Journal of Alloys and Compounds, 176 (1991) 115–121
JAL 0003

Magnetic properties of $Tm_2Fe_{17}N_x$ studied by means of the ^{169}Tm and ^{57}Fe Mössbauer effect

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(Received April 3, 1991)

Abstract

The ^{57}Fe Mössbauer effect in $Tm_2Fe_{17}N_x$ was measured in the temperature range 4.2–600 K. The temperature dependence of the ^{57}Fe Mössbauer spectra shows a hyperfine field anomaly around the spin reorientation temperature ($T_{SR} \approx 190$ K) where the easy magnetization direction changes from parallel to *c* ($T < T_{SR}$) to perpendicular to $c (T > T_{SR})$. At 4.2 K the ^{57}Fe hyperfine field was found to have slightly increased after charging Tm_2Fe_{17} with nitrogen. The ^{169}Tm Mössbauer spectrum of $Tm_2Fe_{17}N_x$ was measured at 4.2 K. From the quadrupolar splitting it was derived that interstitial solution of nitrogen atoms considerably increased the second-order crystal field parameter ($A_2{}^0 \approx 300\ Ka_0{}^{-2}$), although the value reached is not much larger than found before in $Tm_2Fe_{17}C$.

1. Introduction

The rare earth sublattice anisotropy in compounds of the type R_2Fe_{17} is fairly weak. Detailed studies of these materials in the past had shown that the iron sublattice favours an easy magnetization direction perpendicular to the hexagonal *c* axis and that for the R element samarium, erbium, thulium and ytterbium the R sublattice anisotropy favours an easy direction parallel to the *c* axis. Of these four R elements only thulium has a sublattice anisotropy strong enough to dominate the iron sublattice anisotropy. This dominance becomes manifest only at fairly low temperatures, the corresponding spin reorientation temperature being $T_{SR} = 72$ K [1].

Previous studies have shown that the R sublattice anisotropy is considerably enhanced by interstitial of carbon or nitrogen atoms in R_2Fe_{17} [2–7]. As a consequence the temperature regime in which the easy magnetization direction is determined by the R sublattice anisotropy increases strongly towards higher temperatures. In $Tm_2Fe_{17}C_x$ we found a shift from $T_{SR} = 72$ K for $x = 0$ to $T_{SR} = 210$ K for $x = 1$ [2]. Since the interstitial atom concentration in $Tm_2Fe_{17}N_x$ is much larger ($x \approx 2.7$ [8]) than in $Tm_2Fe_{17}C$,

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0925-8388/91/$3.50

one may expect that T_{SR} is substantially higher in the former compound than in the latter. However, from discontinuities of the temperature dependence of the initial susceptibility in $Tm_2Fe_{17}N_x$, indications were obtained that there is no such enhancement of T_{SR} in $Tm_2Fe_{17}N_x$ compared to $Tm_2Fe_{17}C$ [9, 10]. This has led us to investigate the effect of interstitial nitrogen atom solution in Tm_2Fe_{17} on the magnetic properties in more detail using ^{169}Tm and ^{57}Fe Mössbauer spectroscopy.

2. Experimental results

The compound Tm_2Fe_{17} was prepared by arc melting from materials of at least 99.9% purity followed by vacuum annealing at 1000 °C for about 10 days. X-ray diffraction showed this sample to be approximately single phase, a few per cent of elemental iron being present as an impurity phase. The annealed sample was subsequently pulverized and heated in an atmosphere of purified nitrogen gas at 500 °C for about 3 h.

The X-ray diagram of the nitrided sample showed that the nitriding process has reached completion. The lattice constants of the ternary nitride are $a=0.8583$ nm and $c=0.8482$ nm. Compared with the lattice constants of the original Tm_2Fe_{17} compound, there is a volume increase $\Delta V/V$ of more than 6%.

The ^{169}Tm Mössbauer spectra were obtained by means of an acceleration-type spectrometer in sinusoidal mode, the measured points being plotted on a linear scale. Velocity calibration was done in the absolute sense with a laser Michelson interferometer. The ^{169}Tm Mössbauer effect was measured using the 8.4 keV γ rays emitted by ^{169}Er obtained after neutron irradiation of a disk-shaped sample consisting of cubic $^{168}ErAl_3$ grains in an aluminium matrix. The 8.4 keV γ rays were detected by means of an Si(Li) detector, which discriminates very well between the 8.4 keV γ rays and the erbium L lines.

The ^{169}Tm Mössbauer spectrum of $Tm_2Fe_{17}N_x$ measured at $T=4.2$ K is shown in Fig. 1. Since the spectrum does not show clearly distinct magnetically split subspectra that may be associated with the two different thulium sites in the hexagonal Th_2Ni_{17}-type structure or with a distribution of the nitrogen atoms, we did not attempt to resolve the spectrum into more than one subspectrum. The average values of the hyperfine field and quadrupole splitting derived from fitting the spectrum are listed in Table 1.

The ^{57}Fe Mössbauer spectra of $Tm_2Fe_{17}N_x$ were obtained in the range 4.2–600 K by means of a constant-acceleration-type spectrometer equipped with a ^{57}Co–Rh source. The spectra obtained at 4.2 and 350 K are shown in Fig. 2. The various spectra were fitted by means of a standard procedure described elsewhere [1], taking account of four different iron sites of the Th_2Ni_{17}-type structure (Wyckoff notation: $4f$, $6g$, $12j$, $12k$). The temperature dependence of the hyperfine field of the $4f$ site (H_{eff}^{f}), as derived from these fits, has been plotted in Fig. 3. Also shown in this figure is the temperature

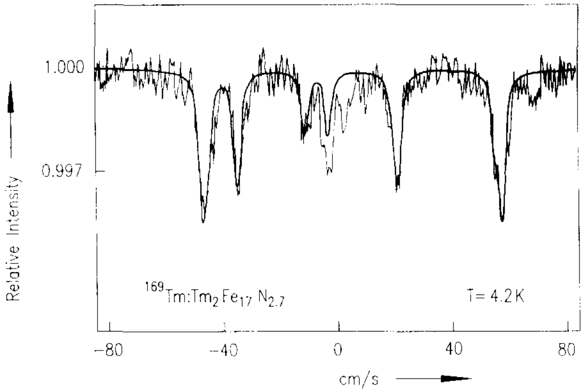

Fig. 1. ^{169}Tm Mössbauer spectrum of $Tm_2Fe_{17}N_x$ at 4.2 K.

TABLE 1

Average values of the hyperfine field and quadrupolar splitting obtained from ^{169}Tm Mössbauer spectroscopy in Tm_2Fe_{17}, $Tm_2Fe_{17}C$ and $Tm_2Fe_{17}N_x$. The values QS^{latt} were obtained from QS after subtracting the free-ion value. $A_2{}^0$ is the corresponding second-order crystal field coefficient. The zero values of QS^{latt} and $A_2{}^0$ in Tm_2Fe_{17} are the result of cancellation between the two different thulium sites

Compound	H_{eff} (T)	QS (cm s^{-1})	QS^{latt} (cm s^{-1})	θ (deg)	$A_2{}^0$ ($Ka_0{}^{-2}$)	T_{SR} (K)
Tm_2Fe_{17}	747 ± 3	12.7 ± 0.3	0 ± 0.3	900	0 ± 50	75
$Tm_2Fe_{17}C$	725 ± 3	13.8 ± 0.4	-1.9 ± 0.4	0	-300 ± 50	210
$Tm_2Fe_{17}N_x$	706 ± 3	13.8 ± 0.4	-1.9 ± 0.4	0	-300 ± 50	190
Free ion	720	15.7				

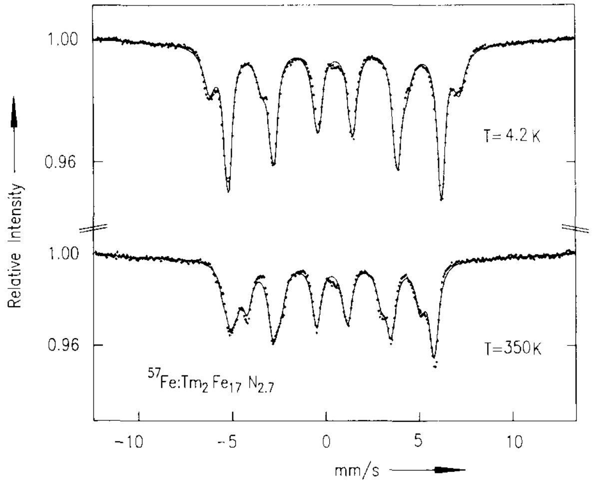

Fig. 2. ^{57}Fe Mössbauer spectra of $Tm_2Fe_{17}N_x$ at 4.2 and 350 K.

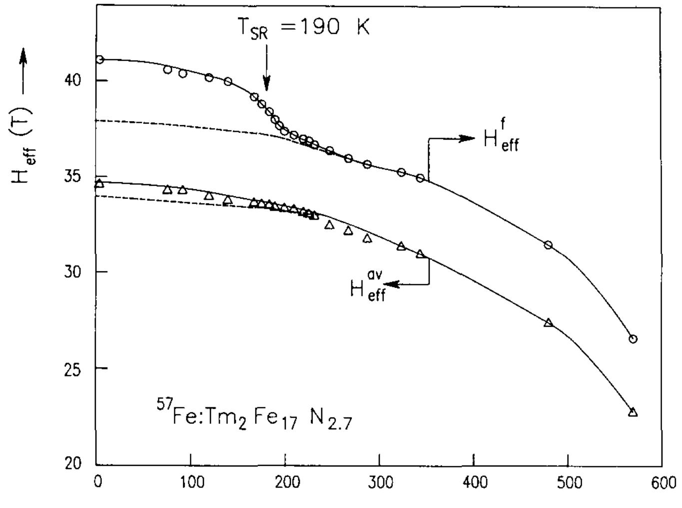

Fig. 3. Temperature dependence of average ^{57}Fe hyperfine field (H_{eff}^{av}) and hyperfine field of 4*f* iron atoms (H_{eff}^{f}).

TABLE 2

Average ^{57}Fe hyperfine fields (H_{eff}^{av}) and hyperfine field at the 4*f* site (H_{eff}^{f}) at 4.2 K in Tm_2Fe_{17}, $Tm_2Fe_{17}C_{0.4}$ and $Tm_2Fe_{17}N_x$. The corresponding values of ΔH_{eff} represent the hyperfine field anomaly discussed in the text

Compound	H_{eff}^{f} (T)	ΔH_{eff}^{f} (T)	H_{eff}^{av} (T)	ΔH_{eff}^{f} (T)
Tm_2Fe_{17}	41.9 ± 0.2	4.4 ± 0.2	32.1 ± 0.2	1.4 ± 0.2
$Tm_2Fe_{17}C_{0.4}$	41.5 ± 0.2	3.7 ± 0.2	32.8 ± 0.2	0.4 ± 0.2
$Tm_2Fe_{17}N_x$	41.0 ± 0.2	3.3 ± 0.2	34.4 ± 0.2	0.5 ± 0.2

dependence of the average hyperfine field (H_{eff}^{av}) obtained by weighing the hyperfine fields of the four subspectra with the corresponding relative intensities. The relative intensities were found to correspond closely to the intensity ratio expected from the Wyckoff symbols, except for the 4*f* site for which the subspectrum had a somewhat larger intensity. Since the latter subspectrum has, however, the largest hyperfine splitting (outermost lines), there is no doubt with regard to the correct assignment of this spectrum.

The large increase of H_{eff}^{f} and the smaller increase of H_{eff}^{av} with decreasing temperature have been interpreted as being due to a spin reorientation from a preferred moment direction perpendicular to the *c* axis ($T > T_{SR}$) to a preferred moment direction parallel to the *c* axis ($T < T_{SR}$). A similar transition was observed before in $Tm_2Fe_{17}C$, but in $Tm_2Fe_{17}N_x$ it has a more smeared-out character. The results shown in Fig. 3 suggest that the spin reorientation of $Tm_2Fe_{17}N_x$ is centred at about 190 K. This value for T_{SR} together with the values of H_{eff}^{f} and H_{eff}^{av} at 4.2 K are listed in Table 2. From the extrapolated high temperature curves of these latter two quantities we have estimated the values $\Delta H_{\mathrm{eff}}^{\mathrm{f}}$ and $\Delta H_{\mathrm{eff}}^{\mathrm{av}}$ due to the spin reorientation; these are also listed in Table 2.

3. Discussion

The increase of the average hyperfine field at the iron sites observed after charging Tm_2Fe_{17} with nitrogen suggests that the interstitial solution of nitrogen atoms in Tm_2Fe_{17} is accompanied by an increase in the iron moments. This conclusion is in agreement with results of magnetic measurements on Y_2Fe_{17} and Lu_2Fe_{17} made before and after charging [9].

The observation by ^{57}Fe Mössbauer spectroscopy of a spin reorientation in $Tm_2Fe_{17}N_x$ at low temperatures is in agreement with results of a.c. susceptibility measurements [9, 10] and high field magnetization measurements, which showed that the easy magnetization direction at 4.2 K is different from that at room temperature [9]. From the a.c. susceptibility measurements it was derived that the spin reorientation temperature occurs at $T_{\mathrm{SR}} = 173$ K, which is slightly lower than the value $T_{\mathrm{SR}} = 190$ K found by us.

The increase of the hyperfine fields $H_{\mathrm{eff}}^{\mathrm{f}}$ and $H_{\mathrm{eff}}^{\mathrm{av}}$ below T_{SR} is similar to that observed earlier in $Tm_2Fe_{17}C_x$ [2]. This hyperfine field anomaly may be an indication of the presence of an orbital contribution to the iron moments, being particularly pronounced for the dumb-bell iron site [11, 12]. It may be inferred from the $\Delta H_{\mathrm{eff}}^{\mathrm{f}}$ data listed in Table 1 that the orbital contribution becomes somewhat less when carbon or nitrogen atoms are dissolved interstitially in the R_2Fe_{17} lattice. If the differences in orbital contribution of the various iron sites are held responsible for the iron sublattice anisotropy, this could be an indication that the (planar) iron sublattice anisotropy in the nitrides is lower than that in the pure R_2Fe_{17} compounds, as argued previously [6].

The quadrupole splitting observed at the thulium site can be attributed to the co-called free-ion contribution (*i.e.* 4f electron contribution of the electric field gradient V_{zz} at the thulium nucleus) and a crystal field contribution experienced by the nucleus when the thulium ions are accommodated in the lattice of an intermetallic compound. The latter contribution is $QS^{\mathrm{latt}} = \frac{1}{4}|e|V_{zz}Q(3\cos^2\theta - 1)$ and can be derived from the experimental value by subtracting the free-ion contribution. In previous investigations we used the corresponding value of V_{zz} to calculate the second-order crystal field parameter A_2^0 by means of the expression

$$A_2^0 = \frac{-\frac{1}{2}|e|V_{zz}(1-\sigma)}{1+\gamma_\infty} = \frac{-V_{zz}}{4c} \qquad (1)$$

where γ_∞ is the Sternheimer antishielding factor and σ is a screening constant.

It was shown recently that the crystal field experienced by the 4f electrons (and hence A_2^0) is mostly determined by the rare earth valence electrons (5d and 6p) [13]. The same situation applies to the corresponding rare earth nucleus. Since the relative contributions of 5d and 6p electrons may be different in the two cases, the applicability of eqn. (1) is limited. This difficulty is largely avoided by using for the constant c a semiempirical value $c = 243$ derived previously for $TmNi_5$ [14]. The value of $A_2{}^0$ obtained in this way for $Tm_2Fe_{17}N_x$ is compared with $A_2{}^0$ values determined in a similar manner for $Tm_2Fe_{17}C_x$ and Tm_2Fe_{17} in Fig. 4. It may be seen that the increase in $|A_2{}^0|$ due to the interstitial solution of about three nitrogen atoms is about the same as that of a single atom. This fact is surprising when viewed against recent results obtained by ^{166}Er and ^{155}Gd Mössbauer spectroscopy on the corresponding $R_2Fe_{17}N_x$ compounds, which indicated that there is a large increase in $A_2{}^0$ when the interstitial hole position around the R atoms is fully occupied [6, 7].

At first sight one might therefore come to the conclusion that the nitrogen concentration x in $Tm_2Fe_{17}N_x$ is substantially lower than in $Er_2Fe_{17}N_x$ and $Gd_2Fe_{17}N_x$, but this conclusion is contradicted by the volume expansion accompanying the nitrogenation, which is almost the same in all three compounds.

It can be shown by means of crystal field theory that the value of $A_2{}^0$ determines the magnitude and sign of the rare earth sublattice anisotropy to the lowest order. In $Tm_2Fe_{17}C$ and $Tm_2Fe_{17}N_x$ the value of $A_2{}^0$ is negative, hence the anisotropy constant $K_1{}^{TM}$ is positive, favouring an easy c axis. This thulium sublattice anisotropy has to compete with the iron sublattice anisotropy which favours an easy magnetization direction perpendicular to the c axis. Owing to the stronger temperature dependence of $K_1{}^{TM}$ than $K_1{}^{Fe}$, the thulium sublattice anisotropy prevails only at low temperatures, which causes a change in the easy magnetization direction at $T = T_{SR}$. By using the same arguments as before [6], it can be shown that the spin reorientation temperature shifts to higher temperatures when $A_2{}^0$ becomes more negative.

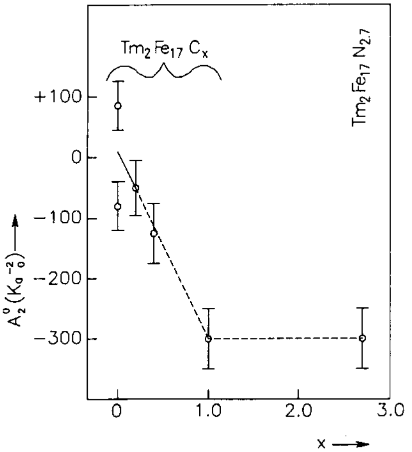

Fig. 4. Second-order crystal field parameter $A_2{}^0$ derived from ^{169}Tm Mössbauer spectroscopy for Tm_2Fe_{17}, $Tm_2Fe_{17}C_x$ and $Tm_2Fe_{17}N_{2.7}$.

The observation that T_{SR} is almost equal in $Tm_2Fe_{17}C$ and $Tm_2Fe_{17}N_x$ is therefore in good agreement with the observation that $A_2{}^0$ reaches about the same value in both compounds. At present we are not able to offer an explanation for the fact that the enhancement of $A_2{}^0$ (and $K_1{}^{TM}$) in $Tm_2Fe_{17}N_x$ remains comparatively low, *i.e.* that it does not surpass the $A_2{}^0$ enhancement found in $Tm_2Fe_{17}C$.

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