Mössbauer effect studies of Dy(Mn_{0.4-x}Al_{x}Fe_{0.6})_2 intermetallics

Paweł Stoch, Jarosław Pszczoła, Piotr Guzdek, Agata Jabłońska, Jan Suwalski, Ludwik Dąbrowski, Antoni Pańta

Abstract Both 3d subbands in the Dy(Mn_{0.4}Fe_{0.6})_2 compound are filled up only partially with 3d electrons. So, it was interesting to study the consequence of Mn/Al substitution in the Dy(Mn_{0.4-x}Al_{x}Fe_{0.6})_2 series. The cubic, MgCu_2-type, Fd3m crystal structure was observed across the series. However, for x = 0.35 and 0.40 a stoichiometric admixture of the hexagonal, MgZn_2-type, P6_3/mmc structure was evidenced. Mössbauer effect measurements at ^{57}Fe nuclei were performed at 77 K. The magnetic hyperfine field decreases vs. the aluminium content x. This dependence is related to the possible 3d-electron band structure.

Key words intermetallics • crystal structure • ^{57}Fe Mössbauer effect • hyperfine interactions • Slater-Pauling curve • band structure

Introduction

Fundamental interest and practical applications are the reason behind the numerous studies of the heavy rare earth (R) – transition metal (M) compounds \[1\]. It was previously found that the magnetic properties of the RM materials are mainly governed by the 3d electrons of the M sublattice \[3\]. In particular, the magnetic hyperfine fields \(\mu_0 H_{hf}\) (\(\mu_0\) is the magnetic permeability), determined at ^{57}Fe nuclei (4.2 and 77 K) in the Dy(Mn_{1-x}Fe_x)_2 and Dy(Fe_{1-x}Co_x)_2 intermetallics treated as functions of the average number \(n\) of 3d electrons calculated per transition metal site behave according to the Slater-Pauling curve \[3\].

Across the Dy(Mn_{1-x}Fe_x)_2 series the 3d subbands are filled-up step by step and consequently the magnetic hyperfine field \(\mu_0 H_{hf}\) increases with \(x\) (or \(n\)) \[3\]. It can be noticed that in this series not even one 3d-subband approaches its completeness.

The Mn/Al substitution introduces the 3s^2p^1 electrons of the Al atom instead of the 3d^4s^2 electrons of manganese atom and thus modifies 3d-bands, magnetic properties and hyperfine interactions of the compounds \[4, 5\].

It was interesting to study the significance of the manganese component in the compounds, with the 3d subbands only partially occupied by 3d electrons. Therefore, the compounds Dy(Mn_{0.4-x}Al_{x}Fe_{0.6})_2 were studied by using ^{57}Fe Mössbauer effect. The obtained data are qualitatively discussed within the frame of the rigid band model \[8\].

Crystal structure

The intermetallics Dy(Mn_{0.4-x}Al_{x}Fe_{0.6})_2 (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40) were prepared by arc melting, in a high purity argon atmosphere from the
appropriate amounts of Dy (99.9% purity), Mn, Fe and Al (all 99.99% purity).

The X-ray patterns evidence the cubic, Fd3m, MgCu2-type (C15) Laves phases [2] across the series. However, for \( x = 0.35 \) and 0.40 an admixture (presumably stoichiometric) of the hexagonal, \( P6_3mmc \), MgZn2-type (C14) Laves phase was observed (42(2)% and 68(3)%, correspondingly). A possible coexistence of the stoichiometrically similar C14 and C15 Laves phases was previously discussed elsewhere [2].

The determined lattice parameter \( a \) is presented in Table 1. For the hexagonal crystal structure of the MgZn2-type for \( x = 0.35 \) the crystal parameters are equal to: \( a = 5.328(1) \text{ Å}, c = 8.630(1) \text{ Å} \) and for \( x = 0.4 \), \( a = 5.320(4) \text{ Å}, c = 8.683(1) \text{ Å} \).

Spectra and analysis

The Mössbauer effect measurements were performed at 77 K by using a standard transmission technique with a source of 57Co in Rh.

The exemplary 57Fe Mössbauer effect spectra for the Dy(Mn0.4−\( x \)Al\( x \)Fe0.6)\( _2 \) series are presented in Fig. 1. The fitting procedure was carried out analogously as for the series Dy(Mn0.4Fe0.6−\( x \)Al\( x \))\( _2 \) described previously [4, 5]. Table 1 and Fig. 2 contain the determined average hyperfine interaction parameters, i.e. the isomer shift IS (related to pure iron metal at 300 K), the magnetic hyperfine field \( \mu_0H_{hf} \) and the quadrupole interaction parameter QS (as defined, for instance, in [4, 5]).

Experimental points follow the fitted formulas: IS(\( x \)) = [0.496(80)\( x \) + 0.012(18)]mm/s, \( \mu_0H_{hf}(x) = [-17.28(90)\( x \) + 16.64(16)]T \) and QS = [0.199(70)\( x \) – 0.030(14)]mm/s.

Fig. 2. Average hyperfine interaction parameters of the Dy(Mn0.4−\( x \)Al\( x \)Fe0.6)\( _2 \) series (77 K): 1 – the isomer shift IS in relation to Fe-metal, 300 K; 2 – the magnetic hyperfine field \( \mu_0H_{hf} \); 3 – the quadrupole interaction parameter QS.

Spectra and analysis

The Mössbauer effect measurements were performed at 77 K by using a standard transmission technique with a source of 57Co in Rh.

The exemplary 57Fe Mössbauer effect spectra for the Dy(Mn0.4−\( x \)Al\( x \)Fe0.6)\( _2 \) series are presented in Fig. 1. The fitting procedure was carried out analogously as for the series Dy(Mn0.4Fe0.6−\( x \)Al\( x \))\( _2 \) described previously [4, 5]. Table 1 and Fig. 2 contain the determined average hyperfine interaction parameters, i.e. the isomer shift IS (related to pure iron metal at 300 K), the magnetic hyperfine field \( \mu_0H_{hf} \) and the quadrupole interaction parameter QS (as defined, for instance, in [4, 5]).

Experimental points follow the fitted formulas: IS(\( x \)) = [0.496(80)\( x \) + 0.012(18)]mm/s, \( \mu_0H_{hf}(x) = [-17.28(90)\( x \) + 16.64(16)]T \) and QS = [0.199(70)\( x \) – 0.030(14)]mm/s.

Branches of the Slater-Pauling curve

The 3d/3d Slater-Pauling curve \( \mu_0H_{hf}(n) \), the result of the substitution of one transition metal by the other, observed at 77 K for the Dy(Mn1−\( x \)Fe\( x \))\( _2 \) and Dy(Fe1−\( x \)Co\( x \))\( _2 \) compounds [6] [Fig. 3, line 1; \( \mu_0H_{hf} = (12.01n – 49.46)T \), \( \mu_0H_{hf} = (-13.22n + 108.06)T \)] is compared with the \( \mu_0H_{hf}(n) \) branch [Fig. 3, line 2; \( \mu_0H_{hf} = (0.49n^2 – 5.82n + 18.69)T \)] obtained for the Dy(Mn0.4−\( x \)Al\( x \)Fe0.6)\( _2 \) series. In the last case, the average number \( n \) of 3d electrons can be expressed as

---

<table>
<thead>
<tr>
<th>( x )</th>
<th>( a ) [Å]</th>
<th>( n )</th>
<th>IS [mm/s]</th>
<th>( \mu_0H_{hf} ) [T]</th>
<th>QS [mm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.391(1)</td>
<td>5.60</td>
<td>–0.002(25)</td>
<td>17.02(3)</td>
<td>–0.020(19)</td>
</tr>
<tr>
<td>0.05</td>
<td>7.409(1)</td>
<td>5.35</td>
<td>0.039(29)</td>
<td>15.41(3)</td>
<td>–0.033(21)</td>
</tr>
<tr>
<td>0.1</td>
<td>7.433(1)</td>
<td>5.10</td>
<td>0.080(9)</td>
<td>14.83(1)</td>
<td>–0.005(26)</td>
</tr>
<tr>
<td>0.15</td>
<td>7.446(1)</td>
<td>4.85</td>
<td>0.087(27)</td>
<td>14.16(6)</td>
<td>–0.005(16)</td>
</tr>
<tr>
<td>0.2</td>
<td>7.465(1)</td>
<td>4.60</td>
<td>0.115(13)</td>
<td>13.08(2)</td>
<td>0.008(18)</td>
</tr>
<tr>
<td>0.25</td>
<td>7.479(1)</td>
<td>4.35</td>
<td>0.124(24)</td>
<td>12.39(5)</td>
<td>0.025(20)</td>
</tr>
<tr>
<td>0.3</td>
<td>7.502(1)</td>
<td>4.10</td>
<td>0.161(31)</td>
<td>11.51(8)</td>
<td>0.031(19)</td>
</tr>
</tbody>
</table>

---

Fig. 1. Exemplary 57Fe Mössbauer effect transmission spectra of the Dy(Mn0.4−\( x \)Al\( x \)Fe0.6)\( _2 \) intermetallics (77 K). Experimental points, fitted lines are presented.
n(x) = (0.4 − x)5 + 0.6/6 where 5, 6 are the numbers of 3d electrons of the Mn, Fe atom, respectively. It can be seen that, as a result of the Mn/Al substitution, the field μH(n) creates a new 3d4s/3sp branch which bifurcates from the 3d/3d Slater-Pauling curve.

Summary

The 3d-subbands of the starting compound x = 0 of the Dy(Mn0.4xAlFe0.6x)2 series are filled-up only partially and both are far away from their completeness. The Mn/Al substitution changes the Fermi energy, the width of 3d band and the energy shift between 3d subbands [8].

The number of manganese atoms in the M sublattice is reduced with x and simultaneously the MgCu2-type crystal lattice parameter a and thus the distance dₘ₋ₘ = a(2)1/2/4 (as defined in [2]) between the transition metal atoms as nearest neighbours increase. It can be noticed that the unit cell parameters a and c also increase with x for the MgZn2-type structure. Additionally, the mean distance Dₘ₋ₘ among the statistically distributed transition metal atoms in the crystal lattice increases. These factors as discussed elsewhere [4] reduce the overlap of the 3d-wave functions of the neighbouring transition metal atoms with x, gradually increase the 3d electron density at a given 3d atom (particularly iron atom) and cause a rise of the isomer shift observed at ⁵₇Fe [7].

The reduction of the magnetic μH(n) field against the decreasing n (Fig. 3, curve 2) can be qualitatively related to the rigid band model [4, 5, 8]. Although the formally calculated number n of 3d electrons per transition metal site decreases with Al-content, it seems, that in fact, there is no considerable 3d electron density at the Al-atoms, if any. A similar problem was discussed previously [4]. It seems reasonable to assume that the 3d-electrons reside mainly at the transition metal atoms area.

As discussed previously [5], the Mn/Al substitution reduces the energy shift ΔE between the 3d-subbands and presumably also lowers the Fermi level Eₘ. In effect, the 3d electrons should become gradually redistributed over the 3d-subbands, the magnetic moment of the 3d-atom and the magnetic hyperfine field μH should decrease across the series and finally the 3d4s/3sp branch of the Slater-Pauling curve is observed (Fig. 3, curve 2).

Since there is no satisfactory background to predict details of the 3d bands at present a more exhaustive discussion is impossible. For a more precise discussion future sound theoretical and numerical studies would be helpful.

Acknowledgment Work supported partially by the State Committee for Scientific Research, grant No. 4T08D03322. M. Mróz and T. Winek are acknowledged for technical assistance.

References