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An x-ray diffraction study and calculation of the exchange interaction constant between the rare-earth sublattice and the 3d sublattice of $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compounds

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Abstract. Aluminium-substituted $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ solid solution has been studied by step x-ray diffraction. A Rietveld analysis of the x-ray diffraction indicates that the Al atoms have a high initial affinity for the 18h site, show a high affinity for the 6c site and 18f site at high Al concentrations and are absent from the 9d site at all Al concentrations. The values of intersublattice magnetic coupling constant, $J_{R,T}/k$, are calculated by the molecular field model according to the result of a Rietveld analysis of the x-ray diffraction.

1. Introduction

The relatively low values of Curie temperature for the binary rare-earth (R)–iron intermetallic compounds with $\text{Th}_2\text{Ni}_{17}$ or $\text{Th}_2\text{Zn}_{17}$ structure and the fact that none of them exhibits an easy-axis anisotropy at room temperature restricts the possible application of these materials as permanent magnets [1]. In recent years, it was found that either introducing interstitial atoms such as carbon and nitrogen into the R_2Fe_{17} compounds or substituting other elements for iron atoms in the R_2Fe_{17} compounds can increase their Curie temperature by increasing the iron–iron distances and can improve their magneto-crystalline anisotropy by changing the crystalline field [2–6]. An important parameter in the description of the magnetic properties of these compounds is the intersublattice magnetic coupling constant. The strength of the intersublattice coupling not only determines to some extent the value of the Curie temperature, but it has considerable influence also on the magneto-crystalline anisotropy and its temperature dependence since it couples the strongly anisotropic rare-earth sublattice to the less anisotropic 3d sublattice.

In the previous study, Jacobs, Buschow *et al* described the magnetic properties including the intersublattice coupling constant of $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compounds from magnetic experiments [7]. In this paper, we investigate the crystallographic structure of $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compounds by x-ray diffraction and try to calculate the intersublattice magnetic coupling constant of $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compounds by the molecular field model according to the result of x-ray diffraction.

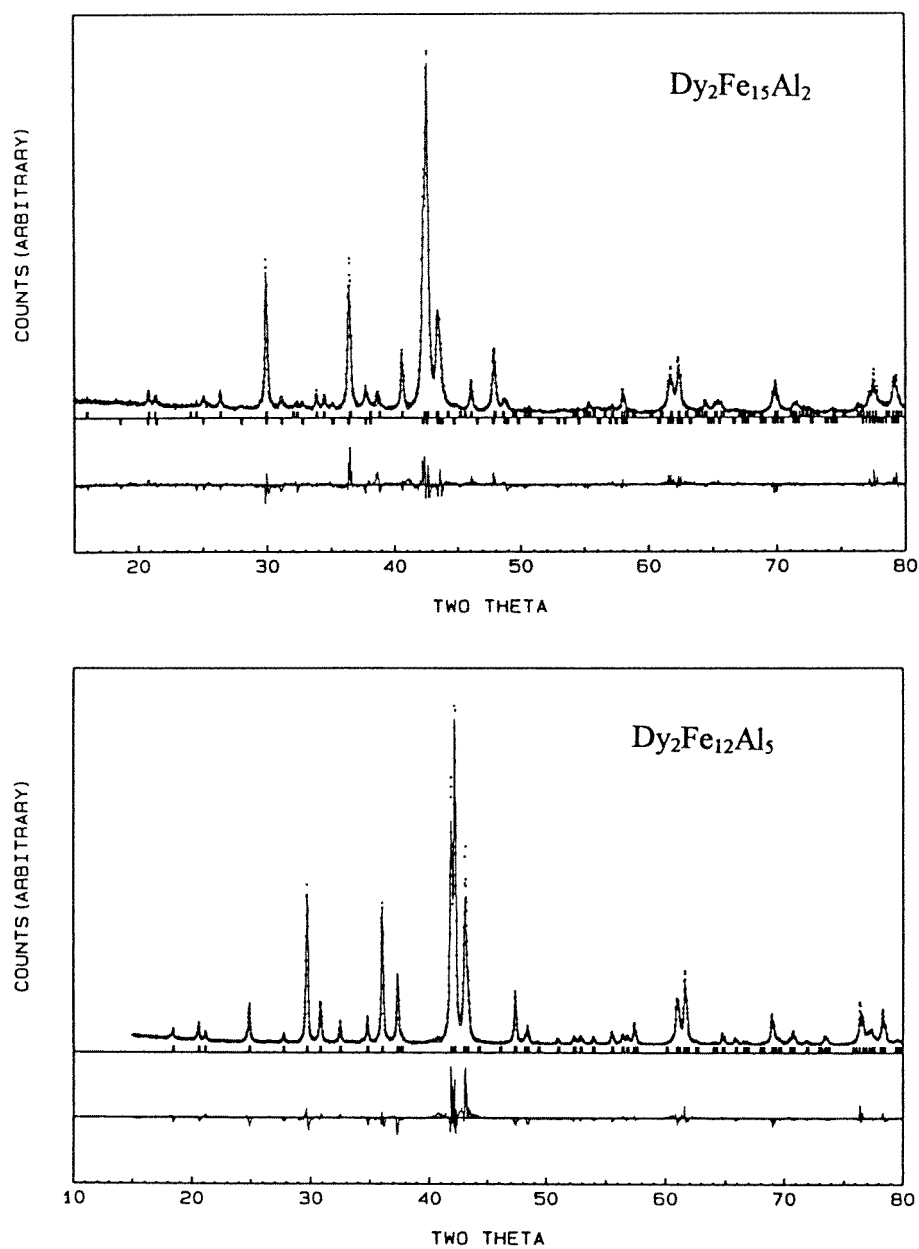


Figure 1. The x-ray powder diffraction patterns for $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ ($x = 2, 5, 8$) at room temperature. The observed and calculated profiles are given by the dotted and solid curves respectively, and the calculated positions are indicated at the bottom. The differences between the observed and calculated data are also given.

2. Experiment

Compounds of $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ with $x = 0, 1, 2, 3, 4, 5, 6, 7, 8$ and 9 were prepared by arc melting in an argon atmosphere of high purity. The raw materials of Dy, Fe and Al were at least

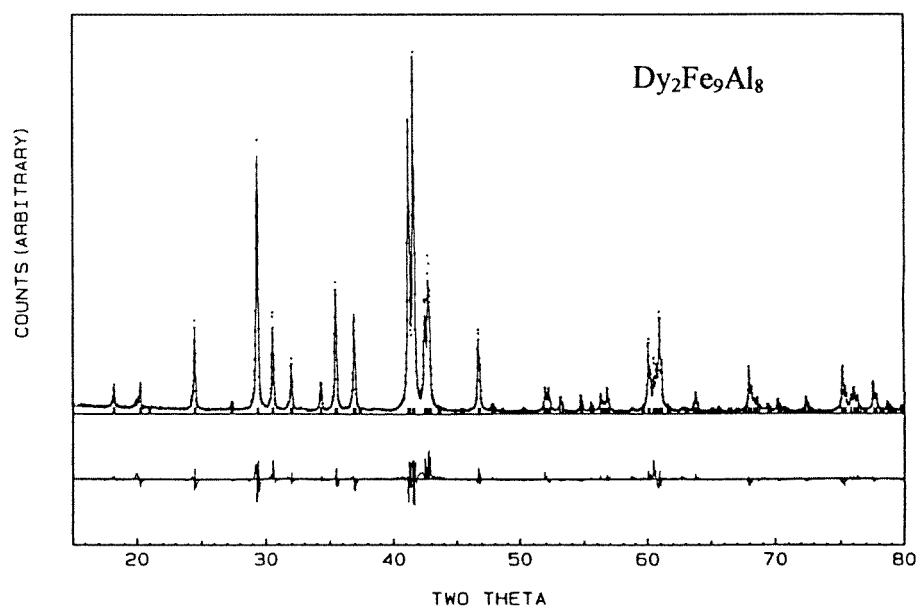


Figure 1. (Continued)

99.9% purity. The ingots were remelted at least three times to ensure their homogeneity. The arc-melted ingots were sealed in a silicon vacuum tube, annealed at 1050 °C for 7 days, and then quenched in water. Powder x-ray diffraction with Cu $K\alpha$ radiation was used to examine the phase structure of the samples.

Step scanning x-ray diffraction patterns were recorded by a Rigaku x-ray diffractometer with Cu $K\alpha$ radiation monochromatized by a single-crystal graphite monochromator. The total (3251 points) data for each sample were collected over 4.5 h by step scanning at 0.02° intervals with 2θ angle from 15 to 80°. The parameters of the crystallographic structure of Th_2Ni_{17} type (for $x = 0$ and 1) and Th_2Zn_{17} type (for $x \geq 4$) or both ($x = 2$ and 3) compounds were used to start the refinement. It was assumed that Fe and Al atoms occupy simultaneously 6g (9d), 12j (18f), 12k (18h) and 4f (6c) sites with the linear condition that the sum of the occupancies of Fe and Al atoms at each of the four sites equals 1.0.

3. Results and discussion

X-ray diffraction patterns show there exists a structure change from the Th_2Ni_{17} hexagonal for $x < 2$ to the Th_2Zn_{17} rhombohedral phase for $x \geq 4$, and coexistence of those two phases for $x = 2$ and 3. Examples of diffraction patterns for $x = 2, 5$ and 8 are shown in figure 1. The results of the refinement of the powder x-ray diffraction patterns for the $Dy_2Fe_{17-x}Al_x$ samples are given in tables 1 and 2. The unit-cell volumes of the $Dy_2Fe_{17-x}Al_x$ compounds derived from the x-ray diffraction show a linear increase with increasing aluminium concentration as can be seen in figure 2; they agree very well with that observed for the same compounds reported elsewhere [7]. The total aluminium content in the $Dy_2Fe_{17-x}Al_x$ compounds, as calculated from the refined fractional occupancies, is in good agreement with the nominal aluminium content.

The concentration dependence of the four crystallographic sites in $Dy_2Fe_{17-x}Al_x$ compounds is shown in figure 3; this is similar to that observed in $Nd_2Fe_{17-x}Al_x$

Table 1. The lattice and positional parameters and site occupancies in the Th₂Zn₁₇ rhombohedral Dy₂Fe_{17-x}Al_x compounds.

	$x = 2.01$	$x = 3.10$	$x = 3.98$	$x = 5.01$	$x = 6.01$	$x = 7.27$	$x = 7.89$	$x = 8.89$
a (Å)	8.5466(3)	8.5783(1)	8.5973(2)	8.6306(2)	8.6665(1)	8.7072(1)	8.7470(2)	8.7794(1)
b (Å)	12.4641(2)	12.4998(3)	12.5515(2)	12.5911(1)	12.6195(3)	12.6404(2)	12.6648(1)	12.7141(1)
v (Å ³)	788.43	796.57	803.41	812.20	820.82	829.92	839.14	848.66
Dy,6c,z	0.3379(2)	0.3385(1)	0.3394(3)	0.3402(2)	0.3439(1)	0.3461(2)	0.3492(2)	0.3494(3)
Fe/Al,6c,z	0.0967(2)	0.0969(4)	0.0968(1)	0.0979(4)	0.0983(2)	0.1023(1)	0.1067(1)	0.1114(1)
Fe/Al,18f,x	0.2954(3)	0.2957(4)	0.2972(3)	0.2976(1)	0.2972(2)	0.2977(1)	0.2978(2)	0.2958(2)
Fe/Al,18h,x	0.1674(3)	0.1678(4)	0.1682(1)	0.1681(4)	0.1682(3)	0.1679(3)	0.1681(3)	0.1676(2)
Fe/Al,18h,z	0.4912(2)	0.4919(2)	0.4923(2)	0.4924(3)	0.4923(1)	0.4902(3)	0.4910(1)	0.4906(1)
% Al,9d	0	0	0	0	0	0	0	0
% Al,6c	10.8(2)	12.3(1)	16.4(2)	23.3(3)	38.0(2)	63.9(3)	77.3(3)	90.2(1)
% Al,18f	7.1(1)	13.9(2)	21.6(1)	30.2(1)	41.3(2)	57.1(1)	68.7(2)	82.8(2)
% Al,18h	22.9(2)	33.7(2)	39.2(4)	45.6(1)	46.2(1)	42.8(2)	37.1(1)	36.3(1)
R_w (%)	12.83	14.09	14.09	12.72	12.74	12.51	12.83	14.90
R_e (%)	6.24	6.48	6.01	6.24	5.95	5.83	5.86	5.69

Table 2. The lattice and positional parameters and site occupancies in the Th₂Ni₁₇ hexagonal Dy₂Fe_{17-x}Al_x compounds.

	$x = 0$	$x = 1.00$	$x = 2.01$	$x = 3.01$
a (Å)	8.4653(2)	8.4901(2)	8.5233(2)	8.5550(2)
c (Å)	8.2962(1)	8.3109(1)	8.3324(1)	8.3601(1)
v (Å ³)	514.85	518.79	524.21	529.87
Fe/Al,4f,z	0.1207(1)	0.1162(2)	0.1104(1)	0.1092(1)
Fe/Al,12k,x	0.1653(2)	0.1638(1)	0.1634(2)	0.1610(2)
Fe/Al,12k,z	0.9890(2)	0.9870(3)	0.9763(3)	0.9642(3)
Fe/Al,12j,x	0.3261(3)	0.3264(2)	0.3284(2)	0.3287(2)
Fe/Al,12j,y	0.9698(3)	0.9677(1)	0.9643(1)	0.9642(2)
% Al,6g	0	0	0	0
% Al,4f	0	7.1(1)	10.8(2)	12.3(1)
% Al,12j	0	3.1(1)	7.1(1)	13.9(2)
% Al,12k	0	11.2(1)	22.9(2)	33.7(2)
R_w (%)	14.49	12.75	12.83	14.09
R_e (%)	6.41	6.19	6.24	6.48

compounds [8]. Because aluminium atoms have larger metallic radii than iron atoms, they avoid the iron 9d, the site which has the smaller Wigner–Seitz cell volume [9–11], for the whole series, and the 6c site, which has the largest Wigner–Seitz cell volume, initially takes up aluminium slowly, but at high aluminium content this site approaches 92% aluminium occupancy. At low aluminium concentration, the aluminium atoms prefer the 18h site, which has a volume next to the largest Wigner–Seitz cell volume [9–11], but the aluminium population of this site appears to saturate at about 47%, and the aluminium occupying the 18f site increases monotonically with increasing aluminium content x . Once a specific site is occupied by aluminium, its near neighbours are less likely, because of crowding, to accept aluminium, except for the 9d site: then its near neighbours are *more* likely to accept aluminium. Thus, because the 9d site has four 18h and four 18f near neighbours: these latter sites are more likely to accept aluminium. Unfortunately there seems to be no simple explanation for the added preference of aluminium for the 18f site at the concentration above $x = 6$. The adjacent atom number of the 6c site are

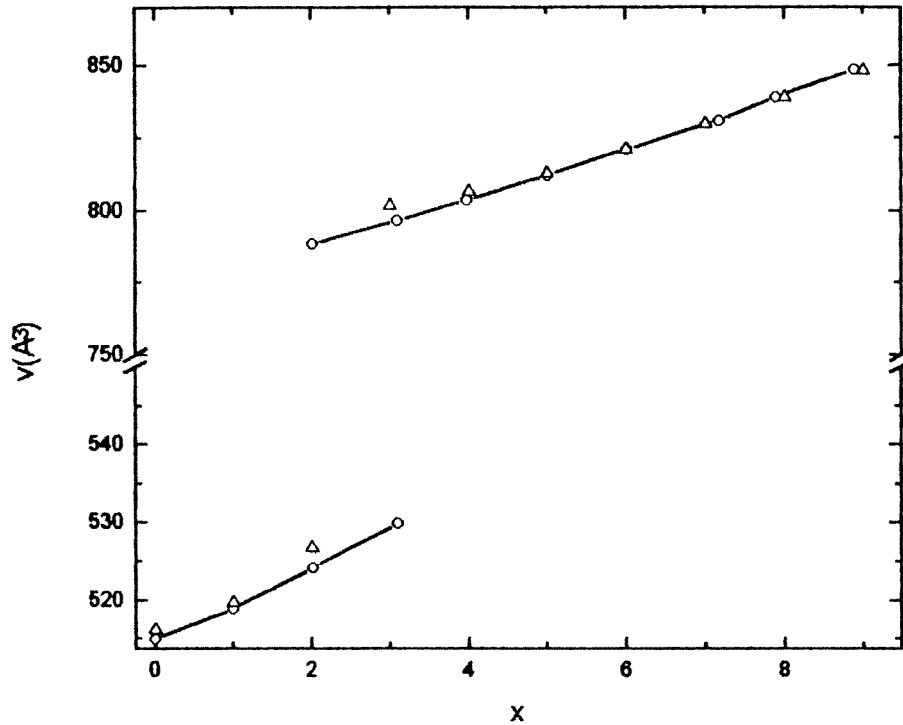


Figure 2. Concentration dependence of the unit-cell volumes of the compounds $Dy_2Fe_{17-x}Al_x$. The values marked by Δ were taken from [7].

Table 3. The exchange interaction constant $J_{Dy,Fe}$ and the magnetic parameters in $Dy_2Fe_{17-x}Al_x$ compounds.

Compounds	T_c [7] (K)	M_S [7] (μ_B fu $^{-1}$)	M_{Fe} (μ_B fu $^{-1}$)	S_{Fe}	$Z_{Dy,Fe}$	$Z_{Fe,Dy}$	$-J_{RT}$ [7]/k (exp) (K)	$-J_{Dy,Fe}/k$ (calc.) (K)
Dy_2Fe_{17}	371	16.0	36.0	1.06	19	2.24	—	8.12
$Dy_2Fe_{16}Al$	404	12.9	32.9	1.03	18.97	2.37	—	7.01
$Dy_2Fe_{15}Al_2$	436	9.5	29.5	0.98	16.41	2.19	—	7.77
$Dy_2Fe_{14}Al_3$	451	7.0	27.0	0.96	15.01	2.14	—	8.69
$Dy_2Fe_{13}Al_4$	436	4.0	24.0	0.92	14.01	2.16	9.04	7.21
$Dy_2Fe_{12}Al_5$	395	0.7	20.7	0.86	12.85	2.14	8.77	9.69
$Dy_2Fe_{11}Al_6$	319	0.8	19.2	0.87	11.98	2.18	9.25	11.34
$Dy_2Fe_{10}Al_7$	237	2.3	17.7	0.89	11.08	2.22	10.1	11.48
$Dy_2Fe_9Al_8$	210	3.7	16.3	0.91	10.78	2.39	10.9	12.52

many including one 6c, six 9d, six 18f and six 18h near neighbours and the distance between the 6c and the 6c site is the shortest distance. Both factors cause the interaction between the Fe atom of the 6c site and its adjacent atoms to be very strong, so the Fe atom of the 6c site is usually difficult to replace by another atom. Thus the 6c site is occupied by aluminium slowly at low aluminium content.

Since Al has no magnetic moment, the intersublattice coupling constant $J_{R,T}$ in the $Dy_2Fe_{17-x}Al_x$ compounds is in fact equal to the intersublattice coupling constant $J_{Dy,Fe}$, of Dy and Fe moments. In the molecular field approximation, values of $J_{Dy,Fe}$ for $Dy_2Fe_{17-x}Al_x$

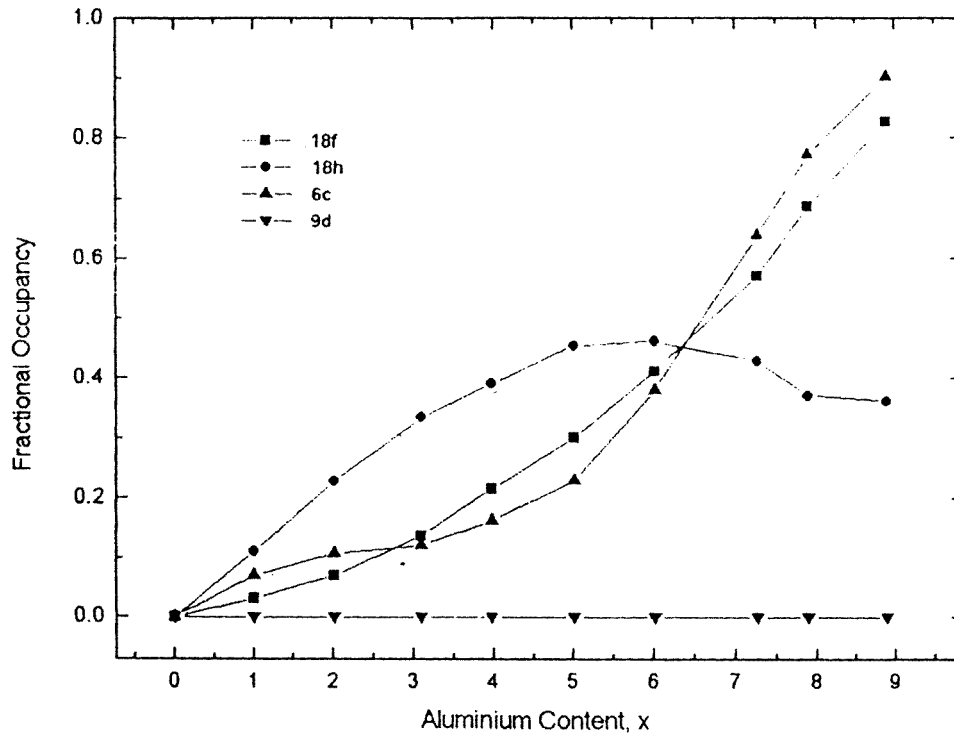


Figure 3. The compositional dependence of the aluminium fractional occupancy on the different crystallographic sites in the $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ solid solutions.

compounds can be estimated by the following expression [12]:

$$\left(\frac{J_{\text{Dy,Fe}}}{k}\right)^2 = \frac{9(T_C - T_{\text{Dy}})(T_C - T_{\text{Fe}})}{4G_{\text{Dy}}G_{\text{Fe}}Z_{\text{Dy,Fe}}Z_{\text{Fe,Dy}}}$$

Here, G_{Dy} is the De Gennes factor $(g_{\text{Dy}} - 1)^2 J_{\text{Dy}}(J_{\text{Dy}} + 1)$ for the rare-earth Dy atom. G_{Fe} is the corresponding De Gennes factor for the transition-metal Fe atom. Usually, the orbital moment of the Fe atom is assumed to be quenched, so one takes $g_{\text{Fe}} = 2$, $J_{\text{Fe}} = S_{\text{Fe}}$ and $G_{\text{Fe}} = S_{\text{Fe}}(S_{\text{Fe}} + 1)$. Furthermore, the interaction between the rare-earth moments is neglected, so T_{Dy} is taken to be zero. The Curie temperature T_{Fe} can be determined from the experimental data obtained on isostructural compounds $\text{Y}_2\text{Fe}_{17-x}\text{Al}_x$ in which the Dy atoms are replaced by non-magnetic atoms Y. The effective spin value S_{Fe} can be determined from the experimental data M_S of $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compounds

$$S_{\text{Fe}} = \frac{1}{2} \frac{M_{\text{Fe}}}{(17-x)\mu_B}$$

where x is the aluminium content in $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compounds. Assuming that in the investigated compounds Dy has a free-ion moment of $10\mu_B$ and that the coupling between the Dy and 3d sublattice is antiparallel, one can obtain values for the magnetization of the transition-metal sublattice, $M_{\text{Fe}} = M_S - 20\mu_B$. $Z_{\text{Dy,Fe}}$ is the number of 'nearest' Fe neighbours of the Dy atom. In the $\text{Dy}_2\text{Fe}_{17}$ compound, Dy (6c site) has 19 iron near neighbours consisting of one Fe 6c, three Fe 9d, six Fe 18f and nine Fe 18h sites. In $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compounds, one

can calculate $Z_{Dy,Fe}$ according to the result of x-ray diffraction refinement.

$$Z_{Dy,Fe} = y_{6c} + 3y_{9d} + 6y_{18f} + 9y_{18h}$$

where y_i ($i = 6c, 9d, 18f$ and $18h$) is the iron fractional occupancy on the i site. The value of $Z_{Fe,Dy}$ is related to $Z_{Dy,Fe}$ via the relation [12]

$$N_{Dy}Z_{Dy,Fe} = N_{Fe}Z_{Fe,Dy}$$

where N_{Dy} ($=2$) is the number of Dy atoms in one unit cell of $Dy_2Fe_{17-x}Al_x$ compounds. N_{Fe} ($=17-x$) is the number of Fe atoms in one unit cell of $Dy_2Fe_{17-x}Al_x$ compounds.

We used the experimental saturation moment, M_S , and Curie temperature, T_C , of $Dy_2Fe_{17-x}Al_x$ compounds in [7] and the experimental Curie temperature $T_{C,Y}$ ($=T_{Fe}$) of $Y_2Fe_{17-x}Al_x$ compounds in [13] to calculate $J_{Dy,Fe}/k$ of $Dy_2Fe_{17-x}Al_x$ compounds. The calculated values, $-J_{Dy,Fe}/k$, of $Dy_2Fe_{17-x}Al_x$ compounds for $x = 4, 5, 6, 7$ and 8 are 7.21, 9.69, 11.34, 11.48 and 12.52, respectively, and are similar to the values, $-J_{R,T}$, derived from the high-field measurement in [7], which are 9.04, 8.77, 9.25, 10.1 and 10.9, respectively, for $x = 4, 5, 6, 7$ and 8 , listed in table 3. One assumes that the difference between the calculated $J_{Dy,Fe}/k$ and the values, $-J_{R,T}$ in [7] is maybe in part correlated with the neglect of the interaction between the rare-earth moments.

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