti_{0.8}}$ has $T_{\mathrm{sr}}\sim381$ K.[9]

The hyperfine field at a given Sn site results from the hybridization of the valence *sp* states of Sn and the polarized *d* states of Mn, and has both isotropic (Fermi contact field) and anisotropic (orbital field) contributions.[7] The anisotropy arises from covalent bonding between Sn and its Mn neighbors and thus is related to the 3*d*-moment direction with respect to the Mn–Sn bond. Such an anisotropic contribution has been observed in binary transition-metal stannides such as $\mathrm{FeSn_2}$.[10] Due to the particular crystallographic and magnetic structures of this compound, the positive and negative isotropic contributions cancel and only the anisotropic contribution is observed. This is not the case for the Sn sites in the $\mathrm{HfFe_6Ge_6}$-type compounds investigated here, where anisotropic contributions can only be detected through spin reorientation. It is worth noting that the reorientation of the moments from the *ab* plane to the *c* axis on cooling through T_{sr} is associated with a decrease of the hyperfine field at the Sn-2*e* site and an increase at the Sn-2*c* and Sn-2*d* sites. The change appears as a significant jump in the case of Sn-2*d* and Sn-2*e* and only a small shift in B_{hf} for Sn-2*c* [Fig. 3(b)]. This evolution is in good accordance with the corresponding angles between the Mn−Sn_i bonds and the *c* axis (~35° for Sn-2*c* and Sn-2*d* and ~73° for Sn-2*e*), indicating that the isotropic and anisotropic contributions add together. Further investigations should enable the determination of quantitative values for the isotropic and anisotropic constants.

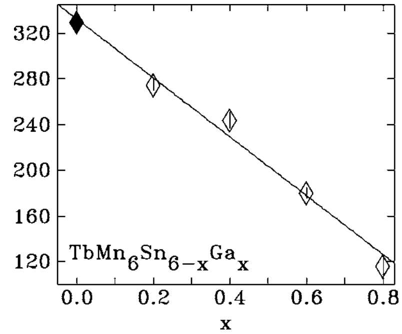

FIG. 4. Decrease in T_{sr} with x by 255 ± 18 K/Ga, from 330 K (Ref. 2) at $x=0$ (filled diamond) to 116(8) K at $x=0.8$.

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