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## On the preferential site occupation of Fe in $RFe_4Al_8$ and related compounds

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**Abstract.** High-resolution neutron powder diffraction studies were performed on several compounds of the type  $YFe_{12-x}Al_x$  ( $x = 8, 7, 6$ ). We observed a strong preferential site occupation of Fe on one of the three non-equivalent transition metal sites of the  $ThMn_{12}$ -type structure. In particular the 8f site is found to be markedly populated by Fe atoms, while there is a strong preference of Al for the 8i site.

### 1. Introduction

The tetragonal  $ThMn_{12}$  structure consists of three different Mn positions, denoted in Wyckoff notation by 8i, 8j and 8f. When the minority element is one of the rare earths (R), binary compounds of this structure type are only formed with Mn as second component, whereas binary rare earth compounds with other 3d elements do not exist. It has been known for many years that there is a large family of ternary compounds of the type  $RT_4Al_8$ , where T can represent Cr, Mn, Fe or Cu (Buschow *et al* 1976, Felner and Nowick 1978). From x-ray diffraction it was derived that the T elements primarily occupy the 8f site. The Fe compounds, in particular, were found to have interesting magnetic properties, although their magnetic ordering temperatures were far below room temperature (Felner and Nowick 1978, Buschow and van der Kraan 1978).

Recently it was discovered that there is another subgroup of ternary intermetallic compounds of the  $RMn_{12}$  structure. The formula composition of these materials can be represented as  $RFe_{12-x}T_x$  where  $T = Ti, V, Cr, Mo, W$  or  $Si$ , and where  $x \approx 2$  for  $T = Cr, Mo$  and  $Si$ , and  $1.5 \leq x \leq 4$  for  $T = V$  (Ohashi *et al* 1988, Buschow 1988). All of these compounds have magnetic ordering temperatures far above room temperature and fairly high magnetisations and anisotropies, so they can be considered as candidates for permanent magnet purposes. This has considerably renewed the interest in  $ThMn_{12}$ -type compounds. Several structural studies have been made using x-ray diffraction as well as neutron diffraction. These studies showed that the T atoms ( $T = Ti, V, Mo$ ) have a strong preference for occupying the 8i site (Buschow 1988, Helmholdt *et al* 1988, Moze *et al* 1988).

For the interpretation of the magnetic properties of the various types of  $ThMn_{12}$  compound it is of paramount importance to have a sound knowledge regarding the positions and occupancies of the various atoms. In a recent model description of the

**Table 1.** Refined atomic position parameters, isotropic temperature factor ( $\text{\AA}^2$ ) and site occupancies in three  $\text{YFe}_{12-x}\text{Al}_x$  compounds:  $\text{YFe}_4\text{Al}_8$ ,  $\text{YFe}_5\text{Al}_7$ ,  $\text{YFe}_6\text{Al}_6$ .

Site	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Occupancy
<b><math>\text{YFe}_4\text{Al}_8</math></b>						
2a	Y	0.000 00	0.000 00	0.000 00	0.85(5)	1
8i	Al	0.342 21(33)	0.000 00	0.000 00	0.34(6)	1.056(6)
	Fe	0.342 21(33)	0.000 00	0.000 00	0.34(6)	-0.056(6)
8j	Al	0.278 01(25)	0.500 00	0.000 00	0.14(8)	1.100(7)
	Fe	0.278 01(25)	0.500 00	0.000 00	0.14(8)	-0.100(7)
8f	Al	0.250 00	0.250 00	0.250 00	0.48(2)	0.090(10)
	Fe	0.250 00	0.250 00	0.250 00	0.48(2)	0.090(10)
<b><math>\text{YFe}_5\text{Al}_7</math></b>						
2a	Y	0.000 00	0.000 00	0.000 00	0.84(6)	1
8i	Al	0.343 92(33)	0.000 00	0.000 00	0.38(9)	1.097(8)
	Fe	0.343 92(33)	0.000 00	0.000 00	0.38(9)	-0.097(8)
8j	Al	0.275 79(22)	0.500 00	0.000 00	0.02(7)	0.953(10)
	Fe	0.275 79(22)	0.500 00	0.000 00	0.02(7)	0.046(10)
8f	Al	0.250 00	0.250 00	0.250 00	0.29(2)	0.158(10)
	Fe	0.250 00	0.250 00	0.250 00	0.29(2)	0.841(10)
<b><math>\text{YFe}_6\text{Al}_6</math></b>						
2a	Y	0.000 00	0.000 00	0.000 00	0.92(9)	1
8i	Al	0.342 92(48)	0.000 00	0.000 00	0.65(13)	1.012(12)
	Fe	0.342 92(48)	0.000 00	0.000 00	0.65(13)	-0.012(12)
8j	Al	0.272 01(33)	0.500 00	0.000 00	0.57(9)	0.680(19)
	Fe	0.272 01(33)	0.500 00	0.000 00	0.57(9)	0.319(19)
8f	Al	0.250 00	0.250 00	0.250 00	0.57(4)	0.073(23)
	Fe	0.250 00	0.250 00	0.250 00	0.57(4)	0.926(23)

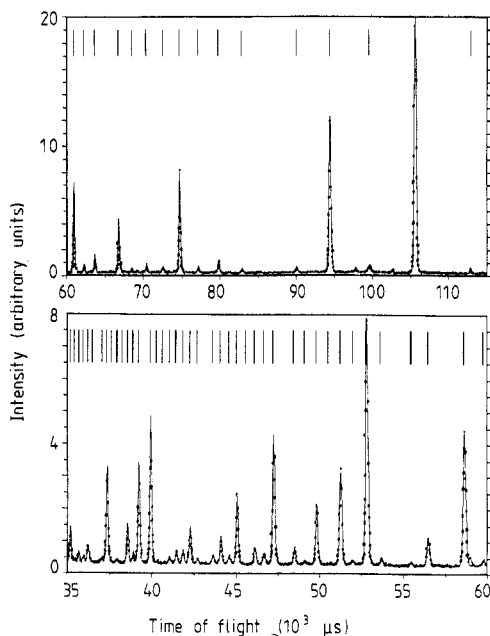
crystallographic and magnetic structures of  $\text{ThMn}_{12}$ -type compounds Melamud *et al* (1987), questioning the experimental structural evidence available, proposed that the majority site for iron in  $\text{RFe}_{12-x}\text{Al}_x$  is the 8i site. This has led us to reinvestigate the crystallographic structure of the latter materials by means of high-resolution neutron powder diffraction (HRPD), the large difference in scattering length between Fe and Al enabling an accurate determination of the Fe (Al) site occupancies to be made.

## 2. Experimental procedures and results

The samples of  $\text{YFe}_4\text{Al}_8$ ,  $\text{YFe}_5\text{Al}_7$  and  $\text{YFe}_6\text{Al}_6$  were prepared by melting the elements (of at least 99.9% purity) in an arc furnace under a reduced Ar atmosphere. The samples were wrapped in Ta foil sealed in a quartz tube in an Ar atmosphere and annealed for 40 days at 800 °C.

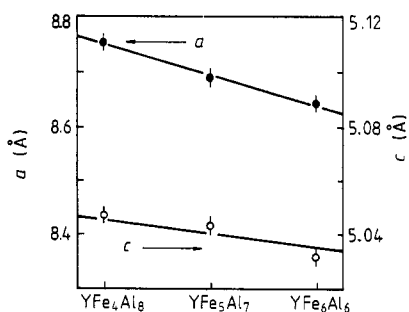
Since the aim of this investigation is to determine the location of the Fe (Al) atoms in  $\text{YFe}_{12-x}\text{Al}_x$  we restricted the neutron diffraction experiments to room temperature. Only nuclear reflections are expected since the magnetic ordering temperature of these compounds is below room temperature.

Neutron diffraction patterns were collected on the high-resolution powder time-of-flight diffractometer HRPD (Johnson and David 1985) connected at the spallation neutron

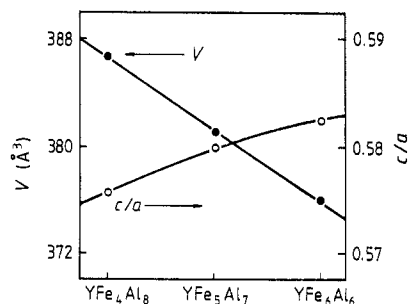


**Figure 1.** Calculated (full curves) and observed (data points) neutron diffraction pattern of  $\text{YFe}_4\text{Al}_8$  at 293 K. The bars at the top correspond to the calculated line positions.

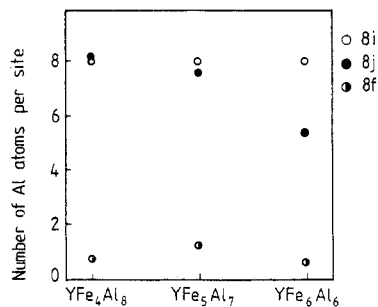
source ISIS, UK. The data were taken in the range of  $d$ -spacing extending from 0.6 to 2.2 Å. In this range of  $d$ -spacing, the diffractometer HRPD is at the optimum condition in terms of both resolution ( $\approx 5 \times 10^{-4}$  in  $d$ -spacing) and intensity. Results obtained for the compound  $\text{YFe}_4\text{Al}_8$  are shown in figure 1. A Rietveld profile refinement (Rietveld 1969) was performed on the HRPD data using the tetragonal  $\text{ThMn}_{12}$  structure as a trial structure. The refined parameters included atomic co-ordinates in the tetragonal unit cell, unit-cell constants and isotropic temperature factors and Fe site populations of the three transition metal sites (8i, 8j, 8f) as well as profile parameters. The profile analysis proceeded routinely to give excellent results which clearly showed a preferential Fe atom occupation of the 8f site. The refined atomic co-ordinates are listed in table 1 which



**Figure 2.** Concentration dependence of the lattice constants of  $\text{YFe}_{12-x}\text{Al}_x$ .



**Figure 3.** Concentration dependence of the unit-cell volume and  $c/a$  ratio of  $\text{YFe}_{12-x}\text{Al}_x$ .



**Figure 4.** Concentration dependence of the Fe (Al) occupancies of the three sites 8f, 8i, 8j, in  $\text{YFe}_{12-x}\text{Al}_x$ .

includes also the refined Fe and Al site populations. The goodness of fit parameters of this refinement are  $R_n = 4.8\%$ ,  $R_{wp} = 6.8\%$ ,  $R_{exp} = 1.9\%$ .

A similar analysis was also made for the compounds  $\text{YFe}_5\text{Al}_7$  and  $\text{YFe}_6\text{Al}_6$ . In the diffraction patterns of these compounds we observed several minor reflection lines not belonging to the  $\text{ThMn}_{12}$  structure type. This was ascribed to the presence of an impurity phase. These additional lines were excluded from the refinement procedure. The refined positional parameters and occupation numbers for  $\text{YFe}_5\text{Al}_7$  and  $\text{YFe}_6\text{Al}_6$  are included in table 1.

### 3. Discussion

The results obtained in the course of the present investigation by means of the HRPD experiments are summarised in figures 2–4. The decrease of the lattice parameters and unit-cell volume with decreasing  $x$  in  $\text{YFe}_{12-x}\text{Al}_x$  reflects the fact that the atomic volume of Al is larger than that of Fe (figures 2 and 3). It follows from the results shown in figure 4 that there is a strong preference of the Al atoms to occupy the 8i site. Alternatively one could say that the Fe atoms are reluctant to occupy the 8i site: the 8f site can be regarded as being fully occupied by Fe atoms in compounds for which  $x > 4$ , so the excess Fe atoms have to be accommodated in the two remaining sites. It follows from figure 4 that, even in this favourable case, the 8i site is largely avoided by the Fe atoms. The question of Fe atom location and Fe moment formation in  $\text{RFe}_{12-x}\text{Al}_x$  was recently addressed by Melamud *et al* (1987). These authors used a Wigner–Seitz analysis and suggested that the occurrence of a substantial magnetic moment at an atomic site in magnetic systems can be related to the occurrence of  $-72^\circ$  disclination lines connecting atoms on this site. These disclinations, or major ligands, are bond lines joining two near-neighbour atoms that have six common nearest neighbours. Applying this model to the  $\text{RFe}_{12-x}\text{Al}_x$  compounds, Melamud *et al* are led to expect that the magnetically ordered Fe atoms are located at the 8i site which requires that a substantial fraction of the Fe will occupy this site. Our data refute these model predictions since they show that the Fe atoms in  $\text{YFe}_4\text{Al}_8$  are located at the 8f site. Moreover, our data show that the Fe atoms are, in fact, strongly avoiding the 8i site.

The results obtained by us for  $\text{YFe}_4\text{Al}_8$  are in good agreement with results obtained from  $^{57}\text{Fe}$  Mössbauer spectroscopy (Buschow and van der Kraan 1978). The  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{RFe}_4\text{Al}_8$  exhibited fairly sharp lines belonging to a single sub-spectrum. These data were interpreted as showing that the Fe atoms are restricted only to a single site, 8f, as has also been derived from the HRPD data.

In situations like those described above, where a given type of atom can occupy more than one site, one has to take into consideration that the degree of site preference does not exclusively depend on enthalpy considerations. Entropic contributions to the stability are important as well. This holds for those compounds, in particular, that are formed at fairly high temperatures (as, e.g., by melting the components together) and in which atomic motion is frozen-in at lower temperatures (owing to limited diffusion of atoms). Very likely this is the case for the compounds  $RFe_4Al_8$  where a full occupancy of the 8f site by Fe atoms would be the most stable situation at 0 K. However, the possibility of site interchange between Fe and Al can be taken to be frozen-in below 700 °C, for example. This means that there may still be a non-negligible occupation of the 8f and 8i site in  $RFe_4Al_8$  samples. Atomic ordering of the Fe atoms into the 8f position will generally be higher the lower the annealing temperature, which necessarily has to be above 700 °C. In unannealed samples, in particular, one may also expect a substantial occupation by Fe of the 8j and 8i sites. This may explain why three different subspectra were needed to fit the  $^{57}Fe$  Mössbauer spectra of as-cast samples (Felner and Nowick 1978), while only a single subspectrum was needed for fitting well-annealed samples (Buschow and van der Kraan 1978).

In conclusion, our results confirm the results obtained previously by means of  $^{57}Fe$  Mössbauer spectroscopy by showing that the Fe atoms in  $RFe_4Al_8$  are located almost exclusively at only one of the three possible sites. We have established now that this site is the 8f site. By combining the results of both investigations it can be stated that the 8f site is the majority site for Fe in  $YFe_4Al_8$  and that the Fe atoms carry a substantial magnetic moment at this site.

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