Effect of hydrogen on the magnetic anisotropy and spin–reorientation transition in ErFe$_{11}$Ti single crystal

I.S. Tereshina[a,*], S.A. Nikitin[a], V.N. Nikiforov[a], L.A. Ponomarenko[a], V.N. Verbetsky[b], A.A. Salamova[b], K.P. Skokov[c]

[a]*Faculty of Physics, Moscow State University, Vorobyevy Gory, 119899 Moscow, Russia*
[b]*Faculty of Chemistry, Moscow State University, Vorobyevy Gory, 119899 Moscow, Russia*
[c]*Faculty of Physics, Tver State University, Zheljabova str. 33, 170000 Tver, Russia*

Abstract

The effect of hydrogenation on the magnetic properties of the intermetallic compound ErFe$_{11}$Ti are studied. Single crystals of the hydrogen-containing compound were obtained. Magnetic characteristics of the ErFe$_{11}$Ti and ErFe$_{11}$TiH single crystals have been investigated in the temperature range 4.2–750 K and in magnetic fields up to 13 kOe. Upon hydrogenation, the uniaxial magnetic anisotropy is observed to increase, while the spin–reorientation temperatures T_{SR} shifted towards lower temperatures.
© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The magnetic properties of iron-rich rare-earth intermetallic RFe$_{11}$Ti compounds have attracted much attention in recent years [1–5]. This series of alloys adopts the tetragonal ThMn$_{12}$-type crystal structure (space group *I4/mmm*). The unit cell contains 26 atoms (two formula units per unit cell). The rare-earth atoms occupy only one kind of high-symmetry site (2*a*) while iron and titanium atoms occupy three different sites (8*i*, 8*j*, and 8*f*). The RFe$_{11}$Ti compounds have high Curie temperatures ranging from 490 to 610 K. Some of them (for example, SmFe$_{11}$Ti) have a large magnetic anisotropy and high saturation magnetization and may be considered as potential candidates for permanent magnet materials.

From a fundamental point of view, these compounds are excellent systems to study the crystalline–electric field effects, spin–reorientation transition (SRT) induced by temperature and applied magnetic field. The small value of the second-order crystal–field coefficients A_2^0 [6] makes these compounds convenient for the modulation of the magnetic anisotropy by the insertion of light interstitial elements such as hydrogen, nitrogen and carbon.

The intrinsic magnetic properties of the ErFe$_{11}$Ti compounds have been previously investigated [7,8]. The magnetic ordering temperature of these compounds is $T_C = 507$ K, and it exhibits an axial-to-conical transition (T_{SR}) on decreasing the temperature at $T = 50$ K [3].

Hitherto the magnetic properties of the ErFe$_{11}$Ti hydrides have been insufficiently investigated. Very recently Isnard et al. [9] have performed high-field magnetization measurements on the magnetically oriented ErFe$_{11}$Ti and its hydride in a field up to 240 kOe in the 4.2–300 K temperature range. The purpose of the present work was to study the effect of interstitial hydrogen on the fundamental magnetic characteristics such as Curie temperatures, saturation magnetisation, magnetic anisotropy and SRT of ErFe$_{11}$Ti and ErFe$_{11}$TiH single crystals.

2. Experimental details

The ErFe$_{11}$Ti polycrystalline samples were prepared by induction-melting under argon atmosphere of constituent elements (Er, Fe, Ti) of purity at least 99.95 wt%. The ingots were crushed and remelted several times to ensure homogeneity. X-ray diffraction was used to check the single phase character of the samples. Then the ingots were melted in an electric resistance furnace with a high

*Corresponding author. Fax: +7-95-932-8820.
E-mail address: irina@rem.phys.msu.su (I.S. Tereshina).

temperature gradient and cooled slowly through the melting point in order to increase the grain size. The single crystals $ErFe_{11}Ti$ extracted from the solidified ingots weighed 2–20 mg and were oriented by the conventional back Laue reflection method. Only the samples with subgrain disorientation less than 2–3° were used for the study.

Hydrogenation was carried out by passing high-purity hydrogen gas for 2 h at atmospheric pressure over the single crystals at 200 °C. Single crystals of the hydrogen containing compound were obtained without destruction of the samples. The amount of absorbed H estimated by a volumetric method was one atom per $RFe_{11}Ti$ formula unit.

Thermomagnetic analysis was used to measure the Curie temperature. The static moments M(T) were measured using a vibrating sample magnetometer, PARC-M-155, in the temperature range 4.2–300 K in magnetic fields up to 7 kOe. The lowest measurable magnetic moment was 10^{-5} emu. The magnetic measurements were also made using a pendulum magnetometer above room temperature (RT) in magnetic fields up to 13 kOe.

3. Results and discussion

The introduction of hydrogen atoms into the compounds changes the lattice constants (*a* and *c*) as indicated in Table 1, but the single phase nature of the compounds is retained. Hydrogenation leads only to a lattice expansion of the compounds and the relative change of the unit-cell volume $\Delta V/V$ is 0.77%. This is a rather common situation in H-modified iron-rich rare earth intermetallic compounds such as R_2Fe_{17}, $R_2Fe_{14}B$ and others.

Fig. 1 shows the σ–T curves of $ErFe_{11}Ti$ and $ErFe_{11}TiH$ in the range 300–620 K for which the Curie temperatures are determined to be 515 and 563 K, respectively. It can be seen from the experimental results that Curie temperature considerably increased upon hydrogenation ($\Delta T = 48$ K). The T_C of $RFe_{11}Ti$ compounds is determined by three kinds of exchange interaction: the Fe–Fe, the R–Fe and the R–R interactions. The exchange interaction can be analyzed by the molecular field model. It is well known, that the ordering temperature of this compounds is mainly governed by the Fe–Fe exchange interaction and is very sensitive to the Fe–Fe distance [1,2,10]. The T_C increase after hydrogenation is presumab-
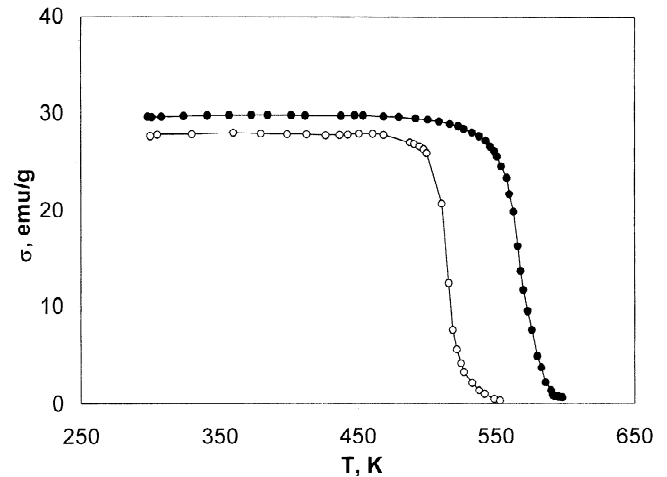

Fig. 1. Thermomagnetic curves of $ErFe_{11}Ti$ (○) and its hydride (●) in a magnetic field of $H = 1$ kOe.

ly related to the increase of the lattice parameters and may be attributed to a reduction of the negative exchange interaction associated with the Fe atom configurations in the $RFe_{11}Ti$ compounds. The exchange coupling constants J_{Fe-Fe} describing the exchange interactions in the Fe sublattice were obtained earlier in Ref. [11] for $YFe_{11}Ti$ and its hydride. Yttrium is not magnetic and the ordering temperature is due only to the Fe sublattice exchange interactions. The Fe–Fe interaction is enhanced by the interstitial hydrogen atoms. Then the J_{RFe} value describing the exchange interactions between the Er and Fe sublattices was calculated [12]. The R–Fe exchange constants slightly increase in $RFe_{11}TiH_x$, when the H content increases. These changes are correlated with the increase of the lattice constants and the Curie temperatures (see Table 1).

The saturation magnetization σ_S of $ErFe_{11}Ti$ and the hydrogen interstitial compounds measured at 77 and 300 K in magnetic fields up to 13 kOe are given in Table 1. The σ_S is found to be higher in the hydride than in the host compounds. It is known [11,13,14] that the iron sublattice magnetization is increased upon hydrogenation. The increase of σ_S results from a narrowing of the 3*d* band due to the volume expansion [11]. The observed increase of the overall magnetization of $ErFe_{11}TiH$ indicates this increase of the Fe sublattice magnetization. The question regarding the magnetic moment change upon interstitial insertion is

Table 1
Structural and magnetic properties of $ErFe_{11}TiH_x$ ($x = 0$ and 1) single crystals

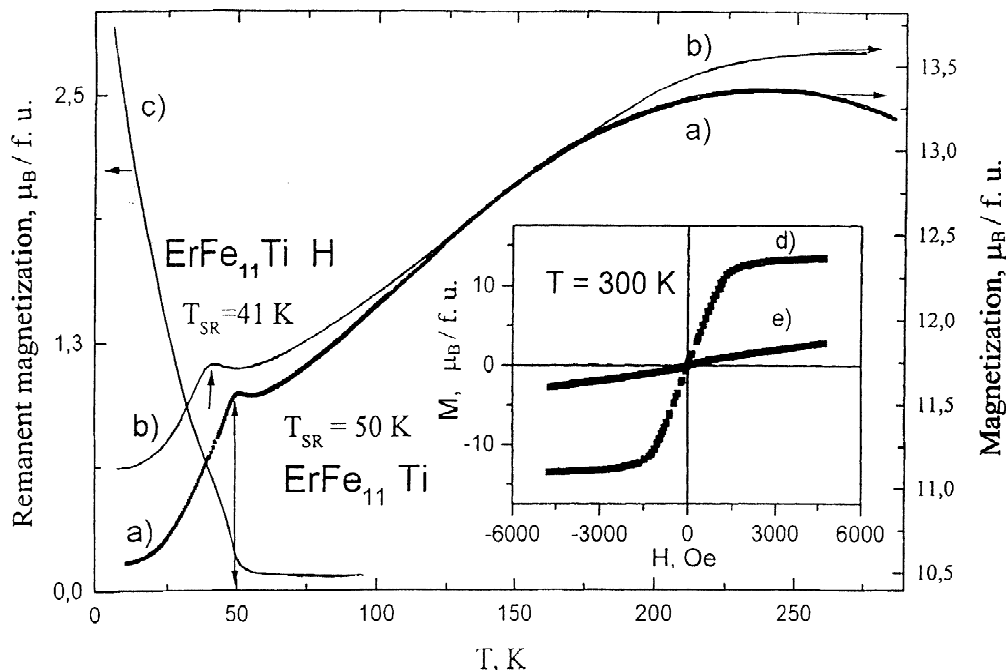| Compounds	a (Å)	c (Å)	c/a	V (Å^3)	$\Delta V/V$ (%)	T_C (K)	σ_S (emu g^{-1}) 295 K	77 K	T_{SR} (K)
$ErFe_{11}Ti$	8.480	4.775	0.563	343.4	–	515	96	81	50
$ErFe_{11}TiH$	8.507	4.781	0.562	346.0	0.77	563	99	86	41

Fig. 2. Temperature dependence of the magnetization of $ErFe_{11}Ti$ (a) and $ErFe_{11}TiH$ (b) and remanent magnetization of $ErFe_{11}Ti$ (c). Inset: the magnetization versus magnetic field curves measured along the easy (d) and hard (e) directions for $ErFe_{11}Ti$ at 300 K.

very difficult and it should be analyzed by a band structure calculation.

Fig. 2 shows the temperature dependencies of the magnetization measured in $H=5$ kOe of $ErFe_{11}Ti$ and $ErFe_{11}TiH$ and the remanent magnetization of the $ErFe_{11}Ti$ single crystal. An anomaly that occurs at about 50 K for the host compound is related to a spin–reorientation transition. In the $ErFe_{11}TiH$ single crystal, the situation is slightly different. An anomaly of the magnetization is found at $T_{SR}=41$ K and T_{SR} is shifted towards lower temperatures. Fig. 2(inset) also shows the magnetization versus magnetic field curves measured along the easy and hard directions for $ErFe_{11}Ti$ at 300 K. The estimation of the anisotropy field obtained by extrapolation of the experimental data leads to the value $H_a=35$ kOe. Our results for $ErFe_{11}Ti$ agree well with the data obtained earlier [9].

Hysteresis loops measured along the c-axis at 4.2 and 113 K for $ErFe_{11}TiH$ are shown in Fig. 3a,b. It is evident that there is no hysteresis at $T=113$ K and also in the whole investigated temperature range $T>T_{SR}$, but broad hysteresis loops are seen at 4.2 K, which means that the value of the coercive force increases at low temperatures where the SRT takes place. Hysteresis is connected with irreversible processes of rotation of the magnetization.

Since Er ion possesses a positive second order Stevens factor ($\alpha_J>0$), this compound would, in a rough approximation, be expected to retain its uniaxial anisotropy and first magnetic anisotropy constant $K_1>0$ at all temperatures, because the second order crystal field coefficients A_2^0

is negative. However, a main feature of the $RFe_{11}Ti$ compounds is the small value of A_{20} and the relevance of higher-order terms in determining SRT. Therefore, the observed SRT in $ErFe_{11}Ti$ are due to the fourth and sixth crystal–field parameters.

Some $RFe_{11}Ti$ compounds mainly with negative second-order Stevens coefficient $\alpha_J<0$ (Nd, Tb, Dy) show different types of spin–reorientation transitions (SRT) originating from the competition between the R and Fe sublattices [5]. It is well known [11,13,14], that the contribution to the total magnetic anisotropy in these compounds from the Fe sublattice is large and favors an easy c-axis. With decreasing temperature, the influence of the rare-earth anisotropy increases, which leads to temperature-induced spin–reorientation transitions. For instance, $TbFe_{11}Ti$ exhibits a direct axis-to-plane transition at $T_{SR}=325$ K [15]. After interstitial H modification, the iron sublattice anisotropy remains uniaxial and becomes slightly enhanced. Hydrogenation also yields an increase of the planar contribution to the anisotropy from the R ($\alpha_J<0$) site, suppresses the easy-axis anisotropy and the SRT disappears in the $TbFe_{11}TiH$ single crystals [16].

The reverse situation is observed in our case for Er ($\alpha_J>0$). It can be seen from the experimental results that the introduction of hydrogen atoms into the host compound leads to an increase in the temperature range where the easy magnetisation direction is parallel to the c-axis. T_{SR} shifts towards lower temperatures. These facts indicate that the rare-earth sublattice contribution to the magnetic anisotropy is increased. In the $ErFe_{11}TiH$, the rare earth
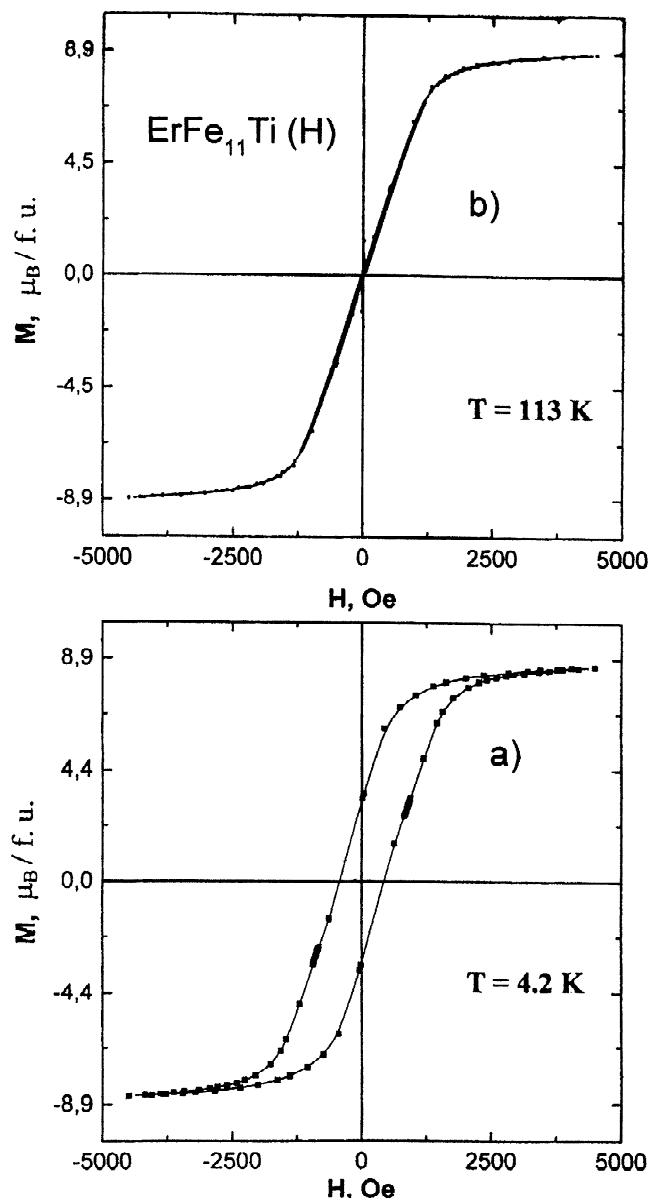
Fig. 3. Hysteresis loops measured at 4.2 (a) and 113 K (b) for ErFe$_{11}$TiH.

atoms have two nearest interstitial neighbors located along the *c*-axis direction in the octahedral 2*b* site. The increase in the rare-earth sublattice contribution to magnetic anisotropy should be due to the effect of the interstitial atoms on the second-order term of the crystal field of Er. The relative importance of higher-order terms in determining the SRT is retained. Thus, at low temperature ($T < 41$ K) the easy magnetization direction favors an intermediate direction in the ErFe$_{11}$TiH single crystals.

4. Conclusion

We have made a systematic study of the effect of hydrogen on the magnetic properties of ErFe$_{11}$Ti single crystals. It is found that the introduction of H increases the lattice parameters and increases the Curie temperature and the saturation magnetization. A second-order SRT from 'easy axis' to 'easy cone' exist in the host compounds at $T_{SR} = 50$ K and in the hydride at $T_{SR} = 41$ K. At temperatures $T > T_{SR}$ both compounds have uniaxial anisotropy and the anisotropy field H_a increases after hydrogenation.

References

[1] J.M.D. Coey, Rare-earth Iron Permanent Magnets, Clarendon Press, Oxford, 1996.
[2] K.H.J. Buschow, in: Handbook of Magnetic Materials, Vol. 10, Elsevier, Amsterdam, 1997, p. 463.
[3] L.Y. Zhang, E.B. Boltich, V.K. Sinha, W.E. Wallace, IEEE Trans. Magn. 25 (1989) 3303.
[4] N.V. Kurevatykh, M.I. Bartashevich, V.A. Reymer, S.S. Sigaev, E.N. Tarasov, Phys. Met. Metall. 70 (1990) 48.
[5] X.C. Kou, T.S. Zhao, R. Grössinger, H.R. Kirchmayr, X. Li, F.R. de Boer, Phys. Rev. B 47 (1993) 3231.
[6] B.-P. Hu, H.-S. Li, J.M.D. Coey, J.P. Gavigan, Phys. Rev. B 41 (1990) 2221.
[7] A.V. Andreev, V. Sechovsky, N.V. Kudrevatykh, S.S. Sigaev, E.N. Tarasov, J. Less-Common Metals 144 (1988) L21.
[8] K.Yu. Guslienko, X.C. Kou, R. Grössinger, J. Magn. Magn. Mater. 150 (1995) 383.
[9] O. Isnard, M. Guillot, J. Appl. Phys. 83 (1998) 6730.
[10] I.S. Tereshina, S.A. Nikitin, T.I. Ivanova, K.P. Skokov, J. Alloys Comp. 275–277 (1998) 625.
[11] J. Yang, S. Dong, W. Mao, P. Xuan, Y. Yang, Physica B 205 (1995) 341.
[12] S.A. Nikitin, I.S. Tereshina, Y. Skourski, V.N. Verbetsky, A.A. Salamova, in: Proceedings of MISM '99 (Moscow International Symposium on Magnetism devoted to the memory of E.I. Kondorskii, June 20–24), Moscow, Russia, 1999, pp. 376–379, Part 1.
[13] I.S. Tereshina, P. Gaczyński, V.S. Rusakov, H. Drulis, S.A. Nikitin, W. Suski, N.V. Tristan, T. Palewski, J. Phys. Condens. Matter 13 (2001) 8161–8170.
[14] S.A. Nikitin, I.S. Tereshina, V.N. Verbetsky, A.A. Salamova, J. Hydrogen Energy 24 (1999) 217.
[15] J. Wang, G. Wu, N. Tang, D. Yang, F. Yang, F.R. de Boer, Y. Janssen, J.C.P. Klaasse, E. Brück, K.H.J. Buschow, Appl. Phys. Lett. 76 (2000) 1170.
[16] S.A. Nikitin, I.S. Tereshina, V.N. Verbetsky, A.A. Salamova, Magnetic anisotropy and coercivity in rare-earth transition metal alloys, in: L. Schultz, K.-H. Müller (Eds.), Proceedings of the 10th International Symposium on Magnetic Anisotropy and Coercivity in Rare-earth Transition Metals Alloys, Werkstoff-informationsgesellschaft, Dresden, 1998, pp. 183–189.