119Sn transferred hyperfine fields in ErMn$_6$Sn$_{6-x}$Ga$_x$

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We present here the Sn anisotropic fields in ErMn$_6$Sn$_{5.89}$Ga$_{0.11}$, studied by $^{119}$Sn Mössbauer spectroscopy. The moments undergo a 90° spin reorientation from the $ab$ plane to the $c$ axis on cooling through $T_{sr}$=38(2) K. We find that the hyperfine field at Sn-2$c$ is totally isotropic, while 5(1)% of $B_{hf}$ at Sn-2$d$ and more than 20% of $B_{hf}$ at Sn-2$e$ arise from anisotropic contributions.

I. INTRODUCTION

The hyperfine field ($B_{hf}$) observed at nonmagnetic probe sites in magnetically ordered materials must arise from the effects of surrounding magnetic moments. The transfer process is generally assumed to be isotropic, driven by the magnitude of the neighboring moments and their magnetic symmetry. However, where the bonding has a partially covalent character, the transferred hyperfine field includes an anisotropic contribution: $B_{hf}$ also depends on the relative orientations of the moments and their connecting bonds. This anisotropic contribution can be a substantial fraction of the total transferred hyperfine field and neglecting the anisotropic contribution to $B_{hf}$ can lead to incorrect site assignments in multicomponent spectra. Attributing the component with the largest $B_{hf}$ to the site with the most magnetic neighbors frequently fails to yield a correct interpretation of the observed spectrum.

To isolate the anisotropic contribution, we need to change the orientation of the surrounding magnetic moments without affecting their symmetry, positions, or magnitudes. In many of the ferrimagnetic RMn$_6$Sn$_6$ compounds, the moments undergo a spontaneous temperature-driven reorientation in which they rotate from the $ab$ plane to the $c$ axis on cooling through $T_{sr}$. The magnetic structures of these compounds are simple and provide three distinct Sn sites at which to study the anisotropic field. As the environment of each site is unique, the spin reorientation affects each Sn site differently. In TbMn$_6$Sn$_{6-x}$Ga$_x$, the size ordering of hyperfine fields changes at $T_{sr}$ so that a site assignment based solely on the magnitudes of $B_{hf}$ does not yield a unique result. Site assignments in this system must be based on the electrostatic environment ($\Delta$), which is unaffected by the reorientation except for a uniform change by a factor of $-2$.

Although the moments in ErMn$_6$Sn$_6$ do not undergo a spin reorientation transition, the transition can be forced with a small amount of Ga doping ($x_{cm}=0.1$), and $T_{sr}$ can be driven as low as 36 K (Ref. 4) (in TbMn$_6$Sn$_{6-x}$Ga$_x$, Ga doping decreases $T_{sr}$ by $\sim$255 K/Ga) where the thermal variation of the moments is negligible, resulting in a clean and simple spin reorientation. We present here a $^{119}$Sn Mössbauer study of the transferred hyperfine fields in ErMn$_6$Sn$_{5.89}$Ga$_{0.11}$. We find that on cooling through $T_{sr}$=38(2) K, the quadrupole splitting changes by a factor of $-2$, within error, for all three Sn sites, consistent with a full 90° rotation of the moments. From the change in $B_{hf}$ through $T_{sr}$, we determine the anisotropic contributions to $B_{hf}$ at each Sn site. Remarkably, more than 20% of the hyperfine field at one site (Sn-2$e$) arises from anisotropic contributions.

II. EXPERIMENTAL METHODS

The ErMn$_6$Sn$_{5.89}$Ga$_{0.11}$ single crystal was synthesized using a flux method similar to that previously reported in Ref. 5. Stoichiometric amounts of ErMn$_6$Sn$_6$ and elemental gallium (atomic ratio ErMn$_6$Sn$_{31.5}$Ga$_{0.5}$) were alloyed in an induction furnace. The resulting ingot was sealed under argon in a silica tube and annealed for two weeks at 1263 K. In RMan$_6$Sn$_{6-x}$Ga$_x$, R and $x$ yield larger single crystals. ErMn$_6$Sn$_{5.89}$Ga$_{0.11}$ grew as a large ($-7\times4\times1$ mm$^3$), faceted, single crystal. Part of it was powdered for x-ray diffraction and Mössbauer spectroscopy. The compound is isotopic with the HfFe$_6$Ge$_6$-type crystal structure (P6/mmm space group), with cell parameters $a=5.508(2)$ Å and $c=8.989(5)$ Å. The crystal cleaves parallel to the $a$ axis so that an oriented piece could be cut for magnetometry.

III. RESULTS AND DISCUSSION

The Mn sublattice of the ternary ErMn$_6$Sn$_6$ compound orders antiferromagnetically at $T_N$=352 K. The material becomes ferrimagnetic when the Er sublattice orders at 75 K. With a small amount of Ga substitution, the ErMn$_6$Sn$_{5.89}$Ga$_{0.11}$ compound is ferrimagnetic over its whole ordered range below $T_N$=372 K. Figure 1 shows the magnetization ($T\leq60$ K) in an applied field of $B_0$=1 T, for $B_0$ both parallel (left) and perpendicular (right) to the $c$ axis. The
anomaly at $T_{sr} = 39(1)$ K marks the spin reorientation transition. The width of the transition is less than 1 K, so the reorientation is an abrupt, well-defined transition. $T_{sr}$ is in close agreement with that measured in the polycrystalline ErMn$_{5.85}$Sn$_{5.89}$Ga$_{0.11}$ compound ($T_{sr} = 36$ K).

The temperature dependence of the reorientation is an abrupt, well-defined transition. The width of the transition is less than 1 K, so the field ordering within error for all three Sn sites (Table II). The moments thus rotate by 90° on cooling through $T_{sr} = 38(2)$ K, from the $ab$ plane to the $c$ axis.

The temperature dependence of $B_{hf}$ at the three Sn sites is shown in Fig. 3 (bottom right). On cooling through $T_{sr}$, $B_{hf}$ decreases at Sn-2e and increases at Sn-2d, while there is very little change at Sn-2c. We can determine the anisotropic field directly from these changes in $B_{hf}$, since it alone is changed by the reorientation. The temperature dependence of $B_{hf}$ for $T > T_{sr}$ ($\mu \perp c$) was fitted to a Brillouin curve and extrapolated to $T_{sr}$. The difference $B_{hf}^{sf}(T_{sr}) - B_{hf}^{sf}(T_{sr})$ was tracked back to 0 K in order to determine the change in hyperfine field due to the reorientation at 0 K, $\delta B_{hf}$. This change in $B_{hf}$ is the anisotropic field, $B_{hf}^A$ given in the second column of Table III for each Sn site.

The first neighbors for all three Sn sites are Mn atoms.
with the Er atoms further away. The anisotropic contribution to \( B_{hf} \) is thought to arise through partially covariant bonding between the magnetic atoms and the Sn.\textsuperscript{1,2} If we therefore ignore contributions to \( B_{hf} \) from second neighbor Er atoms (the observed fields here are comparable to those in alloys with nonmagnetic atoms in the Er position\textsuperscript{10}), the transferred hyperfine field at the Sn sites is given by \textsuperscript{1}

\[
B_{hf} = \left[ \sum_{i=1}^{6} A_p \cdot \mathbf{u}_i \cdot (\mu_i \cdot \mathbf{u}_i) - \frac{3}{2} \sum_{i=1}^{6} \mathbf{u}_i \right] + \sum_{i=1}^{6} \mathbf{A}_s \cdot \mathbf{u}_i, \tag{1}
\]

where \( \mathbf{u}_i \) is the unit vector connecting each Sn atom to a specific Mn atom with moment \( \mu_i \), and \( A_p \) and \( A_s \) are the dipolar and contact fields due to a unit Mn moment. \( A_p \) is also referred to as the anisotropic constant. The last term in Eq. (1) is the isotropic contribution from the Mn shells around the Sn atoms, while the first two terms represent the anisotropic transferred hyperfine field. We will only consider the first term in Eq. (1), denoted as \( A_1 \), as the second is independent of moment orientation. In the \textit{HfFe}\textsubscript{6}Ge\textsubscript{6}-type crystal structure, the Mn–Sn bonds make angles of 35° (Sn-2c and Sn-2d) and 73° (Sn-2e) with the c axis, and in Er\textit{Mn}\textsubscript{6}Sn\textsubscript{5.85}Ga\textsubscript{0.11}, the moments are in the \( ab \) plane for \( T > T_a \) and along \( c \) for \( T < T_a \). \( \Delta A_1 \) is the change in \( A_1 \) due to a rotation from the \( ab \) plane to the \( c \) axis and is listed in Table III (see Ref. 11 for a more detailed description of these constants). Since the signs of \( B_{hf}^{\text{Sn-2c}} \) and \( \Delta A_1/A_p \) agree for the three Sn sites, the anisotropic and isotropic contributions to \( B_{hf} \) must have the same sign. Finally, the anisotropic constant is calculated as \( A_p = B_{hf}^{\text{Sn-2c}}/\Delta A_1 \) and values are given in Table III. From Eq. (1) we can determine the ratio \( A_p/A_s \), and we find that the transferred hyperfine field at Sn-2c is totally isotropic, while \( B_{hf} \) at Sn-2d consists of a 5(1)% anisotropic contribution. By contrast, the anisotropic field constitutes more than 20% of the total transferred hyperfine field at Sn-2e.

The anisotropic constants at the Sn sites in Er\textit{Mn}\textsubscript{6}Sn\textsubscript{5.85}Ga\textsubscript{0.11} are significantly smaller than \( A_p \) measured in MnSn\textsubscript{2} \[ B_{hf}^{\text{Sn-2c}} = 4.9(2) \text{ T} \text{ yielding } A_p = 2.19(9) \text{ T/}\mu_B \] (Ref. 1). Additional anisotropic contributions from Er–Sn bonding [not accounted for in Eq. (1)] could possibly affect the apparent Mn–Sn anisotropic contribution in this system, leading to smaller derived anisotropic constants. An investigation into this possibility is currently underway in the Y\textit{Mn}\textsubscript{6}Sn\textsubscript{5}–In system.

The significant effect of the anisotropic field on the total measured hyperfine field at each site emphasizes the importance of including this term when interpreting the observed spectra. For example, site assignments based simply on matching the sequence of fields with the number of magnetic neighbors (more neighboring moments imply bigger field) fail here as the Sn-2d and Sn-2c change order on cooling through \( T_a = 38(2) \text{ K} \). Furthermore, the Sn-2c site has the most magnetic neighbors (six Mn and three Er) but has a smaller field (below \( T_a \)) than the Sn-2d site which has only six Mn neighbors.

### IV. CONCLUSIONS

Magnetization and \textsuperscript{119}Sn Mössbauer spectroscopy have been used to show that anisotropic contributions to the transferred hyperfine field in Er\textit{Mn}\textsubscript{6}Sn\textsubscript{5.85}Ga\textsubscript{0.11} can be as much as 20% of the total observed field.

\begin{table}[h]
\centering
\caption{Mössbauer parameters at 35 and 40 K in Er\textit{Mn}\textsubscript{6}Sn\textsubscript{5.85}Ga\textsubscript{0.11}.}
\begin{tabular}{|c|c|c|}
\hline
Site & \( T < T_a \) (\( \mu \parallel c \)) & \( T > T_a \) (\( \mu \perp c \))
\hline
\textit{Sn-2c} & 1.11(2) & 31.99(2)
\hline
\textit{Sn-2d} & 1.54(3) & 33.46(3)
\hline
\textit{Sn-2e} & 0.07(2) & 15.45(2)
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Anisotropic field \( B_{hf}^{\text{Sn-2c}} \) change in \( A_1 \) due to a rotation from the \( ab \) plane to the \( c \) axis (Ref. 11), and resulting anisotropic constants for the three Sn sites in Er\textit{Mn}\textsubscript{6}Sn\textsubscript{5.85}Ga\textsubscript{0.11}. From magnetometry, \( \mu = \mu_{\text{Mn}} = 2.11(1) \mu_B \).}
\begin{tabular}{|c|c|c|c|
\hline
Site & \( B_{hf}^{\text{Sn-2c}} \) (T) & \( \Delta A_1/A_p \) & \( A_p \) (T/\( \mu_B \))
\hline
\textit{Sn-2c} & 0.20 (4) & 2.96\( \mu_B \) & 0.03(1)
\hline
\textit{Sn-2d} & 3.1(1) & 3.03\( \mu_B \) & 0.49(2)
\hline
\textit{Sn-2e} & -5.1(1) & -2.31\( \mu_B \) & 1.04(1)
\hline
\end{tabular}
\end{table}