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Neutron diffraction studies of $Ho_2Fe_9Ga_{8-x}Al_x$ $(x = 2, 4)$ at 50 K and 300 K

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Abstract. The crystallographic and magnetic structures of $Ho_2Fe_9Ga_{8-x}Al_x$ $(x = 2, 4)$ were studied by powder neutron diffraction at 50 K and 300 K. The atom fractional occupancies of gallium and aluminium and the magnetic moments of Ho and Fe atoms were obtained by a Rietveld analysis program. The gallium atoms occupy preferentially 18f sites, but aluminium atoms prefer to occupy 6c sites. The magnetic moments of the phase with the $x = 2, 4$ at 50 K and $x = 2$ at 300 K show uniaxial anisotropy. A qualitative explanation for this result is given.

1. Introduction

In recent years, the rare-earth–iron intermetallic compounds R_2Fe_{17} have been extensively investigated as possible high-performance permanent magnets [1–7]. They have two drawbacks: relatively low Curie temperature and few of them exhibit easy-axis magnetocrystalline anisotropy. These drawbacks have restricted the possible applications of these materials as permanent magnets.

In order to improve the room-temperature uniaxial anisotropy of these compounds, many studies have been focused on substituting other elements into the R_2Fe_{17} structure.

Recently Hu *et al* [8] reported that $Tb_2Fe_9Ga_8$ compound exhibits easy-axis anisotropy by the substitution of Ga for Fe element. Because Ho is a near-neighbour element of Tb, then we can expect that for Ho_2Fe_{17} compounds, if the Fe is substituted by Ga, it is also possible to exhibit easy-axis anisotropy.

In this paper, the crystallographic and magnetic structure of $Ho_2Fe_9Ga_{8-x}Al_x$ $(x = 2, 4)$ were studied by neutron diffraction. The neutron diffraction experiments were done at 50 K and 300 K, and the site occupancies of the Al and Ga atoms and the magnetic moments of the Ho and Fe atoms were determined. As was expected, the $Ho_2Fe_9Ga_{8-x}Al_x$ $(x = 2, 4)$ compounds exhibit easy-axis anisotropy.

2. Experiments and results

The samples $Ho_2Fe_9Ga_{8-x}Al_x$ $(x = 2, 4)$ were prepared by arc melting high-purity starting materials Ho (99.9%), Fe (99.9%), Ga (99.9%) and Al (99.9%) in an argon arc furnace and

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were annealed in a quartz tube under an argon atmosphere at 1150 °C for 24 hours. The ingots were then ground to yield fine powder samples. The x-ray diffraction indicated that the samples were all pure Th_2Zn_{17} type structure (space group $R\bar{3}m$).

The neutron diffraction measurements at 50 K were carried out on a high-resolution powder diffractometer with a multi-detector system installed at neutron guide tube No 2 (NGT-2), at the Materials Science Research Centre attached to the multi-purpose research reactor, G A Siwabessy (RSG-GAS), Serpong, Indonesia. The incident neutron wavelength λ was 1.8215 Å. The samples were contained in a vanadium can and stored in the cryostat. The temperature was kept at 50 ± 0.1 K during the measurement period. The neutron diffraction data were collected by step scanning at 0.05° intervals with the range of 2.50–162.45°.

The neutron diffraction patterns at 300 K were measured on a neutron triple-axis spectrometer beside the heavy-water research reactor at the China Institute of Atomic Energy. The incident neutron wavelength is 1.541 Å. The scanning measurements were done with 0.1° step intervals and the scanning range of 10.0–90.0°.

The neutron diffraction data were analysed by Izumi's Rietveld structure refinement program (RIETAN) [9]. The parameters of the crystallographic structure of Th_2Zn_{17} type rare-earth–iron compounds were used to start the refinement [10]. The parameters of the final refined crystallographic and magnetic structure are listed in table 1. The observed and calculated diffraction patterns are shown in figure 1. The magnetic moments of the Ho and Fe atoms exhibit an easy-axis anisotropy for the phase with $x = 2, 4$ at 50 K and $x = 2$ at 300 K. The magnetic moments of all iron atoms display ferromagnetic coupling, but the coupling of magnetic moments of Ho and Fe is ferrimagnetic. The final refined result shows that the total occupancies of gallium and aluminium atoms on both 18f and 6c sites for our samples coincides with the chemical concentration of the compounds.

3. Discussion

The Rietveld structure analysis shows an obvious concentration dependence of the Al and Ga fractional occupancies on each of the four crystallographic sites (18f, 18h, 9d and 6c) in $Ho_2Fe_9Ga_{8-x}Al_x$ ($x = 2, 4$) at 50 K and 300 K. It is impossible for the occupancies of Gal and Al to be influenced by different temperatures, thus the occupation factors of Ga and Al at 300 K are kept the same as those at 50 K.

According to the results from neutron diffraction measurement, Al and Ga atoms prefer 6c sites and 18f sites, but avoid 9d sites. This can be explained as due to both Ga and Al atoms having larger atomic radii than Fe: they avoid occupying 9d sites that have the smallest Wigner–Seitz cell volume and prefer 6c sites that have the largest one [11]. It is still not clear why Ga and Al do not occupy the 18h sites that have the next largest Wigner–Seitz cell volume. From table 1, it can be deduced that the unit-cell volumes of samples at 300 K are bigger than those at 50 K. It is reasonable that the unit-cell volume expands with increasing temperature.

In general, T_C in rare-earth–iron intermetallic compounds is mainly dominated by the Fe–Fe exchange interaction. Increasing Fe–Fe interatomic distance may improve the exchange interaction by means of the volume effect, but the content of Fe decreases due to higher concentration of Ga and Al. The T_C is still low: $T_C = 327$ K and 166 K for $Ho_2Fe_9Al_2$ and $Ho_2Fe_9Ga_4Al_4$ respectively. However, it is difficult to explain the magnetic intrinsic relation of the reciprocal substitution between non-magnetic elements (Al and Ga) in $Ho_2Fe_9Ga_{8-x}Al_x$. But to separately study how T_C value was affected by substitution of Ga and Al for Fe, we have done the magnetic experiments for $Ho_2Fe_{17-x}Ga_x$, $Y_2Fe_{17-x}Ga_x$

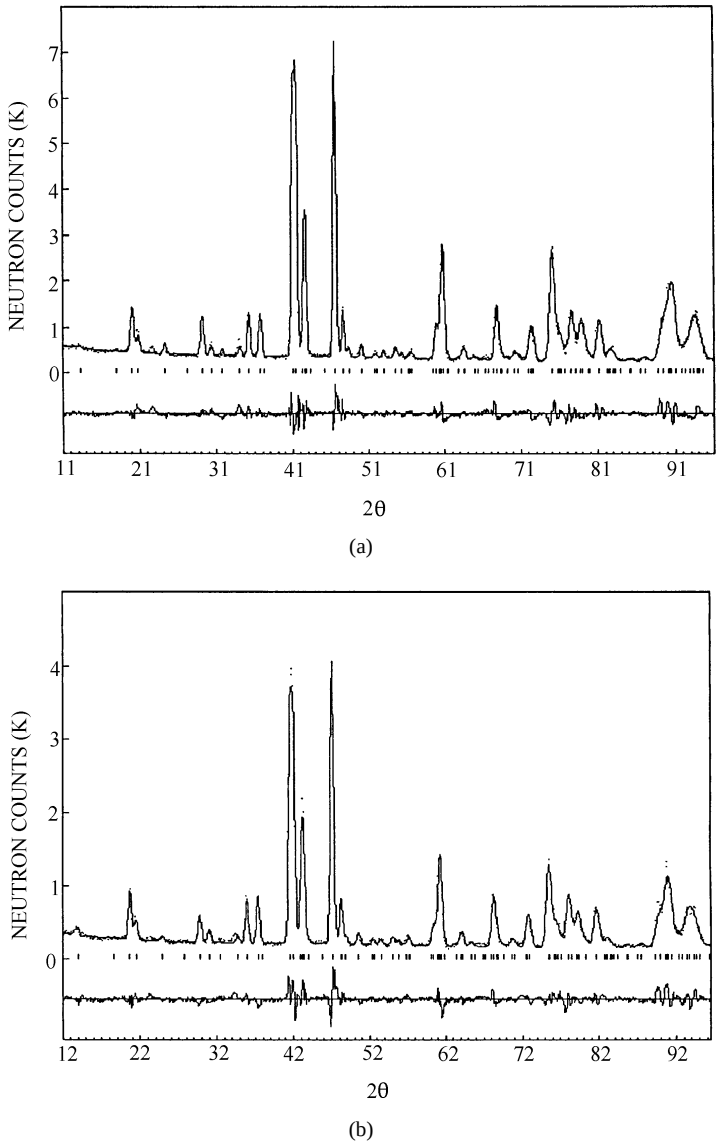
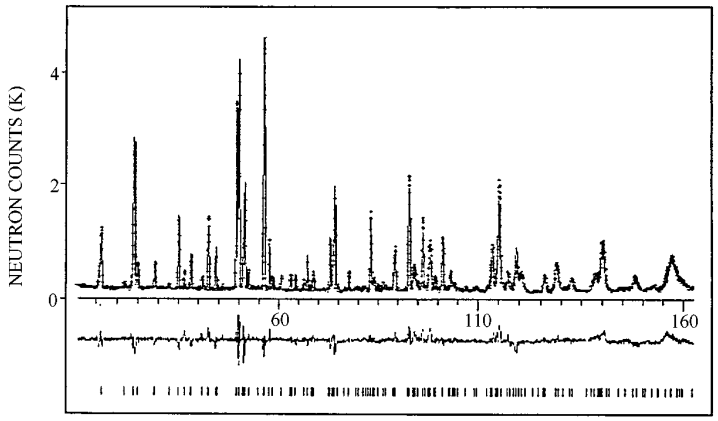


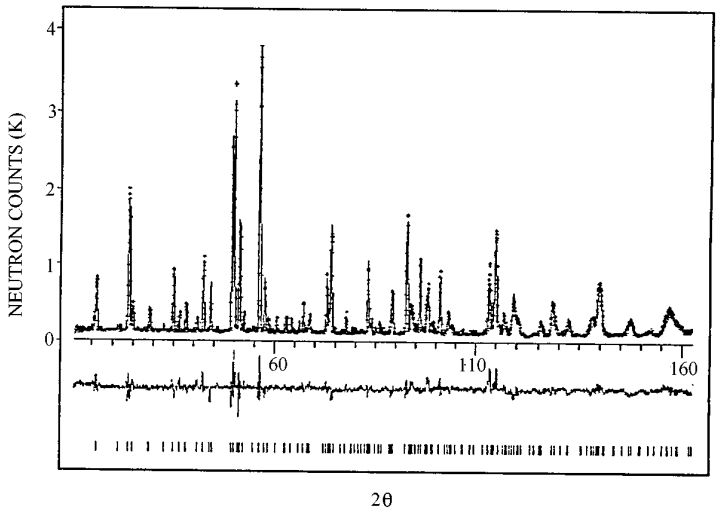
Figure 1. The observed and calculated diffraction patterns (a) $Ho_2Fe_9Ga_4Al_4$ at 300 K; (b) $Ho_2Fe_9Ga_6Al_2$ at 300 K; (c) $Ho_2Fe_9Ga_4Al_4$ at 50 K; (d) $Ho_2Fe_9Ga_6Al_2$ at 50 K.

and of course, $Ho_2Fe_9Ga_{8-x}Al_x$. Compared to the similar experiments for $Ho_2Fe_{17-x}Al_x$ and $Y_2Fe_{17-x}Al_x$ reported by Jacobs *et al* [1]. It can be seen that an enhancement of T_C appeared in the samples of $R_2Fe_{17-x}Ga_x$ with $x > 6$, which is different from the case in the Al-containing samples. Because they are not very important for our conclusion, we will explain the details of these experiments in other papers.

Although the T_C of $Ho_2Fe_9Ga_{8-x}Al_x$ ($x = 2, 4$) is not high enough, it is very interesting that both of them exhibit uniaxial anisotropy. It is well known that, to a first approximation, the total magnetocrystalline anisotropy constant K(total) is the sum of the first-order anisotropy constants of the rare-earth and iron sublattices, $K(\text{total}) = K_1(\text{R}) + K_1(\text{Fe})$.



(c)



(d)

Figure 1. (Continued)

Generally, K_1(Fe) is negative for the R_2Fe_{17} compound, i.e. the anisotropy of the Fe sublattice is easy planar [12].

In the view of the single-ion model [12], the magnitude and sign of K_1(R) are mainly determined by the product of the second-order crystal field parameter, A_2^0, and the second-order Stevens coefficient, α_J, $K_1(\mathrm{Ho}) \propto -A_2^0\alpha_J$. A negative $A_2^0\alpha_J$ gives a uniaxial anisotropy for the rare-earth sublattice, whereas a positive $A_2^0\alpha_J$ gives a planar anisotropy.

From previous investigation, A_2^0 is negative in the R_2Fe_{17} compounds, while $\alpha_J(\mathrm{Ho}) = -22.2 \times 10^4$, so K_1(Ho) is negative. Then the sum of K_1(Ho) and K_1(Fe) will produce a more negative K_1(total). But the uniaxial magnetic anisotropy of $Ho_2Fe_9Ga_{8-x}Al_x$ ($x = 2, 4$) indicates that K_1(total) is positive. The reason may be that A_2^0 and thus K_1(Ho) have changed from negative to positive.

Why is the change of A_2^0 so large? It is well known that A_2^0 is determined predominantly by the charge density asphericity of rare-earth valence electrons [13]. Because of the

Table 1. Crystallographic and magnetic parameters of $Ho_2Fe_9Ga_6Al_2$ and $Ho_2Fe_9Ga_4Al_4$ at 50 K and 300 K (rhombohedral cell; space group $R\bar{3}m$).

Atom site	Occupancy factor	x	y	z	M (μ_B)
$Ho_2Fe_9Ga_6Al_2$ (50 K)		$a = b = 8.742(1)$ Å	$c = 12.657(1)$ Å	$R_1 = 5.68\%$	$R_F = 3.35\%$
Ho (6c)	1	0	0	0.349(2)	−8.6(5)[a]
Fe (9d)	1	0.5	0	0.5	+ 0.59(29)[a]
Fe (18h)	1	0.500(1)	0.500(1)	0.156(1)	+ 0.60(20)[a]
Ga (18f)	0.80	0.298(1)	0	0	0
Ga (6c)	0.60	0	0	0.106(1)	0
Al (18f)	0.20	0.298(1)	0	0	0
Al (6c)	0.40	0	0	0.106(1)	0
$Ho_2Fe_9Ga_6Al_2$ (300 K)		$a = b = 8.759(3)$ Å	$c = 12.651(3)$ Å	$R_1 = 5.45\%$	$R_F = 3.78\%$
Ho (6c)	1	0	0	0.353(2)	−0.50(12)[a]
Fe (9d)	1	0.5	0	0.5	+ 1.76(21)[a]
Fe (18h)	1	0.500(1)	0.500(1)	0.157(1)	+ 2.53(48)[a]
Ga (18f)	0.80	0.300(1)	0	0	0
Ga (6c)	0.60	0	0	0.113(2)	0
Al (18f)	0.20	0.300(1)	0	0	0
Al (6c)	0.40	0	0	0.113(2)	0
$Ho_2Fe_9Ga_4Al_4$ (50 K)		$a = b = 8.738(1)$ Å	$c = 12.635(1)$ Å	$R_1 = 4.57\%$	$R_F = 2.62\%$
Ho (6c)	1	0	0	0.350(2)	−9.3(6)[a]
Fe (9d)	1	0.5	0	0.5	+ 0.44(23)[a]
Fe (18h)	1	0.500(1)	0.500(1)	0.155(1)	+ 0.51(28)[a]
Ga (18f)	0.67	0.301(1)	0	0	0
Al (18f)	0.33	0.301(1)	0	0	0
Al (6c)	1	0	0	0.107(1)	0
$Ho_2Fe_9Ga_4Al_4$ (300 K)		$a = b = 8.765(3)$ Å	$c = 12.699(4)$ Å	$R_1 = 5.47\%$	$R_F = 3.43\%$
Ho (6c)	1	0	0	0.353(2)	0
Fe (9d)	1	0.5	0	0.5	0
Fe (18h)	1	0.500(1)	0.500(1)	0.157(1)	0
Ga (18f)	0.67	0.295(1)	0	0	0
Al (18f)	0.33	0.295(1)	0	0	0
Al (6c)	1	0	0	0.111(1)	0

[a] The atom magnetic moment is oriented along [0 0 1].

hybridization of the rare-earth 5d and 6p valence electrons with the valence electrons of their neighbour atoms, and because iron atoms were preferentially substituted by Ga and Al on specific crystallographic sites, for example 6c and 18f sites, from table 1, the charge density asphericity of Ho valence electron will be changed largely. The change of asphericity will have a strong influence on the magnitude and sign of A_2^0.

In addition, recently we have also studied $Y_2Fe_{10}Ga_7$ [14] by powder neutron diffraction at room temperature. It exhibits unaxial magnetic anisotropy, too. The Y atom is non-magnetic. So the contribution for anisotropy is only from the Fe–Ga sublattice. This shows that K_1(Fe) is changed from negative to positive due to the substitution of Ga for Fe. Although the Ga-concentration dependence of the easy magnetization direction is not well understood, it can be simply discussed in terms of the individual site anisotropy (ISA) model. In the frame of the ISA model, the concentration dependence of the anisotropy constant $K_{1,\mathrm{Fe}}(x)$ can be expressed as follows [15]: $K_{1,\mathrm{Fe}}(x) = \Sigma n_i f_i(x) K_{l,i}$, where $K_{l,i}$ is the anisotropic constant of the 3d Fe atom at a given site i; n_i is the number of equivalent positions of 3d Fe atoms at the ith site; m is the number of non-equivalent positions of Fe atoms in a unit cell; $f_i(x)$ is the occupation factor of Fe atoms at the ith site. We have also prepared a series of $Y_2Fe_{17-x}Al_x$ recently, and found that they change anisotropy direction

from easy plane to easy axis at high ($x > 7$) concentration. The neutron powder diffraction of $Y_2Fe_9Al_8$ was carried out by HRPD at 10 K [16]. Compared with $Y_2Fe_{10}Ga_7$, similar results were found for $Y_2Fe_9Al_8$. The result of the above neutron diffraction measurements shows that Ga and Al atoms prefer 6c and 18f sites. The contribution of Fe atoms in 6c and 18f sites should have planar anisotropy. So when the Fe atoms at these sites were substituted by non-magnetic Ga and Al, the sign of $K_{1,\mathrm{Fe}}(x)$ may be changed from negative to positive. The magnetocrystalline anisotropy of Fe sublattice becomes uniaxial.

From the above, it is concluded that the contributions to the uniaxial orientation of the magnetization in $Ho_2Fe_9Ga_{8-x}Al_x$ ($x = 2, 4$) compounds is not only from the rare earth sublattice, but also may be from the iron sublattice. In any case, we found that the contribution to magnetic anisotropy from Fe–Fe is comparable to that from the rare earth sublattice *near* the Curie temperature from our experiment on $Y_2Fe_{17-x}Al_x$ mentioned above. There are also some other explanations of the change of magnetic anisotropy by substitution: one of them suggests that the large increase in the anisotropy field can be induced by changes in overall electronic structure due to the Ga and Al substitution. Obviously, it is necessary to do further detailed research into the real mechanism of uniaxial anisotropy in $Ho_2Fe_9Ga_{8-x}Al_x$ ($x = 2, 4$).

At the end of this work, it should be mentioned that the magnetic moment of $Ho_2Fe_9Ga_6Al_2$ at 50 K is surprisingly small. This neutron diffraction data were refined repeatedly and the results did not change, but the refinement of $Y_2Fe_9Al_8$ at low temperature gave reasonable magnetic moments of Fe atoms. Then, it can deduced that the small magnetic moments may come from the reorientation of the magnetic moments near 50 K, so that the projection of Fe magnetic moment on the *c*-axis will be smaller than itself. The further research on magnetic anisotropy should be performed by a proper magnetic experiment facility.

Acknowledgments

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