

^{155}Gd Mössbauer effect and magnetic properties of Al-substituted $\text{Gd}_2\text{Fe}_{17}$

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Abstract

We have investigated the effect of Al substitution on the magnetic properties and the ^{155}Gd Mössbauer spectra of $\text{Gd}_2\text{Fe}_{17-x}\text{Al}_x$. Marked changes were observed in the values of the electric field gradient derived from the quadrupole splitting of the spectra, the effective Gd hyperfine field and the isomer shift. The implications of the sign reversal of the electric field gradient on the crystal field-induced magnetic anisotropy is discussed. The variation in the hyperfine field across the series has been attributed to a gradual reduction in the transferred hyperfine field, owing to the Fe moments. The variation in the isomer shift was shown to be in agreement with model predictions.

1. Introduction

Rare-earth-Fe compounds of the type R_2Fe_{17} have been known to be amenable to substantial substitution of Al for Fe without losing their crystal structure. Neutron diffraction has shown that the substitution of Al atoms is not completely random but proceeds initially into mainly the 18h site, whereas substitutions into the 6c and 18f sites predominate at high Al concentrations, with no Al atoms going into the 9d site [1]. The ultimate Al concentration that can be reached in $\text{R}_2\text{Fe}_{17-x}\text{Al}_x$ corresponds generally to about $x=10$ and there is only a relatively small reduction in the Fe atomic moments in these systems [2]. This favourable property has been employed in several investigations to tune the relative magnitudes of the rare earth and Fe sublattice magnetizations, so that information on the intersublattice interaction strength can be obtained from high field measurements [2–4].

In the present investigation, we have extended a previous investigation of the $\text{Gd}_2\text{Fe}_{17-x}\text{Al}_x$ series to higher Fe concentration and focused our attention mainly on the changes in hyperfine parameters observed by means of ^{155}Gd Mössbauer spectroscopy.

2. Experimental details

The $\text{Gd}_2\text{Fe}_{17-x}\text{Al}_x$ compounds were prepared by arc melting from starting materials of at least 99.9% purity.

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They were vacuum annealed at 900 °C for four weeks and subsequently examined by X-ray diffraction to check whether or not single-phase compounds had formed. The rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure was observed for all samples with $x \leq 10$. Magnetic measurements were made on a SQUID magnetometer in the temperature range 4.2–600 K.

The Mössbauer spectra of the various $\text{Gd}_2\text{Fe}_{17-x}\text{Al}_x$ compounds were taken using the 86.5 keV resonance of ^{155}Gd . The source was neutron-irradiated SmPd_3 prepared from Sm enriched to 98% in ^{154}Sm . Details of the spectrometer can be found elsewhere [5]. All the spectra have been analysed by means of a least-squares fitting procedure involving the diagonalization of the full nuclear hamiltonian and using a transmission integral. The independently refined variables consisted of the isomer shift, the effective hyperfine field (H_{eff}) and the quadrupole splitting

$$\text{QS} = \frac{1}{4} eQV_{zz}(3 \cos^2 \theta - 1)$$

using the value $Q_g = 1.30 \times 10^{-28} \text{ m}^2$ given by Tanaka *et al.* [6]. The angle θ between H_{eff} and the c axis was kept as an adjustable parameter. The line widths of the absorber and source were constrained to 0.25 and 0.36 mm s^{-1} for the transmission integral. These parameters have to be regarded as being averages over the distributions of hyperfine parameters associated with various types of different coordinations of the Gd sites by Fe and Al atoms.

In some cases (for $x=3$ and $x=4$), slightly better fits were obtained by considering two subspectra – one subspectrum with a positive value for the average electric field gradient and one subspectrum with a negative value. However, the intensity of the ‘negative’ subspectrum was much larger than that of the ‘positive’ subspectrum in both cases. For the sake of simplicity, and also to make a comparison of the hyperfine values obtained for various Al concentrations easier, we chose to analyse all the spectra in the same way, discarding the possibility of two separate hyperfine distributions and using a single subspectrum in all cases for the fitting procedures.

3. Experimental results

The substitution of Al for Fe in Gd_2Fe_{17} is accompanied by a substantial increase in the unit cell volume. This may be seen from Fig. 1(a), where the concentration dependence of the unit cell volume of $Gd_2Fe_{17-x}Al_x$ has been plotted. The values of the unit cell volumes were derived from the corresponding lattice constants determined by X-ray diffraction.

From the temperature dependence of the magnetization σ measured in low applied fields (i.e. $\mu_0 H = 0.05$ T), we have determined the Curie temperatures by plotting σ^2 vs. T and extrapolating to $\sigma^2 = 0$.

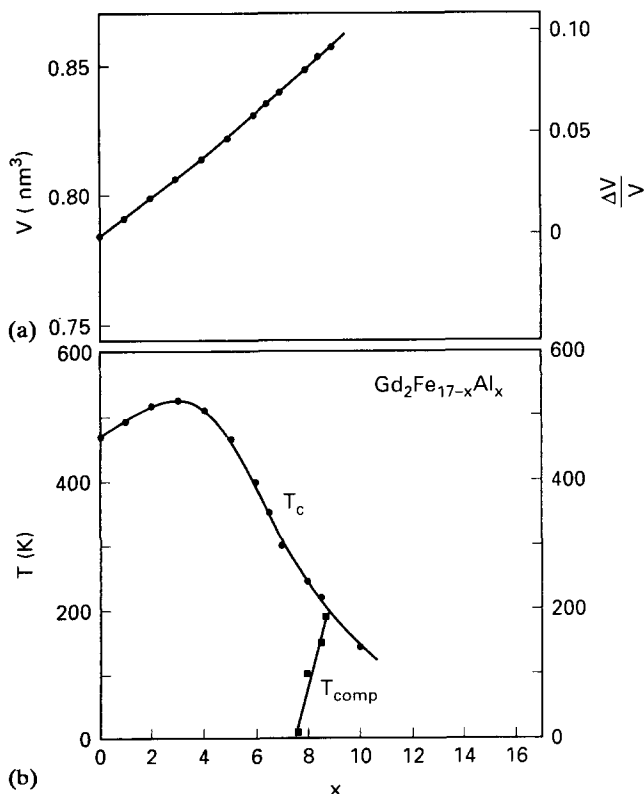


Fig. 1. (a) Concentration dependence of the unit cell volume in $Gd_2Fe_{17-x}Al_x$ and (b) concentration dependence of the Curie temperature T_c and compensation temperature T_{comp} .

The concentration dependence of T_c is shown in Fig. 1(b).

In a previous investigation of the magnetic properties of $Gd_2Fe_{17-x}Al_x$ compounds in high magnetic fields, it has been shown that the Fe sublattice magnetization at 4.2 K is dominant for low x values but that, close to $x=8$, there is a change-over to a dominant Gd sublattice magnetization [4]. Examples of the temperature dependences of the magnetization of compounds close to $x=8$ are shown in Fig. 2. The curve in Fig 2(a) is a typical example for compounds in which the Gd sublattice magnetization dominates at low temperatures and where one may expect compensation temperatures T_{comp} between 4.2 K and T_c . (The concentration dependence of T_{comp} has been included in Fig. 1(b).)

The ^{155}Gd Mössbauer spectra of various $Gd_2Fe_{17-x}Al_x$ compounds are displayed in Fig. 3. The continuous lines through the data points represent fits. The corresponding hyperfine parameters have been listed in Table 1.

4. Discussion

The magnetic properties of the $Gd_2Fe_{17-x}Al_x$ compounds closely resemble those found in other systems

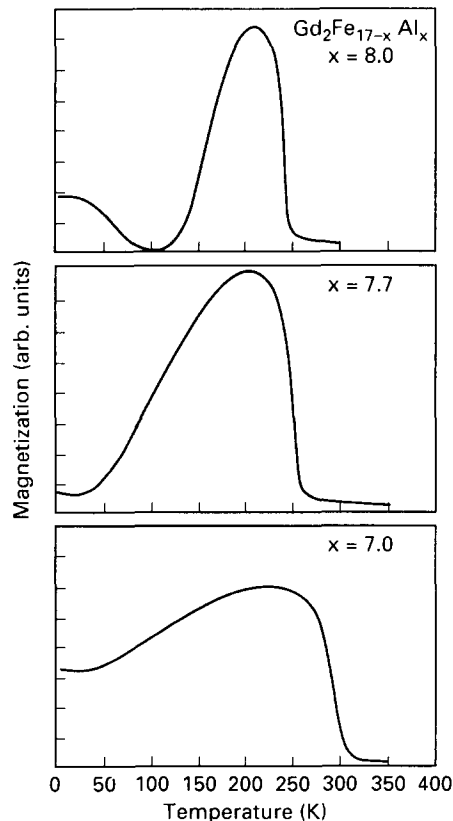


Fig. 2. Temperature dependence of the magnetization of $Gd_2Fe_{17-x}Al_x$ for (a) $x=7.0$, (b) $x=7.8$ and (c) $x=8.0$ measured in $\mu_0 H = 0.05$ T. Measurements were made after cooling the samples from 300 K to 4.2 K in a field of 1 T.

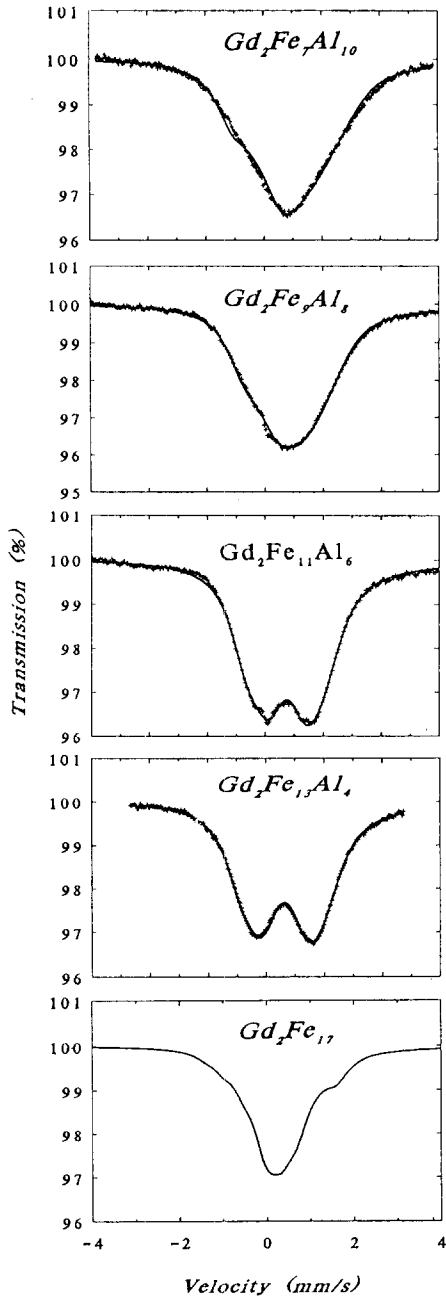


Fig. 3. Variation of the ^{155}Gd Mössbauer spectra at 4.2 K across the series $\text{Gd}_2\text{Fe}_{17-x}\text{Al}_x$. The curves through the data points represent fits to the spectra (see main text).

of the type $\text{R}_2\text{Fe}_{17-x}\text{Al}_x$ [2–4]. The initial increase in T_c with the Al concentration is a result of the volume expansion, which is counteracted by the effect of magnetic dilution of the Fe sublattice. This dilution effect eventually becomes predominant and leads to a continuous decrease in T_c up to the limit of the stability range of the $\text{Th}_2\text{Zn}_{17}$ -type structure.

The comparatively low Curie temperature of the R_2Fe_{17} compounds frequently has been attributed to the rather small Fe–Fe interatomic distances associated with the 6c (dumbell) site in the $\text{Th}_2\text{Zn}_{17}$ structure,

TABLE 1. Hyperfine parameters derived from fits of the ^{155}Gd Mössbauer spectra of various $\text{Gd}_2\text{Fe}_{17-x}\text{Al}_x$ compounds having the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure

Composition x	V_{zz} (10^{21} V m $^{-2}$)	$ B_{\text{eff}} $ (T)	IS (mm s $^{-1}$)	θ (deg)
0	+4.4	21	0.27	90
3	−4.9	7.3	0.31	90
4	−5.0	5.8	0.31	90
6	−4.3	6.1	0.37	90
8	−3.8	7.6	0.40	90
9	± 4.6	10.1	0.41	90
10	± 4.8	10.9	0.42	90

The quantities listed are the composition x , electric field gradient V_{zz} , effective hyperfine field B_{eff} , isomer shift (IS) and angle θ between V_{zz} and B_{eff} .

which are supposed to favour antiferromagnetic exchange interactions and reduce T_c . It is tempting, therefore, to attribute increases in T_c in various $\text{R}_2\text{Fe}_{17-x}\text{T}_x$ series to a preferential substitution of the element T into the 6c sites, which would remove the antiferromagnetic exchange interactions. However, recent results of neutron diffraction, performed on several compounds of the series $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$, showed that the Al atoms initially avoid the 6c sites [1]. A substantial occupation of the 6c site by Al atoms occurs only for $x > 5$, which makes it unlikely that the initial increase in T_c is due to a substitution effect of Al into the dumbell sites.

From the hyperfine parameters listed in Table 1, it follows that the electric field gradient at the nuclear Gd site changes sign when Al substitution into $\text{Gd}_2\text{Fe}_{17}$ takes place. Therefore, it is likely that a similar change in sign (from negative to positive) also occurs for the second-order crystal field parameter A_2° in $\text{R}_2\text{Fe}_{17-x}\text{Al}_x$ compounds. Furthermore, using the relationship

$$K_1 = -\frac{3}{2} N \alpha_j \langle r^2 \rangle A_2^\circ \langle 3J_z^2 - J(J+1) \rangle$$

one would expect that the rare earth sublattice anisotropy also changes its sign. In the equation, N represents the number of rare earth atoms, α_j the second order Stevens factor characteristic for a certain rare earth element, and $\langle r^2 \rangle$ is the expectation value for $\langle r_{4f}^2 \rangle$. For instance, in the series $\text{R}_2\text{Fe}_{17-x}\text{Al}_x$ ($\alpha_j < 0$ for $\text{R} \equiv \text{Pr, Nd, Tb, Dy, Ho}$), one expects the rare earth sublattice magnetization to have a preferred magnetization direction perpendicular to the c axis for small x values ($V_{zz} > 0$; $A_2^\circ < 0$; $K_1 < 0$) but for it to be along a direction parallel to the c axis for larger x values ($V_{zz} < 0$; $A_2^\circ > 0$; $K_1 > 0$). However, it is still an open question whether or not the rare earth sublattice anisotropy will be strong enough to overcompensate the Fe sublattice anisotropy, which favours an easy direction perpendicular to the c axis in the R_2Fe_{17} compounds.

There are indications that the rare earth sublattice anisotropy is successful in this respect in the system $Dy_2Fe_{17-x}Al_x$, since Oesterreicher and McNeely [7] reported the observation of a strong coercivity ($\mu_0 H_c = 6.25$ T) in $Dy_2Fe_{11}Al_8$. Such strong coercivities can develop only in systems where the preferred magnetization direction is along the uniaxial direction.

The concentration dependence of the effective hyperfine field B_{eff} has been plotted in Fig. 4. Here, we have tacitly assumed that B_{eff} changes its sign for increasing x values. In a previous analysis of the hyperfine field in Gd_2Fe_{17} , it was shown that the total hyperfine field can be decomposed into various contributions of different sign and magnitude [8], *i.e.*

$$B_{\text{eff}} = B_{\text{CP}} + B_{\text{OP}} + B_{\text{N}}^{\text{Af}} + B_{\text{N}}^{\text{3d}}$$

where the core polarization (B_{CP}) (as observed in insulators based on Gd^{3+} ions) equals -33.2 T and where the contributions resulting from the polarization of the conduction electrons originate from the polarizing effect of the on-site Gd spin (B_{OP}), the neighbouring Gd spins (B_{N}^{Af}) and the neighbouring Fe moments (B_{N}^{3d}). The contribution of the Fe moments predominates and equals $B_{\text{N}}^{\text{3d}} = +50.2$ T, whereas the sum of the two Gd contributions is much smaller, *i.e.* $B_{\text{OP}} + B_{\text{N}}^{\text{Af}} = +4.0$ T. Recent band structure calculations have largely confirmed the important role of the 6s conduction electrons in determining the hyperfine field in Gd_2Fe_{17} and other intermetallic compounds of Gd [9].

When forming compounds of the type $Gd_2Fe_{17-x}Al_x$, it will be clear that the 6s electron polarization resulting from the Fe moments (50.2 T) will gradually disappear. Indeed, this is suggested by the curve drawn through the data points in the lower curve in Fig. 4, the concave character of the curve being explained by the fact that,

apart from dilution of the Fe sublattice, there is also a small decrease in the size of the Fe moments with x [2].

The concentration dependence of the isomer shift (IS) has been plotted in the upper curve of Fig. 4. This behaviour may be compared with a simple model based on chemical effects (charge transfer and intra-atomic s-d electron redistribution) and volume effects [10]. On the basis of this model, one expects that the ultimate value of the isomer shift that would be reached for $x = 17$ is 0.52 mm s $^{-1}$. There is satisfactory agreement between this value and that obtained by extrapolation of the upper curve shown in Fig. 4.

5. Conclusions

In conclusion, we have studied the magnetic properties of the system $Gd_2Fe_{17-x}Al_x$ and shown that the magnetic phase diagram of this system (as presented in Fig. 1(b)) is similar to that observed in other $R_2Fe_{17-x}Al_x$ systems. From the quadrupolar splitting of the ^{155}Gd Mössbauer spectra, we derived the sign and magnitude of the electric field gradient V_{zz} at the nuclear site and found that V_{zz} changes from positive to negative upon Al substitution into Gd_2Fe_{17} . We discussed the possibility that the corresponding sign change of the second-order crystal field parameter A_2^0 can lead to a dominating rare earth sublattice anisotropy, with an easy c axis for R components with $\alpha_j < 0$. The variation of the Gd hyperfine field in $Gd_2Fe_{17-x}Al_x$ was explained in terms of a reduced 6s electron polarization resulting from the Fe moments. The isomer shift was found to behave in good agreement with model predictions presented earlier.

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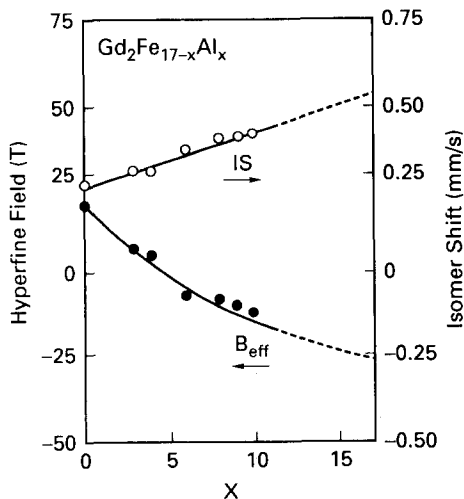


Fig. 4. Concentration dependence of the isomer shift (IS) and effective ^{155}Gd hyperfine field B_{eff} in $Gd_2Fe_{17-x}Al_x$.