Neutron diffraction study of the magnetic structure of $ErFe_{11.5}Ta_{0.5}$

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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 $T \to 0$ 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.%,

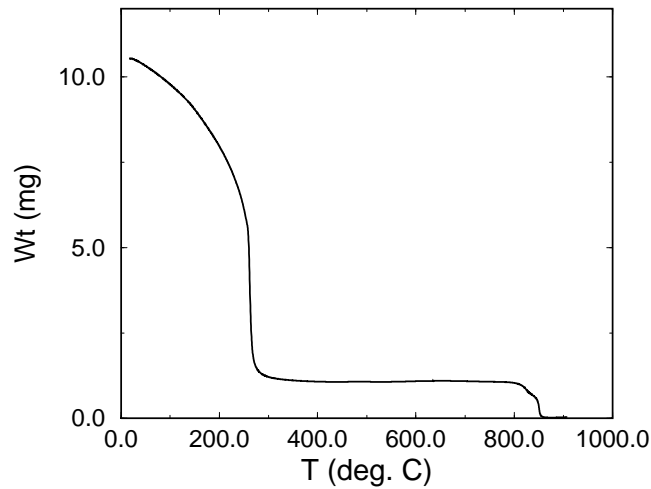**Figure 1.** TGA trace of $ErFe_{11.5}Ta_{0.5}$.

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
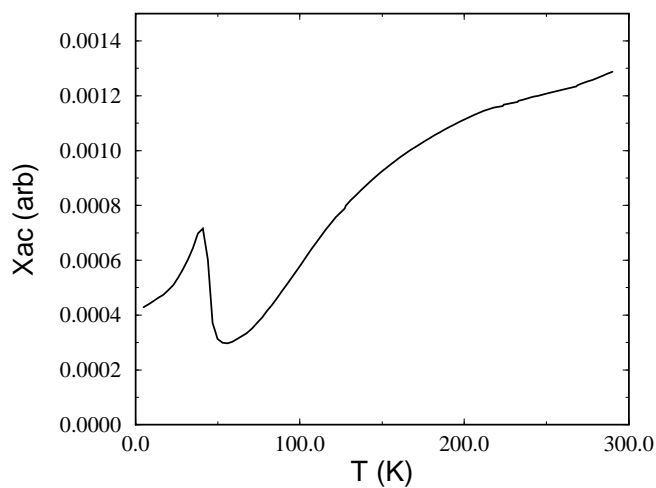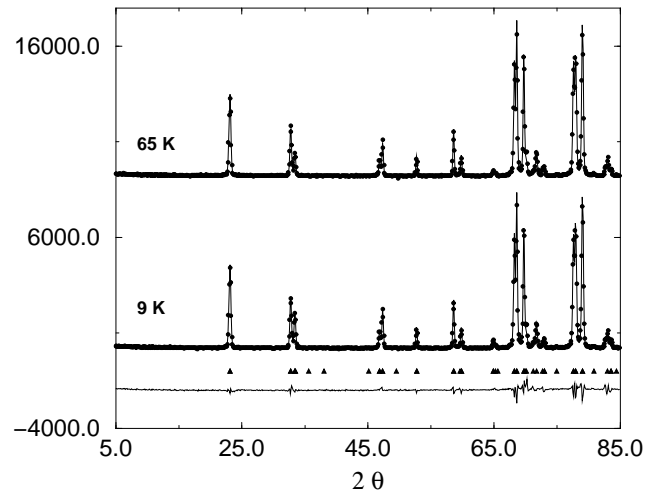

Figure 2. ac-susceptibility of $ErFe_{11.5}Ta_{0.5}$.

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(Å)	c(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}(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
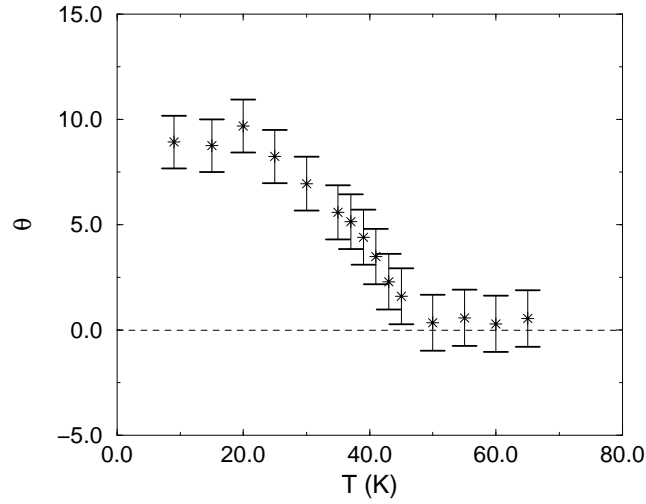
Figure 4. Canting angle (in degrees) of the net magnetization of $ErFe_{11.5}Ta_{0.5}$ relative to the *c*-axis.

$RFe_{11.35}Nb_{0.65}$ 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 $T \rightarrow 0$ K. The neutron diffraction results also confirm that the Ta occupies the $8i$ crystallographic site.

Acknowledgments

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