NUKLEONIKA 2004;49(Supplement 3):S23–S25

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

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

Abstract Both 3*d* subbands in the $Dy(Mn_{0.4}Fe_{0.6})_2$ compound are filled up only partially with 3*d* electrons. So, it was interesting to study the consequence of Mn/Al substitution in the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ series. The cubic, $MgCu_2$-type, *Fd*3*m* 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 3*d*-electron band structure.

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

P. Stoch, J. Pszczoła✉, P. Guzdek
Solid State Physics Department,
AGH University of Science and Technology,
30 A. Mickiewicza Ave., 30-059 Kraków, Poland,
Tel.: +48 12/ 617 29 90, Fax: +48 12/ 634 12 47,
e-mail: pszczola@uci.agh.edu.pl

A. Jabłońska, J. Suwalski, L. Dąbrowski
Institute of Atomic Energy,
05-400 Otwock-Świerk, Poland

A. Pańta
Department of Metallurgy and Materials Engineering,
AGH University of Science and Technology,
30 A. Mickiewicza Ave., 30-059 Kraków, Poland

Received: 6 June 2004, Accepted: 23 July 2004

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 3*d* electrons of the M sublattice [3]. In particular, the magnetic hyperfine fields $\mu_0 H_{hf}$ (μ_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 3*d* 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 3*d* 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 3*d*-subband approaches its completeness.

The Mn/Al substitution introduces the $3s^2p^1$ electrons of the Al atom instead of the $3d^54s^2$ electrons of manganese atom and thus modifies 3*d*-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 3*d* subbands only partially occupied by 3*d* electrons. Therefore, the compounds $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ 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

Table 1. The average hyperfine interaction parameters (77 K) for $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$.

x	a [Å]	n	IS [mm/s]	$\mu_0 H_{hf}$ [T]	QS [mm/s]
	295 K			77 K	
0	7.391(1)	5.60	–0.002(25)	17.02(3)	–0.020(19)
0.05	7.409(1)	5.35	0.039(29)	15.41(3)	–0.033(21)
0.1	7.433(1)	5.10	0.080(9)	14.83(1)	–0.005(26)
0.15	7.446(1)	4.85	0.087(27)	14.10(6)	–0.005(16)
0.2	7.465(1)	4.60	0.115(13)	13.08(2)	0.008(18)
0.25	7.479(1)	4.35	0.124(24)	12.39(5)	0.025(20)
0.3	7.502(1)	4.10	0.161(31)	11.51(8)	0.031(19)

appropriate amounts of Dy(99.9% purity), Mn, Fe and Al (all 99.99% purity).

The X-ray patterns evidence the cubic, *Fd*3*m*, $MgCu_2$-type (C15) Laves phases [2] across the series. However, for $x = 0.35$ and 0.40 an admixture (presumably stoichiometric) of the hexagonal, $P6_3mmc$, $MgZn_2$-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 $MgZn_2$-type for $x = 0.35$ the crystal parameters are equal to: a = 5.328(1) Å, c = 8.630(1) Å and for $x = 0.4$, a = 5.320(4) Å, c = 8.683(1) Å.

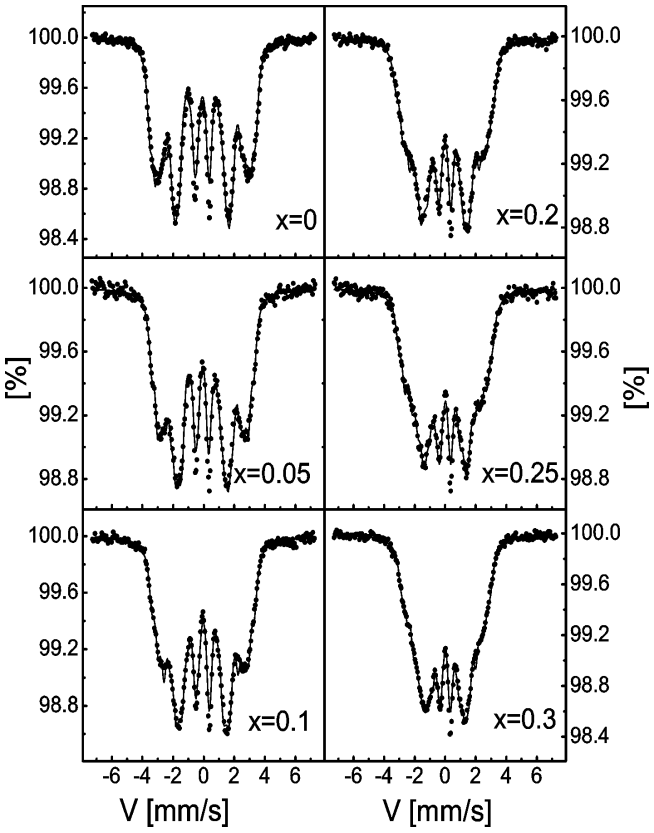

Fig. 1. Exemplary ^{57}Fe Mössbauer effect transmission spectra of the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ intermetallics (77 K). Experimental points, fitted lines are presented.

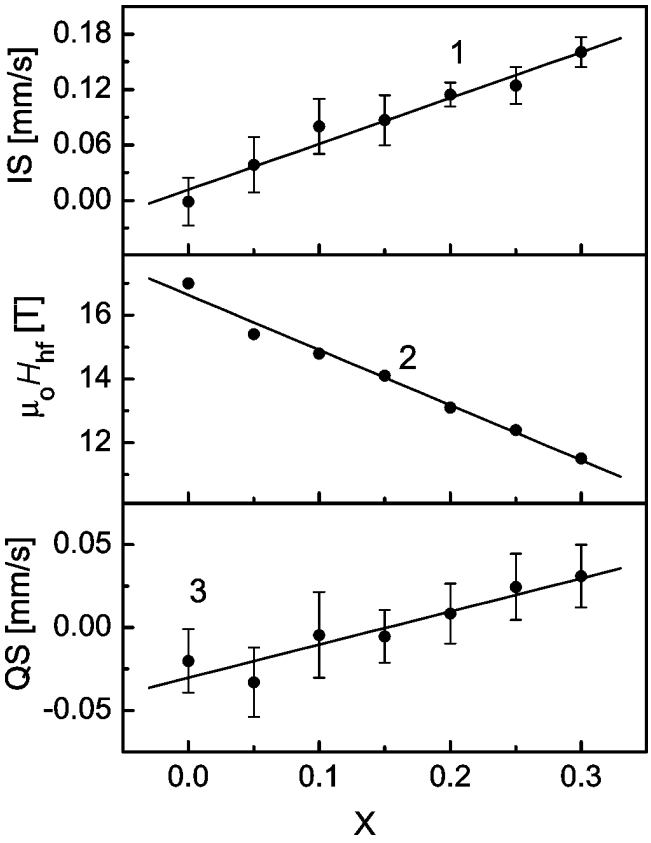

Fig. 2. Average hyperfine interaction parameters of the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ series (77 K): 1 – the isomer shift IS in relation to Fe-metal, 300 K; 2 – the magnetic hyperfine field $\mu_0 H_{hf}$; 3 – the quadrupole interaction parameter QS.

Spectra and analysis

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

The exemplary ^{57}Fe Mössbauer effect spectra for the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ series are presented in Fig. 1. The fitting procedure was carried out analogously as for the series $Dy(Mn_{0.4}Fe_{0.6-x}Al_x)_2$ 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 $\mu_0 H_{hf}$ 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, $\mu_0 H_{hf}(x) = [-17.28(90)x + 16.64(16)]$T and $QS = [0.199(70)x - 0.030(14)]$mm/s.

Branches of the Slater-Pauling curve

The 3*d*/3*d* Slater-Pauling curve $\mu_0 H_{hf}(n)$, the result of the substitution of one transition metal by the other, observed at 77 K for the $Dy(Mn_{1-x}Fe_x)_2$ and $Dy(Fe_{1-x}Co_x)_2$ compounds [6] [Fig. 3, line 1; $\mu_0 H_{hf} = (12.01n - 49.46)$T, $\mu_0 H_{hf} = (-13.22n + 108.06)$T] is compared with the $\mu_0 H_{hf}(n)$ branch [Fig. 3, line 2; $\mu_0 H_{hf} = (0.49n^2 - 5.82n + 18.69)$T] obtained for the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ series. In the last case, the average number n of 3*d* electrons can be expressed as

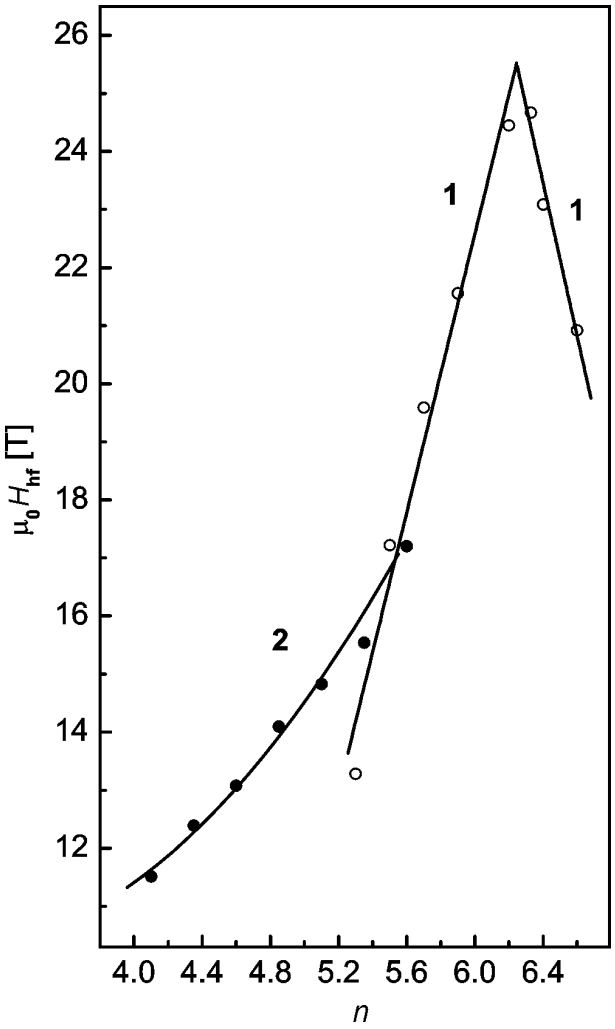

Fig. 3. Magnetic hyperfine fields $\mu_0 H_{hf}(n)$ (77 K) compared for series: 1 – $Dy(Mn_{1-x}Fe_x)_2$, $Dy(Fe_{1-x}Co_x)_2$ [3]; 2 – $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$.

$n(x) = (0.4 - x)^*5 + 0.6^*6$ where 5, 6 are the numbers of 3*d* electrons of the Mn, Fe atom, respectively. It can be seen that, as a result of the Mn/Al substitution, the field $\mu_0 H_{hf}(n)$ creates a new 3*d*4*s*/3*sp* branch which bifurcates from the 3*d*/3*d* Slater-Pauling curve.

Summary

The 3*d*-subbands of the starting compound $x = 0$ of the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ 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 3*d* band and the energy shift between 3*d* subbands [8].

The number of manganese atoms in the M sublattice is reduced with *x* and simultaneously the $MgCu_2$-type crystal lattice parameter *a* and thus the distance $d_{M\text{-}M} = a(2)^{1/2}/4$ (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 $MgZn_2$-type structure. Additionally, the mean distance $D_{M\text{-}M}$ among the statistically distributed transition metal atoms in the crystal lattice increases. These factors as discussed elsewhere [4] reduce the overlap of the 3*d*-wave functions of the neighbouring transition metal atoms with *x*, gradually increase the 3*d* electron density at a given 3*d* atom (particularly iron atom) and cause a rise of the isomer shift observed at ^{57}Fe [7].

The reduction of the magnetic $\mu_0 H_{hf}(n)$ 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 3*d* electrons per transition metal site decreases with Al-content, it seems, that in fact, there is no considerable 3*d* electron density at the Al-atoms, if any. A similar problem was discussed previously [4]. It seems reasonable to assume that the 3*d*-electrons reside mainly at the transition metal atoms area.

As discussed previously [5], the Mn/Al substitution reduces the energy shift ΔE between the 3*d*-subbands and presumably also lowers the Fermi level E_f. In effect, the 3*d* electrons should become gradually redistributed over the 3*d*-subbands, the magnetic moment of the 3*d*-atom and the magnetic hyperfine field $\mu_0 H_{hf}$ should decrease across the series and finally the 3*d*4*s*/3*sp* branch of the Slater-Pauling curve is observed (Fig. 3, curve 2).

Since there is no satisfactory background to predict details of the 3*d* bands at present a more exhausative 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.

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