Neutron diffraction study of the magnetic structure of ErFe$_{11.5}$Ta$_{0.5}$

J M Cadogan†¶, D H Ryan‡, I P Swainson§ and R Gagnon‡

† School of Physics, The University of New South Wales, Sydney NSW 2052, Australia
‡ Department of Physics, McGill University, Montreal, Quebec, Canada H3A 2T8
§ Neutron Programme for Materials Research, Steacie Institute for Molecular Sciences, National Research Council, Chalk River Laboratories, Ontario, Canada K0J 1J0

E-mail: `j.cadogan@unsw.edu.au`

Abstract.   We have used high-resolution neutron powder diffraction over the temperature range 9–65 K to determine the magnetic structure of ErFe$_{11.5}$Ta$_{0.5}$. Above 49 K the magnetic structure is a collinear ferrimagnet with an easy c-axis. Below 49 K, the magnetization cants away from the c-axis and eventually reaches a canting angle of $9.0(1.3)°$ from the c-axis, as $T \rightarrow 0$ K. This behaviour may be understood in terms of the competition between different order terms in the Er^{3+} crystal-field Hamiltonian: the spin-reorientation away from the c-axis is driven by the 6th-order crystal-field term.

1. Introduction

The ThMn$_{12}$ structure is tetragonal with the space group *I4/mmm* (#139). There are two formula units ($f.u.$) per unit cell and the site occupancies are *2a* for Th and *8f, 8i* and *8j* for Mn. This structure forms the basis for many series of iron-rich, rare-earth–iron intermetallic phases, some of which become potential permanent magnet materials after interstitial modification with nitrogen or carbon [1]. The R atom takes the place of Th and the Fe takes the place of Mn. Unfortunately, binary RFe$_{12}$ compounds do not form and a third element is required to stabilize this structure. To date, RFe$_{12-x}$M$_x$ compounds have been formed with M = Ti, V, Cr, Mn, Nb, Mo, W, Re, Al and Si. Minimizing the M content while retaining the ThMn$_{12}$ structure is important as it maximizes the Fe content and thus the net magnetization of the phase. The minimum M content is around 0.5–0.7 for M = Mo and Nb [2].

Recently, Piquer *et al* [3] reported on the preparation of RFe$_{12-x}$Ta$_x$ compounds with $x \sim 0.5$. They found that this Ta-stabilized phase only forms with the heavier rare-earth elements Tb, Dy, Ho, Er and Lu. Single-phase samples could not be produced and all samples contained impurities, the most common being α-Fe and Fe$_2$Ta. The Curie temperatures of the RFe$_{11.5}$Ta$_{0.5}$ compounds range from 499 K (R = Lu) to 576 K (R = Tb) and the easy direction of magnetization at room temperature is the tetragonal c-axis for all R except Tb, which is planar at room temperature. Magnetometry and ac-susceptometry work showed that both ErFe$_{11.5}$Ta$_{0.5}$ and DyFe$_{11.5}$Ta$_{0.5}$ undergo spin-reorientations at 40 K for R = Er, and at 185 K and 265 K for R = Dy. This group also used x-ray diffraction to show that Ta occupies the *8i* site [4].

¶ Author to whom any correspondence should be addressed.

The $RFe_{12-x}Ta_x$ compounds can accommodate interstitial elements as shown by Vert *et al* [5], who studied $HoFe_{11.4}Ta_{0.6}X_{0.6}$ with X = H and C. Both interstitials lead to a volume expansion (1.0% with H and 2.9% with C), resulting in an increase in Curie temperature from 526 K to 716 K and an increase in magnetization (at 4 K) from 11.4 $\mu_B/f.u.$ to 13.0 $\mu_B/f.u.$ for $HoFe_{11.4}Ta_{0.6}C_{0.6}$. Interestingly, a spin-reorientation at 118 K was observed for $HoFe_{11.4}Ta_{0.6}H_{0.6}$, although the parent $HoFe_{11.4}Ta_{0.6}$ shows no such behaviour.

Vert *et al* [6] also studied the phase compositions of samples as a function of Ta starting content. They confirmed that single-phase samples do not form, with the usual impurities being α-Fe and Fe_2Ta, as mentioned earlier. Furthermore, significant amounts (>15 at.%) of hexagonal R_2Fe_{17} can also form and a rather narrow Ta content range of $0.5 \leqslant x \leqslant 0.7$ is required to maximize the $R(Fe, Ta)_{12}$ content.

From a fundamental point of view, the tetragonal $R(Fe, M)_{12}$ compounds have provided much useful information on (i) the crystal-field interactions at the R^{3+} ion, (ii) the R–Fe and Fe–Fe exchange interactions and (iii) the complex interplay between the crystal-field and the exchange. Much of this information has been deduced from the numerous spin-reorientations which occur in the $R(Fe, M)_{12}$ compounds at low temperatures. Such changes in the magnetic structure of a compound are generally due to either (i) competition between the R and Fe anisotropies and/or (ii) competition between the 2nd-, 4th- and 6th-order terms in the crystal-field acting on the R^{3+} ion, with the higher-order terms playing a more significant role as the temperature is reduced. Thus, the determination of both spin-reorientation temperatures and canting angles of the magnetic structure has provided valuable data for the characterization of both crystal-field and exchange interactions.

In this paper we present the results of our study of the spin-reorientation in $ErFe_{11.5}Ta_{0.5}$ using high-resolution neutron powder diffraction. Our results confirm the existence of a spin-reorientation below 49 K, during which the magnetization gradually tips away from the c-axis, reaching an angle of $\theta = 9.0(1.3)°$ from the c-axis as $T \rightarrow 0$ K.

2. Experimental methods

The $ErFe_{11.5}Ta_{0.5}$ sample was prepared by arc-melting stoichiometric amounts of the pure elements under Ti-gettered argon. The sample was subsequently annealed at 900 °C for 2 weeks, sealed under vacuum in a quartz tube. Powder x-ray diffraction patterns were obtained using Cu-K_α radiation on an automated Nicolet–Stoe diffractometer. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA-7 in a small magnetic field gradient to determine the magnetic ordering temperature. ac-susceptibility was measured on a Quantum Design PPMS system at a frequency of 377 Hz with an ac magnetic field amplitude of 398 A m^{-1}.

Neutron powder diffraction experiments were carried out on $\sim$ 4 g samples on the DUALSPEC C2 high-resolution powder diffractometer located at the NRU reactor, Chalk River Laboratories, Ontario, operated by Atomic Energy Canada Ltd. The neutron wavelength was 2.3688(1) Å. A detailed review of the neutron scattering facilities at Chalk River, including a description of C2, can be found in [7]. A total of 15 diffraction patterns were obtained over the temperature range 9–65 K and all diffraction patterns were analysed using the Rietveld method with the FULLPROF program [8].

3. Results and discussion

It proved impossible to prepare single-phase $ErFe_{11.5}Ta_{0.5}$ in agreement with the findings of Vert *et al* [5, 6]. Our sample contained α-Fe and Fe_2Ta in the amounts 3 wt.% and 4wt.%,

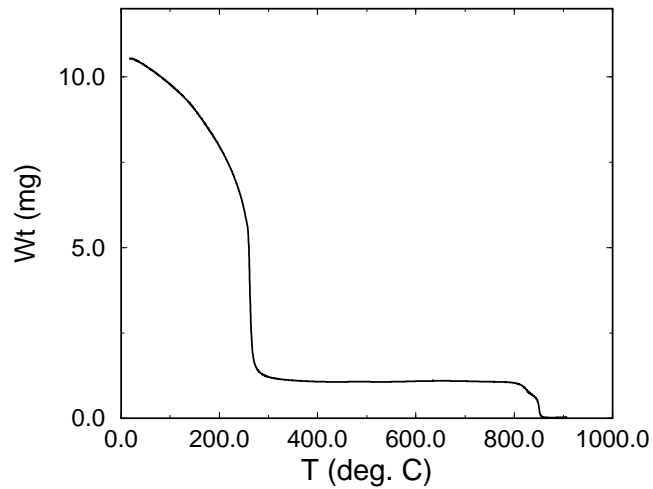**Figure 1.** TGA trace of $ErFe_{11.5}Ta_{0.5}$.

respectively, as determined from the fits to the neutron diffraction patterns.

In figure 1 we show the TGA trace of $ErFe_{11.5}Ta_{0.5}$, from which we derive a magnetic ordering temperature of 541(5) K for $ErFe_{11.5}Ta_{0.5}$. The residual magnetic order of the impurity α-Fe is clear. Fe_2Ta is a Pauli paramagnet [9] and does not contribute to the TGA data.

In figure 2 we show the ac-susceptibility trace of $ErFe_{11.5}Ta_{0.5}$. The spin-reorientation is clear with an onset temperature of 49(2) K and a peak temperature of 41(2) K.

In figure 3 we show neutron diffraction patterns of $ErFe_{11.5}Ta_{0.5}$ obtained at 65 K and 9 K, i.e., above and below the spin-reorientation temperature, respectively. Most of the 1:12-stabilizing elements studied to date show preferential occupation of the *8i* site and our neutron work confirms this for Ta. The refined Ta content in the 1:12 phase is slightly larger than the nominal starting composition of $Ta_{0.5}$, corresponding to $ErFe_{11.38}Ta_{0.62}$. The refined atomic
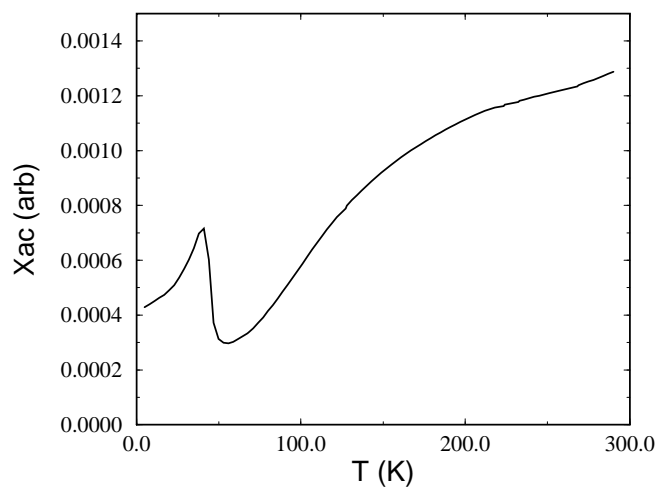

Figure 2. ac-susceptibility of $ErFe_{11.5}Ta_{0.5}$.

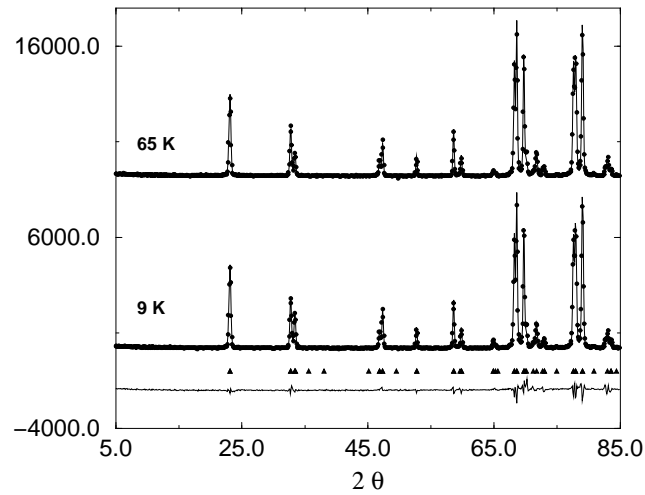**Figure 3.** Neutron powder diffraction patterns of nominal $ErFe_{11.5}Ta_{0.5}$ at 9 K and 65 K.

and magnetic parameters are given in table 1. The refinement 'R-factors (%)' for all 15 patterns obtained during this study lie within the following ranges: R(Bragg) = 2.9–4.5, R(F-structure) = 1.9–3.0, R(wp) = 9.4–12.1, R(exp) = 4.4–4.7 and R(mag) = 3.3–5.1.

Table 1. Lattice parameters, atomic positions, magnetic moments (in μ_B), magnetization and canting angle (degrees) of $ErFe_{11.5}Ta_{0.5}$ deduced from the neutron diffraction pattern obtained at 9 K.

$a(\text{Å})$	$c(\text{Å})$	$x(8j)$	$x(8i)$
8.4847(5)	4.7747(3)	0.276(1)	0.359(1)

$\mu(Er)$	$\mu(Fe-8f)$	$\mu(Fe-8j)$	$\mu(Fe-8i)$
8.35(17)	1.67(8)	1.89(9)	2.21(13)

$M(\mu_B/f.u.)$	θ	$B_{iso}(\text{Å}^2)$
13.6(7)	8.9(11)	0.08(6)

In figure 4 we show the canting angle of the net magnetization of $ErFe_{11.5}Ta_{0.5}$ relative to the crystal c-axis, derived from our neutron diffraction data.

The magnetocrystalline anisotropy of the R^{3+} sublattice in the $R(Fe, M)_{12}$ compounds is determined by the crystal-field Hamiltonian appropriate to the *4/mmm* point symmetry of the R^{3+} site

$$\mathcal{H}_{cf} = B_{20}O_{20} + B_{40}O_{40} + B_{44}O_{44} + B_{60}O_{60} + B_{64}O_{64} \tag{1}$$

where the B_{nm} are the crystal-field parameters and the O_{nm} are the standard Stevens spin-operators [10].

From experiments on numerous $R(Fe, M)_{12}$ systems it is well established that the Fe sublattice has easy c-axis anisotropy over the entire magnetically-ordered temperature range. Hu *et al* [11] have determined a set of crystal-field energy terms from a study of the
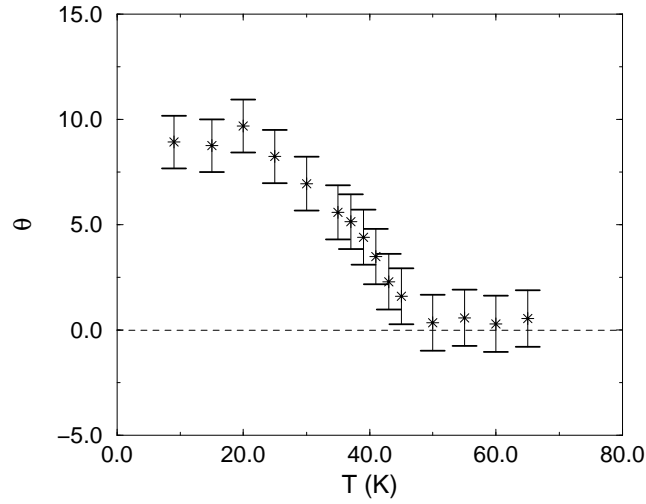
Figure 4. Canting angle (in degrees) of the net magnetization of $ErFe_{11.5}Ta_{0.5}$ relative to the *c*-axis.

$RFe_{11.35}Nb_{0.65}$ series, and for $ErFe_{11.35}Nb_{0.65}$ in the limit $T = 0$ K they find: $B_{20}\langle O_{20}\rangle = -6.12$ K, $B_{40}\langle O_{40}\rangle = -11.4$ K, $B_{44}\langle O_{40}\rangle = 109$ K, $B_{60}\langle O_{60}\rangle = 23.0$ K and $B_{64}\langle O_{60}\rangle = 5.7$ K. The axial or planar anisotropy is determined principally by the diagonal terms such as $B_{20}\langle O_{20}\rangle$, while the anisotropy *within* the *a–b*-plane is determined by the off-diagonal terms $B_{44}\langle O_{40}\rangle$ and $B_{64}\langle O_{60}\rangle$. The 2nd- and 4th-order diagonal crystal-field energy terms for Er^{3+} are negative and thus favour easy *c*-axis anisotropy, whereas the 6th-order diagonal term $B_{60}\langle O_{60}\rangle$ is positive and favours easy *a–b*-plane anisotropy. Hence, it is clear that the observed spin-reorientation away from the *c*-axis observed in $ErFe_{11.5}Ta_{0.5}$ is driven by the 6th-order crystal-field term acting on the Er^{3+} ion.

Finally, the rotational transformation properties of the spin-operators O_{nm} in the above crystal-field Hamiltonian (tabulated by Rudowicz [12]) may be used to show that the anisotropy of the R^{3+} sublattice can be written in the phenomenological form [13]:

$$E_a = K_1\sin^2\theta + (K_2 + K_2'\cos 4\phi)\sin^4\theta + (K_3 + K_3'\cos 4\phi)\sin^6\theta \tag{2}$$

where θ and ϕ are the polar angles of the R^{3+} magnetization relative to the crystal axes. The *in-plane* terms K_2' and K_3' are related to the crystal-field energy terms by

$$K_2' = \frac{1}{8}[B_{44}\langle O_{40}\rangle + 5B_{64}\langle O_{60}\rangle] \tag{3}$$

$$K_3' = -\frac{11}{16}[B_{64}\langle O_{60}\rangle] \tag{4}$$

and, if the relative magnitudes and signs of the crystal-field parameters deduced for the $Er(Fe, Nb)_{12}$ compound are applicable to $Er(Fe, Ta)_{12}$, then the fact that both off-diagonal terms in (1) are positive indicates that in the canted or tipped magnetic state the planar projection of the net magnetization is along the [110] direction, a fact inaccessible to neutron diffraction due to the tetragonal symmetry [14].

4. Conclusion

ErFe$_{11.5}$Ta$_{0.5}$ is a collinear ferrimagnet with an ordering temperature of 541(5) K. The easy direction of magnetic order is the *c*-axis in the temperature range $\sim$50 $\leqslant T$(K) $\leqslant$ 541. A spin-reorientation commences at 49(2) K below which temperature the net magnetization is canted away from the *c*-axis. Using high-resolution neutron powder diffraction we have determined the temperature dependence of the canting angle and find a maximum canting of 9.0(1.3)$^\circ$ as $T \to 0$ K. The neutron diffraction results also confirm that the Ta occupies the 8*i* crystallographic site.

Acknowledgments

References

[1] Coey J M D, Sun H and Hurley D P F 1991 *J. Magn. Magn. Mater.* **101** 310–6
[2] See, for example, Szytula A and Leciejewicz J 1994 *Handbook of Crystal Structures and Magnetic Properties of Rare Earth Intermetallics* (Boca Raton: CRC) pp 193–202
[3] Piquer C, Artigas M, Rubin J and Bartolomé J 1998 *J. Phys.: Condens. Matter* **10** 11055–65
[4] Artigas M, Piquer C, Rubin J and Bartolomé J 1999 *J. Magn. Magn. Mater.* **196–197** 653–4
[5] Vert R, Bououdina M, Fruchart D, Gignoux D, Kalychak Y, Ouladdiaf B and Skolozdra R V 1999 *J. Alloys and Compounds* **285** 56–63
[6] Vert R, Bououdina M, Fruchart D, Gignoux D, Kalychak Y and Skolozdra R V 1999 *J. Alloys and Compounds* **287** 38–44
[7] Powell B M 1990 *Neutron News* **1** 16–20
[8] Rodríguez-Carvajal J 1993 *Physica* B **192** 55–69
[9] Wijn H P J (ed) 1991 *Magnetic Properties of Metals—d-elements, Alloys and Compounds* (Berlin: Springer) p 72
[10] Hutchings M T 1964 *Solid State Physics* **16** 227–73
[11] Hu B P, Wang K Y, Wang Y Z, Wang Z X, Yan Q W, Zhang P L and Sun X D 1995 *Phys. Rev.* B **51** 2905–19
[12] Rudowicz C 1985 *J. Phys. C: Solid State Phys.* **18** 1415–30
[13] Hu B P, Li H S, Gavigan J P and Coey J M D 1989 *J. Phys.: Condens. Matter* **1** 755–70
[14] Shirane G 1959 *Acta Crystallogr.* **12** 282–3