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Neutron structure analysis and magnetic properties of $Ho_2Fe_{17-x}Ga_x (x = 5, 8)$

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Abstract. The crystallographic and magnetic structures of $Ho_2Fe_{17-x}Ga_x (x = 5, 8)$ compounds at room temperature were refined by Rietveld analysis of the neutron powder diffraction data. The analysis indicates that $Ho_2Fe_{17-x}Ga_x (x = 5, 8)$ compounds have Th_2Zn_{17} type structure (SG $R\bar{3}m$). For $x = 5$ Ga atoms partially occupy 18h and 18f sites with the occupancies of 0.40 and 0.43, and for $x = 8$ they occupy 18h, 18f and 6c sites with the occupancies of 0.20, 0.80 and 1.0 respectively. The magneto-anisotropy changes from easy planar to easy-axial when the Ga content x increases from 5 to 8. The magnetic measurements show that the magnetic ordering temperature T_c increases abnormally with Ga content x increasing from 6.5 to 8. This paper gives a reasonable explanation for this phenomenon.

1. Introduction

The rare earth–iron compounds of R_2Fe_{17} type have attracted much attention in recent years as possible high-performance permanent magnetic materials. The high Fe concentration yields high saturation magnetization while maintaining a low cost. However these series of alloys have two drawbacks: relatively low values of Curie temperature and the fact that none of them exhibits easy-axis magneto-anisotropy at room temperature. Extensive studies showed that substitutions of other elements (for example Al, Ga) for Fe in R_2Fe_{17} type compounds increase Curie temperature [1–7], but only $Sm_2Fe_{17-x}Al_x$ for $x > 2$ [2] and $Sm_2Fe_{17-x}Ga_x$ for $x > 1$ [7] exhibit easy-axial anisotropy.

Recently Hu *et al* [8] reported that $Tb_2Fe_{17-x}Ga_x$ compounds exhibit easy-axis anisotropy for Ga content $x = 8$. Shen *et al* [9, 10] found that the magnetic ordering temperature T_c of $R_2Fe_{17-x}Ga_x$ (R=Y, Sm, Gd, Dy, Ho, Er and Tb) compounds increases significantly when Ga content x increases from $x = 6.5$ to $x = 8$.

This paper reports a neutron structure analysis on $Ho_2Fe_{17-x}Ga_x$ ($x = 5, 8$) and presents a physical explanation of the relation between the structural and magnetic properties in the compounds with high Ga contents.

2. Experiment and refinement

The samples $Ho_2Fe_{17-x}Ga_x$ ($x = 1, 2, \ldots, 8$) were prepared by arc melting high-purity Ho (99.9% purity), Fe (99.9% purity) and Ga (99.99% purity) in an argon furnace. The

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ingots were then ground to yield powder samples. The samples were examined by x-ray diffraction. The x-ray patterns show that these samples crystallize into a single phase with R_2Fe_{17} type structure. The magnetic ordering temperatures T_c of these compounds were measured by means of a vibrating sample magnetometer. The dependence of T_c on Ga content x is shown in figure 1. First, the T_c increases due to the volume expanding effect in the compounds [8]. Then, it decreases with Ga content x increasing from 3 to 6.5: the reason is that the magnetic dilution effect (magnetic Fe atoms are replaced by non-magnetic Ga atoms), which reduces total magnetic exchange interaction [8], becomes a predominant factor in this case. Finally, T_c increases unusually again when Ga content x increases from 6.5 to 8. This means there must be some effect which compensates the magnetic dilution effect of Ga and plays an important role in increasing T_c.

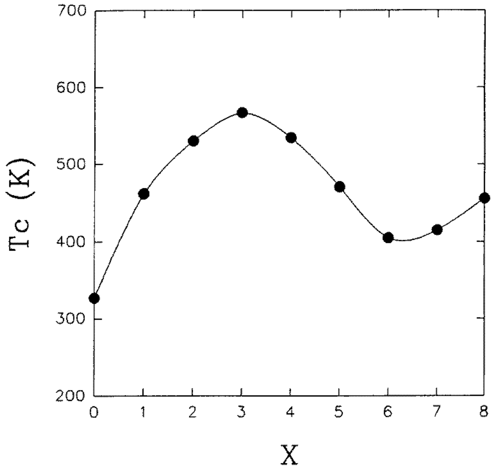


Figure 1. Magnetic ordering temperature T_c against Ga content x for $Ho_2Fe_{17-x}Ga_x$ ($x = 5, 8$).

In the experiments for preparing samples, it was found that it was extremely hard to obtain a single-phase sample with Ga content $x = 6.5$. The sample with $x = 6.5$ may be a multiphase mixture and was unsuitable for neutron Rietveld refinement. Here, the samples with $x = 5$ and $x = 8$ were used in neutron structural analyses.

The neutron powder diffraction data were collected using a high-resolution powder diffractometer with a multi-detector system installed at neutron guide No 2 (NGT-2), Material Science Research Centre, attached to the multi-purpose research reactor GA Siwabessy (RSG GAS), Serpong, Indonesia. The neutron wavelength $\lambda = 1.8215$ Å, monochromatized using a 'hot-pressed' Ga(331) single crystal, was used for data collection. About 10 g of the powder sample were used and placed in a vanadium tube. The total 3200-point data were collected with a step counting method, 0.05°/step. The powder diffraction patterns of $Ho_2Fe_{17-x}Ga_x$ ($x = 5, 8$) are shown in figure 2. The data were analysed with Rietveld structure refinement program RIETAN94 [11]. The parameters of the crystallographic structure [12] of Th_2Zn_{17} type rare earth–iron compounds were used to start the refinement. Initially, only the parameters describing zero point, background, full width at half maximum of the reflections and unit cell dimensions were refined, assuming Ga and Fe atoms occupy 9d, 18f, 18h and 6c sites according to the chemical composition and with all the magnetic moments in collinear arrangement. Secondly, we refined the occupancies of Ga and Fe atoms at four sites and the magnetic moments of all magnetic atoms. The result implied that Ga atoms occupy only 18h and 18f sites, and are absent from the other two sites for the sample with $x = 5$. Nevertheless, they occupy 18h, 18f and 6c sites for the sample of $x = 8$. After that, the atomic coordinates of Ho, Fe and Ga atoms and the temperature factors on different sites were refined. The last refinement included all parameters and the weighted pattern R-factor R_{wp} converged to 11.88 and 10.68% (expected R-factor $R_{exp} = 7.13$ and 4.21%) corresponding to $x = 5$ and $x = 8$ respectively.

The refined crystallographic and magnetic parameters are listed in table 1 and the Fe–Fe bond lengths in table 2. Refined magnetic structure parameters show that the magnetic moments of all Fe atoms display ferromagnetic coupling, but the magnetic moments of Ho antiferromagnetically couple to those of Fe atoms. The magnetic moments of all atoms lie in the planes perpendicular to the sixfold axes and display easy-planar anisotropy for $x = 5$. Nevertheless, the magnetic moments of all atoms oriented to sixfold axes and exhibit an easy-axial anisotropy for $x = 8$. The most remarkable change in structure is the positions of Ga atoms. For $x = 5$ Ga only substitute the Fe on 18f and 18h sites with nearly the same occupancies (0.42 and 0.40 respectively), but for $x = 8$, Ga substitute all the Fe on 6c, 80% of Fe on 18f and 20% of Fe on 18h sites. The schematic plots of Ga and Fe positions are shown in figure 3.

3. Discussion

The dependence of T_c on Ga content in the $Tb_2Fe_{17-x}Ga_x$ compounds has been discussed when $x < 6.5$ [1, 8]: the volume expansion effect is predominant and increases T_c for $x < 3.0$; T_c reaches a maximum value at $x = 3$, then the magnetic dilution effect (due to Ga substitution) is predominant and decreases T_c for $3 < x < 6.5$. The abnormal increase of T_c for $6.5 < x < 8$ is a new phenomenon and will be discussed within the molecular field theory.

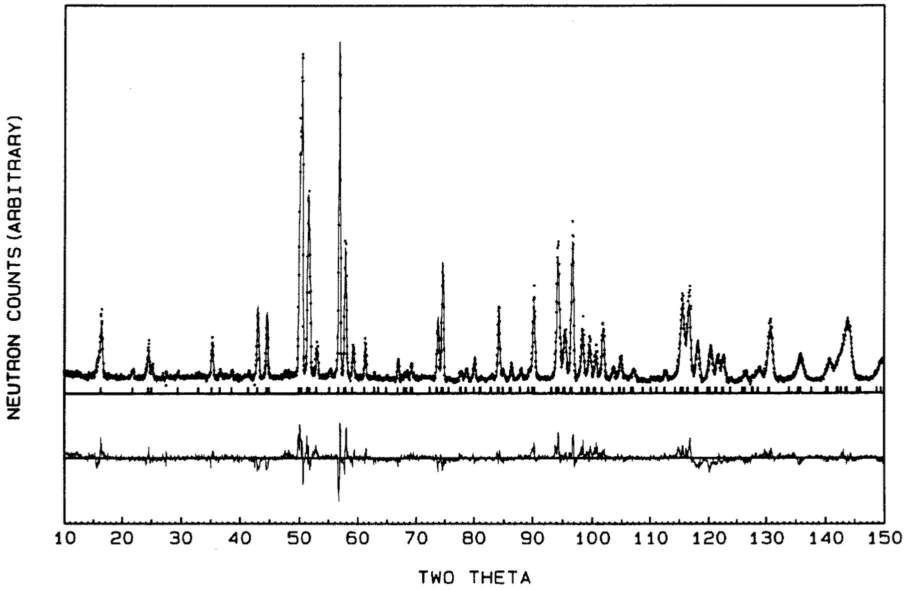
Néel molecular field theory expressed the proportional relation between magnetic ordering temperature T_c and Fe–Fe, R–Fe magnetic exchange interactions α_{tt}, α_{rt} (α_{tr}) of rare earth–iron compounds as follows:

$$\begin{aligned} 3kT_c &= \alpha_{tt} + [\alpha_{tt}^2 + 4\alpha_{rt}\alpha_{tr}]^{1/2} \\ \alpha_{tt} &= Z_{tt}J_{tt}S_t(S_t+1) \\ \alpha_{rt}\alpha_{tr} &= Z_{rt}J_{tr}S_t(S_t+1)(g_t+1)^2J(J+1)J_{rt} \end{aligned} \tag{1}$$

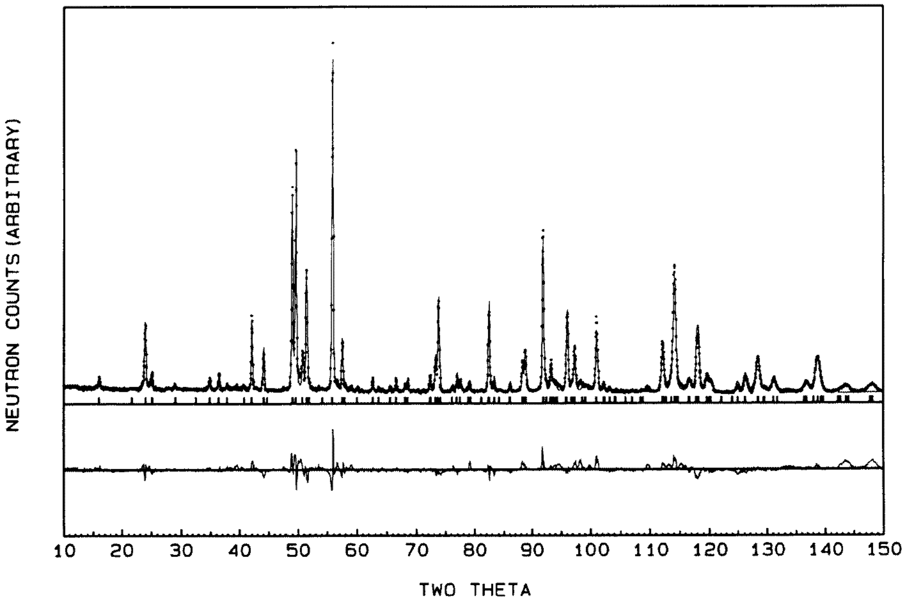
where Z_{tt} and Z_{tr} are mean Fe neighbour numbers around Fe and R atoms respectively.

The total magnetic exchange interaction can be obtained from the summation of Fe–Fe, R–R and R–Fe magnetic interactions. In rare earth–iron compounds, comparing with the Fe–Fe and R–Fe direct magnetic interactions, the indirect (RKKY type) R–R exchange interaction is so weak that it is neglected in formula (1). In most cases, the contribution of R–Fe interaction to T_c is relatively weaker than that of the Fe–Fe exchange interaction, so the Fe–Fe interactions predominantly determine the magnetic ordering temperature T_c in rare earth–iron compounds if T_c of the compounds is much higher than the T_c of rare earth elements. For example, the T_c of R_2Fe_{17} compounds depend weakly on rare earth elements.

Fe–Fe exchange interaction (or T_c) increases with Ga content x in the region of $6.5 \leqslant x \leqslant 8$. This shows that the substitution of Ga for Fe in this region contributes a net positive effect on T_c after compensating the negative magnetic dilution effect of the Ga atom. According to formula (1), Fe–Fe exchange interaction in $Ho_2Fe_{17-x}Ga_x$ depends mainly on Fe–Fe exchange integral J_{tt} and mean Fe–Fe neighbour number Z_{tt}. Although the mean Fe–Fe neighbour number Z_{tt} for $x = 8$ is less than that for $x = 6.5$, yet T_c



(a)



(b)

Figure 2. Powder diffraction patterns for $Ho_2Fe_{12}Ga_5$ (a) and $Ho_2Fe_9Ga_8$ (b). Observed and calculated profiles are given by dotted and solid curves. The calculated peak positions are indicated at the bottom. The differences between observed and calculated data are given.

for $x = 8$ is higher than that for $x = 6.5$. So, J_{tt} for $x = 8$ should be far greater than that for $x = 6.5$, because it needs to compensate the loss of Z_{tt}. The Bethe–Slater curve

Table 1. Crystallographic and magnetic parameters of $\mathrm{Ho_2Fe_{17-x}Ga_x}$ ($x = 5, 8$). Rhombohedral cell. Space group: $R\bar{3}m$.

Atom		$x = 5$	$x = 8$
Cell constant	a	8.627(2)	8.7838(2)
	c	12.623(2)	12.603(2)
Ho(6c)	$x = y = 0$		
	z	0.3406(18)	0.3549(13)
	B	0.3(3)	0.14(4)
	$M(\mu_B)$	−3.5(7)	−2.6(4)
Fe(9d)	$x = z = 0.5,\ y = 0$		
	B	0.6(3)	0.6(3)
	$M(\mu_B)$	0.8(5)	1.2(5)
Fe(18h)	o.f.	0.60	0.80
	$x = -y$	0.1686(8)	0.1659(10)
	z	0.4882(9)	0.4919(10)
	B	0.4(2)	0.5(2)
	$M(\mu_B)$	0.6(8)	1.5(5)
Fe(18f)	o.f.	0.57	0.20
	x	0.2915(9)	0.3117(16)
	$y = z = 0$		
	B	0.2(2)	1.0(3)
	$M(\mu_B)$	1.2(9)	1.0(8)
Fe(6c)	o.f.	1	0
	$x = y = 0$		
	z	9.6488(14)	
	B	0.8(3)	
	$M(\mu_B)$	1.5(6)	
Ga(18f)	occupy Fe(18f)		
	o.f.	0.43	0.80
Ga(18h)	occupy Fe(18h)		
	o.f.	0.40	0.20
Ga(6c)	o.f.	0	1
	$x = y = 0$		
	z		0.1182(20)
	B		1.0(5)
polar angle	ϕ	90	0

[13] described the dependence of the exchange integral of a pure 3d transition metal on the ratio of R/R_d (where R represents the interatomic distance, and R_d the mean radius of the electron clouds). It reveals that bond length plays an important role in affecting the exchange integral. Table 2 shows the Fe–Fe bond lengths for $x = 5$ and $x = 8$. When Ga content x increases from 5 to 8, the Fe–Fe bond lengths which are larger than 2.54 Å become shorter (the average bond lengths larger than 2.54 Å are 2.670 and 2.603 Å corresponding to $x = 5$ and 8 respectively), and the Fe–Fe bond lengths which are shorter than 2.54 Å become longer (the average bond lengths shorter than 2.54 Å are 2.487 and 2.532 Å corresponding to $x = 5$ and 8 respectively). The only obvious exception is the bond length between Fe(18f) and Fe(18f), but the concentration of Fe on the 18f site becomes quite small (20%) in the case of $x = 8$, so its contribution to T_c is rather smaller. It seems that all the Fe–Fe bond lengths converge to some value around 2.54 Å, which is the value of the Fe–Fe bond length in α-Fe.

In the case of $x = 5$ the Ga atom only occupies 18f and 18h sites with nearly the same occupancies, but in the case of $x = 8$ Ga atoms substitute all the Fe atoms in 6c sites, and

Table 2. Fe–Fe bond lengths (Å) of $Ho_2Fe_{17-x}Ga_x$ $(x = 5, 8)$.

	$x = 5$	$x = 8$
Fe(9d)–Fe(18f)	2.468(4)	2.512(7)
Fe(9d)–Fe(18h)	2.481(5)	2.544(7)
Fe(9d)–Fe(6c)	2.643(5)	
Fe(18f)–Fe(18h)(1)	2.592(10)	2.593(11)
Fe(18f)–Fe(18h)(2)	2.654(11)	2.598(11)
Fe(18f)–Fe(6c)	2.793(10)	
Fe(18h)–Fe(6c)	2.669(10)	
Fe(18f)–Fe(18f)	2.515(6)	2.738(9)
Fe(18h)–Fe(18h)	2.537(8)	2.532(10)
Fe(6c)–Fe(6c)	2.432(23)	
average(< 2.54)	2.487(7)	2.532(10)
average(> 2.54)	2.670(9)	2.603(9)

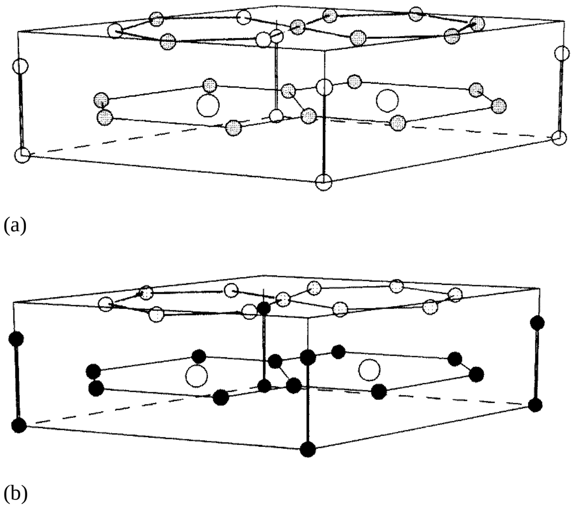


Figure 3. Schematical plots of Fe and Ga positions for $Ho_2Fe_{12}Ga_5$ (a) and $Ho_2Fe_9Ga_8$ (b). Large circles represent Ho atoms and small circles represent Fe/Ga atoms with intensity of shading representing Ga concentration.

occupy 18f and 18h sites with occupancies of 0.80 and 0.20 respectively. The configurations of Fe and Ga atoms for $x = 5$ and $x = 8$ are plotted schematically in figure 3(a) and (b) respectively. Large circles represent Ho atoms, and small circles represent Fe and Ga atoms with intensity of shading representing Ga concentration. For $x = 8$, the configuration of Fe and Ga atoms is nearly a magnetic/non-magnetic layer stacking structure, which might be better for exchange interaction.

Neutron structure analysis indicated that the samples of $x = 5$ and 8 exhibit easy-planar and easy-axial anisotropy respectively at room temperature (the following discussions are all for room temperature). Yan *et al* [14] reported that the samples of $Y_2Fe_{12}Ga_5$ and $Y_2Fe_{10}Ga_7$ also exhibit easy-planar and easy-axial anisotropy respectively. This means that this phenomenon is independent of rare earth element. In $R_2Fe_{17-x}Ga_x$ compounds, the total magnetocrystalline anisotropy is the sum of the contribution of rare earth sublattices and Fe sublattices. For R=Y, the non-magnetic element Y makes no contribution to the total magnetocrystalline anisotropy, but Fe sublattices determine it. Increasing Ga content x from 5 to 7, it is the contribution of Fe sublattices that reverses the sign of total magnetocrystalline anisotropy. In the case of R=Ho, total magnetocrystalline anisotropy varies in a similar manner as R=Y. Therefore, it is reasonable to propose that Fe sublattices dominate the total magnetocrystalline anisotropy. As Ga content x increases from 5 to 8, all the Fe atoms at 6c sites are substituted by Ga atoms and Fe occupancies at 18f and 18h vary from about 0.4 to 0.2 and 0.8 respectively; only the Fe occupancy at the 9d site maintains unchanged. These nonuniform substitutions of Ga atoms may be related to the change of magnetocrystalline anisotropy. The sum of the magnetocrystalline anisotropy of 9d, 18f and 18h sites must be positive for $x = 8$, and that of the 6c site might be negative for $x = 5$.

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