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# Structural and Mössbauer effect studies of $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ intermetallics

**Paweł Stoch,
Jarosław Pszczoła,
Jan Suwalski,
Antoni Pańta**

**Abstract** The magnetic hyperfine fields observed at the $^{57}Fe$ nuclei (77 K) in the $Dy(Mn_{1-x}Fe_x)_2$ and $Dy(Fe_{1-x}Co_x)_2$ intermetallics form a Slater-Pauling curve. In order to study the effect of cobalt atoms on crystal structure and hyperfine interactions, the new Co/Al substituted series $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ was prepared and data of X-ray powder analysis are presented (300 K). From the $^{57}Fe$ Mössbauer measurements at 77 K the hyperfine parameters were obtained. The magnetic hyperfine fields form a branch of the Slater-Pauling curve.

**Key words** crystal structure • hyperfine interactions • Mössbauer spectroscopy • rare earth • Slater-Pauling curve • transition metal

P. Stoch✉, J. Pszczoła
Solid State Physics Department,
University of Mining and Metallurgy,
30 Mickiewicza Ave., 30-059 Kraków, Poland,
Tel.: +48 12/ 617 29 90, Fax: +48 12/ 634 12 47,
e-mail: stoch@novell.ftj.agh.edu.pl

J. Suwalski
Institute of Atomic Energy,
05-400 Otwock-Świerk, Poland

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

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## Introduction

The heavy rare earth (R) – transition metal (M) ferrimagnets ($RM_2$) are widely studied for their fundamental interest and practical applications [1, 2, 12]. The electronic band structure of these intermetallics, and in particular of their transition metal sublattice, is rather complex and poorly understood up to now. In order to check the effect of cobalt atoms on the crystal structure and hyperfine interactions, the new intermetallics $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ with Co/Al substitution were synthesized and detailed X-ray crystallographic studies and $^{57}Fe$ Mössbauer effect measurements were performed. Magnetic properties of $Dy(Mn\text{-}Fe)_2$, $Dy(Fe\text{-}Co)_2$ series and especially of the studied series are poorly known up to now. Nevertheless the ordering temperatures for $x = 0$ and for $x = 0.6$ can be appreciated as being equal to 620 K and 109 K, correspondingly [9, 11].

## Materials, crystal structure

The series of intermetallics $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ ($x = 0$, 0.1, ..., 0.5 and 0.6) was prepared by arc melting with contactless ignition [7], in a high purity argon atmosphere, from the appropriate amounts of Dy (99.9% purity), Fe, Co and Al (all 99.999% purity) starting materials. After 48 h treatment at 1150 K, good quality X-ray diffraction patterns were obtained at room temperature for all the samples, using Mo $K_\alpha$ radiation. For the compounds with $x = 0$–0.2, the cubic, *Fd3m*, $MgCu_2$-type Laves phase was evidenced. For $0.3 \le x \le 0.5$ a mixture of two Laves phases was observed [8], the second one corresponding to the hexagonal, $P6_3/mmc$, $MgZn_2$-type structure. For $x = 0.6$ only the $MgZn_2$-type phase was observed. The phase contribution, lattice parameters and unit cell volume for both Laves phases are presented in Table 1.

**Table 1.** Crystal data (300 K) for the $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ intermetallics: the phase contribution (%), parameters $a$ and $V$ for the $MgCu_2$-type phase and $a$, $c$, $V$ for the $MgZn_2$-type phase.

| $x$ | % | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) |
|---|---|---|---|---|
| 0 | 100 | 7.274(8) | – | 384.81(7) |
| 0.1 | 100 | 7.315(6) | – | 391.36(6) |
| 0.2 | 100 | 7.366(7) | – | 399.61(6) |
| 0.3 | 44(3) | 7.4(2) | – | 409.10(2) |
| | 55(4) | 5.27(3) | 8.589(3) | 206.40(2) |
| 0.4 | 4(1) | 7.56(4) | – | 432.00(4) |
| | 96(6) | 5.31(1) | 8.640(1) | 211.34(7) |
| 0.5 | 0.2(5) | 7.67(4) | – | 451.40(5) |
| | 99(4) | 5.36(2) | 8.690(2) | 216.40(1) |
| 0.6 | 100 | 5.432(3) | 8.759(2) | 223.90(2) |

## Mössbauer effect studies

The Mössbauer effect measurements (at 77 K) were performed by using a standard transmission technique, with a $^{57}$Co source in Rh. The experimental spectra of the $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ series are presented in Fig. 1. The spectra are complex which can be related principally to the Fe/Co/Al substitution and also to the crystallography of the constituent $MgCu_2$- and $MgZn_2$-type phases and to the direction of the easy axis of magnetization [10]. In the present complex case the general Bernoulli law [4] was used to find probabilities of particular local Fe/Co/Al configurations of atoms. During fitting procedure the used starting amplitude distribution of subspectra followed the Bernoulli distribution, considering, as an approximation, only significant probabilities. This approximation results in change of the halfwidth ($\Gamma/2$) of the Mössbauer line. Namely, it varies across the series from 0.137(5) mm/s ($x$ = 0) to 0.23(1) mm/s ($x$ = 0.5) and even to 0.33 mm/s ($x$ = 0.6). The average values of the hyperfine interaction parameters are the fitted amplitude weighted data. These parameters, i.e. the isomer shift IS (with respect to pure iron metal, at 300 K), the magnetic hyperfine field $\mu_0 H_{hf}$ ($\mu_0$ is magnetic permeability) and the quadrupole interaction parameter $eQ/2$ (as defined in [13]) obtained for the $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ series are

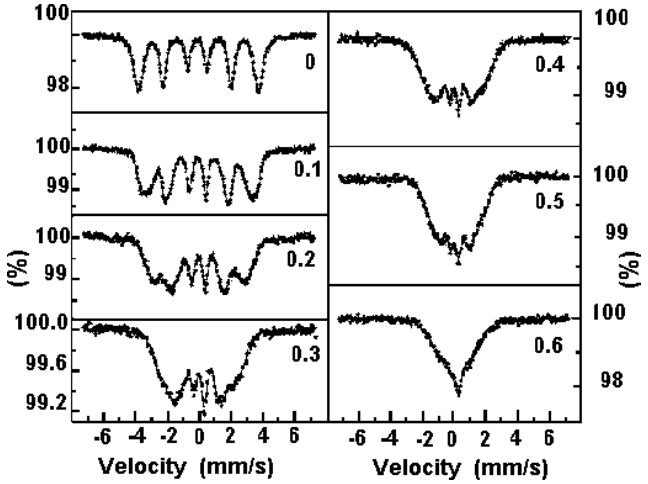


**Fig. 1.** $^{57}$Fe Mössbauer spectra of the $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ intermetallics (77 K) for several $x$ values.

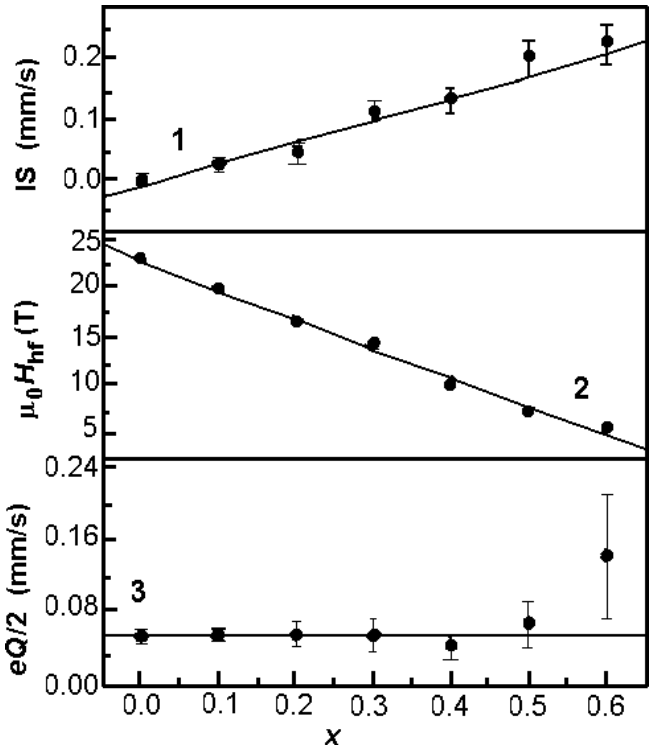


**Fig. 2.** Evolution of the hyperfine parameters of the $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ series (77 K) with the aluminium content ($x$): 1 – the isomer shift; 2 – the magnetic hyperfine field; 3 – the quadrupole interaction parameter.

presented in Fig. 2. The errors $\delta(\mu_0 H_{hf})$ of the $\mu_0 H_{hf}$ parameters are less than dimensions of experimental points. For instance, $\pm\delta(\mu_0 H_{hf})$ = 0.09 T ($x$ = 0), 0.1 T ($x$ = 0.3), 0.13 T ($x$ = 0.5). The magnetic hyperfine field $\mu_0 H_{hf}$ equals 23.4(1) T for $Dy(Fe_{0.4}Co_{0.6})_2$ and decreases with increasing Al content $x$. The line through the experimental points corresponds to a linear fit: $\mu_0 H_{hf} = -30.28x + 23.03$ T. The isomer shift, IS, increases with $x$ (IS = $0.37x - 0.011$ mm/s), whereas the quadrupole interaction parameter $eQ/2$ remains constant, except perhaps for $x$ = 0.6. Although the crystal structure changes across the series, the observed average hyperfine interaction parameters do not reflect these crystal transitions since they vary continuously with $x$ (IS and $\mu_0 H_{hf}$) or do not significantly vary ($eQ/2$). This behaviour can be understood by considering that the nearest neigbourhoods of the studied iron atoms are similar in both the Laves structures [3].

## The Slater-Pauling curve

Figure 3 gives the 3*d*/3*d* Slater-Pauling curve $\mu_0 H_{hf}(n)$ for the $Dy(M\text{-}M)_2$ compounds (M-M = Mn-Fe, Fe-Co) at 77 K, (analogous to the curve previously reported for these compounds at 4.2 K [5]) (lines 1) and the $\mu_0 H_{hf}(n)$ dependence for the $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ series (line 2). Lines 1 are fitted using the formulae: $\mu_0 H_{hf}(n) = 11.55n - 47.87$ T and $\mu_0 H_{hf}(n) = -5.89n - 61.73$ T. Line 2 is fitted using the formula $\mu_0 H_{hf}(n) = 4.33n - 5.52$ T. The average number $n$ of 3*d* electrons, calculated per site of the M – sublattice, equals $n(x) = 0.4 \cdot 6 + (0.6 - x)7$, where 6 and 7 are the numbers of 3*d* electrons for iron and cobalt atoms, respect-

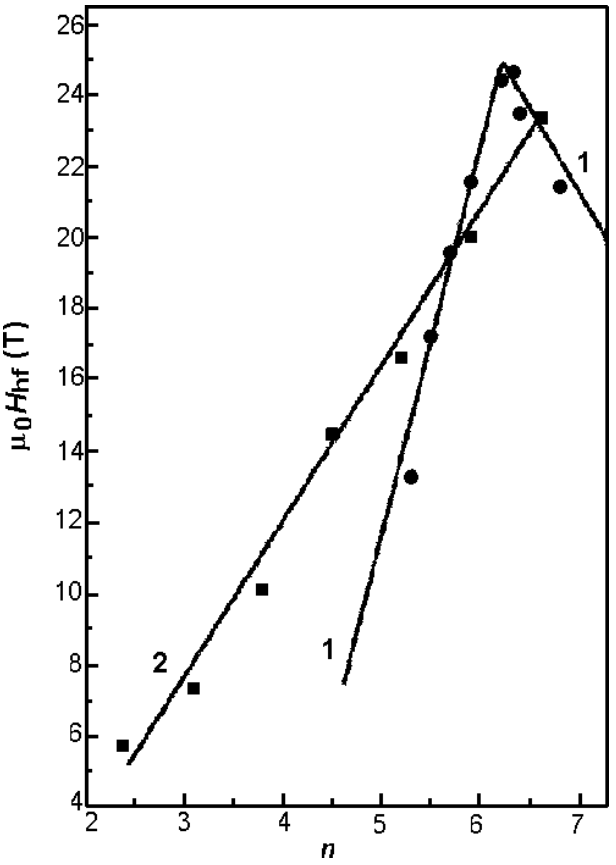


**Fig. 3.** Magnetic hyperfine fields $\mu_0 H_{hf}(n)$ (77 K) compared for series: 1 – $Dy(M\text{-}M)_2$ (M-M = Mn-Fe, Fe-Co) and 2 – $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ ($n$ is the average number of 3$d$ electrons).

ively. The obtained fields create a new $\mu_0 H_{hf}(n)$ 3$d$4$s$/3$sp$ branch (line 2) which differs from the 3$d$/3$d$ Slater-Pauling curve. Namely, for this branch there is no maximum and the field decreases approximately linearly with $n$-reducing. The slope of line 2 equals $\eta = \Delta\mu_0 H_{hf}(n)/\Delta n = = 4.33$ T/electron.

## Summary and discussion

The influence of Al substitution on the crystal lattice, magnetic properties and hyperfine interactions observed in several intermetallics was previously discussed elsewhere [6, 10]. The main problem to discuss below is the $\mu_0 H_{hf}(n)$ dependence. The series $Dy(Fe_{0.4}Co_{0.6-x}Al_x)_2$ starts from the $Dy(Fe_{0.4}Co_{0.6})_2$ compound with the majority subband totally filled up, and the minority subband only partly filled [8, 10]. We did not observe the Slater-Pauling mechanism since the typical maximum does not occur on our $\mu_0 H_{hf}(n)$ curve.

This type of $\mu_0 H_{hf}(n)$ dependence could be understood qualitatively considering that the Al substitution of Co – atoms reduces the average number $u$ of the magnetic nearest neighbours surrounding the probed Fe atom and thus reduces the energy shift $\Delta E \sim J_{M\text{-}M} u m_M$ between the 3$d$-subbands, where $J_{M\text{-}M}$ is the exchange integral and $m_M$ is an average magnetic moment of transition metal (M) atom. As a result the 3$d$ electrons should become gradually redistributed over the 3$d$ subbands [8, 10] and the difference between the spin-up $\rho^+_{3d}$ and spin down $\rho^-_{3d}$ densities should become reduced step by step with $x$. Consequently, the magnetic moment $m_M$, the magnetic hyperfine field $\mu_0 H_{hf}$ should also decrease and finally the 3$d$/3$sp$ branch is observed. A more advanced explanation including the change of Fermi energy needs further experimental, theoretical and numerical studies.

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## References

1. Burzo E, Kirchmayr HR (1989) Physical properties of $R_2F_{14}B$-based alloys. In: Gschneidner KA Jr, Eyring L (eds) Handbook on the physics and chemistry of rare earths, vol. 12. North-Holland, Amsterdam, pp 71–132
2. Buschow KHJ (1980) Rare earths compounds. In: Wohlfarth EP (ed.) Ferromagnetic materials, vol. 1. North-Holland, Amsterdam, pp 297–414
3. Chojnacki J (1966) Structural metallography. Śląsk Press, Katowice
4. Feller W (1961) An introduction to probability theory and its applications. Wiley, New York
5. Gicala B, Pszczoła J, Kucharski Z, Suwalski J (1994) Two Slater-Pauling dependences for Dy-3$d$ metal compounds. Phys Lett A 185:491–494
6. Maletta H, Crecelius G, Zinn W (1974) Spin and charge density transfer in the series $Dy(Fe_xAl_{1-x})_2$. J Phys C, Suppl 35;6:279–283
7. Onak M, Pszczoła J (2000) Synthesis of rare earth-transition metal compounds using arc melting. In: XXVIII School of Materials Engineering, Kraków–Szczawnica, pp 211–216 (in Polish)
8. Pszczoła J, Feret A, Winiarska B, Dąbrowski L, Suwalski J (2000) Mössbauer effect studies of $Dy[(Fe_{0.7}Co_{0.3})_{1-x}Al_x]_2$ intermetallics. J Alloys Compd 299:59–67
9. Pszczoła J, Suwalski J (2000) Mössbauer effect studies of $Dy[(Fe_{1-c}Co_c)_{1-x}Al_x]_2$ ferrimagnets. Molecular Physics Reports 30:113–126
10. Pszczoła J, Winiarska B, Suwalski J, Kucharski Z (1998) Slater-Pauling dependence of $Dy[(Fe_{0.4}Co_{0.6})_{1-x}Al_x]_2$ intermetallics. J Alloys Compd 265:15–22
11. Pszczoła J, Żukrowski J, Suwalski J, Pańta A (2000) $^{161}Dy$ and $^{57}Fe$ Mössbauer effect studies of $Dy[(Fe_{0.4}Co_{0.6})_{1-x}Mn_x]_2$ intermetallics. J Alloys Compd 306:56–65
12. Taylor KNR (1971) Intermetallic rare-earth compounds. Adv Phys 20:551–600
13. Wertheim GK (1964) Mössbauer effect. Academic Press, London