Magneetoelastic properties of substituted Er$_{1-x}$Gd$_x$Mn$_6$Sn$_6$
intermetallic system

Sh. Tabatabai Yazdia, N. Tajabora, M. Rezaee Roknabadi, M. Behdani, F. Pourarian

Abstract

The forced magnetostriction of polycrystalline samples of Er$_{1-x}$Gd$_x$Mn$_6$Sn$_6$ ($0 \leq x \leq 1$) intermetallics with hexagonal HFes$_6$Ge$_6$-type structure is investigated in the temperature range of 77–480 K. Gd substitution has a significant effect on interatomic distances and especially on inter-sublattice R–Mn couplings. The replacement of Er by Gd results in increasing the ordering temperature followed by reinforcement of the R–Mn coupling, as well as decreasing the magnetostriction values owing to the S-state character of Gd$^{3+}$ ions. The results show that the contribution of Er sublattice to anisotropic magnetoelastic effects is positive, while that of Gd and Mn is negative. All the examined samples exhibit considerable magnetovolume anomalies at the ordering temperature ($T_c=338, 381, 412$ and $434$ K for the samples with $x=0, 0.2, 0.6$ and 1.0, respectively). While the unsubstituted sample exhibits metamagnetic transitions, Gd-contained compounds do not show this behavior, owing to the strong Gd–Mn coupling. The experimental results obtained are discussed in the framework of the two-magnetic sublattice by bearing in mind the lattice parameter dependence of the interlayer Mn–Mn exchange interaction in these layered compounds. From the temperature dependence of magnetostriction values and considering the magnetostriction equation for a hexagonal structure, we attempt to determine the signs of some of the magnetostriction constants for these compounds and the influence of Gd substitution on them.

1. Introduction

RMn$_6$Sn$_6$ ternary intermetallic compounds with R=Sc, Y and rare-earth elements (except for R=Pr and Eu whose compounds have never been prepared) have attracted considerable attention in recent years, owing to their interesting magnetic properties. They have been extensively studied using a wide variety of methods including magnetization measurements [1–3], neutron diffraction [4], Mössbauer spectroscopy [4], neutron spectroscopy [5], transport, magnetotransport [6] and magneto-optical measurements [7], and also by theoretical studies on their electronic structure [8]. All these compounds crystallize in the hexagonal HFes$_6$Ge$_6$-type structure with space group P6/mmm (Fig. 1). This crystal structure can be described as layers of R and Mn atoms alternately stacked along the c-axis in the sequence Mn–(R,Sn)–Mn–Sn–Sn–Sn–Mn. The magnetic structure of RMn$_6$Sn$_6$ compounds consists of two interacting subsystems: one of them is composed of R atoms whereas Mn atoms form the other. The observed complex magnetic behavior of these compounds with various magnetic phase transitions originate from the temperature-dependent competition between the Mn–Mn, R–Mn and R–R interactions, as well as from the magnetocrystalline anisotropies of the R and Mn sublattices. Both the intralayer Mn–Mn interaction ($J_{fi}$) which is the strongest, and the interlayer Mn–Mn exchange interaction through the Mn–Sn–Sn–Sn–Mn slab ($J_{sl}$) are always positive (ferromagnetic), while the nature of that of within the Mn–(R,Sn)–Mn slab ($J_{sl}$) depends on the Mn–Mn interatomic distances and so is very sensitive to the R element [9,10]. The R–Mn coupling is negative for heavy R elements and strongest for R=Gd [11,12], with the same order of magnitude as the interlayer Mn–Mn. Among the RMn$_6$Sn$_6$ family, the compound with R=Er has a complex behavior displaying several transitions: spontaneous (temperature-induced) transitions characterized by antiferromagnetism below $T_N=352$ K and a transition to ferrimagnetic state at about 75 K, as well as metamagnetic (field-induced) ones in its ordered state [11]. In order to better understand the contributions of the two sublattices to these magnetic behaviors, we decided to study the effect of Gd substitution for Er on structure and on certain magnetic and magnetoelastic properties of Er$_{1-x}$Gd$_x$Mn$_6$Sn$_6$ ($0 \leq x \leq 1$) compounds. Since the Mn sublattice favors an easy plane anisotropy and Er and Gd both reveal an easy plane behavior in the whole ordered state as well [4], there will be no competition between the two sublattice anisotropies and consequently no spin reorientation process is expected in the compounds studied. As a result of the strong dependence of Mn–Mn interlayer...
interactions on interatomic distance, one may expect that these magnetic transitions involving variation of arrangement of Mn moments, are likely to be accompanied by anomalies in the magnetelastic behaviors. Therefore, in the present work, we report the effect of Gd substitution for Er on the field-induced magnetovolume effects of Er<sub>1-x</sub>Gd<sub>x</sub>Mn<sub>6</sub>Sn<sub>6</sub> (0 < x < 1) compounds. The influence of this substitution on their structure, thermal expansion and spontaneous magnetostriction has been reported elsewhere [13].

2. Experiments

Er<sub>1-x</sub>Gd<sub>x</sub>Mn<sub>6</sub>Sn<sub>6</sub> (0 < x < 1) polycrystalline samples were prepared by arc melting of the constituent elements under high-purity argon atmosphere in a water-cooled copper hearth. The details of samples preparation have been described previously in Ref. [13]. The purity and microstructure of the prepared samples were examined using X-ray powder diffraction (XRD) with monochromatic Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 20–90° in a continuous scan mode with a step width of 0.05° and using scanning electron microscopy (SEM) (Leo 1450VP, Carl Zeiss SMT, Germany). For structural characterization, analysis of the obtained XRD data was performed using the Rietveld refinement method, through the Fullprofi software. The Linear thermal expansion (TE) was normalized to 77 K (T<sub>n</sub>) through the Fullprof software. The Linear thermal expansion d/t of Er<sub>1-x</sub>Gd<sub>x</sub>Mn<sub>6</sub>Sn<sub>6</sub> samples was measured as a function of the temperature range of 77–520 K [13] has revealed considerable anomalies (notable volume expansions) at Néel-like transition points of the related compounds (T<sub>N</sub>) and also at T<sub>M</sub> = 309–311 K where the Mn moments experience collapse-like reduction [15], whereas trivial anomalies occurred at Curie-like transition points (T<sub>C</sub>). Consequently, with regard to the magnetic arrangement of sublattices at the transition temperatures of the samples, it can be concluded that the spontaneous magneto-volume effects in these compounds originate mainly from the antiferromagnetic interlayer Mn–Mn exchange interactions, whereas the intralayer ferromagnetism does not influence these magneto-volume effects. The values of the transition temperatures of the studied samples estimated from the thermal expansion measurements are summarized in Table 1. As seen, the ordering temperature increases with increasing Gd content. This behavior has been discussed in detail in our previous paper [13].

The longitudinal λ<sub>y</sub> and transverse λ<sub>xy</sub> magnetostrictions of Er<sub>1-x</sub>Gd<sub>x</sub>Mn<sub>6</sub>Sn<sub>6</sub> samples were measured as a function of the applied magnetic field at certain typical temperatures. As representatives, the λ<sub>y</sub> and λ<sub>xy</sub> isotherms of the samples at two selected temperatures are presented in Fig. 2. For the ErMn<sub>6</sub>Sn<sub>6</sub> sample, except for the region near to the antiferromagnetic–ferrimagnetic transition point (about 77 K), there is no significant difference between the MS measured parallel (λ<sub>y</sub>) and perpendicular (λ<sub>xy</sub>) to the applied magnetic field. This means that, apart from the low temperature region, MS is almost isotropic. As seen, Gd substitution causes the longitudinal and transverse MS to be opposite in sign (except for the region around the ordering temperature), and whereas for the sample with x = 0.2 there is no significant difference between their magnitudes, the difference grows with Gd content so that for the sample with x = 1, Δμ = 3μ<sub>y</sub>. Furthermore, the comparison of the results shows that the linear MS decreases with Gd substitution. This is reasonable since Gd<sup>3+</sup> is an S state ion (L = 0) with a spherical symmetric 4f charge density. Consequently, loss of the interaction of the anisotropic electronic cloud of 4f electrons with the crystalline field which is the origin of MS effect in heavy rare earths makes the MS of Gd approximately two orders of magnitude smaller than the other rare earth

### Table 1

<table>
<thead>
<tr>
<th>Gd context (x)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>c/a</th>
<th>TE</th>
<th>MS</th>
<th>Magnetic order</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.52743</td>
<td>9.02036</td>
<td>238.671</td>
<td>1.6319</td>
<td>T&lt;sub&gt;T1&lt;/sub&gt; (K)</td>
<td>T&lt;sub&gt;n&lt;/sub&gt; (K)</td>
<td>T&lt;sub&gt;C&lt;/sub&gt; (K)</td>
</tr>
<tr>
<td>0.2</td>
<td>5.52835</td>
<td>9.01982</td>
<td>238.736</td>
<td>1.6316</td>
<td>164</td>
<td>335</td>
<td>383</td>
</tr>
<tr>
<td>0.6</td>
<td>5.53266</td>
<td>9.02602</td>
<td>239.274</td>
<td>1.6314</td>
<td>–</td>
<td>–</td>
<td>419</td>
</tr>
<tr>
<td>1</td>
<td>5.54671</td>
<td>9.04348</td>
<td>240.956</td>
<td>1.6304</td>
<td>–</td>
<td>–</td>
<td>434</td>
</tr>
</tbody>
</table>
elements [16]. It is noteworthy in Fig. 2 that the MS isotherms, except those around the ordering temperature, increase rapidly in the low magnetic field region and then tend towards saturation. The observed abrupt change of MS (say the enhanced magnetization) in low magnetic fields can be attributed to the conventional domain extension relevant to the domain-wall motion in the ferrimagnetic state. As seen, the saturation behavior of MS isotherms for the ErMn₆Sn₆ compound occurs at different threshold magnetic fields \( H_{\text{th}} \), for which the thermal variation has been discussed in detail in our previous paper [17]. With Gd substitution in the samples, \( H_{\text{th}} \) does not reveal significant changes for different temperatures. The low and almost temperature-independent values of \( H_{\text{th}} \) in the samples with \( x \neq 0 \) may indicate the easy movement of domain-walls and absence of any pinning center in these compounds. In the rare-earth/transition metal intermetallic compounds, the local 4f orbitals of the rare-earth atoms creating large magnetocrystalline anisotropy are generally responsible for providing strong pinning centers [18]. As known, Gd⁴⁺ in the involved samples is an S state ion with a spherical symmetric 4f charge density and consequently is not influenced by the crystal field, so the observed behavior is logical. In this situation, by increasing the applied magnetic field through \( H_{\text{th}} \) as well as domain extension, the Gd magnetic moments rotate readily towards the field direction. Therefore, the magnetic field forces the linear ferrimagnetically anisotropic of the compound to the nonlinear one. This rotation of antiparallel moments of the two sublattices is accompanied by considerable volume strain effects. In the compounds with high Gd content (\( x \geq 0.6 \)) MS effects are suggested to be involved with a negative magnetoelastic coupling constant in the direction parallel to the applied magnetic field and with a positive one in the perpendicular direction (except for the ordering region). It is worth noting that the high temperature MS isotherms, as seen in Fig. 2, increase continuously with magnetic field, with no sign of saturation up to 1 T. It means that higher fields are needed for saturation at temperatures in the ordering region. These linear MS curves exhibit \( H^2 \) dependence up to 1 T, which is the expected behavior of the paramagnetic MS at low magnetic fields [19].

The temperature dependence of the anisotropic magnetostriction \( \lambda \) of \( \text{Er}_{x} \text{Gd}_{x} \text{Mn}_{6} \text{Sn}_{6} \) samples, calculated from \( \lambda_{t} \) and \( \lambda_{p} \) measurements, at some typical applied magnetic fields up to 1.5 T is depicted in Fig. 3. At first glance, it is observed that \( \lambda_{t} \) is almost field-independent. For the samples with \( x \leq 0.6 \), from a value of about \( 4 \times 10^{-3} \) at low temperatures, \( \lambda_{t} \) drops continuously to zero at a temperature denoted by \( T_{p} \). Above this point, after a sign change, it tends to zero once again around the ordering temperature of each sample, owing to the decrease of the magnetization due to the thermal fluctuations. The observed zero MS at \( T_{p} \) may be attributed to the magnetostriction compensation of the two sublattices involved. For \( \text{ErMn}_{6}\text{Sn}_{6} \) above \( T_{p} \approx 160 \text{ K} \), the Er sublattice is in its paramagnetic state and so the negative values of \( \lambda_{t} \) originate from the Mn sublattice anisotropy. Therefore, it can be concluded that the Er and Mn sublattice contributions to the anisotropic MS of these compounds are positive and negative, respectively. The observation that with Gd substitution in the compounds, \( T_{p} \) shifts towards lower temperatures, and the \( \lambda_{t} \) positive values decrease while its negative values increase, confirms the above conclusion. For the \( \text{GdMn}_{6}\text{Sn}_{6} \) sample, \( \lambda_{t} \) is negative over the whole temperature range, with no MS compensation of the two sublattices; so following from the above discussion, it can be concluded that the Gd sublattice contribution in the anisotropic MS of these compounds is negative, similar to the case of Mn sublattice. Furthermore, it is observed that by Gd substitution, the magnitude of \( \lambda_{t} \) decreases at low temperatures. This was expected since the anisotropy constants \( K_{1} \) and \( K_{2} \) for Gd (an S state ion) are two orders of magnitude smaller than for Er [16].

In Fig. 3, some trivial anomalies can also be seen in the anisotropic MS behavior at the Curie points (\( T_{C} \)= 423, 419 and 383 K for the samples with \( x=1.0, 0.6 \) and 0.2, respectively) while other transitions are not accompanied by any anomalies in \( \lambda_{t} \) behaviors.

For further discussion, we consider the Callen and Callen relation for the magnetostriction in a direction with cosines \( \beta_{1} = (x, y, z) \) in a hexagonal structure when magnetized in a direction described by cosines \( \alpha_{1} = (x, y, z) \) in terms of magnetostrictive coefficients \( \lambda_{ij}(T, H) \) [20]

\[
\lambda = 1/3 \lambda_{11}^{\alpha} + 1/2 \sqrt{3} \lambda_{12}^{\alpha} (\alpha_2^2 - 1/3) + 2 \lambda_{22}^{\alpha} (\beta^2 - 1/3) + \sqrt{3} \lambda_{23}^{\alpha} (\beta_2^2 - 1/3) \alpha_2^2 - 1/3\]

\[
+ 2 \lambda_{23}^{\alpha} \left( \frac{1}{3} (\beta_2^2 - \beta_3^2) (\alpha_2^2 - \alpha_3^2) + \beta_3 \beta_3 \alpha_3 \alpha_3 \right) + 2 \lambda_{23}^{\alpha} (\beta_3 \alpha_3 + \beta_3 \alpha_3) \beta_3 \alpha_3
\]

(1)

where the \( \lambda_{ij}(T, H) \) coefficients describe the deformations originating either from the single-ion crystal electric field interaction (\( \lambda_{11}^{\alpha}, \lambda_{22}^{\alpha}, \lambda_{23}^{\alpha} \)) and \( \lambda' \), or from the two-ion exchange interaction (\( \lambda_{12}^{\alpha} \) and \( \lambda_{13}^{\alpha} \)). In this relation, the modes with the superscript \( \Gamma=\alpha \) indicate the fully
symmetric volume change preserving the hexagonal structure, and those with superscripts $\Gamma=\gamma$ and $\epsilon$ represent shearing strains in the basal plane and in planes parallel to the $c$-axis, respectively. The first subscript $j$ denotes the degree of measurement direction cosines pertaining to that particular term, i.e., for the terms with $\lambda_j^{\alpha_j}$, $(j=1, 2)$ coefficients are independent of measurement direction (the basal plane volume modes). The second subscript $j^\prime$ relates to the degree of magnetization direction cosines exactly in the same way. In a single crystal sample, all $\lambda_{j^\prime}$ coefficients are responsible for the different types of deformation and distortion, while for a polycrystalline sample, MS expression must be averaged over all directions within a sphere. Following Mason [21], we calculate the $\lambda_t$ expression for a polycrystalline hexagonal sample to be

$$\lambda_t = \lambda_{||} - \lambda_{\perp} = \frac{2\sqrt{3}}{15} \lambda_{22}^{\alpha_{22}} \left( 2\lambda^\prime + 2\lambda^\prime \right)$$

(2)

where the $\lambda_{22}^{\alpha_{22}}$ mode is associated with a longitudinal change in the $c/a$ ratio for the fixed volume upon the magnetization rotation from the basal plane to the $c$-axis. This mode maintains the hexagonal symmetry. The $\lambda^\prime$ and $\lambda^\prime$ modes refer to a shear breaking of the circular symmetry of the basal plane by magnetization rotation in the plane and to a shear tilting the $c$-axis, respectively. Notice that no exchange striction terms are present in the $\lambda_t$ expression. For our samples, being compounds possessing easy planes with high anisotropy fields (about 9 T, for GdMn$_6$Sn$_6$ [22]), the magnetization rotation in low temperatures and fields is restricted to the basal plane. Therefore, $\lambda^\prime$ is the dominant term under the conditions of low temperatures and fields. Hence, regarding the $\lambda_t$ results presented in Fig. 3, one can conclude that $\lambda^\prime$ is positive for Er$_{1-x}$Gd$_x$Mn$_6$Sn$_6$ compounds with $x \leq 0.6$, and it decreases with increasing Gd content so that it becomes negative for GdMn$_6$Sn$_6$. As temperature increases and consequentially the planar anisotropy field decreases, the magnetization vector experiences all directions leading $\lambda^\prime$ to decrease. Therefore, from Eq. (2) along with Fig. 3 and considering that $\lambda^\prime$ can be neglected in easy plane compounds, as for the present samples, we conclude that at higher temperatures, $\lambda_{22}^{\alpha_{22}}$ is negative for all the samples studied. Moreover, the observed anomalies around $T_F$ in $\lambda_t$ isofields can be attributed to the thermal variations of $\lambda_{22}^{\alpha_{22}}$ coefficient.

The temperature dependence of the volume magnetostriction $\omega$ of Er$_{1-x}$Gd$_x$Mn$_6$Sn$_6$ samples at selected applied magnetic fields up to 1.5 T is presented in Fig. 4. At first glance, it is observed that in contrast to $\lambda_t$ behaviors, $\omega$ results depend strongly on the magnitude of the applied field especially in the transition regions. The volume MS behavior of the ErMn$_6$Sn$_6$ sample seems different from the Gd substituted compounds. The $\omega(T)$ of Er$_{1-x}$Gd$_x$Mn$_6$Sn$_6$ samples with $x \geq 0.2$ peaks drastically at the ordering temperature (independent of the applied magnetic field), while the $\omega(T)$ behavior of the compound with $x=0$, in addition to anomalies at the ordering temperature, depends strongly on the magnitude of the applied field in the antiferromagnetic state. As seen, upon increasing the field intensity, the temperature range of the antiferromagnetic state decreases. The low temperature metamagnetic transition shifts to higher temperatures, while the high temperature one occurs at lower temperatures. Meanwhile, the transition to the paramagnetic state undergoes no change ($T_N=338$ K). This behavior, which is well consistent with the magnetic phase diagram of the compound [2], has been discussed in detail in our previous paper [17]. The isofield curves of volume MS for Er$_{1-x}$Gd$_x$Mn$_6$Sn$_6$ compounds with $x \geq 0.2$ reveal just a pronounced peak around the ordering temperature ($T_C=434, 412$ and $381$ K for the samples with $x=1.0, 0.6$ and 0.2, respectively). This indicates that with magnetic fields up to 1.5 T no metamagnetic transition results in these compounds. This is reasonable since one expects that the strong Gd–Mn exchange coupling ($J_{Gd-Mn}=0.107$ K [23]) makes the Gd- and Mn-sublattice moments remain strictly antiparallel under magnetic fields available in these measurements. The occurrence of the observed magnetovolume effects in the ordering region of the samples (notable volume shrinkage upon magnetic field application) can be explained as follows: the magnetic field causes the loss of the magnetic ordering in the $T_C$ region to occur with a delay, so that in a limited temperature interval there exists an enhanced number of nearest R–Mn neighbors with the negative exchange (say attractive interaction), and hence the crystal volume decreases. It is obvious that the maximum value of $\omega(T)$ increases with magnetic field. The values of the transition temperatures of the studied samples estimated from the $\omega(T)$ results are listed in Table 1. The comparison of the volume MS curves reveals the effect of Gd substitution in these compounds as a decrease in the maximum value of $\omega(T)$ as well as an increase in $T_C$ values. (The latter observation, which is consistent with the result obtained from thermal expansion measurements, has been previously discussed [13].) Recalling that Gd$^{3+}$ is an S state ion, its substitution for Er results reasonably in weakening of the magnetoelastic properties of the compounds.

For further discussion on volume MS of these compounds, we obtain the expression for $\omega$ of a hexagonal polycrystalline sample.
As mentioned, magnitude larger than single-ion strain $[16]$. 

$\omega_\text{obs} \approx \omega_\text{applied} \text{ magnetic}$ $\text{ term depends only on the magnitude of the magnetization (or the interaction (depending just on the interatomic distances). This for the basal plane originating from the two-ion isotropic exchange interaction (depending just on the interatomic distances). This term depends only on the magnitude of the magnetization (or the applied magnetic field), and not on its direction. From the observed $\omega(T)$ behaviors (Fig. 4), one can conclude that the $\lambda_{11}^{\alpha}$ coefficient is negative for these compounds, and its magnitude decreases with Gd substitution. The observed anomalies in the $\omega$ curves at the ordering temperature are also ascribed to the thermal variations of this coefficient. Furthermore, as the anomalies around $T_c$ in the $\omega$ behavior are observed to be larger than those in the $\lambda_t$ behavior, it can be concluded that the $\lambda_{11}^{\alpha}$ coefficient (related to the contribution of the isotropic two-ion exchange interaction in MS) is about one order of magnitude larger than $\lambda_{22}^{\alpha}$ (the anisotropic single-ion crystal electric field contribution). It is consistent with the fact that the absolute value of strain caused by two-ion interactions such as exchange striction is one order of magnitude larger than single-ion strain $[16]$. 

4. Conclusions

Pure single-phase polycrystalline samples of $\text{Er}_{1-x}\text{Gd}_x\text{Mn}_6\text{Sn}_6$ $(0 \leq x \leq 1)$ intermetallics were prepared by the arc melting method. All the compounds are isotypic and possess a hexagonal $\text{HfFe}_2\text{Ge}_2$-type structure (S.G. P6/mmm). The replacement of $\text{Er}$ by $\text{Gd}$ causes the lattice constants to increase; this is related to the larger atomic radius of $\text{Gd}$ compared with $\text{Er}$. Apart from the influence of this substitution on the interatomic distances, it has a significant effect on inter-sublattice $\text{R-Mn}$ couplings. The study of the forced magnetostriction of samples in the temperature range of 77–480 K showed that $\text{Gd}$ substitution resulted in increasing the ordering temperature following reinforcement of the $\text{R-Mn}$ coupling, as well as decreasing the magnetostriction values owing to the $\text{S}$-state character of $\text{Gd}^{3+}$ ions. The anisotropic magnetostriction behaviors lead us to conclude that the contribution of the $\text{Er}$ sublattice in anisotropic effects is positive, while that of $\text{Gd}$ and $\text{Mn}$ is negative. All the examined samples exhibit considerable magnetovolume anomalies at the ordering temperature ($T_c = 338$, 381, 412 and 434 K for the samples with $x=0$, 0.2, 0.6 and 1.0, respectively). While the unsubstituted sample exhibits magnetic transitions, the $\text{Gd}$-contained compounds do not show this behavior, owing to the strong $\text{Gd-Mn}$ coupling. The experimental results obtained are discussed in the framework of the two-magnetic sublattice by bearing in mind the behavior of the lattice parameter dependence of the interlayer $\text{Mn-Mn}$ exchange interaction in these layered compounds. From the temperature dependence of magnetostriction values and considering the magnetostriction relation of a hexagonal structure, the signs of some of the magnetostriction constants are determined and the effect of $\text{Gd}$ substitution on them is discussed.

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