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A neutron powder diffraction study of the structure of Ho$_2$Fe$_{17-x}$Ga$_x$C$_2$ ($x = 4.0$ and 5.5)

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Abstract. The crystallographic and magnetic structures of Ho$_2$Fe$_{17-x}$Ga$_x$C$_2$ ($x = 4.0$ and 5.5) at room temperature were refined by the Rietveld analysis of neutron powder diffraction data. The analysis indicates that Ho$_2$Fe$_{17-x}$Ga$_x$C$_2$ has a Th$_2$Zn$_{17}$-type structure space group, ($R\bar{3}m$); the gallium atoms occupy only 18h sites with an occupancy of 0.66 for $x = 4.0$, they occupy both 18h and 6c sites with occupancies of 0.66 and 0.75, respectively, for $x = 5.5$ and they are absent from the 9d and 18f sites at all gallium concentrations. The carbon atoms occupy 9e sites. For the $x = 4.0$ compound, the magnetic moments of all atoms lie in a plane perpendicular to the sixfold axes and have a parallel arrangement. The magnetic moments of all Fe atoms display ferromagnetic coupling, but the magnetic moments of Ho and Fe are antiferromagnetically oriented. The $x = 5.5$ compound is paramagnetic at room temperature.

1. Introduction

The rare-earth–iron compounds of R$_2$Fe$_{17}$ have attracted much attention in recent years as possible high-performance permanent magnetic materials. The high Fe concentration yields a high saturation magnetization while maintaining a low cost. However, this series of alloys has two drawbacks: the relatively low Curie temperatures and the fact that none of these alloys exhibits an easy-axis anisotropy at room temperature. Many studies have centred on either substituting other elements into the R$_2$Fe$_{17}$ structure of preparing materials with additional atoms located interstitially. Extensive studies of the substitution of other elements for Fe (e.g. Co, Al or Si) in R$_2$Fe$_{17}$ will increase the Curie temperature [1–3], but only the Sm$_2$Fe$_{17-x}$Al$_x$ compounds with $x > 2.0$ [2] exhibit easy-axis anisotropy. In many cases, large increases in the Curie temperature have been observed in materials with interstitial nitrogen or carbon [4–6] and, in the case of Sm$_2$Fe$_{17}$N$_x$ ($x > 0.8$) and Sm$_2$Fe$_{17}$C$_x$ ($x > 0.5$), only easy-axis anisotropy is observed [4–6].

Some studies of the structure of R$_2$Fe$_{17-x}$Al$_x$ were carried out in order to understand the relation between the structure and the magnetic properties; the aluminium atoms occupy randomly 18f, 18h, 9d and 6c sites [7] or they occupy only 9d and 6c sites [2]. This neutron diffraction structure analysis shows that in the Ho$_2$Fe$_{17-x}$Ga$_x$C$_2$ compounds the gallium atoms occupy only 18h sites with an occupancy of 0.66 for $x = 4.0$ and occupy both 18h and 6c sites with occupancies of 0.66 and 0.75, respectively, for $x = 5.5$. Some magnetic information on the compounds was reported and discussed.

2. Experiment and refinement

The $Ho_2Fe_{17-x}Ga_xC_2$ ($x = 4.0$ and 5.5) samples were prepared by arc melting high-purity Ho (99.9% purity), Fe–C alloy (99.9% purity) and Ga (99.99% purity) in an argon arc furnace, sealing in quartz tubes under an argon atmosphere and annealing at 1150 °C for 24h. The ingots were then ground to yield powder samples. The samples were examined using x-ray diffraction. The x-ray patterns show that the samples are a single phase with a Th_2Zn_{17}-type structure. The magnetic measurements show that the $x = 5.5$ sample exhibits paramagnetism at room temperature.

Neutron powder diffraction data were collected using the triple-axis spectrometer at Institute of Atomic Energy, Beijing, at a wavelength of 1.541 Å. About 15 g of the powder sample were used and placed in a vanadium tube. The triple-axis spectrometer was used as a two-axis powder spectrometer in order to improve the resolution. With a PG-Graphite monochromator (004 plane), an analyser (002 plane) and four collimators of 30′ divergence. The powder diffraction patterns of $Ho_2Fe_{17-x}Ga_xC_2$ are shown in figures 1(*a*) and 1(*b*) for $x = 4.0$ and 5.5, respectively. The data were analysed with the Rietveld structure refinement program RIETAN [8]. The parameters of the crystallographic structure [9] of the Th_2Zn_{17}-type rare-earth–iron compound was used to start the refinement. Initially, the zero-point, the background, the parameters of the full width at half-maximum, the cell parameters and the profile parameters were refined. It was assumed that the carbon atoms were on 9e sites [4–6] and that the gallium atoms and iron atoms occupy 18h, 18f, 9d and 6c sites simultaneously, according to the chemical concentration and with the linear constraint condition; the sum of the occupancies of Fe and Ga atoms on these four sites equals 1.0, the overall temperature factors take the value 1.0, the magnetic moments of all magnetic atoms are $2.0\mu_B$ and $-1.0\mu_B$ for Fe and Ho atoms, respectively, and all magnetic moments are in a parallel arrangement, lying in a plane perpendicular to the sixfold axes [9]. At this time the refinement has the weighted pattern R factor $R_{wp} = 18.3\%$ and 16.8% corresponding to $x = 4.0$ and $x = 5.5$, respectively. Here the weighted pattern factor $R_{wp} = \sum_i \{w_i [y_i(0) - y_i(c)]^2 / [y_i(0) - y_i(c)]^2\}$, where w_i, $Y_i(0)$ and $Y_i(c)$ are the weighted factor, the observed and the calculated values at the ith point of the pattern, respectively; the summation was done for all points of the pattern. Secondly we refined the occupancies of Ga and Fe atoms at the four sites, and the magnetic moments of magnetic atoms; the result implied that the gallium atoms occupy only 18h sites with an occupancy of 0.66 and are absent from the other three sites for the $x = 4.0$ sample, and that they occupy both 18h and 6c sites with occupancies of 0.66 and 0.75, respectively, and are absent from 9d and 18f sites for the $x = 5.5$ sample. The weighted pattern factor R_{wp} decreases to 9.2% and 8.7% for the $x = 4.0$ and $x = 5.5$ samples, respectively. This refinement starts from the very general initial situation; so the results are unique. We tried some initial modes; for example the Ga atoms occupy preferentially 9d and/or 18f sites, and the results of the refinement confirmed this point. Subsequently we refined the temperature factors for the Ho, Ga and Fe atoms on different sites, and the atomic coordinates; the refinement shows that the occupancies of Ga and Fe on the four sites do not change, and that $R_{wp} = 7.2\%$ and 7.0% correspond to $x = 4.0$ and 5.5, respectively.

The last refinement includes all parameters; the parameters of the final refined structure are listed in table 1. The magnetic moments of all atoms lie in a plane perpendicular to the sixfold axes with a parallel arrangement. The magnetic moments of all iron atoms display ferromagnetic coupling, but the magnetic moments of Ho and Fe are antiferromagnetically oriented. The final refined total occupancies of gallium atoms on both 18h and 6c sites correspond to the chemical concentration of the compounds. It is found that $R_{wp} = 0.070$ and 0.065 correspond to $x = 4.0$ and 5.5, respectively.
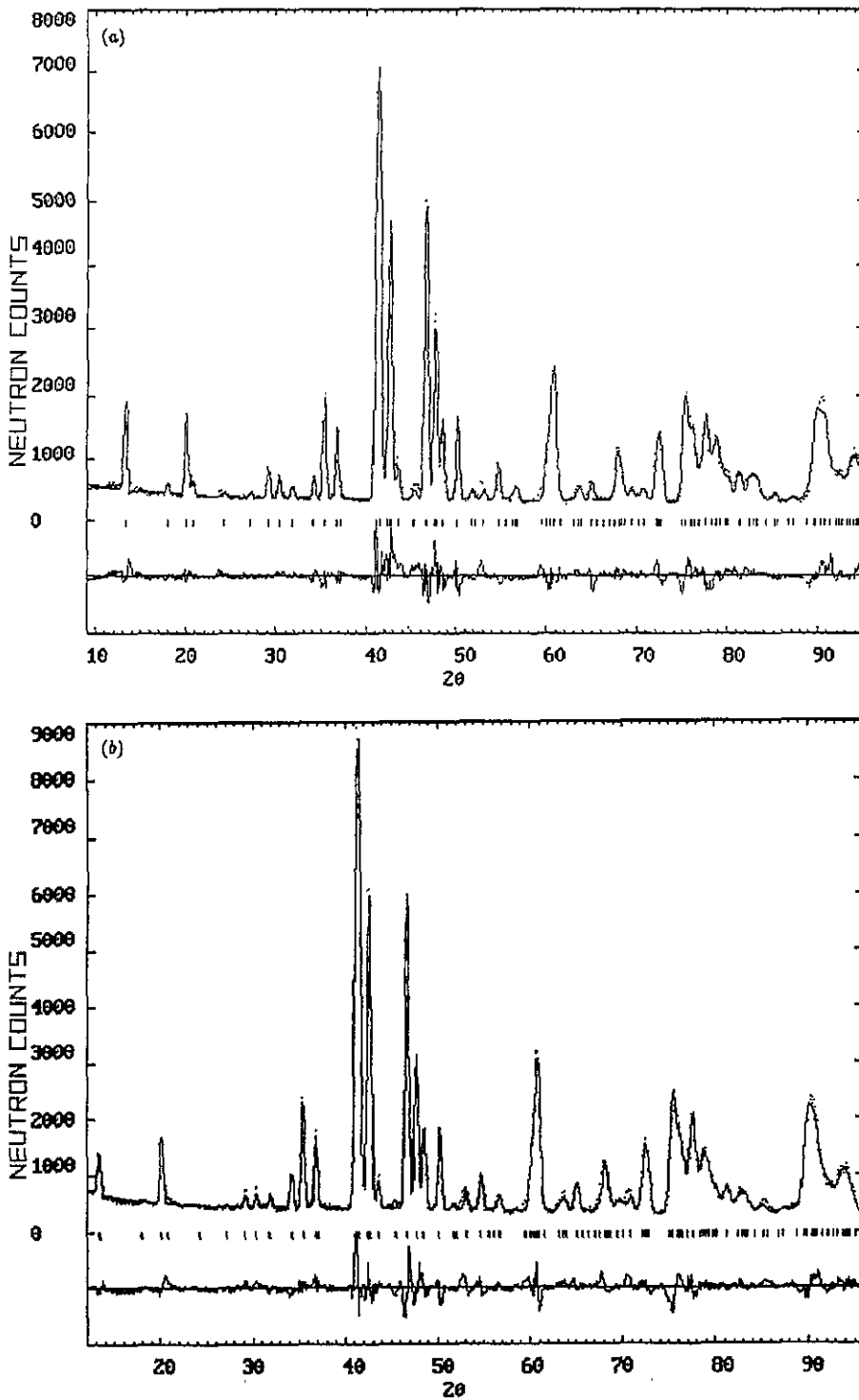
**Figure 1.** Powder diffraction patterns for $Ho_2Fe_{17-x}Ga_xC_2$ ($x = 4.0$ and 5.5). The observed and calculated profiles are given by the dotted and solid curves, respectively, and the calculated positions are indicated at the bottom. The differences between the observed and calculated data are given.

Table 1. Crystallographic and magnetic parameters of $Ho_2Fe_{17-x}Ga_xC_2$ ($x = 4.0$ and 5.5) (rhombohedral cell; space group, $R\bar{3}m$).

Atom (site)	Occupancy	x	y	z	B (Å^2)	M (μ_B)
$x = 4.0$ $a = b = 8.688(3)$ Å, $c = 12.592(5)$ Å						
Ho (6c)	1.0	0	0	0.343(2)	0.91(7)	−2.84(15)
Fe (6c)	1.0	0	0	0.0938(3)	1.69(5)	0.41(10)
Fe (18f)	1.0	0.284(1)	0	0	0.78(9)	0.83(9)
Fe (18h)	0.34(2)	0.503(2)	0.497(2)	0.151(1)	0.40(5)	2.0(2)
Ga (18h)	0.66(2)	0.503(2)	0.497(2)	0.151(1)	0.40(5)	
Fe (9d)	1.0	0.5	0	0.5	1.20(8)	0.55(9)
C (9e)	0.66(3)	0.5	0	0	0.67(3)	
$x = 5.5$ $a = b = 8.696(4)$ Å, $c = 12.627(5)$ Å						
Ho (6c)	1.0	0	0	0.343(2)	0.80(7)	0
Fe (6c)	0.25	0	0	0.099(2)	0.41(5)	0
Ga (6C)	0.75	0	0	0.099(2)	0.41(5)	
Fe (18f)	1.0	0.284(2)	0	0	0.96(12)	0
Fe (18h)	0.33(2)	0.501(2)	0.499(2)	0.154(3)	0.33(6)	0
Ga (18h)	0.66(2)	0.501(2)	0.499(2)	0.154(3)	0.33(6)	
Fe (9d)	1.0	0.5	0	0.5	1.40(9)	0
C (9e)	0.66	0.5	0	0	0.83(7)	

The magnetic ordering temperature T_c of the compounds was measured with a vibrating-sample magnetometer; T_c according to the Ga content is shown in figure 2. The magnetic ordering temperatures $T_c = 475$ K and 242 K correspond to Ga contents $x = 4.0$ and $x = 5.5$, respectively. The saturation magnetization per molecule μ_s was measured using an extracting-sample magnetometer at 1.5 K, and variation in μ_s with the Ga content is shown in figure 3.
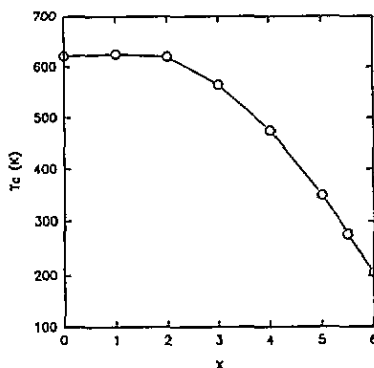
Figure 2. The magnetic ordering temperature T_c according to Ga content x in the compounds $Ho_2Fe_{17-x}Ga_xC_2$.

3. Discussion

The Rietveld structure analysis shows clearly that the gallium atoms occupy only 18h sites for $0 < x < 4.0$ and that they occupy both 18h and 6c sites for $4.0 < x < 5.5$.
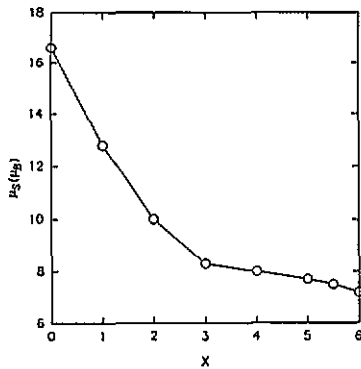
Figure 3.   The variation in saturation magnetization μ_s with Ga content x in the $Ho_2Fe_{17-x}Ga_xC_2$ compounds.

The substitution of gallium atoms for iron atoms on 18h sites reaches a maximum for $x = 4.0$ (corresponding to an occupancy of 0.66), and 18f and 9d sites exclude gallium at all concentrations. The Ga atoms preferentially occupy 18h and 6c sites which provides the possibility of convenient research on the magnetic exchange interactions between 18h or/and 6c, and other sites.

Figures 2 and 3 demonstrate that the magnetic ordering temperature T_c and the saturation magnetization μ_s decreased monotonically when the Ga content increases; because magnetic Fe atoms were replaced by non-magnetic Ga atoms, this decreased the magnetic exchange interactions. However, the saturation magnetization μ_s decreased with two different slopes, the larger slope corresponding to a Ga content $x < 4.0$ and the smaller slope corresponding to $4.0 > x > 6.0$. It is obvious that the magnetic moment of Fe atoms will be larger on 18h sites than on 6c sites (see table 1); only Fe atoms on 18h sites were replaced by non-magnetic atoms when $x < 4.0$, and so μ_s decreased rapidly; however, when $6.0 > x > 4.0$ the non-magnetic atoms began to occupy 6c sites too, but the moments of Fe atoms on 6c sites were smaller (see table 1), and so μ_s decreased more slowly. There was a middle region $4.0 > x > 3.0$ showing an intermediate slope; we assume that in this region the total Fe–Fe ferromagnetic interactions decreased more slowly because of the greater Ga substitution, and the decrease in Ho–Fe antiferromagnetic interactions was more rapid simultaneously; the result of this competition may result in a region with an intermediate slope. The μ_s–x curve shown in figure 3 is different from that in [3]; in [3], μ_s–x (Al content) is a straight line for $Y_2Fe_{17-x}Al_x$ and $Ho_2Fe_{17-x}Al_x$ because Al atoms randomly occupy these four sites.

It is well known that the ion diameter of gallium is larger than that of iron. So table 1 shows that the volume of the unit cell of the Ga-substituted alloy increases with increasing Ga concentration, and the z coordinate of the 6c sites increases from 0.094 (for the $x = 4.0$ sample) to 0.099 (for the $x = 5.5$ sample); it also confirms that the gallium atoms occupy partly 6c sites in the $x > 4.0$ case.

The carbon atoms occupying 9e sites effectively prevent gallium atoms from substituting for iron on 18f sites, because it is impossible for a reasonable Ga–C bond length to exist there.

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