Note on the crystal field and intersublattice coupling in $Er_2Fe_{17}C$ and $Tm_2Fe_{17}C$ studied by means of the ^{166}Er and ^{169}Tm Mössbauer effect

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Abstract

The temperature dependence of the ^{166}Er and ^{169}Tm hyperfine fields in $Er_2Fe_{17}C$ and $Tm_2Fe_{17}C$ was studied in extended temperature regions on both sides of the spin reorientation temperature. From fits of these temperature dependences we obtained values of the second-order crystal field parameter ($A_2^{\,0} = -300$ K a_0^{-2}) and the intersublattice coupling constants ($J_{ErFe}/k = -6.3$ K, $J_{TmFe}/k = -6.0$ K). The value of $A_2^{\,0}$ obtained in this way agrees with an earlier determination based on the quadrupolar splitting of the ^{166}Er and ^{169}Tm Mössbauer spectra.

1. Introduction

It is well known that the Curie temperature and the rare earth sublattice anisotropy of R_2Fe_{17} compounds can be increased substantially by interstitial solution of C and N atoms [1]. Accurate values for the crystal field parameters and intersublattice coupling constants cannot be obtained easily for these materials, which is partly due to the fact that single crystals are not available. It is the purpose of the present investigation to obtain more experimental information on these quantities by studying the temperature dependence of the ^{166}Er and ^{169}Tm hyperfine fields by means of Mössbauer spectroscopy.

2. Experimental details

The compounds of $Er_2Fe_{17}C$ and $Tm_2Fe_{17}C$ were prepared by arc melting from starting materials of at least 99.9% purity, followed by vacuum annealing at 1100 °C for about 2 weeks. X-Ray diffraction showed the samples to be approximately single phase (Th_2Ni_{17}-type structure), a few per cent of elemental iron being present as an impurity phase. The annealed samples were subsequently pulverized and used for Mössbauer spectroscopy.

The ^{169}Tm and ^{166}Er Mössbauer spectra were obtained at various temperatures between 4.2 and 300 K by means of an acceleration-type spectrometer in the sinusoidal mode, with the measured points being plotted on a linear scale. The velocity calibration was done in the absolute sense by means of a laser Michelson interferometer. The ^{169}Tm (^{166}Er) Mössbauer effect was measured using the 8.4 (80.6) keV γ rays emitted by ^{169}Er (^{166}Ho) after neutron irradiation of a disk-shaped sample consisting of cubic $^{168}ErAl_3$ ($^{166}HoPd_3$). 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–X lines. For the 80.6 keV γ rays we employed a Ge detector.

3. Results and discussion

The ^{169}Tm (^{166}Er) Mössbauer spectra of $Tm_2Fe_{17}C$ ($Er_2Fe_{17}C$) measured at $T = 4.2$ K have already been reported [2, 3]. Since the spectra do not show clearly distinct magnetically split subspectra that may be associated with the two different rare earth sites in the hexagonal Th_2Ni_{17}-type structure or with a distribution of the C atoms, we did not attempt to resolve the spectrum into more than one subspectrum. The reason for the absence of two different subspectra in these carbides is that the electric field gradient at the rare earth nuclei and the concomitant quadrupole splittings are mainly determined by the interstitial C atoms. In other words, the change in the electric field gradient

due to the presence of the C atoms leads to almost equal quadrupole splittings for both sites in $R_2Fe_{17}C$, as was studied in more detail as a function of x in $Tm_2Fe_{17}C_x$ in ref. 2. The average values of the hyperfine field and quadrupole splitting derived from fitting the spectra at 4.2 K are listed in Table 1. These data are the same as those obtained in previous investigations. The hyperfine fields derived from fitting the spectra obtained for $Tm_2Fe_{17}C$ and $Er_2Fe_{17}C$ at various temperatures have been plotted as a function of temperature in Figs. 1 and 2 respectively. It may be seen from Fig. 1 that there is a distinct discontinuity in the temperature dependence of the ^{169}Tm hyperfine field at $T_{SR} = 210$ K. This discontinuity corresponds to the spin reorientation transition [2] where the easy magnetization direction changes from parallel to the c axis ($T < 210$ K) to perpendicular to the c axis ($T > 210$ K). A similar spin reorientation occurs at $T_{SR} = 82$ K in $Er_2Fe_{17}C$ [3], although this is hardly seen in the temperature dependence of the ^{166}Er hyperfine field shown in Fig. 2.

TABLE 1. Data obtained from Mössbauer spectroscopy on $Tm_2Fe_{17}C$ and $Er_2Fe_{17}C$ as reported in refs. 2 and 3. The values listed for the effective hyperfine fields H_{eff}^R and electric field gradient V_{zz}^{latt} correspond to 4.2 K

Compound	$\mu_0 H_{eff}^R$ (T)	V_{zz}^{latt} (10^{17} V cm^{-2})	A_2^0 (K a_0^{-2})	T_{SR} (K)
$Er_2Fe_{17}C$	824 ± 7	9.9 ± 1.5	−290	110
$Tm_2Fe_{17}C$	725 ± 3	9.7 ± 1.5	−320	210

Fig. 2. Temperature dependence of the ^{166}Er hyperfine field in $Er_2Fe_{17}C$. The full and broken curves represent fits (see main text) for the two temperature regimes around the spin reorientation temperature $T = 110$ K.

For describing the temperature dependence of the hyperfine fields we have used the formula

$$H_{eff}(T) = \frac{H_{eff}(T=0)\langle J_{z,x}\rangle}{J} \tag{1}$$

where $H_{eff}(T=0)$ was taken to be equal to the experimental value observed at 4.2 K and listed in Table 1. The expectation values $\langle J_z \rangle$ and $\langle J_x \rangle$ were obtained as thermal averages at each temperature. The corresponding energy levels and eigenfunctions were obtained after diagonalization of the hamiltonians

$$H = B_2^0 O_2^0 + B_2^2 O_2^2 - g_J \mu_B H_m(T) J_z \quad (T < T_{SR}) \tag{2}$$

$$H = B_2^0 O_2^0 + B_2^2 O_2^2 - g_J \mu_B H_m(T) J_x \quad (T > T_{SR}) \tag{3}$$

where $B_2^n = \alpha_J \langle r_{4f}^2 \rangle A_2^n$, the O_2^n are the standard operator equivalent expressions and $H_m(T) = H(T=0)\mu_{Fe}(T)$ is the molecular field experienced by the R atoms. For the temperature dependence of the Fe moments $\mu_{Fe}(T)$ we used data obtained from ^{57}Fe Mössbauer spectroscopy [2, 3]. The terms $B_2^2 O_2^2$ are zero in the pure compounds R_2Fe_{17} but may take nonzero values in the carbides because the presence of the C atoms has broken the trigonal site symmetry.

In order to reduce the number of fitting parameters, we used $A_2^2 = 100$ K a_0^{-2}, which corresponds to the asymmetry parameter $\eta = 0.35$ found in an earlier ^{166}Gd Mössbauer spectroscopy investigation of $Gd_2Fe_{17}C$ [4]. For A_2^0 we used the values obtained from the experimental value of the lattice contribution to the quadrupole splitting in $Tm_2Fe_{17}C$ and $Er_2Fe_{17}C$. The electric field gradient V_{zz} present at the R nuclei corresponding to this lattice contribution can be transformed to obtain values of A_2^0 via the semiempirical relation
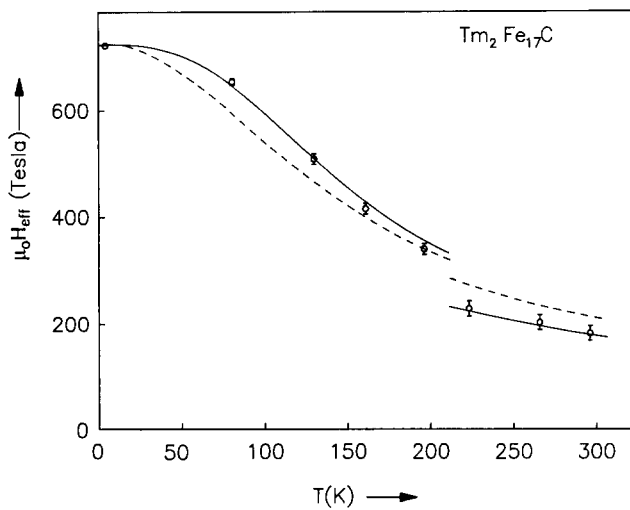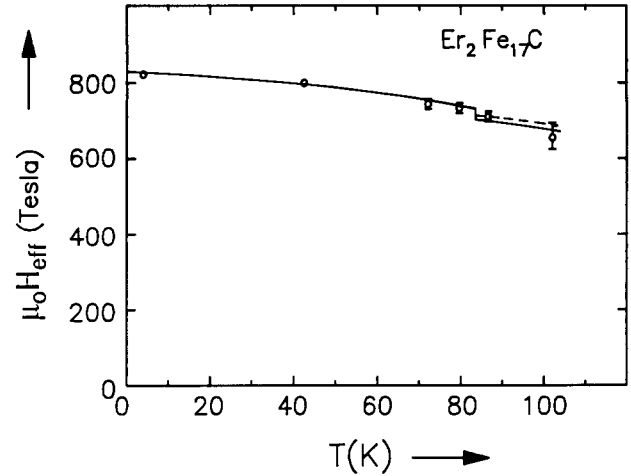
$$eV_{zz}^{latt} = 4cA_2^0 \tag{4}$$

Fig. 1. Temperature dependence of the ^{169}Tm hyperfine field in $Tm_2Fe_{17}C$. The full and broken curves represent fits (see main text) for the two temperature regimes around the spin reorientation temperature $T_{SR} = 210$ K.

where c is a dimensionless constant when eV_{zz}^{latt} and A_2^0 are expressed in eV cm^{-2}. The values of this constant c are 243 and 270 for $Tm_2Fe_{17}C$ and $Er_2Fe_{17}C$ respectively [5]. In both cases (see Table 1) we found values close to $A_2^0 = -300$ K a_0^{-2} [2, 3], which value was used in the diagonalization procedure described above. Satisfactory fits to the temperature dependence of H_{eff} shown in Figs. 1 and 2 were obtained with $g_J\mu_B H_m(T=0)/k = 50 \pm 10$ K in the case of $Er_2Fe_{17}C$ and $g_J\mu_B H_m T=0)/k = 40 \pm 5$ K in the case of $Tm_2Fe_{17}C$. The fits corresponding to these parameters are displayed by the full curves in Figs. 1 and 2. For completeness we mention that these fits are not very sensitive with regard to the values of A_2^2. By contrast, the temperature dependence of H_{eff} is very sensitive to the value of A_2^0. This holds for the case of $Tm_2Fe_{17}C$ in particular, Tm having a value of α_J about four times larger than that of Er. The broken curve shown as an example in Fig. 1 corresponds to the value $A_2^0 = -100$ K a_0^{-2}. Clearly the fit of the temperature dependence is significantly less satisfactory.

On using the values of $H_m(T=0)$ in the expression for the intersublattice coupling constant J_{RFe},

$$\frac{J_{RFe}}{k} = \frac{g_J\mu_B H_m}{2(g_J-1)\mu_{Fe}Z_{RT}}$$

one finds with $Z_{RT} = 19$ nearest Fe atom neighbours and $\mu_{Fe} = 2.1$ μ_B/Fe the values $J_{ErFe}/k = -6.3$ K and $J_{TmFe}/k = -6.0$ K. These values are not much different from those found in the pure compounds [6, 7].

4. Conclusions

We have fitted the temperature dependence of the ^{166}Er and ^{169}Tm hyperfine fields in $Er_2Fe_{17}C$ and $Tm_2Fe_{17}C$ in two separate temperature regions around the spin reorientation temperatures. Independent proof has been obtained that the values of the second-order crystal field parameter in these materials, obtained earlier by means of the semiempirical relation (4) from the field gradient V_{zz} at the nuclear Er and Tm sites, have the correct sign and magnitude.

The values of the intersublattice coupling constants J_{RFe} in $R_2Fe_{17}C$ derived from the fitting of the temperature dependence of the ^{166}Er and ^{169}Tm hyperfine fields are close to the intersublattice constants obtained for the pure compounds.

References

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