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Crystal fields and spin reorientation transitions in $R_2Fe_{17}C_{3-\delta}$ ($R \equiv Sm$, Er, Tm)

Qi-nian Qi, M. D. Kuz'min, Hong Sun and J. M. D. Coey
Department of Pure and Applied Physics, Trinity College, Dublin 2 (Ireland)

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Abstract

The interstitial carbides $R_2Fe_{17}C_{3-\delta}$ with $\delta \approx 0.8$ prepared by gas-phase reaction with butane at 550 °C exhibit spin reorientations at 125 K when $R \equiv Er$ and 225 K when $R \equiv Tm$ in measurements of a.c. magnetic susceptibility and Mössbauer spectra. The effective average value of A_{20} in these hexagonal compounds is -95 K a_0^{-2}.

1. Introduction

Of the 2:17 rare earth iron intermetallics, only Tm_2Fe_{17} exhibits *c* axis anisotropy [1]. This is below $T_{sr} = 72$ K. All other R_2Fe_{17} compounds and Tm_2Fe_{17} at temperatures greater than T_{sr} show easy-plane anisotropy. A recent suggestion, based on a.c. susceptibility measurements, that Sm_2Fe_{17} may have a spin reorientation at about 164 K [2] was not confirmed in a subsequent Mössbauer study of the compound as a function of temperature [3].

The interstitial carbides $R_2Fe_{17}C_{3-\delta}$ with $\delta > 1.5$ have been prepared by arc melting. T_{sr} for $Tm_2Fe_{17}C_{3-\delta}$ rises with increasing carbon content, due to an increasing crystal field interaction at the rare earth site [4]. We recently found that it is possible to prepare interstitial carbides with substantially greater carbon content by a low-temperature (about 550 °C) reaction of 2:17 intermetallic powder with a hydrocarbon gas [5].

The samarium compound exhibits strong uniaxial anisotropy at room temperature and probably remains uniaxial at all temperatures up to the Curie point. The anisotropy field B_a is 5.3 T for $Sm_2Fe_{17}C$ [6] and $B_a = 16$ T for $Sm_2Fe_{17}C_{2.3}$ [7]. From ref. 8, we deduce a value of the second-order crystal field coefficient $A_{20} = -180$ K a_0^{-2} where a_0 is the Bohr radius. Here we examine compounds of two other rare earths with a positive second-order Stevens coefficient α_J, erbium and thulium. By analogy with the interstitial nitrides $R_2Fe_{17}N_{3-\delta}$ [9], these compounds may be expected to exhibit spin reorientation below room temperature.

2. Experimental details

The 2:17 compounds were first prepared by arc melting the 99.9% pure elements. A fine powder was then carbonated by heating at 550 °C for about

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2 h in 1 bar of butane in the thermopiezic analyser, and then pumping to remove any hydrogen or unreacted butane before cooling to room temperature. Both compounds had a Th_2Ni_{17}-related structure after carbonation. The value of δ was determined from the weight gain to be 0.8(1). Increases in unit cell volume determined by X-ray diffraction were 6.1% for R≡Er and 6.7% for R≡Tm. The Curie temperatures of the carbides were 663 K and 656 K compared with 296 K and 260 K respectively for the parent compounds.

3. Results and discussion

The a.c. magnetic susceptibility, measured at 1000 Hz in a field of magnitude 30 μT, is shown in Fig. 1 for R≡Er. There are sharp changes at 125 K for R≡Er and at 225 K for R≡Tm. That these anomalies are actually associated with a reorientation of the magnetization is confirmed by the Mössbauer spectra as a function of temperature shown in Fig. 2. The structure visible in the spectra around +4 and −6 mm s^{-1} changes distinctly at the temperature of the susceptibility anomaly. These data were fitted using a model with seven lorentzian sextets, previously used to fit spectra of the $R_2Fe_{17}N_{3-\delta}$ series [10]. The hyperfine fields and the quadrupole interaction at 12j and 12k sites are plotted in Fig. 3. There is an increase of about 2 T in the average hyperfine field $\langle B_{hf} \rangle$ below T_{sr}, which is probably due to the anisotropy in the iron hyperfine field associated with a small orbital moment of about $0.05\mu_B$. The hyperfine field associated with the orbital moment in iron is 42 T μ_B^{-1} [11]. The change in sign of the quadrupole splitting at the majority iron sites also indicates a reorientation of the iron magnetization direction.

The spin reorientations reflect the balance of the anisotropy of the iron and rare earth sublattices. The close similarities in the transition temperatures of the carbides and nitrides (Table 1) are probably fortuitous. The anisotropy difference increases smoothly with increasing carbon content, as shown by the variation of T_{sr} in Fig. 4. The iron sublattice anisotropy measured in the

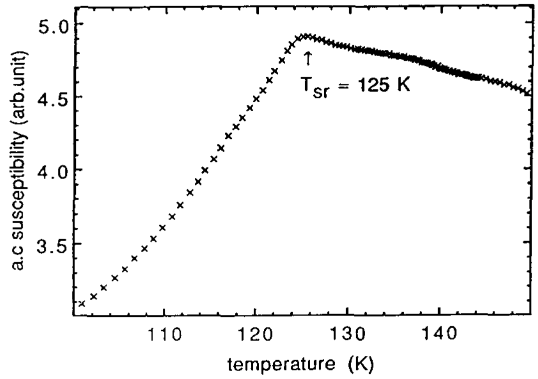


Fig. 1. The a.c. magnetic susceptibility of $Er_2Fe_{17}C_{3-\delta}$.

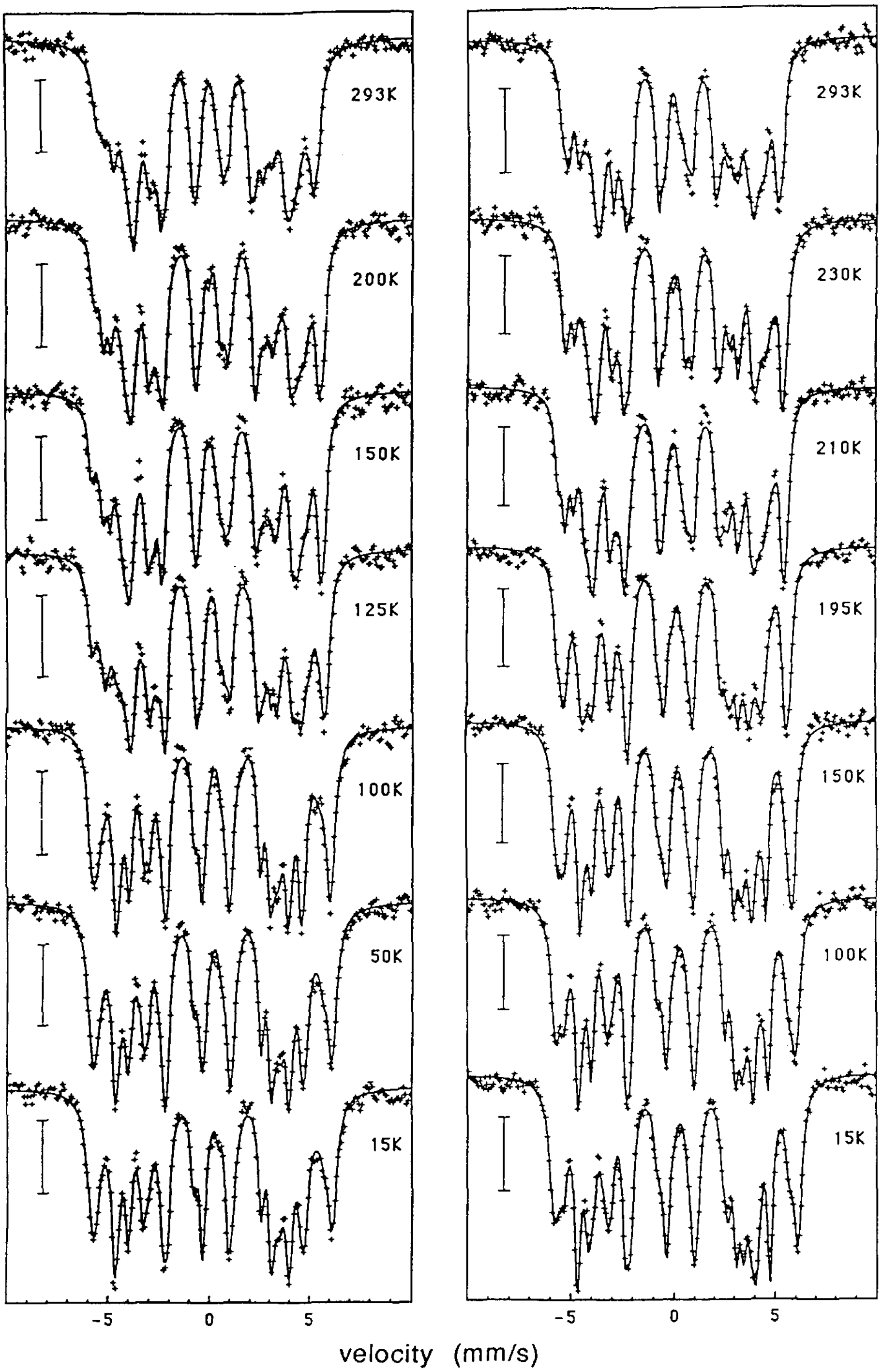
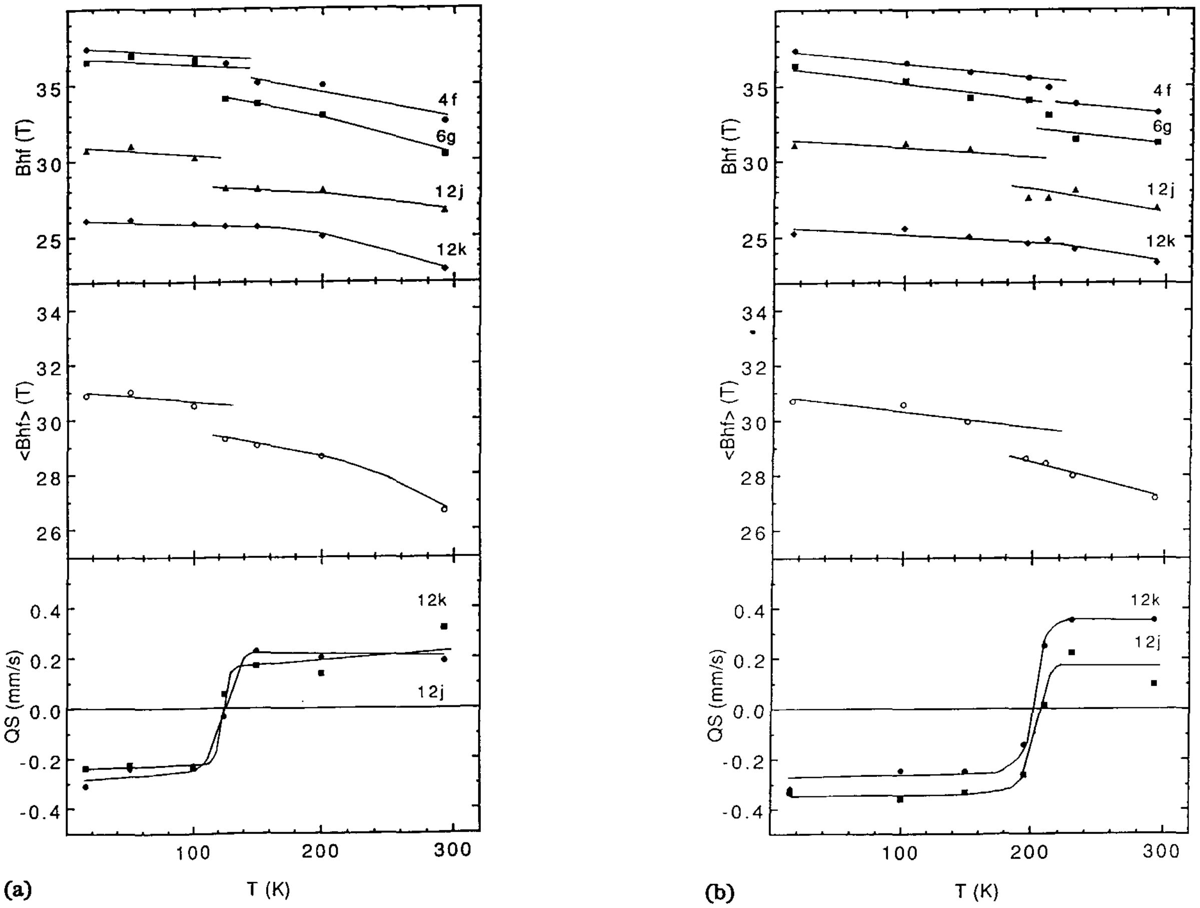


Fig. 2. Mössbauer spectra of $Er_2Fe_{17}C_{3-\delta}$ (left) and $Tm_2Fe_{17}C_{3-\delta}$ (right) at different temperatures: ——, fits to the data (vertical bars represent 1% absorption).



(a) (b)

Fig. 3. Hyperfine fields at the four sites, the average hyperfine field and quadrupole interaction for (a) $Er_2Fe_{17}C_{3-\delta}$ and (b) $Tm_2Fe_{17}C_{3-\delta}$ as functions of temperature.

TABLE 1

Structure and magnetic properties of R_2Fe_{17}, $R_2Fe_{17}C_{2.2}$ and $R_2Fe_{17}N_{2.7}$ (R≡Sm, Tm, Er)

Compound	Structure	a (nm)	c (nm)	T_c (K)	T_{sr} (K)	$\bar{A}_{20}$ (K a_0^{-2})
Sm_2Fe_{17}	Th_2Zn_{17}	0.854	1.243	389	c plane	> −36
$Sm_2Fe_{17}C_{2.3}$	Th_2Zn_{17}	0.875	1.257	668	c axis	−180[a]
$Sm_2Fe_{17}N_{2.3}$	Th_2Zn_{17}	0.873	1.264	749	c axis	−242[a]
Er_2Fe_{17}	Th_2Ni_{17}	0.842	0.827	296	c plane	> −74
$Er_2Fe_{17}C_{2.2}$	Th_2Ni_{17}	0.860	0.841	663	125	−83
$Er_2Fe_{17}N_{2.7}$	Th_2Ni_{17}	0.861	0.846	697	120	−65
Tm_2Fe_{17}	Th_2Ni_{17}	0.840	0.828	260	72	−34
$Tm_2Fe_{17}C_{2.2}$	Th_2Ni_{17}	0.860	0.843	656	226	−107
$Tm_2Fe_{17}N_{2.7}$	Th_2Ni_{17}	0.858	0.847	690	220	−52

[a] Values deduced from the anisotropy fields [8].

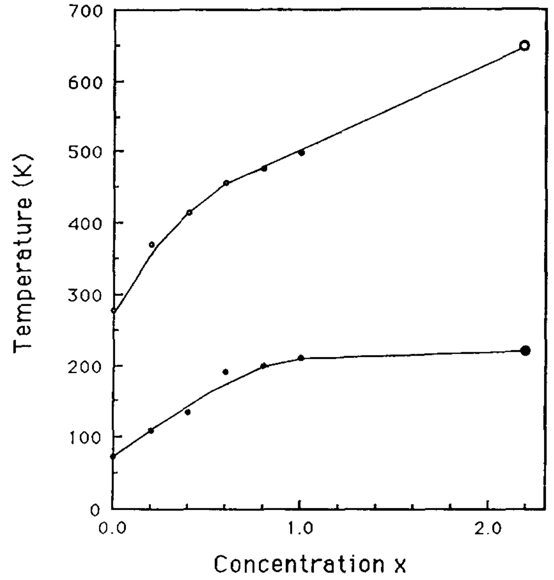


Fig. 4. Magnetic phase diagram of $Tm_2Fe_{17}C_{3-\delta}$: ○, ◯, $S\perp c$; •, ●, $S\parallel c$; ○, •, taken from ref. 4; ◯, ●, this work.

carbide with R≡Y is $K_1 = -1.2(2)$ MJ m^{-3} at 4.2 K and $-0.2(1)$ MJ m^{-3} at 293 K [7], but the rare earth term varies more rapidly with temperature on account of the relatively small spin moments of erbium or thulium and their weak exchange coupling to the iron sublattices.

There are two rare earth sites in the Th_2Ni_{17} structure, and A_{20} is initially of opposite sign, although it becomes negative at both sites with increasing carbon concentration [12]. Following our previous analysis for the nitrides, we deduce an average effective value neglecting all but the second-order crystal field term and averaging over the two sites.

The spin reorientation occurs when the sum of the anisotropy associated with the iron and rare earth sublattices is zero. The former is obtained by using the measured temperature dependence of K_1 for Y_2Fe_{17} [13] to interpolate between the above values for $Y_2Fe_{17}C_{2.2}$. The latter is calculated from the rare earth hamiltonian (in Kelvins per rare earth)

$$H_R = B_{20}\hat{O}_{20} + 2(g_J - 1)\mu_B k^{-1} n_{RFe} M_{Fe} \hat{J}_z$$

where $B_{20} = \alpha_J \langle r^2 \rangle \bar{A}_{20}$, $\hat{O}_{20} = 3\hat{J}_z{}^2 - J(J+1)$, n_{RFe} is the intersublattice molecular field coefficient ($136\mu_0$ in the carbides [7]) and M_{Fe} is taken as 1.5 T. The resulting values are $\bar{A}_{20} = -83$ K $a_0{}^{-2}$ for R≡Er and $\bar{A}_{20} = -107$ K $a_0{}^{-2}$ for R≡Tm. Applying the same analysis to the spin reorientation in Tm_2Fe_{17} with $n_{RFe} = 225\mu_0$ [14] yields $\bar{A}_{20} = -34$ K $a_0{}^{-2}$. The absence of a spin reorientation in Sm_2Fe_{17} implies that the $\bar{A}_{20} > -36$ K $a_0{}^{-2}$.

Much larger negative values, $\bar{A}_{20} \approx -300$ K $a_0{}^{-2}$, have been inferred from the electric field gradient measured at the ^{169}Tm nucleus [4, 12]. However, large differences between values of $\bar{A}_{20}$ inferred from the principal component V_{zz} of the electric field gradient at the nucleus, and those determined more directly from the magnetocrystalline anisotropy of the 4f shell, are now understood to arise from the different weighting of contributions from p and d electrons to the electric field gradient at the nucleus and at the 4f shell [15].

4. Conclusion

In conclusion, we find the following.

(1) The values of $\bar{A}_{20}$ are similar in magnitude for the erbium and thulium carbides, as might be expected. They are approximately 50% higher than those of the corresponding nitrides.

(2) A substantial increase in the second-order crystal field is attributable to the presence of the carbon interstitials.

(3) The average effective crystal field is weaker by a factor of 2 for carbides with a Th_2Ni_{17}-related structure (Er, Tm) than for those with a Th_2Zn_{17}-related structure (Sm).

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