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Middleton, D.P.; Mulder, F.M.; Thiel, R.C.; Buschow, K.H.J.

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\[ ^{155} \text{Gd Mössbauer effect studies and magnetic properties of GdFe}_{12-x}\text{Mo}_x(N_y) \] compounds

D.P. Middleton \(^a, \ast\), F.M. Mulder \(^b\), R.C. Thiel \(^b\), K.H.J. Buschow \(^c\)

\(^a\) Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands
\(^b\) Kamerlingh Onnes Laboratory, Leiden University, 2300 RA Leiden, The Netherlands
\(^c\) Van der Waals–Zeeman Laboratory, University of Amsterdam, NL-1018 XE Amsterdam, The Netherlands

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Abstract

Structural and magnetic properties of the GdFe\(_{12-x}\)Mo\(_x\) compounds having the ThMn\(_{12}\) type of structure were studied. Rare-earth nitrides of the composition GdFe\(_{12-x}\)Mo\(_x\)N\(_y\) were prepared by the reaction of GdFe\(_{12-x}\)Mo\(_x\) with nitrogen gas at 475°C. The crystal structure and lattice constants have been determined for all compounds. The lattice expansion of the nitrogenated compounds is mainly along the a-axis, the Curie temperatures are increased by about 110 K. We investigated the effect of interstitial nitrogen on the magnetic properties and the \(^{155}\text{Gd Mössbauer spectrum of GdFe}_{12-x}\text{Mo}_x\). Values of the electric field gradient \(V_{zz}\) derived from the quadrupole splitting of the spectra were strongly negative, with \(V_{zz} = -21.3 \times 10^{-21} \text{ V m}^{-2}\) and \(V_{zz} = -19.9 \times 10^{-21} \text{ V m}^{-2}\) for \(x = 1.5\) and \(3.0\), respectively. Nitrogenation is shown to lead to a sign reversal of the 4f as well as of the 3d sublattice anisotropies.

1. Introduction

Ternary compounds of rare-earth and iron having the tetragonal ThMn\(_{12}\) structure can be formed by stabilizing the non-existent RFe\(_{12}\) (R = rare-earth) with an additional element M (e.g. V, Mo, Ti). The compounds RFe\(_{12-x}\)M\(_x\) are characterized by fairly high values of the Curie temperature and saturation magnetization, and the magnetocrystalline anisotropy is of sufficiently high magnitude to consider them as candidates for permanent magnet applications.

These compounds have already been known for many years [2,4], but the discovery that nitrogen can lead to considerable improvements in the magnetic properties, has led to renewed interest in this class of compounds. Recent investigations [6,8] have indicated that nitrogenated RFe\(_{11}\)Ti and RFe\(_{10.5}\)V\(_{1.5}\) compounds are promising as permanent magnets.

The ThMn\(_{12}\) structure (space group I\(_4/mmm\)) is a simple one (Fig. 1). The Mo atoms preferentially occupy the 8i site [2] and interstitial nitrogen the 2b site in the tetragonal lattice, which is located on the c-axis in between two rare-earth sites. Nitrogenation leads to an increases in the Curie temperature and the saturation magnetization. Also important is the change of the magnetocrystalline anisotropy upon nitrogenation. The anisotropy is related to the second-order crystal field parameter, \(A_2^0\) by the expression: \(K_1 = -3/2 \alpha_j A_2^0 \langle r^2 \rangle \langle O^0_2 \rangle\), where \(\alpha_j\) is the second-order Stevens factor and \(O^0_2\) is the corresponding operator equivalent. The second-order crys-
Fig. 1. Schematic representation of the unit cell of compounds of the tetragonal ThMn\(_{12}\) structure.

The crystal field term is related to the electrical field gradient tensor element \(V_{zz}\) by the empirical relation: 
\[ A_{20} \approx -\omega V_{zz}, \]
where \(\omega\) is an empirical factor which varies from 30-35 Kao \(^2\) mV\(^{-1}\) [12]. Although there is no thorough physical basis for this relation, there are several groups of compounds for which this empirical relation holds [13].

Uniaxial symmetry in permanent magnets, which owe their magnetocrystalline anisotropy to the rare-earth sublattice, arises as a consequence of the electrostatic interaction of the crystal field with the asymmetric charge cloud of the 4f electrons. The 4f moment of Gd does not contribute to the magnetocrystalline anisotropy, due to the absence of an orbital moment \((S = 0)\). The 4f electrons of Gd, however, experience a crystal field similar to those of other rare-earth atoms in the same type of compounds. In this report we present a study of the effect of nitrogen on the crystallographic and magnetic properties, as well as the crystal field, by means of 155Gd Mössbauer spectroscopy in the RFe\(_{10}\)Mo\(_{2}\) compounds. The effect of nitrogen on the second-order crystal field parameter is expected to be large, due to the short distance between the interstitial N-atoms and the R-atoms.

2. Experimental procedures

The GdFe\(_{12-x}\)Mo\(_{x}\) compounds studied in these investigations were prepared by arc melting from starting materials of at least 99.9% purity. The compounds were wrapped in tantalum foil and vacuum annealed in quartz tubes at 1050°C for several days and then quenched in water. The annealed samples were pulverized and heated at 475°C in an atmosphere of purified N\(_2\) gas (at ambient pressure) for about 5 days. All samples were examined by X-ray powder diffraction, using CuK\(_{\alpha}\) radiation at room temperature.

Magnetic measurements were performed on a superconducting quantum interference device (SQUID) magnetometer in the temperature range 4.2-300 K. Measurements above 300 K were performed on a home-built magnetometer based on the Faraday balance method. 155Gd Mössbauer spectra of GdFe\(_{10.5}\)Mo\(_{1.5}\)(N\(_y\)) and GdFe\(_9\)Mo\(_3\)(N\(_y\)) were measured on a spectrometer described in detail elsewhere [5], using the 86.5 keV resonance of 155Gd. The source was neutron-irradiated SmPd\(_3\), for which we employed samarium enriched to 98% in 154Sm. The spectra have been analyzed by means of a least squares fitting procedure that involved diagonalization of the full nuclear Hamiltonian and use of a transmission integral. The independently refined variables considered in the fitting procedure are the isomer shift (IS), the effective hyperfine field \((H_{eff})\), and the quadrupole splitting (QS). From the latter quantity we obtained the electric field gradient tensor element \(V_{zz}\), via the relation:
\[ QS = \frac{1}{4}eQV_{zz}(3\cos^2\theta - 1) \]
using the value \(Q = 1.30 \times 10^{-28} \text{ m}^2\) given by Tanaka et al. [7]. The angle \(\Theta\) between \(H_{eff}\) and the c-axis was 0° for the parent compounds. For the nitrogenated compounds the angle \(\Theta\) was kept at 90°. The line width of absorber and source were constrained for the transmission integral to 0.25 and 0.36 mm s\(^{-1}\), respectively, for GdFe\(_{10.5}\)Mo\(_{1.5}\)(N\(_y\)). For GdFe\(_9\)Mo\(_3\)(N\(_y\)), the absorber line width was kept as an adjustable parameter.

3. Results and discussion

3.1. Crystallographic and magnetic properties

X-ray diffraction of GdFe\(_{12-x}\)Mo\(_{x}\) showed these samples to be approximately single phase, with the tetragonal ThMn\(_{12}\) structure. The samples contained a few percent of elemental Fe as an impurity phase for \(x = 1.5\) and elemental Mo for \(x = 3.0\). For higher Mo concentrations, the samples were not single...
phase. The lattice constants were derived from the diffraction diagrams of GdFe$_{10.5}$Mo$_{1.5}$ and GdFe$_9$Mo$_3$, respectively (Table 1).

The magnetic isotherms at 5.0 K have been measured for Mo concentrations of $x = 1.5$ and 3.0 (Fig. 2). From the isotherms, the saturation magnetization $M_s$ was derived (Table 1). Values of the saturation magnetization were obtained by extrapolating the $M(1/B)$ curves to $1/B = 0$. The values of $\mu_{Fe}$ were derived from the corresponding values of $M_s$ by assuming a moment of $7\mu_B$ per Gd atom and an antiparallel coupling between the Gd sublattice magnetization and the d-metal sublattice magnetization. The substitution of Mo for Fe leads to a strong reduction in the iron moments. Besides magnetic dilution, the reduction of the Fe moments is mainly due to the occupation by Mo of the 8i site [1], at which Fe normally is expected to have the largest moment [11, and references therein].

From the temperature dependence of the magnetization $\sigma(T)$ of GdFe$_{10.5}$Mo$_{1.5}$ and GdFe$_9$Mo$_3$, as shown in Fig. 3, the Curie temperature of these compounds was calculated (Table 1). Mo strongly decreases the Curie temperature, more than one would expect from simple magnetic dilution of Fe by Mo. The pronounced peak in the magnetization at about 150 K for GdFe$_9$Mo$_3$ can be understood as being due to a temperature-induced magnetic transition in the Fe sublattice [10].

Nitrogenation of the GdFe$_{12-x}$Mo$_x$ compounds has strong effects on the crystallographic and magnetic properties. The expansion of the unit cell volume is about 3% for the nitrogenated compounds. From the increase in the unit cell dimensions we estimate the nitrogen concentration to correspond to $y \approx 1$. The lattice expansion is known to be anisotropic for the 1:12 interstitial compounds of

Table 1
Structural and magnetic properties of several GdFe$_{12-x}$Mo$_x$(N$_y$) compounds. The nitrogen concentration is estimated to be $y \approx 1$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$\Delta a/a_0$ (%)</th>
<th>$\Delta c/c_0$ (%)</th>
<th>$\Delta V/V_0$ (%)</th>
<th>$T_C$ (K)</th>
<th>$M_s$ ($\mu_B$/f.u.) at 5.0 K</th>
<th>$\mu_{Fe}$ ($\mu_B$/Fe) at 5.0 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdFe$<em>{10.5}$Mo$</em>{1.5}$</td>
<td>8.563</td>
<td>4.792</td>
<td>351.43</td>
<td>1.04</td>
<td>0.79</td>
<td>2.88</td>
<td>505.6</td>
<td>14.1</td>
<td>2.0</td>
</tr>
<tr>
<td>GdFe$<em>{10.5}$Mo$</em>{1.5}$N$_y$</td>
<td>8.652</td>
<td>4.830</td>
<td>361.56</td>
<td>1.04</td>
<td>0.79</td>
<td>2.88</td>
<td>618.2</td>
<td>14.9</td>
<td>2.1</td>
</tr>
<tr>
<td>GdFe$_9$Mo$_3$</td>
<td>8.593</td>
<td>4.826</td>
<td>356.39</td>
<td>1.04</td>
<td>0.79</td>
<td>2.88</td>
<td>291.9</td>
<td>3.3</td>
<td>1.1</td>
</tr>
<tr>
<td>GdFe$_9$Mo$_3$N$_y$</td>
<td>8.702</td>
<td>4.854</td>
<td>367.55</td>
<td>1.27</td>
<td>0.58</td>
<td>3.13</td>
<td>401.9</td>
<td>7.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Fig. 2. Magnetic isotherms at 5.0 K of GdFe$_{12-x}$Mo$_x$. The solid line is a guide for the eye.

Fig. 3. Temperature dependence of the magnetization $\sigma(T)$ of GdFe$_{10.5}$Mo$_{1.5}$ (right scale) and GdFe$_9$Mo$_3$ (left scale) measured at 0.1 T. The samples were field-cooled.
the Mo system containing nitrogen [11]. As can be seen from Table 1, the lattice constants increase is mainly along the $a$-axis. This anisotropic expansion may be due to the strong hybridization of the N 2p-electron states with the Gd 4d-electron states rather than the Fe 3d-electron states [11,6]. In this case the expansion is larger in the direction of the $a$-axis.

The magnetic isotherms at 5.0 K for the nitrogenated compounds are shown in Fig. 4. The saturation magnetization of the nitrogenated compounds is enhanced (Table 1), as a net result of the increase of the Fe moments, due to volume expansion (which leads to a narrowing of the 3d bands) and the opposing effect of Fe moment reduction by hybridization of N-2p and Fe-3d orbitals on the 8j site [11]. The Curie temperature derived from the $\sigma(T)$ curves (Fig. 5) is enhanced by about 110 K upon nitrogenation, which we attribute to a magneto-volume effect. For the compound with $x = 3.0$, the temperature-induced magnetic transition in the Fe sublattice (Fig. 3) is no longer present in the nitrogenated compound. We ascribe the transitions at 550 K to the onset of the decomposition reaction (Gd(N) and Fe(Mo) compounds are probably formed).

3.2. $^{155}$Gd Mössbauer effect study

The $^{155}$Gd Mössbauer spectra measured at 4.2 K for the GdFe$_{12-x}$Mo$_x$N$_x$ compounds with $x = 1.5$ and 3.0 are shown in Fig. 6. The full line through the data points represents a fit to the spectrum. From the X-ray diffraction diagrams, it was impossible to distinguish any additional phases in the nitrogenated samples. This is due to the low penetration depth of the CuK$_\alpha$ radiation. However, the Mössbauer spectra of these samples clearly show contributions of the parent compound and of a partially nitrogenated compound. The contribution of the parent compound can be clearly observed in Fig. 6B (the central peak).

These phases have been accounted for by the use of three different Gd subspectra in the fitting procedure. For GdFe$_x$Mo$_y$(N$_z$), the absorber line width was kept as an adjustable parameter, which we justify by noting that the 8j sites are randomly occupied by Mo.

The hyperfine parameters corresponding to these fits are listed in Table 2. There is a little variation in the isomer shift in going from $x = 1.5$ to 3.0. This seems plausible, since the nearest-neighbour coordination of the Gd site is changed. For the nitrogenated compounds the isomer shift seems to be dominated by the neighbouring N atoms on the Gd site.

The direction of the effective hyperfine field is dominated by the Fe sublattice anisotropy. For the GdFe$_{12-x}$Mo$_x$ compounds, the easy axis of magnetization is along the $c$-axis [1], therefore $\theta = 0^\circ$. A fit with the magnetization perpendicular to the $c$-axis
gave the most acceptable fit for the GdFe$_{12-x}$Mo$_x$N$_y$. This remarkable feature of a nitrogen-induced change in the easy magnetization direction of the 3d sublattice, closely corresponds to the results obtained by Tomey et al. [14].

The hyperfine field in the GdFe$_{12-x}$Mo$_x$(N$_y$) compounds is reduced in going from $x = 1.5$ to 3.0, which seems plausible if there is a reduced 6s and 5d electron polarization due to the reduction of the Fe moments. A decomposition of the various hyperfine fields into their different contributions is beyond the scope of the present report.

![Graph](image)

**Fig. 6.** $^{155}$Gd Mössbauer spectrum of the GdFe$_{12-x}$Mo$_x$(N$_y$) compounds at 4.2 K, for (A) GdFe$_{10.5}$Mo$_{1.5}$, (B) GdFe$_{10.5}$Mo$_{1.5}$N$_y$, (C) GdFe$_9$Mo$_3$, and (D) GdFe$_9$Mo$_3$N$_y$. The solid curve through the data points represents a fit.

### Table 2

| Compound       | $V_{zz}$ $(10^{21}$ V m$^{-2}$) | $\mu_0 | H_{eff} | IS | $\theta$ |
|----------------|---------------------------------|---------|-----|--------|
| GdFe$_{10.5}$Mo$_{1.5}$ | 1.6                              | 9.2     | 0.21 | 0      |
| GdFe$_{10.5}$Mo$_{1.5}$N$_y$ | -21.3                            | 7.2     | 0.35 | 90     |
| GdFe$_9$Mo$_3$    | 1.9                              | 4.3     | 0.18 | 0      |
| GdFe$_9$Mo$_3$N$_y$ | -19.9                            | 6.9     | 0.35 | 90     |

The electric field gradient is mainly determined by the on-site valence electron asphericities. It is positive and increases slightly with increasing Mo concentration for the parent compounds. Nitrogenation leads to a sign reversal of the electric field gradient. The absolute value of $V_{zz}$ exceeds the large electric field gradient value measured in Gd$_2$(Co, Fe)$_{17}$N$_x$ compounds [15]. An easy axis type of anisotropy can be expected when, instead of Gd, rare-earths having a negative second-order Stevens coefficient $\alpha_J$ are employed (e.g. Nd or Pr) [16]. This in fact makes the compounds interesting for permanent magnet applications. Further studies on the Mo 1:12 system are now in progress.

### 4. Conclusions

Ternary GdFe$_{12-x}$Mo$_x$ compounds having the ThMn$_{12}$ type of structure can be formed for $0 < x \leq 3.0$. The magnetic properties are generally improved upon nitrogenation. Nitrogenation has a drastic effect on the second-order crystal field parameter $A_0^0$, which is changed from negative to positive. An easy axis type of anisotropy can be expected when rare-earths having a negative second-order Stevens coefficient $\alpha_J$ are employed. Appropriate substitutions of 3d metals in these ternary compounds might also lead to interesting magnetic properties for permanent magnet applications.

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