Magnetic structure of the Zr₆CoAs₂-type Er₆TX₂ compounds 
(T = Mn, Fe, Co and X = Sb, Bi)

A.V. Morozkin a,∗, R. Nirmalab, S.K. Malikb

a Department of Chemistry, Moscow State University, Leninskie Gory, House 1, Building 3, Moscow, GSP-2 119992, Russia
b Tata Institute of Fundamental Research, Mumbai 400 005, India

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Abstract

Investigations were made by neutron diffraction on the Zr₆CoAs₂-type (space group P6b2m, No. 189) Er₆FeSb₂, Er₆MnSb₂, Er₆CoBi₂, Er₆FeBi₂, Er₆MnBi₂ and Zr₆MnBi₂ compounds. The Er₆FeSb₂, Er₆MnSb₂, Er₆CoBi₂ and Er₆MnBi₂ compounds show a ferromagnetic type of ordering below 21(5), 110(5), 30(2) and 100(5) K, respectively. Below the ferromagnetic transition the magnetic structure of these compounds consist of Er ferromagnetic (1 0 0) layers.

Below 33(25) K, the Er₆MnBi₂ compound has an incommensurate magnetic structure with constant propagation vectors [0.596(2), 0, 0]. The propagation vector coincides with the a-axis of the unit cell. The magnetic moments of the Er atoms make an angle with the c-axis (µ_Er = 7.5(2) µ_B, β_Er = 6.7(4)° at 2 K).

The Er₆FeBi₂ compound displays a ferromagnetic transition below 15(5) K. The magnetic structure of the Er₆FeBi₂ compound is not clear.

In the Er₆TX₂ compounds, no local moment was detected on the transition metal site. Furthermore, no magnetic transition was detected in the Zr₆CoAs₂-type Zr₆MnBi₂ compound.

Both, the type of transition metal and the distortion of the unit cell strongly influence the ferromagnetic type of ordering temperature and the magnetic structure in these compounds.

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1. Introduction

It is known that the Er₆TX₂ compounds (T = Mn, Fe, Co and X = Sb, Bi) adopt the Zr₆CoAs₂-type structure [1–3]. The Zr₆CoAs₂-type is a superstructure of the Fe₆P₆-type structure (space group P6b2m, No. 189) [4]. In the Zr₆CoAs₂-type structure, the Er atoms occupy the 3(g) site (X_Er₁, 0, 1/2) and 3(f) site (X_Er₂, 0, 0), transition metal atoms occupy the special position 1(b) (0, 0, 1/2) and antimony (bismuth) atoms occupy the special position 2(c) (1/3, 2/3, 0). It is known that the Er₆MnBi₂ compound gives rise to a ferromagnetic type of ordering below 115(5) K [5].

This paper reports on a neutron diffraction study of novel Er₆TX₂ compounds.

2. Experimental details

In the present investigation, the compounds were prepared in an electric arc furnace under an argon atmosphere using a non-consumable tungsten electrode and a water-cooled copper tray. Antimony, bismuth, zirconium (purity all components 99.99%), erbium, iron, cobalt and manganese (purity all components 99.9%) were used as the starting components. Titanium was used as a getter during melting. Subsequently, the compounds were annealed at 1170 K for 240 h in an argon atmosphere and quenched in ice-cold water.
The quality of the samples before the neutron diffraction study was determined using X-ray phase analysis and microprobe X-ray analysis. The X-ray data were obtained on a diffractometer DRON-3.0 (Cu Kα radiation, 2θ = 20–70°, step 0.05°, for 5 s per step). The diffractograms obtained were identified by means of calculated patterns using the Rietan program [6, 7] in the isotropic approximation. A “Camebax” microanalyser was employed to perform microprobe X-ray spectral analyses of the samples.

The ac magnetization measurements on the Er₅TX₃ compounds were carried out in the temperature range of 2–300 K in a commercial magnetometer (MPMS and PPMS, Quantum Design, USA).

The neutron diffraction study was carried out on a powder D1B diffractometer (Institute Laue-Langevin, Grenoble, France).

Fig. 1. Neutron diffraction patterns of the Er₅MnBi₃ compound at (a) 150 K (paramagnetic state), (b) 70 K (ferromagnetic collinear type ordering FC) and (c) 2 K (ferromagnetic non-collinear type ordering FNC).
France) from 300 to 2 K. The neutron diffraction patterns (Fig. 1) were identified and calculated using the Fullprof 98-program [8].

3. Results and discussion

The Zr₆CoAs₂-type Er₆TX₂ compounds can be regarded as having a structure based on the Mg-type rare earths solid solutions. We can describe the Mg-type rare earth structure in terms of the Zr₆CoAs₂-type structure as follows: the rare earth atoms occupy the special positions 3(f) (1/3, 0, 0) and 3(g) (2/3, 0, 1/2), and the occupation factors for the transition metal and antimony (bismuth) atoms are zero; cell parameters \(a = \sqrt{3}a_{\text{Mg}}\) and \(c = c_{\text{Mg}}\), space group \(P6\bar{b}2m\), No. 189 (\(a = 0.616402\) nm, \(c = 0.55874\) nm, \(c/a = 0.90645\), \(V = 0.18385\) nm³ for pure Er [9]). Insertion of the transition metal atoms and p-elements atoms into the Mg-type rare earths leads to formation of the Zr₆CoAs₂-type compounds with a strong distortion of the unit cell (Fig. 2a). The \(a, c, V\) and \(c/a\) cell parameters decrease with decreasing temperature for all compounds. However, \(c/a\) increases for the Er₆MnBi₂ compound below second magnetic transition at 33(2) K (Table 1).

Preliminary measurements of the magnetic susceptibility show that the temperature of the magnetic transition is the same as the temperature of the magnetic transition obtained from the neutron diffraction experiment. The temperature dependences of the ac magnetic susceptibility of the Er₆FeSb₂ and Er₆MnBi₂ compounds are given in Fig. 3.

Fig. 2. (a) Unit cell of the Zr₆CoAs₂-type Er₆TX₂ compounds and their magnetic structures at (b) \(T < T_{FC}\) and (c) \(T < T_{FNC}\) for Er₆MnBi₂.

\( T = \text{Mn, Fe, Co}; X = \text{Sb, Bi} \)
In the Er$_6$TX$_2$ compounds, no local moment was detected on the transition metal site. Furthermore no magnetic transition was detected in the Zr$_6$CoAs$_2$-type Zr$_6$MnBi$_2$ compound.

Below the ferromagnetic transition, the magnetic structure of Er$_6$FeSb$_2$, Er$_6$MnSb$_2$, Er$_6$CoBi$_2$ and Er$_6$MnBi$_2$ compounds consist of Er ferromagnetic (100) layers (Fig. 2b). The magnetic moments of the Er atoms are collinear and oriented along the $a$-axis. The crystallographic data and magnetic data of the Er$_6$TX$_2$ compounds and the Zr$_6$MnBi$_2$ compound at different temperatures are given in Table 1. The thermal variation of the Er moments in the Er$_6$FeSb$_2$, Er$_6$MnSb$_2$, Er$_6$MnBi$_2$ and Er$_6$CoBi$_2$ compounds are given in Fig. 4.

It is obvious that the Er$_6$FeBi$_2$ compound has another magnetic structure. This compound needs following investigation.

Below $T_{NC}$ = 33(2) K, the Er$_6$MnBi$_2$ compound has an incommensurate magnetic structure with a constant propagation vector $[0.596(2), 0, 0]$ (Fig. 1c). The magnetic moment of the Er atoms make an $\beta$ angle with the $a$-axis (Fig. 2c). $M_{p}^{\beta} = \mu_{0} \sin \beta \sin \text{sin}(2\pi n, R_{p}^{\beta})$, $M_{y}^{\beta} = \mu_{0} \sin \beta \sin \text{sin}(2\pi n, R_{y}^{\beta})$, where $R_{p}^{\beta}$ is the position of the $p$th atom of Er along the $a$-axis. The value of propagation factor $k_{p} = 0.596(2)$ corresponds to the magnetic unit cell with parameters $a_{u} = 5 \delta_{\text{ErMnBi}}$, $b_{u} = 6 \delta_{\text{ErMnBi}}$, $c = c_{\text{ErMnBi}}$, $\alpha = 90^\circ$ and $\gamma = 120^\circ$.

The Mg-type Er has a sine wave modulated spin structure along the $c$-axis with the magnetic moment coinciding with the $c$-axis below $T_{NC}$ = 85 K. Below the ferromagnetic

### Table 1

<table>
<thead>
<tr>
<th>Magnetic type</th>
<th>$T_{NC}$</th>
<th>Compound</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>$c/a$</th>
<th>$V$ (nm$^3$)</th>
<th>$X_{c(1)}$</th>
<th>$X_{c(2)}$</th>
<th>$R_{B}$</th>
<th>$\alpha_{B}$</th>
<th>$\beta$</th>
<th>$R_{B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Para</td>
<td>30(5)</td>
<td>Er$_6$MnSb$_2$</td>
<td>0.805(7)</td>
<td>0.42115(3)</td>
<td>0.52369</td>
<td>0.23564</td>
<td>0.5965(8)</td>
<td>0.238(8)</td>
<td>3.5</td>
<td>8.0(6)</td>
<td>9.4</td>
<td></td>
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<tr>
<td>Para</td>
<td>2(5)</td>
<td>Er$_6$FeSb$_2$</td>
<td>0.80004(9)</td>
<td>0.41050(6)</td>
<td>0.51310</td>
<td>0.22755</td>
<td>0.591(1)</td>
<td>0.231(2)</td>
<td>8.8</td>
<td>7.2(6)</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>FNC$^b$</td>
<td>33(2)</td>
<td>Er$_6$MnBi$_2$</td>
<td>0.81306(9)</td>
<td>0.42354(6)</td>
<td>0.52094</td>
<td>0.24266</td>
<td>0.607(1)</td>
<td>0.236(1)</td>
<td>4.6</td>
<td>7.4(3)</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>FNC$^b$</td>
<td>30(2)</td>
<td>Er$_6$CoBi$_2$</td>
<td>0.80088(6)</td>
<td>0.41276(4)</td>
<td>0.52131</td>
<td>0.23911</td>
<td>0.601(9)</td>
<td>0.220(2)</td>
<td>7.5</td>
<td>6.7(3)</td>
<td>6.7(4)</td>
<td></td>
</tr>
<tr>
<td>Para</td>
<td>30(2)</td>
<td>Zr$_6$CoAs$_2$</td>
<td>0.7828(8)</td>
<td>0.37147(3)</td>
<td>0.47435</td>
<td>0.19714</td>
<td>0.604(2)</td>
<td>0.234(3)</td>
<td>4.2</td>
<td>9.0(3)</td>
<td>6.4</td>
<td></td>
</tr>
</tbody>
</table>

* Para, the paramagnetic state, FC, the ferromagnetic cationic type ordering and FNC the ferromagnetic non-collinear type ordering.

$^b$ Propagation vector [0.596(5), 0, 0]

$^c$ Propagation vector [0.596(2), 0, 0]
Fig. 4. Thermal variation of the Er moments in the Er₆FeSb₂, Er₆MnSb₂, Er₆MnBi₂ and Er₆CoBi₂ compounds.

transition at $T_C = 20 \text{K}$, the magnetic structure of Er is a ferromagnetic cone [10].

The formation of the Zr₆CoAs₂-type compound leads to a strong distortion of the initial Mg-type unit cell. The magnetic structures of the Er₆TX₂ compounds strongly differ from the magnetic structure of pure Er. The temperatures of the ferromagnetic type of ordering of Er₆FeSb₂ and Er₆CoBi₂ are close to the temperature of the ferromagnetic transition of pure Er. The presence of Mn strongly increases the temperature of the magnetic transition in the Er₆MnSb₂ and Er₆MnBi₂ compounds. The Sb-containing Er₆TX₂ compounds have ferromagnetic transition temperatures higher than the Bi-containing compounds, as a rule.

4. Conclusions

(1) The type of transition metal strongly influences the magnetic transition temperature of the Er₆TX₂ compounds.

(2) In the Er₆TX₂ compounds, the Er-sublattice has a magnetic structure different from the magnetic structure of pure Er.

(3) The Zr₆CoAs₂-type $R_6T_{1-x}Mn_xX_2$ solid solutions makes it possible to change the magnetic structure and magnetic transition temperature of the compounds over wide ranges.

Acknowledgments

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