

Effect of hydrogen insertion on the magnetic properties of $\text{Er}(\text{Fe},\text{Co})_{11}\text{Ti}$ single crystals

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Abstract

Magnetocrystalline anisotropy and spin-reorientation transitions (SRT) of the $\text{ErFe}_{11-x}\text{Co}_x\text{TiH}_y$ ($x = 0, 2, 4$; $y = 0, 1$) compounds with the ThMn_{12} -type structure were studied. The investigation of $\text{ErFe}_{11-x}\text{Co}_x\text{TiH}_y$ compounds with $x \leq 2$ show an “easy axis” anisotropy at room temperature and an “easy cone” anisotropy at temperatures below the spin-reorientation temperature (T_{SR}). The $\text{ErFe}_7\text{Co}_4\text{Ti}$ with $x = 4$ below the SRT exhibits an “easy plane” anisotropy with the easy direction oriented along the $[1\ 0\ 0]$ axis. Hydrogen insertion into $\text{ErFe}_9\text{Co}_2\text{Ti}$ leads to an increase of T_{SR} whereas hydrogenation of $\text{ErFe}_7\text{Co}_4\text{Ti}$ causes T_{SR} decreasing down to 40 K and essential change of SRT character. $\text{ErFe}_7\text{Co}_4\text{TiH}$ hydride has an “easy cone” anisotropy below T_{SR} . It was found that the replacement of the Fe by Co and hydrogen insertion into the crystal lattice of $\text{Er}(\text{Fe},\text{Co})_{11}\text{Ti}$ compounds has an opposite influence on the SRT temperature.

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1. Introduction

Spin-reorientation transitions (SRT) in magnetically ordered materials arise from the rotation of spontaneous magnetisation with respect to the crystallographic axes under the variation of temperature or magnetic field. Further investigations of the SRT are necessary for understanding these phenomena in the rare-earth intermetallic compounds and their hydride phases. The magnetic properties of iron-rich rare-earth intermetallic RFe_{11}Ti and compounds with the tetragonal ThMn_{12} -type structure (space group $I4/mmm$) have been investigated recently [1–3]. It is interesting to note that the in-

sertion of light interstitial elements (hydrogen, nitrogen) into the crystal lattice of the $\text{RFe}_{12-x}\text{M}_x$ compounds results in a drastic effect on the SRT and magnetocrystalline anisotropy (MCA) [1,4–7].

In this work, the SRT in $\text{ErFe}_{11-x}\text{Co}_x\text{Ti}$ ($x = 0, 2, 4$) compounds and their hydrides have been studied. From a fundamental point of view, these compounds are convenient model objects because at the first approximation the magnetic system can be separated into two magnetic sublattices: the rare-earth and the 3d-transition elements. Partial substitution of the Fe by Co is known to change the magnetic anisotropy [8,9]. The hydrogen atoms in the ThMn_{12} -type structure occupy only the 2b crystallographic sites. The intrinsic magnetic properties of $\text{Er}(\text{Fe},\text{Co})_{11}\text{Ti}$ compounds have recently been investigated on magnetically oriented powdered sam-

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ples [10,11]. The aim of the present work is to study the effect of hydrogen insertion on MCA and SRT values of $\text{Er}(\text{Fe},\text{Co})_{11}\text{Ti}$ single crystals.

2. Experimental

The $\text{ErFe}_{11-x}\text{Co}_x\text{Ti}$ ($x = 0, 2, 4$) alloys were prepared by melting the elements with purity higher than 99.95% in an induction furnace. Details of the single crystal preparation have been described previously [12]. The metal hydride syntheses were carried out in a high-pressure reactor chamber of a conventional Sieverts-type volumetric system. The samples were activated for 4 h in vacuum (4×10^{-4} Pa) at 670 K. At this temperature high purity hydrogen gas obtained from the LaNi_5H_6 hydrogen storage was admitted at a pressure of 1.2 MPa to the sample. To achieve a good homogenisation,

the samples were slowly cooled (about 4 K/h) down to room temperature. The amount of the absorbed hydrogen was determined from the hydrogen pressure change in the reactor chamber. The hydrogen concentration of $\text{Er}(\text{Fe},\text{Co})_{11}\text{TiH}_y$ was equal to about 1 H atom per formula unit (f.u.), with an accuracy of ± 0.02 H atoms/f.u.

X-ray diffraction investigation (Co $K\alpha$ radiation) was made on the powder samples for the phase identification both the parent compound and their hydrides and to determine the unit cell parameters. The ac magnetic susceptibility was measured with an ac-susceptometer (Lake Shore 7229) at a frequency of 133 Hz and field amplitude of 1 Oe in the temperature range of 4.2–150 K. The magnetisation measurements were carried out with a SQUID (Quantum Design MPMS 5-S) magnetometer from 5 to 300 K in magnetic fields up to 50 kOe at the IFW Dresden and with a capacitance magnetometer at the International Laboratory of High Magnetic

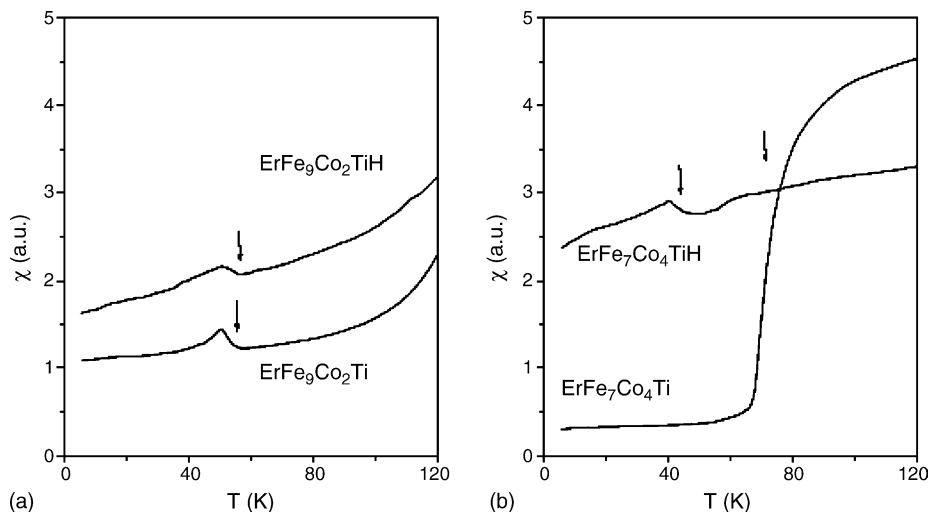


Fig. 1. Temperature dependence of the ac susceptibility for $\text{ErFe}_9\text{Co}_2\text{Ti}$ and $\text{ErFe}_7\text{Co}_4\text{Ti}$ and their hydrides measured on single crystal samples with field applied along the c -axis.

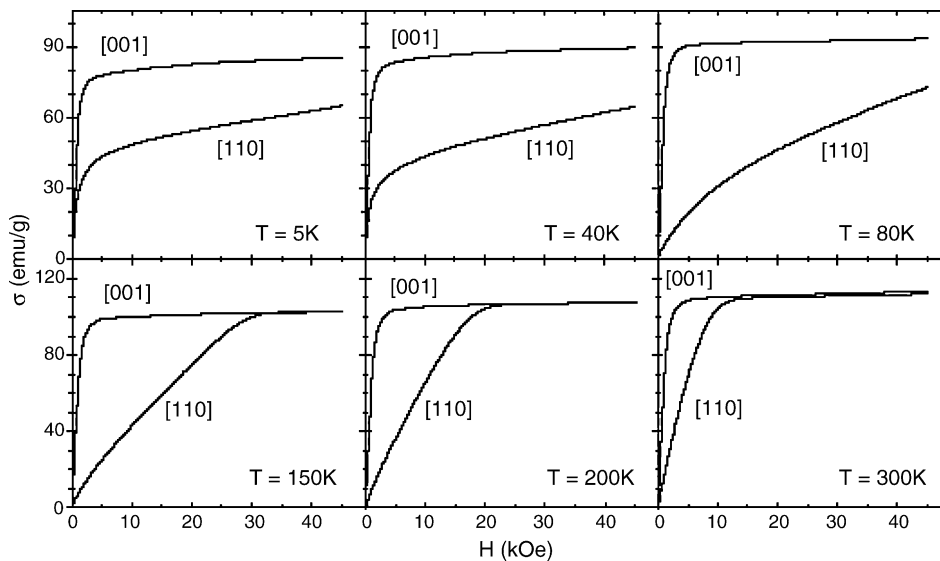


Fig. 2. Magnetisation curves of the $\text{ErFe}_9\text{Co}_2\text{TiH}$ single crystal measured at various temperatures.

Fields and Low Temperatures (Wrocław, Poland) in fields up to 100 kOe.

3. Results and discussion

It was found that the ThMn_{12} -type crystal structure of initial $\text{Er}(\text{Fe},\text{Co})_{11}\text{Ti}$ compounds is retained upon hydrogenation. The introduction of hydrogen atoms changes the lattice constants only (Table 1). It leads to an isotropic volume expansion with the c/a ratio being almost unchanged.

Fig. 1 shows the temperature dependence of susceptibility $\chi(T)$ of $\text{ErFe}_9\text{Co}_2\text{Ti}$ and $\text{ErFe}_7\text{Co}_4\text{Ti}$ single crystals and their hydrides measured along the $[001]$ axis. Sharp peaks on the $\chi(T)$ curves at 52 and 54 K for the $\text{ErFe}_9\text{Co}_2\text{Ti}$ and its monohydride, respectively are induced by SRT. These transitions are similar to a second order axial-to-conical SRT in the $\text{ErFe}_{11}\text{Ti}$ compound and its hydride reported in [4–6]. The magnetisation curves versus magnetic field measured at various temperatures for the $\text{ErFe}_9\text{Co}_2\text{TiH}$ single crystal are shown in Fig. 2. They demonstrate that the $\text{ErFe}_9\text{Co}_2\text{TiH}$ has an easy cone anisotropy below $T_{\text{SR}} = 54$ K and easy

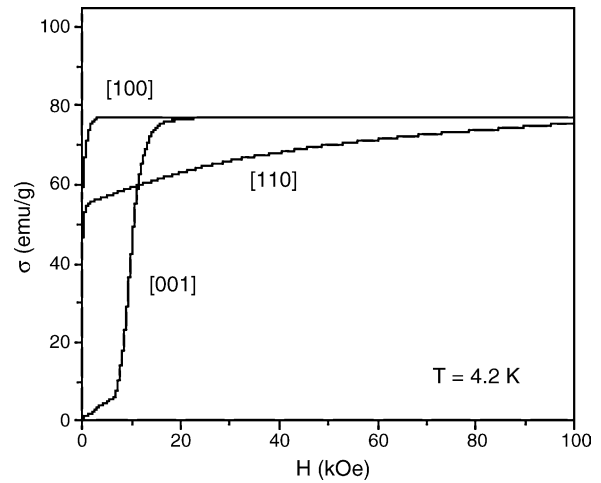


Fig. 3. Magnetisation curves of the $\text{ErFe}_7\text{Co}_4\text{Ti}$ single crystal measured at 4.2 K.

axis anisotropy at temperatures above 80 K. The character of SRT in $\text{ErFe}_9\text{Co}_2\text{Ti}$ remains unchanged and T_{SR} slightly shifts towards a higher temperature upon hydrogenation (see Table 1).

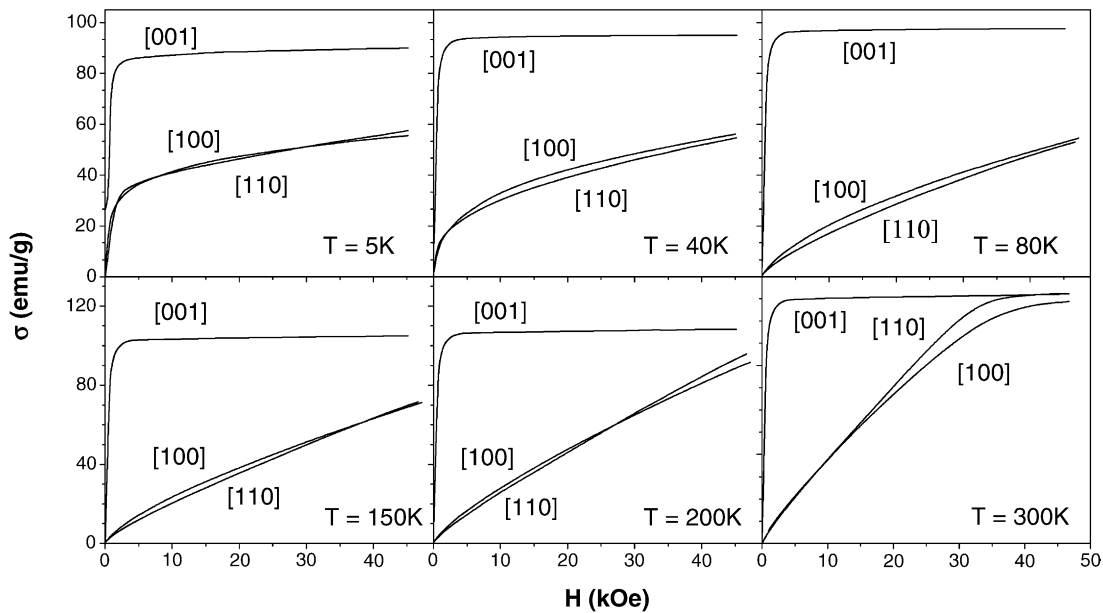


Fig. 4. Magnetisation curves of the $\text{ErFe}_7\text{Co}_4\text{TiH}$ single crystal measured at various temperatures.

Table 1

Lattice parameters, spin-reorientation temperatures, saturation magnetisation, and orientation of the easy magnetisation direction (EMD) at 4.2 K of $\text{ErFe}_{11-x}\text{Co}_x\text{Ti}$ and their hydrides

Compounds	a (Å)	c (Å)	T_{SR} (K)	ΔT_{SR} (K)	σ_{S} (emu/g)		EMD (4.2 K)
					80 K	300 K	
$\text{ErFe}_{11}\text{Ti}$	8.493	4.783	50	–	81	96	cone
$\text{ErFe}_{11}\text{TiH}$	8.507	4.781	41	–9	86	99	cone
$\text{ErFe}_9\text{Co}_2\text{Ti}$	8.479	4.783	52	–	97	117	cone
$\text{ErFe}_9\text{Co}_2\text{TiH}$	8.485	4.780	54	2	98	119	cone
$\text{ErFe}_7\text{Co}_4\text{Ti}$	8.477	4.770	64	–	91	111	$[100]$
$\text{ErFe}_7\text{Co}_4\text{TiH}$	8.506	4.772	41	–23	97	112	cone

The temperature dependence of susceptibility $\chi(T)$ of $\text{ErFe}_7\text{Co}_4\text{Ti}$ single crystal differs dramatically from that of $\text{ErFe}_9\text{Co}_2\text{Ti}$ (see Fig. 1). A strong increase of the susceptibility of $\text{ErFe}_7\text{Co}_4\text{Ti}$ compounds is observed at $T_{\text{SR}} = 64$ K. Magnetisation $\sigma(H)$ of $\text{ErFe}_7\text{Co}_4\text{Ti}$ along the three main crystallographic directions (Fig. 3) show an easy plane anisotropy at 4.2 K with a large basal plane anisotropy (more than 100 kOe). Hence the Co induces a first order axial-to-plane SRT in $\text{ErFe}_7\text{Co}_4\text{Ti}$ with replacement of the Fe.

A drastic change of MCA and SRT by hydrogen was found in $\text{ErFe}_7\text{Co}_4\text{TiH}$ very similarly to those observed in $\text{ErFe}_{11-x}\text{Co}_x\text{Mo}$ [4,13]. As appears from Fig. 4, $\text{ErFe}_7\text{Co}_4\text{TiH}$ has an “easy cone” anisotropy at temperatures below $T_{\text{SR}} = 41$ K. Due to the hydrogenation the SRT type has been changed to a second order axial-to-conical transition. The cone of the easy magnetisation axis is clearly observed in the $\sigma(H)$ curves at $T = 4.2$ K, which manifests itself in the presence of the spontaneous magnetic moment component not only along the $[001]$ axis, but also along the $[110]$ and $[100]$ axes as well. These spontaneous moments can be found by an extrapolation of the $\sigma(H)$ curves to $H = 0$. With cooling, spontaneous magnetisation deviates from the $[001]$ direction and the angle θ_0 between c -axis and magnetisation is equal to 19° at 5 K. The apex angle of the cone can be defined as $\theta_0 = \arctan(\sigma_{0\perp}/\sigma_{0\parallel})$, where $\sigma_{0\parallel}$ and $\sigma_{0\perp}$ are the spontaneous magnetic moments measured along the tetragonal axis in the basal plane. There is no distinction between the $\sigma(H)$ curve along the $[100]$ and $[110]$ directions. At room temperature the $\text{ErFe}_{11-x}\text{Co}_x\text{Ti}$ compounds and their hydrides show the “easy axis” anisotropy.

4. Conclusion

The Co substitution for the Fe in $\text{Er}(\text{Fe},\text{Co})_{11}\text{Ti}$ similarly as have been observed previously in $\text{ErFe}_{11-x}\text{Co}_x\text{Mo}$ [4,14] leads to the increase of the easy plane anisotropy. This is because the Co ions have a negative single-ion anisotropy constant, whereas the Fe ions favour a positive single-ion anisotropy. The introduction of hydrogen atoms into the crystal lattice of the $\text{ErFe}_7\text{Co}_4\text{Ti}$ compound suppresses a plane anisotropy. Under hydrogenation T_{SR} is shifted down what is caused by an enhancement of the second order crystal electric

field term. These facts indicate that under hydrogenation in the $\text{Er}(\text{Fe},\text{Co})_{11}\text{Ti}$ the change of magnetic properties in both the Er and the 3d-transition sublattices take place.

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References

- [1] J.M.D. Coey, Rare-earth Iron Permanent Magnets, Clarendon Press, Oxford, 1996.
- [2] K.H.J. Buschow, Handbook of Magnetic Materials, vol. 10, Elsevier, Amsterdam, 1997, p. 463.
- [3] W. Suski, K.A. Gschneidner Jr., L.R. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare-earths, vol. 22, Elsevier Science, Amsterdam, 1996, pp. 143–294.
- [4] E. Tomey, M. Bacmann, D. Fruchart, D. Gignoux, J.L. Souberoux, J. Alloys Compd. 262–263 (1997) 194.
- [5] O. Isnard, M. Guillot, J. Appl. Phys. 83 (1998) 6730.
- [6] I.S. Tereshina, S.A. Nikitin, V.N. Nikiforov, L.A. Ponomarenko, V.N. Verbetsky, A.A. Salamova, K.P. Skokov, J. Alloys Compd. 345 (2002) 16.
- [7] S.A. Nikitin, I.S. Tereshina, Yu.V. Skourski, N.Yu. Pankratov, K.P. Skokov, V.V. Zubenko, I.V. Telegina, Phys. Solid State 43 (2) (2001) 290–299.
- [8] F. Luis, R. Burriel, L.M. Garcia, E. Palacios, J. Bartolome, E. Tomey, D. Fruchart, J.L. Souberoux, S. Miraglia, R. Fruchart, D. Gignoux, IEEE Trans. Magn. 30 (1994) 583.
- [9] R. Burriel, E. Palacios, L.M. Garcia, D. Gignoux, E. Tomey, D. Fruchart, J. Magn. Mater. 140–144 (1995) 1091.
- [10] Z.F. Gu, D.C. Zeng, Z.Y. Liu, S.Z. Liang, J.C.P. Klaasse, E. Brück, F.R. de Boer, K.H.J. Buschow, J. Alloys Compd. 321 (2001) 40.
- [11] J.L. Wang, N. Tang, B. Fuquan, W.H. Wang, W.Q. Wang, G.H. Wu, F.M. Yang, J. Phys.: Condens. Matter 13 (2001) 1617.
- [12] I.S. Tereshina, S.A. Nikitin, T.I. Ivanova, K.P. Skokov, J. Alloys Compd. 275–277 (1998) 625.
- [13] L.M. Garcia, R. Burriel, F. Luis, E. Palacios, J. Bartolome, E. Tomey, D. Fruchart, J.L. Souberoux, D. Gignoux, IEEE Trans. Magn. 30 (1994) 595.
- [14] E. Palacios, R. Burriel, D. Fruchart, J.L. Souberoux, J. Magn. Mater. 140–144 (1995) 1095.