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# Atomic distribution in $RFe_xAl_{12-x}$ compounds with R = Tb, Dy, Ho, Er, Tm and Fe concentrations $x \approx 5$ studied by neutron diffraction

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## Abstract

The ternary intermetallic rare earth–iron–aluminium compounds crystallize isostructurally in the tetragonal $ThMn_{12}$-type structure, space group *I4/mmm*. Neutron diffraction reveals atomic distributions, with R on 2a sites and nearly 100% occupancy of 8f sites by Fe and of 8i sites by Al. 8j sites are occupied by both Fe and Al according to stoichiometry. There are indications of a clustering of iron atoms on 8j positions. Refined structural parameters and interatomic distances are discussed with respect to the preferential site occupations of Fe and Al. Unit cell contractions due to lanthanides and different Fe/Al mixing ratios are observed.

## 1. Introduction

Ternary intermetallic heavy rare earth (R) compounds $R(Fe,Al)_{12}$ are known to crystallize in the tetragonal $ThMn_{12}$ structure over a rather wide range of mixing ratios of iron to aluminium [1–3]. The $ThMn_{12}$ structure is characterized by three different symmetry sites of four equivalent positions each to be occupied by the Mn atoms. When changing monoatomic conditions, *e.g.* exchanging manganese with the two different substitutes iron and aluminium, the question arises of an ordered or a statistically disordered occupation of those three non-equivalent sites. So far, most information exists on compounds with an iron to aluminium mixing ratio of 1:2. Lattice constants and unit cell volumes of $RFe_4Al_8$ compounds, as obtained from X-ray diffraction, are summarized in ref. 4.

Structure refinements on $RFe_4Al_8$ compounds were performed using neutron diffraction. Neutron diffraction is an adequate method to distinguish Fe and Al from the heavy rare earth and to investigate simultaneously the magnetic properties of the 4f-3d compounds. $RFe_xAl_{12-x}$ with $x = 4$ (Fe/Al mixing ratio of 1:2) reveals a rather well ordered distribution of iron on one and aluminium on two symmetry sites [5]. Preparation dependent variations and/or stoichiometry conditioned vacancies of about 5–8% were found in some specimens [6,7]. Structural defects are assumed to be responsible for finding spin glass behaviour in some of these compounds [8]. Neutron diffraction on $RT_4Al_8$ compounds (T = Cr, Mn) revealed also a strong preferential site occupation of the 3d-transition element (T) at one of the three non-equivalent sites [9].

This paper deals with $RFe_xAl_{12-x}$ compounds with $x \approx 5$. Due to the Fe/Al mixing ratio of 1:1.4, a completely ordered atomic distribution on three symmetry sites is not possible. We have applied neutron diffraction to determine the real structure and to compare the neutron results with predictions made by a Wigner–Seitz analysis [10]. In a separate paper, we report on the magnetic structures in this series of compounds [11].

## 2. Experimental details

The structure investigations were performed on polycrystalline material, which was prepared by arc melting in a dry argon atmosphere using the nominal amounts of atomic constituents. Subsequently, the material was annealed at 800 °C for 1 week. Preliminary X-ray tests of the powder showed that the specimens were of single phase.

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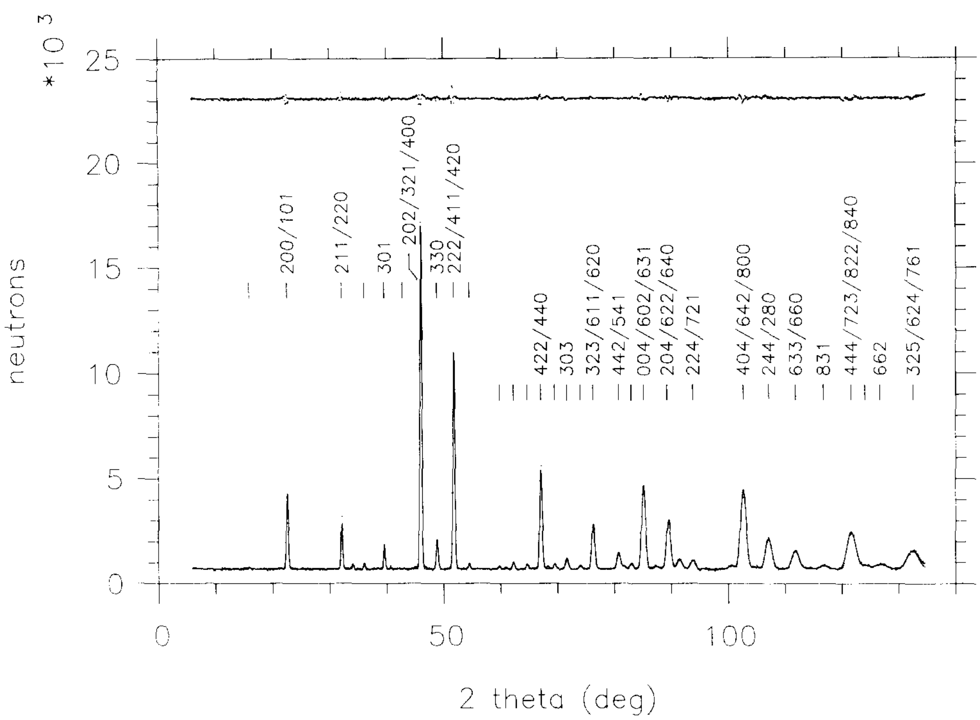

Fig. 1. Profile analysed neutron diffraction pattern of $TbFe_5Al_7$; deviations between observed and calculated count rates according to the Rietveld refinement are given at the top. Insignificant impurities of a FeAl-phase (space group *Pm3m*) are found.

The neutron diffraction measurements were performed on the multicounter powder diffractometer DMC at the SAPHIR-reactor of the LNS in Würenlingen [12]. The neutron wavelength was 1.704 Å. The sample material was contained in vanadium cans of 8 mm diameter and 50 mm height; the measurements were done in a temperature variable He-cryostat. Data analysis was performed by full pattern Rietveld refinements on diagrams taken at 250 K (Fig. 1). Neutron scattering lengths used were: $b(\mathrm{Al}) = 3.449$ fm, $b(\mathrm{Fe}) = 9.45$ fm, $b(\mathrm{Tb}) = 7.38$ fm, $b(\mathrm{Dy}) = 16.9$ fm, $b(\mathrm{Ho}) = 8.01$ fm, $b(\mathrm{Er}) = 7.79$ fm and $b(\mathrm{Tm}) = 7.07$ fm.

## 3. Structural results

The $RFe_xAl_{12-x}$ compounds with $x \approx 5$ crystallize in space group *I4/mmm* with two formula units per cell. R atoms occupy site 2a (0,0,0); the three non-equivalent positions at the Fe and Al atom's disposal are 8f (1/4,1/4,1/4), 8i ($x$,0,0) and 8j ($x$,1/2,0). Refined lattice constants, positional parameters and atomic site occupancies are summarized in Table 1.

The data indicate a more or less pure occupation of sites 8f and 8i with Fe and Al atoms, respectively; 8j positions are of mixed type, occupied with the remaining Fe and Al. The Fe–Al occupancy values are obtained following the refinement calculations, where the scattering power of the 8f-, 8i- and 8j-positions each is initially defined by a sum of iron and aluminium scattering lengths; the scattering lengths on each site are multiplied by individual weighting factors, which represent the individual atomic site occupancies to be refined. According to this procedure, the real stoichiometry of the $RFe_xAl_{12-x}$ specimens was derived by calculating the characteristic values. As can be seen from Table 1, there are some deviations from the nominal value $x = 5$.

Refined lattice and positional parameters were used to calculate interatomic distances (Table 2) and to establish distinct differences in the coordination between rare earth sites and 8f, 8j and 8i positions, respectively; the structural network is depicted in Fig. 2. Each rare earth atom is directly coordinated with four of the 8i aluminium atoms, which lie inside the tetragonal basis plane. The next nearest coordination is with the mixed occupied 8j positions, while the 8f sites of pure iron are characterized by largest distances to the rare earth. Furthermore, it can be stated that 8j–8f distances are very similar to those of 8f–8f, whereas 8j–8i distances are definitely larger. These findings hold for all the compounds investigated, *i.e.* independent of the rare earth partner.

## 4. Discussion

Our neutron diffraction results of the $RFe_5Al_7$ compounds reveal clearly that the iron atoms are placed on those symmetry positions of the $ThMn_{12}$ structure

TABLE 1. Refined structural parameters of ternary rare earth (R)–iron aluminium compounds accordint to neutron diffraction Rietveld refinements; Bragg $R$ values, $R_B$, are given; parameters are related to space group $I4/mmm$; standard deviations in parentheses

| $RFe_xAl_{12-x}$ | R=Tb<br>$x=4.8$ | R=Dy<br>$x=4.6$ | R=Ho<br>$x=5.0$ | R=Er<br>$x=4.4$ | R=Tm<br>$x=4.7$ |
|---|---|---|---|---|---|
| Cell constants | | | | | |
| $a$ (Å) | 8.701(10) | 8.689(10) | 8.663(10) | 8.640(10) | 8.680(10) |
| $c$ (Å) | 5.038(10) | 5.038(10) | 5.029(10) | 5.016(10) | 5.033(10) |
| Atomic positions | | | | | |
| $x$(8i) | 0.343(1) | 0.341(1) | 0.341(2) | 0.342(1) | 0.343(1) |
| $x$(8j) | 0.275(1) | 0.273(1) | 0.276(1) | 0.277(1) | 0.277(1) |
| Site occupation | | | | | |
| R in 2a | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Fe in 8f | 1.00(1) | 0.99(5) | 1.00(1) | 1.00(1) | 0.99(1) |
| Al in 8f | 0.00(1) | 0.01(5) | 0.00(1) | 0.00(1) | 0.01(1) |
| Fe in 8j | 0.19(1) | 0.15(4) | 0.21(1) | 0.18(1) | 0.17(1) |
| Al in 8j | 0.81(1) | 0.85(4) | 0.79(1) | 0.92(1) | 0.83(1) |
| Fe in 8i | 0.02(1) | 0.00(3) | 0.03(1) | 0.02(1) | 0.00(1) |
| Al in 8i | 0.98(1) | 1.00(3) | 0.97(1) | 0.98(2) | 1.00(1) |
| $R_B$ (%) | 3.8 | 9.2 | 6.5 | 4.4 | 6.5 |

TABLE 2. Interatomic distances and coordination numbers CN of $RFe_5Al_7$ compounds; distances in Å of nearst atomic neighbours on sites 2a (R=Tb, Dy, Ho, Er, Tm), 8f (Fe), 8j (Fe and Al), and 8i (Al) of space group $I4/mmm$

| $RFe_5Al_7$ | CN | R=Tb | R=Dy | R=Ho | R=Er | R=Tm |
|---|---|---|---|---|---|---|
| 2a–8f | 8 | 3.324 | 3.320 | 3.311 | 3.302 | 3.317 |
| –8j | 8 | 3.190 | 3.199 | 3.176 | 3.162 | 3.175 |
| –8i | 4 | 2.984 | 2.963 | 2.954 | 2.955 | 2.977 |
| 8f–2a | 2 | 3.324 | 3.320 | 3.311 | 3.302 | 3.317 |
| –8f | 2 | 2.519 | 2.519 | 2.515 | 2.508 | 2.516 |
| –8j | 4 | 2.523 | 2.519 | 2.514 | 2.508 | 2.519 |
| –8i | 4 | 2.641 | 2.633 | 2.626 | 2.621 | 2.635 |
| 8j–2a | 2 | 3.190 | 3.199 | 3.176 | 3.162 | 3.175 |
| –8f | 4 | 2.523 | 2.519 | 2.514 | 2.508 | 2.519 |
| –8j | 2 | 2.768 | 2.789 | 2.744 | 2.725 | 2.737 |
| –8i | 2 | 2.720 | 2.707 | 2.711 | 2.710 | 2.723 |
| –8i | 2 | 2.755 | 2.745 | 2.759 | 2.755 | 2.764 |
| 8i–2a | 1 | 2.984 | 2.963 | 2.954 | 2.955 | 2.977 |
| –8f | 4 | 2.641 | 2.633 | 2.626 | 2.621 | 2.635 |
| –8j | 2 | 2.720 | 2.707 | 2.711 | 2.710 | 2.723 |
| –8j | 2 | 2.755 | 2.745 | 2.759 | 2.755 | 2.764 |
| –8i | 1 | 2.732 | 2.763 | 2.755 | 2.730 | 2.726 |
| –8i | 4 | 3.175 | 3.188 | 3.181 | 3.165 | 3.170 |

with largest possible distances to the rare earths. Within the statistical accuracy of our data, all 8f sites are occupied by iron. The surplus of Fe atoms is found on the 8j sites. This seems reasonable when considering the equivalency of 8f–8f and 8f–8j distances within the structure (Table 2) and the non-equivalency to the 8i–8i distances; there is a strong preference of aluminium for the 8i sites. Our findings are in full agreement with neutron diffraction results on $RFe_4Al_8$ compounds by Moze *et al.* [5] and with X-ray results on $RFe_6Al_6$ compounds by Felner [2]. Predictions by Melamud *et al.* [10], that, according to a Wigner–Seitz analysis, the magnetic iron is placed on the 8i site, cannot be confirmed.

The reluctance of Fe atoms to occupy 8i sites in the $ThMn_{12}$ structure, a fact that was also found by Yang *et al.* on $Y(Mn_{1-x}Fe_x)_{12}$ [13], seems to be a general steric constraint and cannot simply be attributed to the slightly smaller metallic radius of iron compared to aluminium. The effect due to the different atomic radii can be seen when comparing lattice parameters of $RFe_4Al_x$ compounds [7] with those of $RFe_5Al_7$ (Fig. 3). The higher amount of iron causes an average reduction in the basis plane lattice parameter by about

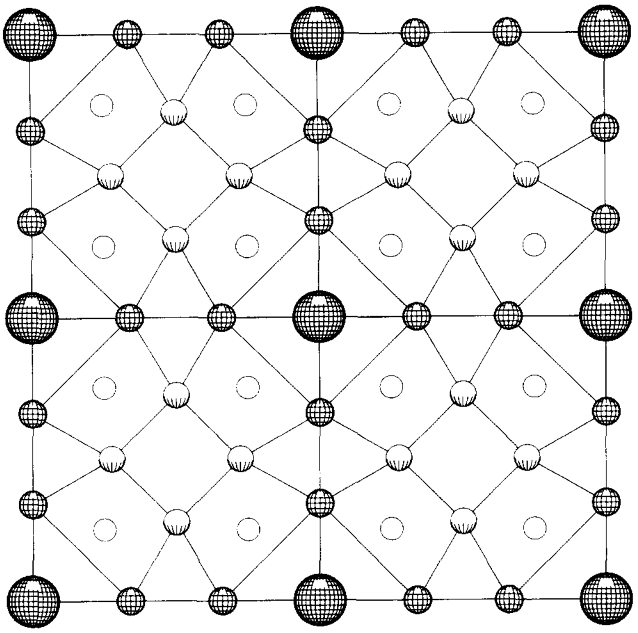

Fig. 2. Projection of four neighbouring unit cells of the $RFe_5Al_7$ structure into the tetragonal basis plane; R atoms at $z=0$ (large spheres), Al in 8i at $z=0$ (small filled spheres), Al and Fe at $z=0$ in 8j (small half-filled spheres), Fe at $z=1/4$ in 8f (open spheres).

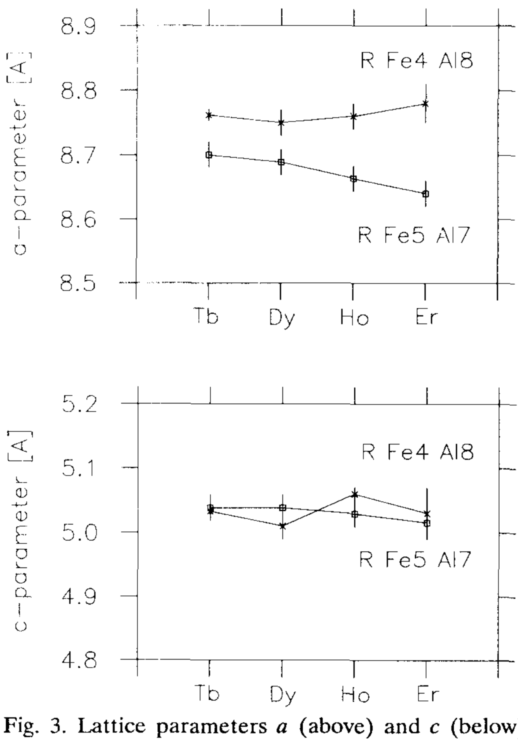

Fig. 3. Lattice parameters *a* (above) and *c* (below) of $RFe_5Al_7$ (squares) and $RFe_4Al_8$ (crosses) as refined from neutron diffraction data.

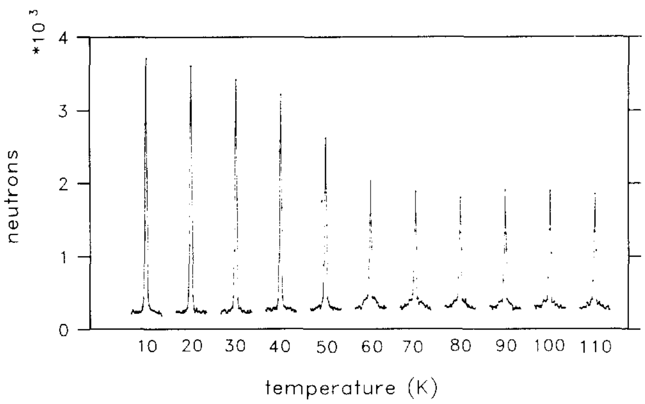

Fig. 4. Temperature dependence of the (2 0 0/1 0 1) neutron diffraction peak profiles of $HoFe_5Al_7$; diffuse scattering beyond the Bragg peaks is observed well above the magnetic ordering temperature of about 60 K.

0.1 Å for the corresponding rare earth compounds; the lattice parameter *c*, however, is almost unchanged. Effects due to the lanthanide contraction in the $RFe_5Al_7$ compounds can be seen again especially inside the basis plane (see Table 1 and Fig. 3); but this effect is contaminated by the observed deviations from stoichiometry.

As far as the 8j positions of the $RFe_5Al_7$ compounds are concerned, there arises the question of a statistical distribution of the remaining Fe and Al atoms. There are indications of a clustering of iron at these positions. This is deduced from low temperature neutron diffraction measurements carried out during the present investigation. Beyond the Bragg reflections, we observed broad peaks well above the Curie temperatures (Fig. 4). This diffuse scattering is attributed to magnetic short range order initiated by iron on 8j positions, because such effects are not observed on $RFe_4Al_8$ compounds with no iron on 8j. The assumption of iron clusters on 8j is in accordance with similar findings for $RFe_6Al_6$ compounds [14]. It is evident that the iron distribution on the 8j sites and observed effects of spin-glass behaviour in several $R(Fe,Al)_{12}$ compounds are correlated to each other.

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