Electrical resistivity and Mössbauer effect studies of $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ and $Dy(Mn_{1-x}Fe_x)_2$ intermetallics

P. Stoch[a], J. Pszczoła[a,*], P. Guzdek[a], J. Chmist[a], W. Bodnar[a], A. Jabłońska[b],
J. Suwalski[b], A. Pańta[c]

[a] *Solid State Physics Department, AGH, Al. Mickiewicza 30, 30-059 Kraków, Poland*
[b] *Institute of Atomic Energy, 05-400 Świerk-Otwock, Poland*
[c] *Department of Metallurgy and Materials Engineering, AGH, Al. Mickiewicza 30, 30-059 Kraków, Poland*

Abstract

Electrical resistivity measurements for the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ intermetallics were performed in a wide temperature region and the parameters characterising the resistivity dependence on temperature were determined. Mössbauer effect studies were performed in the temperature range around the Curie temperatures. From both the methods the magnetic ordering temperatures were estimated. For the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ and $Dy(Mn_{1-x}Fe_x)_2$ series the splitting energies between the 3d subbands were estimated. It was found that the Curie temperatures obtained for the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ intermetallics and the Curie temperatures reported in the literature for the $Dy(Mn_{1-x}Fe_x)_2$ series correlate linearly with the squared energy splitting between the 3d subbands.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Intermetallics; Electric resistivity; [57]Fe Mössbauer effect; Magnetic hyperfine field; Curie temperatures; 3d Subband splitting energy

1. Introduction

The ferrimagnetic properties of the heavy rare earth (R)–transition metal (M) compounds result from the coexistence between the 4f (5d) and 3d electron magnetism [1–6]. It was previously found that the magnetic properties of the R–M intermetallics are mainly governed by the 3d band-type electrons of the transition metal sublattice [4–6]. However, the electronic band structure of the R–M intermetallics, especially of their transition metal constituent, is less known up to date.

Al-substitution is a widely used suitable method to modify 3d bands and thus to modify the magnetic properties or hyperfine interactions, as for instance in Refs. [7,8]. The influence of the Mn/Al substitution on the crystal structure and the hyperfine interactions was studied recently in the series $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ (both the 3d subbands are populated only partially) using [57]Fe Mössbauer spectroscopy [9]. An Al atom substituted into the M-sublattice introduces $3s^2p^1$ electrons instead of $3d^54s^2$ electrons of a manganese atom. The cubic, $Fd3m$, $MgCu_2$-type (C15) Laves phases [9–11] were observed across the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ series. Nevertheless, for $x = 0.35$ and 0.40 an admixture (presumably stoichiometric) of the hexagonal, $P6_3mmc$, $MgZn_2$-type (C14) Laves phase was evidenced. A possible coexistence of the stoichiometric locally similar C14 and C15 Laves phases in the compounds was previously discussed elsewhere [12]. The unit cell parameters of the crystal lattice increase with the Al content x in the series [9].

This Mn/Al replacement strongly influences the 3d band and thus the magnetism and hyperfine interactions of the compounds [7,8,13–16]. For instance, the magnetic hyperfine field $\mu_0 H_{hf}$ (μ_0 is magnetic permeability) decreases considerably with x.

As the Mn/Al substitution reduces a number of 3d electrons in the M sublattice across the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ series it was interesting to study the influence of the manganese

* Corresponding author.
E-mail address: pszczola@uci.agh.edu.pl (J. Pszczoła).

atoms on the 4f–5d–3d magnetism, on the magnetism of the 3d sublattice and especially on the magnetic ordering temperatures T_C.

For this purpose the magnetic ordering temperatures $T_C(x)$ were determined from electric resistivity and from ^{57}Fe Mössbauer effect measurements. The obtained magnetic ordering temperatures are discussed qualitatively on the basis of the rigid band model [17–19].

2. Electrical resistivity (ER) measurements

The synthesis of the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ compounds using arc melting method was described previously [9]. Fragile materials resistant against oxidation, were obtained. A small part of the synthesized ingot was used each time to test the crystal structure of the compound by the X-ray powder diffraction method. Bar (cuboid) shaped specimens with typical dimensions 1 mm× 1 mm× 15 mm, were delicately and precisely cut from the ingots for electrical measurements. Electrical contacts to the bars were established by point spark-welding of high purity thin copper wires onto the ends of the bars. If after the welding procedure there was no microscopically observable cracks the resistivity measurements were performed on the sample. The four probe ac method was used at temperatures below ambient temperature and the dc method above this temperature. The data of the measurements of both the used methods were found to match with each other at the same temperature in the common temperature region.

The successfully obtained good quality electrical resistivities ρ as functions of temperature T for the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ intermetallics are presented in Fig. 1. The resistivity $\rho(T)$ changes slightly with x. Following the Matthiesen formula [20,21]:

$$\rho = \rho_0 + \rho_f + \rho_m \tag{1}$$

the observed resistivity $\rho(T)$ can be divided into three contributions: the residual resistivity ρ_0, the phonon scattering resistivity $\rho_f(T)$ and the magnetic contribution $\rho_m(T)$ (Fig. 1) [17,19–21].

The phonon scattering resistivity $\rho_f(T)$ can be expressed using the Bloch–Grüneisen formula [19–21]:

$$\rho_f(T) = D\left(\frac{T}{\theta}\right)^5 \int_0^{\theta/T} \frac{z^5}{(e^z - 1)(1 - e^{-z})}\, dz \tag{2}$$

where D is a temperature-independent constant and θ a parameter close to the Debye temperature.

Assuming that for the low temperature region ($T \ll T_C$), the resistivity $\rho_m(T)$ of metallic ferrimagnets can be described by the following formula [19]:
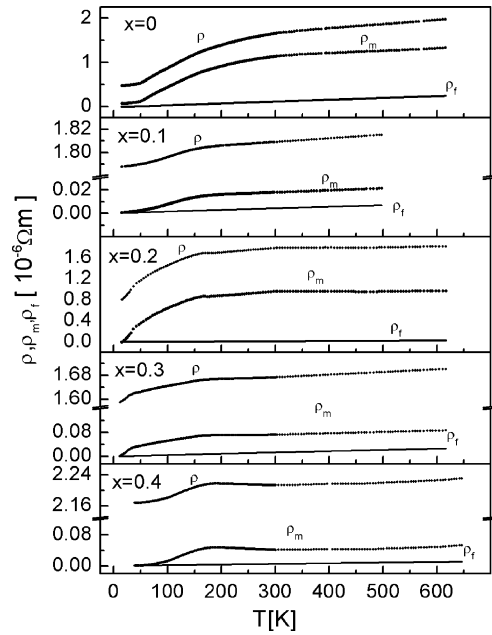
$$\rho_m(T) = AT^2 + BT \tag{3}$$

Fig. 1. Electric resistivities: the total $\rho(T)$, the phonon $\rho_f(T)$ and the magnetic $\rho_m(T)$ observed against temperature for the intermetallics $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$.

with A, B being constants, the expression (1) for temperatures $T \ll \theta$ and $T \ll T_C$ can be rewritten in the form [19,20]:

$$\rho(T) = 497.6D\left(\frac{T}{\theta}\right)^5 + AT^2 + BT + \rho_0 \tag{4}$$

On the other hand for the high temperature region ($T \gg \theta$ and $T \gg T_C$) the total resistivity can be approximated by the formula [19,20]:

$$\rho(T) = D\left(\frac{T}{\theta}\right) + C \tag{5}$$

After fitting formula (4) to the experimental data $\rho(T)$ for low temperatures and formula (5) to the experimental data for high temperatures the parameters appearing in the above equations were obtained, especially the parameters D, θ and ρ_0. Afterwards, the determined parameters D and θ were used to calculate $\rho_f(T)$ following formula (2). Then after subtracting from the experimental $\rho(T)$ curves the fitted ρ_0 values and the calculated temperature dependence of $\rho_f(T)$, the magnetic contribution versus temperature, i.e. the $\rho_m(T)$ curve was obtained for particular compounds. The fitted values ρ_0 for the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ series were equal to 0.448(5), 1.787(1), 0.813(18), 1.589(3) and 2.167(1) ($\times 10^{-6}$ Ω m) for $x = 0$, 0.1, 0.2, 0.3 and 0.4, respectively. An approximately by growing tendency for ρ_0 across the series seems to exist. The residual resistivity ρ_0 depends on both the crystal lattice imperfections and the statistical imperfections introduced by the random Mn/Fe substitution. It is expected that the statistical disorder, a result of the Mn/Al substitution, increasing with x is the origin of the mentioned growing tendency for ρ_0. The fitted temperatures θ were equal to 251(6), 153(23),
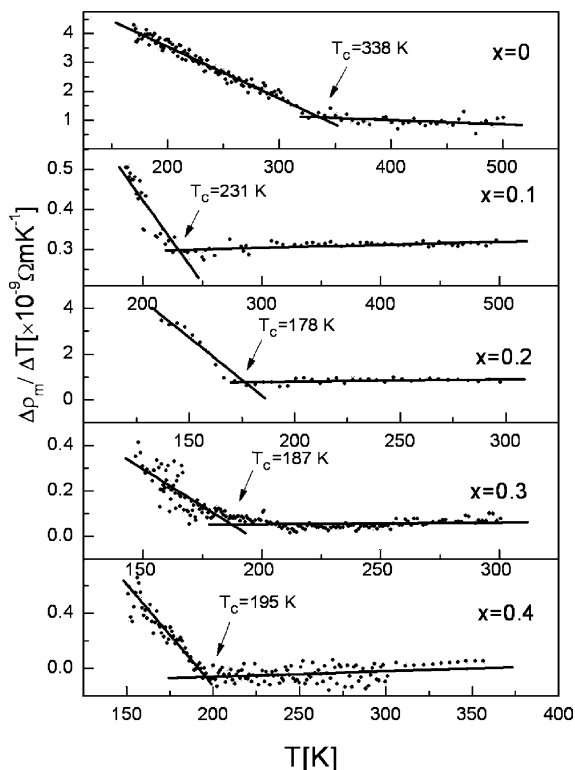
Fig. 2. The $\Delta\rho_m/\Delta T$ functions of temperature for the Dy(Mn$_{0.4-x}$Al$_x$Fe$_{0.6}$)$_2$ compounds.

Table 1
Magnetic hyperfine field $\mu_0 H_{hf}$, average number n_{3d} of 3d electrons, splitting energy ΔE and Curie temperature T_C of the Dy(Mn$_{0.4-x}$Al$_x$Fe$_{0.6}$)$_2$ [9,24] and Dy(Mn$_{1-x}$Fe$_x$)$_2$ [25,26] intermetallics

| x	$\mu_0 H_{hf}$ [T]	n_{3d}	ΔE [eV]	T_C [K]	
				ME	ER
Dy(Mn$_{0.4-x}$Al$_x$Fe$_{0.6}$)$_2$					
0	17.34(6) [9]	5.6	1.53	361, 382 [24]	338
0.05	16.13(7) [9]	5.35	1.40	301	–
0.1	15.54(6) [9]	5.1	1.37	276	231
0.15	14.92(5) [9]	4.85	1.31	245	–
0.2	14.24(8) [9]	4.6	1.27	229	178
0.3	13.09(5) [9]	4.1	1.15	181	187
0.4	12.98(70) [9]	3.6	1.14	173 [24]	195
Dy(Mn$_{1-x}$Fe$_x$)$_2$					
0.2	12.68 [24]	5.2	1.12	158 [25]	–
0.3	14.13 [24]	5.3	1.25	197 [25]	–
0.5	17.63 [24]	5.5	1.55	344 [25]	–
0.7	20.01 [24]	5.7	1.76	457 [25]	–
0.8	20.54 [24]	5.8	1.81	514 [25]	–
0.9	21.87 [24]	5.9	1.92	576 [25]	–
1.0	22.68 [24]	6.0	2.0	635 [25]	–

ME: Mössbauer effect; ER: electrical resistivity measurements.
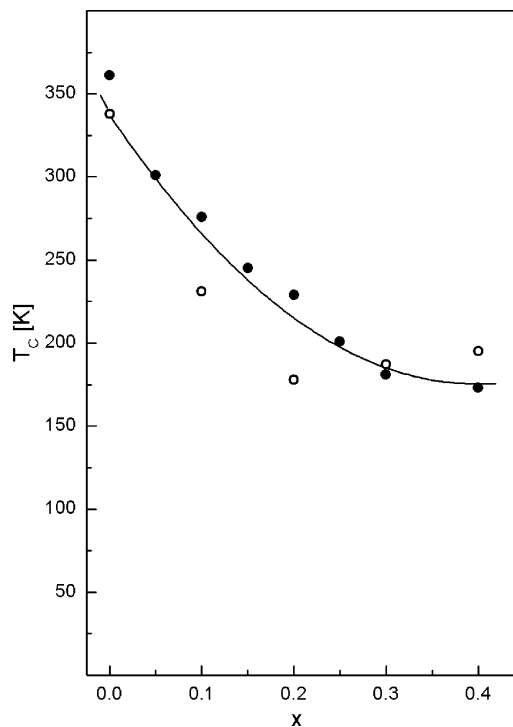
Fig. 3. The Curie temperatures $T_C(x)$ of the Dy(Mn$_{0.4-x}$Al$_x$Fe$_{0.6}$)$_2$ intermetallics. Open points: resistivity measurements; points: Mössbauer data.

212(6), 194(11) and 119(27) K for $x = 0$, 0.1, 0.2, 0.3 and 0.4, respectively. In this case, an approximately decreasing tendency with x can be deduced. These θ values seem to be reasonable as compared to the Debye temperatures 420 K (for Fe), 400 K (for Mn), 394 K (for Al) or 140 K (for Dy) [20]. The Mn/Al substitution reduces the parameter θ. The values for ρ_0 and θ are effected by errors arising from numerical procedure. It can be expected that the physical errors in some cases considerably surpass the numerical errors.

As well as for ferromagnets [17,19] the dependence $\rho_m(T)$ can be used to determine the magnetic ordering temperatures of the intermetallics. In fact, there is no a sharp rule, especially for metallic ferrimagnets, to relate $\rho_m(T)$ and T_C. Nevertheless, it seems that the magnetic ordering temperature T_C is placed in the temperature region with a maximal change of the parameter $\Delta\rho_m/\Delta T$. For the observed $\rho(T)$ curves this sort of approach to determine T_C seems to be a relatively satisfactory method. Fig. 2 presents the numerically determined, $\Delta\rho_m/\Delta T$ functions of temperature for the compounds of the Dy(Mn$_{0.4-x}$Al$_x$Fe$_{0.6}$)$_2$ series. The intersection of the two fitted straight lines gives the magnetic ordering temperature. Unfortunately, the experimental error of the method is quite considerable and for the particular compounds can be appreciated as $\Delta T_C = 20$–30 K. The lack of sharp changes in $\rho_m(T)$ in the T_C region of the Dy(Mn$_{0.4-x}$Al$_x$Fe$_{0.6}$)$_2$ ferrimagnets prevents to reach a better accuracy. The T_C temperatures obtained by using the $\Delta\rho_m/\Delta T$ plots are contained in Table 1 and in Fig. 3 (open circles). All the Curie temperature data follow nonlinearly the fitted polynomial formula $T_C(x)$ (K) $= 1032(99)x^2 - 817(50)x + 337(10)$.

3. Mössbauer effect studies

The Mössbauer effect (ME) measurements were performed versus temperature T for the Dy(Mn$_{0.4-x}$Al$_x$Fe$_{0.6}$)$_2$

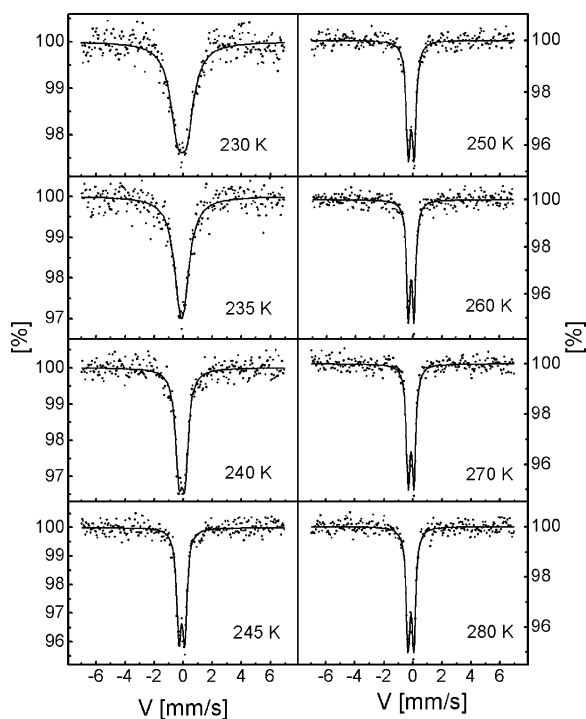Fig. 4. ^{57}Fe Mössbauer effect transmission spectra of the Dy-$(Mn_{0.25}Al_{0.15}Fe_{0.6})_2$ compound vs. temperature. Experimental points and fitted lines are presented.

Fig. 5. The half-width of the Mössbauer line against temperature for the exemplary compounds of the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ intermetallics. T_C: magnetic ordering temperatures.

series ($x = 0$, 0.05, 0.10, 0.15, 0.20 and 0.30) by using a standard transmission technique with a source of ^{57}Co in Rh.

As examples, ^{57}Fe Mössbauer effect spectra (points) observed in the temperature region of the Curie temperature for the $Dy(Mn_{0.25}Al_{0.15}Fe_{0.6})_2$ compound are presented in Fig. 4. During the fitting procedure the particular spectra were treated as doublets composed of two independent lines. Experimental values of G (G is 0.5 halfwidth of the Mössbauer line) at various temperatures were obtained from a fitting procedure for the $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ compounds. Typical examples of the temperature dependency of the halfwidth $G(T)$ for $x = 0.15$ and 0.25 are presented in Fig. 5. A method to determine the magnetic ordering temperatures was described previously elsewhere [22,23]. For instance, for the compound with the Al content $x = 0.15$ the $G(T)$ curve was fitted using two lines: $G(T)$ (mm/s) $= -0.030(5) \, \text{K}^{-1} \, T + 7.422(1.259)$ and $G(T)$ (mm/s) $= -0.001(4) \, \text{K}^{-1} \, T + 0.385(111)$. The lines intersect each other at the magnetic ordering temperature $T_C = 245$ K. The procedure was repeated for the other compounds of the series. The magnetic ordering temperatures T_C obtained for the series using this method are presented in Fig. 3 (black points). The T_C values are also given in Table 1. Table 1 contains also the literature data [24,25]. The error ΔT_C can be estimated to be equal to 5–20 K depending on x. The differences between the corresponding T_C values obtained from the Mössbauer spectra and those obtained from resistivity measurements should be related to experimental errors and to imperfections of the evaluation methods. At
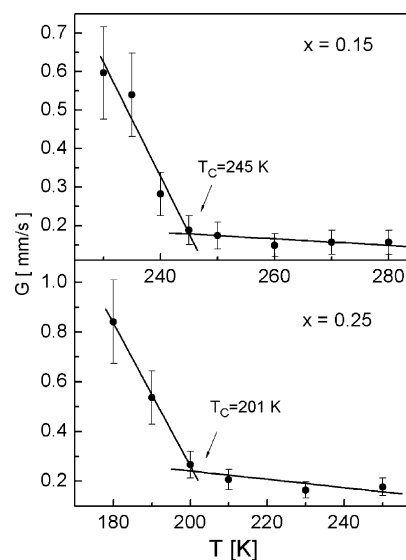
this stage the Mössbauer effect temperature scan seems to be a better method.

4. Summary and discussion

To explain the magnetic ordering temperatures of the R–M intermetallics is an interesting and open topic up to date. In Ref. [1] an empirical approximate formula for the ordering temperature of the R–M compounds was introduced in the form $T_C = T_R + T_M$ with the T_R contribution originating from the rare earth sublattice and the T_M term originating from the transition metal sublattice. It was assumed that $T_R = BG$, where B is a certain constant and G is the de Gennes factor [3]. The conditions necessary for the validity of this formula were discussed later elsewhere [3]. It seems that this approximate formula can be carefully applied also to the substituted compounds discussed above. Following the ideas of Refs. [1,3] it is expected that the influence of the Mn/Fe or the Mn/Al substitution on the T_R term is of the second order, if any. Thus the change of T_C across the series can be approximately ascribed to the T_M term. However, the T_M contribution depends on the changes in the M sublattice originating from the substitutions.

It will be helpful for further discussion to consider some previously published data for the $Dy(Mn_{1-x}Fe_x)_2$ series, reported again in Table 1 [26]. The Mn/Fe substitution in the series $Dy(Mn_{1-x}Fe_x)_2$ or the Mn/Al substitution in the series $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ is expected to introduce a number of changes in the 3d band [17–19]. Namely, these substitutions should change the Fermi energy, the width of 3d bands, the position of the 3d bands in relation to the Fermi level, the 3d electron populations of the 3d subbands and the energy shift ΔE between the 3d subbands [17–19]. It is an open and
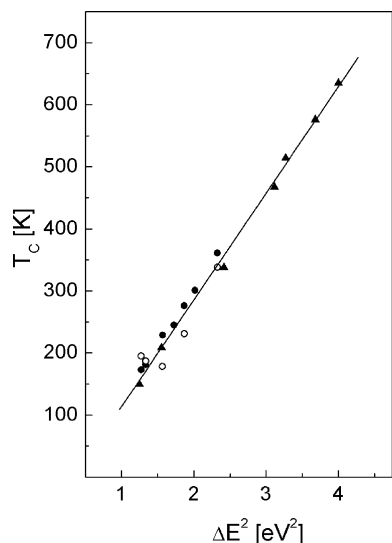
Fig. 6. The correlation between the Curie temperature $T_C(x)$ and the square value ΔE^2 of the splitting energy between the 3d subbands for the series $Dy(Mn_{1-x}Fe_x)_2$ (triangles), $Dy(Mn_{0.4-x}Al_xFe_{0.6})_2$ (points: ME; open points: ER).

in general not easy task to find all these 3d band properties in future studies. Nevertheless, some modest results in this area can be currently approached. It was already found elsewhere for the $DyFe_2$ compound that the magnetic moment m_{3d} of the 3d electrons calculated per Fe atom equals to $2\mu_B$ [27]. Assuming that the magnetic hyperfine field μ_0H_{hf} is approximately proportional to the m_{3d} moment a calibration constant $K_1 = m_{3d}/\mu_0H_{hf} = 2\mu_B/22.68T$ can be found (μ_0H_{hf} for $DyFe_2$ – Table 1).

This constant can be used to calculate the $m_{3d}(x)$ moments for the compounds of the considered substituted series from the known $\mu_0H_{hf}(x)$ data (Table 1). It was found later elsewhere for a number of 3d metals and alloys containing 3d metals that there is a linear correlation between the m_{3d} magnetic moment and the splitting energy ΔE of 3d subbands [28,29]. Namely, it was found that this linear correlation can be described by the ratio $K_2 = \Delta E/m_{3d} = eV/\mu_B$ [28,29]. Thus employing the ratios K_1 and K_2 and using the μ_0H_{hf} values it was possible to calculate the splitting energies between the 3d subbands at iron atoms across the considered series. Assuming additionally that the average ΔE_{av} splitting between the 3d subbands in the M sublattice is proportional to the ΔE splitting ($\Delta E_{av} = K_3\,\Delta E$) an effort can be made to relate the magnetic ordering temperatures T_C and the splitting energies ΔE. It was found that a linear correlation between the magnetic ordering temperature T_C and the squared energy ΔE^2 can be observed for both the studied series of the RM_2 type intermetallics, as presented in Fig. 6. The line in Fig. 6 is described by the numerical formula $T_C(\Delta E^2)\,(K) = 171.781(3.029)\,(eV)^{-2}\Delta E^2 - 58.023(11.769)$. Here, it should be mentioned that the crystal structures for these series are the same or almost the same. The compounds of the $Dy(Mn_{1-x}Fe_x)_2$ series have the cu-

bic Laves phase, $Fd3m$, $MgCu_2$ type (C-15) crystal structure [26]. Since there is no analytical formula for T_C, the above linear $T_C(\Delta E^2)$ dependence should, at best, be treated semi-qualitatively. The discussed compounds are relatively new and thus the knowledge related to the 3d band structure is incomplete. Therefore at present a more exhaustive discussion is impossible. In fact, the electronic structures of certain rare earth–transition metal compounds were previously studied experimentally, theoretically and numerically, the band structures were discussed and proposed, for instance in Refs. [30–33]. However, systematic theoretical and numerical studies of the band structure of transition metal/transition metal substituted series and of transition metal/aluminium substituted series, similar to those series considered in the present paper, have not yet been carried out. Thus for a more precise discussion, the knowledge of the band structure of the substituted metallic series would be necessary. For this purpose further sound experimental, theoretical and numerical studies would be helpful.

Acknowledgements

References

[1] K.N.R. Taylor, Adv. Phys. 20 (1971) 551.
[2] K.H.J. Buschow, in: E.P. Wohlfarth (Ed.), Ferromagnetic Materials, vol. 1, North-Holland, Amsterdam, 1980.
[3] E. Burzo, H.R. Kirchmayr, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 12, North-Holland, Amsterdam, 1989.
[4] I.A. Campbell, J. Phys. F: Met. Phys. 2 (1972) L47.
[5] B. Gicala, J. Pszczoła, Z. Kucharski, J. Suwalski, Phys. Lett. A185 (1984) 491.
[6] B. Gicala, J. Pszczoła, Z. Kucharski, J. Suwalski, Solid State Commun. 96 (1995) 511.
[7] H. Maletta, G. Crecelius, W. Zinn, J. Phys. Suppl. 35 (1974) C-6-279.
[8] J. Bara, A. Pędziwiatr, W. Zarek, D. Konopka, U. Gacek, J. Magn. Magn. Mater. 27 (1982) 159.
[9] P. Stoch, J. Pszczoła, P. Guzdek, M. Wzorek, A. Jabłońska, J. Suwalski, L. Dąbrowski, A. Pańta, J. Alloys Compd. 384 (2004) 25.
[10] F. Laves, Naturwissenschaften 27 (1939) 65.
[11] J. Chojnacki, Structural Metallography, Śląsk Press, Katowice, 1966.
[12] J. Pszczoła, A. Feret, B. Winiarska, L. Dąbrowski, J. Suwalski, J. Alloys Compd. 299 (2000) 59.
[13] J. Pszczoła, B. Winiarska, J. Suwalski, Z. Kucharski, J. Alloys Compd. 265 (1998) 15.
[14] J. Pszczoła, B. Gicala, J. Suwalski, J. Alloys Compd. 274 (1998) 47.
[15] J. Pszczoła, J. Żukrowski, J. Suwalski, Z. Kucharski, M. Łukasiak, J. Magn. Magn. Mater. 40 (1983) 197.
[16] A. Ślebarski, J. Less Common Met. 72 (1980) 231.
[17] R.M. Bozorth, Ferromagnetism, Van Nostrand, Princeton, 1968.
[18] J.M. Ziman, Principles of the Theory of Solids, Cambridge University Press, London, 1972.

[19] W. Vonsovskij, Magnetizm, Nauka, Moscow, 1971 (in Russian).
[20] F.J. Blatt, Physics of Electronic Conduction in Solids, McGraw-Hill, Michigan, 1968.
[21] H. Ibach, H. Lüth, Solid State Physics, Springer, Berlin, 1995.
[22] M.A.S. Kobeissi, C. Hohenemser, Hyp. Int. 4 (1978) 480.
[23] C. Hohenemser, N. Rosov, A. Kleinhammes, Hyp. Int. 49 (1989) 267.
[24] J. Pszczoła, Acta Phys. Polon. 96 (1999) 113.
[25] J. Pszczoła, J. Suwalski, Mol. Phys. Rep. 30 (2000) 113.
[26] B. Gicala, J. Pszczoła, Z. Kucharski, J. Suwalski, Nukleonika 39 (1994) 195.
[27] O. Gunnarson, J. Phys. F: Met. Phys. 6 (1976) 587.
[28] F.J. Himpsel, J.E. Ortega, G.J. Mankey, R.F. Willis, Adv. Phys. 47 (1998) 511.
[29] F.J. Himpsel, J. Magn. Magn. Mater. 102 (1991) 261.
[30] K.H.J. Buschow, J. Less Common Met. 43 (1975) 55.
[31] R. Coehoorn, J. Magn. Magn. Mater. 99 (1991) 55.
[32] R. Coehoorn, K.H.J. Buschow, J. Magn. Magn. Mater. 118 (1993) 175.
[33] R.F. Sabirianov, S.S. Jaswal, J. Appl. Phys. 79 (1996) 5942.