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Neutron diffraction study of the ferrimagnetic structures of RFe_5Al_7 compounds with R = Tb, Dy, Ho, Er, Tm

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Abstract

Long range order of ternary RFe_5Al_7 (R = Tb, Dy, Ho, Er, Tm) intermetallics of $ThMn_{12}$-type structure is analysed by neutron powder diffraction. Ferromagnetic order is found for both the heavy rare earth and the iron sublattices. Rare earth and iron moments are oriented antiparallel to each other, resulting in ferrimagnetic structures. The ordering temperatures are about 235 K for the Tb, Dy and Tm compounds and about 60 K for the Ho and Er compounds. Magnitudes and orientations of ordered magnetic rare earth and iron moments are determined; a moment modulation is observed in $TbFe_5Al_7$. The formation of the ferrimagnetic structures is preceded by short range or frozen magnetic states. The temperature behaviour of the magnetization is discussed.

1. Introduction

A great variety of unusual magnetic phenomena is displayed by magnetization curves and Mössbauer spectra reported on heavy rare earth (R) intermetallic compounds RFe_5Al_7 [1,2]. These findings are consistent with similar observations by magnetization and Mössbauer measurements reported on compounds RFe_xAl_{12-x} with different Fe/Al mixing ratios [3] and specifically on those with $x = 4$ [4,5] and $x = 6$ [6,7]. Explanations are given in terms of long range magnetic order comprising ferro-, antiferro- and ferrimagnetic structures as well as in terms of spin glass states. Neutron diffraction was applied to establish the magnetic structures of RFe_4Al_8 compounds [8,9]. Neutron diffraction in combination with magnetization and Mössbauer data also revealed similar spin glass behaviour in $HoFe_4Al_8$ [10,11] and some isostructural actinide compounds [12].

RFe_xAl_{12-x} compounds crystallize in the $ThMn_{12}$-type structure in the tetragonal space group *I4/mmm* with R on the 2a position and three non-equivalent sites 8f, 8i and 8j to be occupied by Fe and Al. The exact knowledge of atomic site occupancies is considered essential for the physical understanding of the different magnetic phenomena in this series of compounds; all conclusions drawn by bulk magnetic measurements must be related to the specific structural parameters of the specimens involved. Neutron diffraction revealed different deviations from ordered site occupancies and from nominal values of stoichiometry which is attributed to specific preparation conditions (see [9,10,13]).

This paper deals with the neutron diffraction analysis of the magnetic ordering behaviour of RFe_5Al_7 compounds. The specimens used for this investigation had been analysed before for their structural characteristics also using neutron diffraction which is considered to be an adequate method to distinguish between Fe and Al atoms in the neighbourhood of heavy rare earths [13].

2. Experimental details

RFe_xAl_{12-x} sample material existed in form of polycrystalline specimens of R = Tb, Dy, Ho, Er and Tm with x-values of the iron content of 4.8, 4.6, 5.0, 4.4 and 4.7, respectively. All specimens revealed well ordered structures according to space group *I4/mmm* with R on 2a and nearly 100% occupancies of 8f and 8i sites by Fe and Al, respectively; 8j positions are occupied by the remaining Fe and Al atoms [13].

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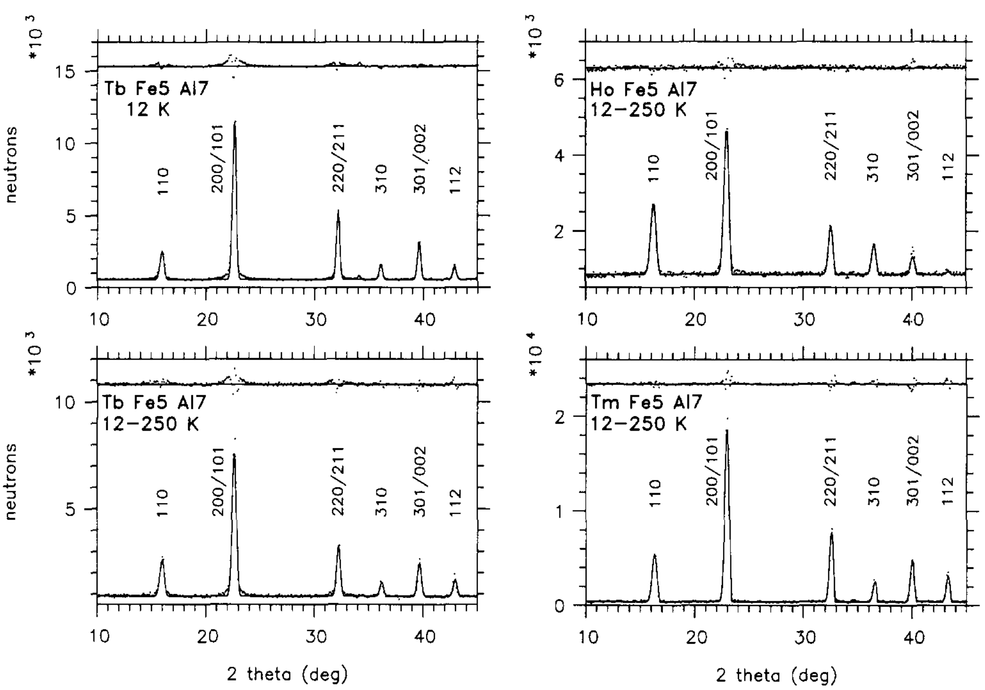

Fig. 1. Front part of profile analysed 12 K neutron diffraction pattern (top left) and temperature difference pattern 12–250 K (bottom left) of $TbFe_5Al_7$. Equivalent difference patterns of $HoFe_5Al_7$ and $TmFe_5Al_7$ containing pure magnetic intensities are shown on the right.

Low temperature neutron diffraction measurements were performed on the multicounter powder diffractometer DMC at the SAPHIR-reactor of the LNS in Würenlingen [14]; the neutron wavelength was 1.704 Å. The specimens were contained in cylindrical vanadium cans of 8 mm diameter and 50 mm height and inserted into a temperature variable He-cryostat. Complete diffraction patterns were run at 250 K and at low temperatures between 15 and 5 K. Temperature dependences of the diffraction peaks were measured during several cooling-down and warming-up cycles. The magnetic structures were analysed from the 12 K intensities and refined by Rietveld calculations taking into account atomic positions and site occupancies as obtained from the 250 K patterns in the paramagnetic phase (see [13]).

3. Magnetic structure results

The low temperature diffraction patterns of all compounds investigated are characterized by additional magnetic intensities to be found only on allowed nuclear reflection positions; temperature difference patterns are shown in Fig. 1. The magnetic reflections are consistent with long range ferromagnetic order of both the rare earth and the iron sublattices; the non-extinction conditions are $h+k+l=2n$ and additionally $h, k, (l)=2n$ for ferromagnetic Fe on the 8f positions (see [15]). Intensity refinement calculations revealed antiparallel orientations of the magnetic moments on the rare earth and the iron sites resulting in ferrimagnetic structures (Fig. 2).

The collinear magnetic moments are oriented inside the tetragonal basis plane in all compounds with the exception of $HoFe_5Al_7$ where the moments are directed along the tetragonal c-axis as seen by the much lower (1 1 2)-intensity (see Fig. 1). The magnetic neutron intensities are also used to determine the magnitudes of the atomic moments which are listed in Table 1. $TbFe_5Al_7$ exhibits weak satellite reflections at tem-

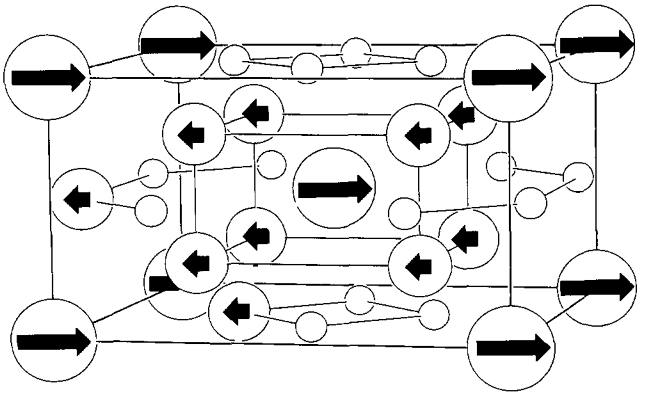

Fig. 2. Ferrimagnetic unit cell of RFe_5Al_7 compounds (R = Tb, Dy, Er, Tm) with antiparallel orientations of collinear rare earth moments (long arrows) on 2a sites and iron moments (short arrows) on 8f sites and some 8j positions; the other 8j positions (empty circles) and 8i sites (not shown) are occupied by non-magnetic Al.

TABLE 1. Curie temperatures T_c in K, magnitudes of magnetic moments μ in μ_B at $T=12$ K for the Tb, Ho and Tm compounds and at $T=15$ K for $DyFe_5Al_7$ and $T=5$ K for $ErFe_5Al_7$. Fe moments on 8f and 8j positions have been constrained to have the same value because their error margins are strongly correlated. Moment orientations are given with respect to the tetragonal c-axis

RFe_5Al_7	R=Tb	R=Dy	R=Ho	R=Er	R=Tm
Ferrimagnetic	$\mu \perp c$	$\mu \perp c$	$\mu \parallel c$	$\mu \perp c$	$\mu \perp c$
T_c	235(10)	230(23)	61	62(1)	235(20)
μ(R)	8.12(9)	9.5(1)	6.29(8)	8.96(8)	9.79(7)
μ(Fe)	1.64(6)	1.60(8)	1.65(4)	1.78(5)	1.21(5)

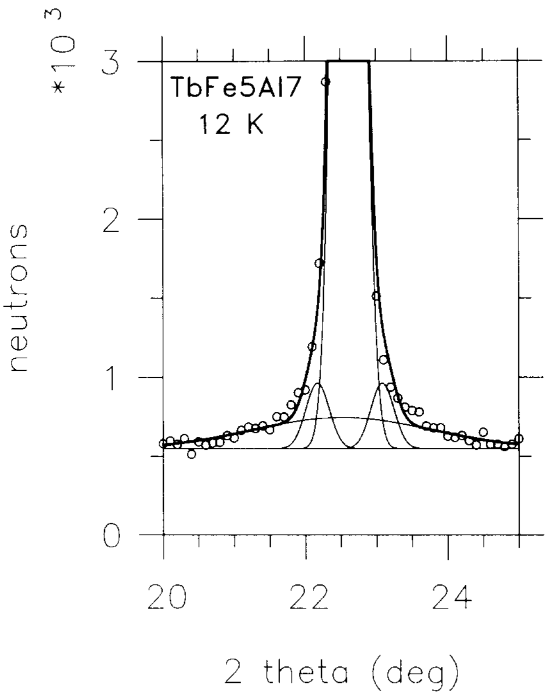

Fig. 3. Profile analysed (2 0 0/1 0 1) peak of $TbFe_5Al_7$ at $T=12$ K. Satellite reflections originating from an incommensurate magnetic structure component as well as a broad background peak of diffuse magnetic scattering are observed with the central Bragg peak.

peratures below 100 K in the ferrimagnetically ordered state (Fig. 3). These satellites are consistent with a modulation of the ferrimagnetic moments along the tetragonal basis plane direction; the periodicity of the modulation is about 20 unit cells. The reliability values of the Bragg intensities R_B as obtained by the Rietveld refinements of the low temperature neutron diffraction patterns are 4.8%, 6.6%, 6.5%, 4.5% and 6.1% for the Tb, Dy, Ho, Er and Tm compounds, respectively.

4. Temperature behaviour of magnetic ordering

Although all compounds are characterized by similar ferrimagnetic structures at low temperatures, we observe distinct differences in the temperature behaviour of the magnetic ordering processes. There are two classes of compounds differing strongly by the Curie temperatures, as seen in Table 1; on the one hand $TbFe_5Al_7$, $DyFe_5Al_7$ and $TmFe_5Al_7$ with ordering temperatures around 235 K and on the other hand, $HoFe_5Al_7$ and $ErFe_5Al_7$ showing long range order only below 60 K.

We have used neutron diffraction to study the development of the magnetic order by following the temperature dependences of several magnetic intensities (Fig. 4). Reflections (1 1 0) and (1 0 1) stand for ferromagnetic order of the rare earth site; reflection (2 0 0) which cannot be separated from (1 0 1) by conventional powder diffraction represents both ferromagnetic rare earth and iron sublattices. The experimental curves were fitted according to

$$I/I_0 \approx (1-T/T_c)^{2\beta} \qquad (1)$$

and exponents β were determined (Fig. 4). Again we observe a similar behaviour of $HoFe_5Al_7$ and $ErFe_5Al_7$ with $\beta=0.34(6)$ and substantially different magnetization processes in $TbFe_5Al_7$, $DyFe_5Al_7$ and $TmFe_5Al_7$ with β values of 0.53(7), 0.7(2) and 0.8(1), respectively.

Additional information is obtained by analysing the total neutron peak profiles. In some compounds, we observe broad peaks of diffuse magnetic scattering below the magnetic Bragg reflections (*cf.* Fig. 3). The diffuse peaks can be attributed to short range ferrimagnetic order, which occurs well above the Curie temperatures and the diffuse scattering disappears with increasing long range order (Fig. 5). Magnetic short range order is marked most strongly in $HoFe_5Al_7$ and $ErFe_5Al_7$, those compounds with the low Curie temperatures.

5. Discussion

As a common characteristic of the heavy rare earth compounds RFe_5Al_7, we can state collinear long range ferrimagnetic order at low temperatures. With the exception of Tm, the ordered iron and rare earth moments are observed lower than the corresponding free ion values (*cf.* Table 1). There are two indications that long range order is driven by the iron atoms: (1) neutron diffraction reveals only one common Curie temperature for both the individual rare earth and the iron sublattices; and (2) the ordering temperatures are higher than those of similar RFe_4Al_8 compounds with less iron. The additional iron on 8j positions acts as a strengthening partner in the magnetic interaction. It is assumed and verified by corresponding model refinements that Fe atoms on the mixed occupied 8i positions are ordered in the same way as those on the pure iron sites 8f.

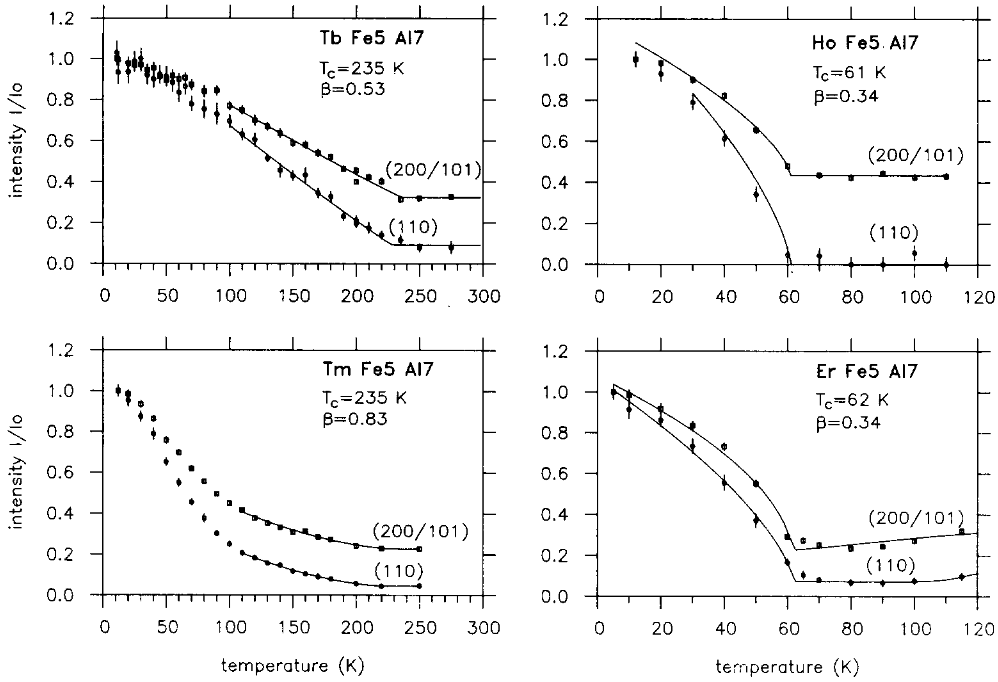

Fig. 4. Measured temperature dependence (points) of magnetic reflection intensities (1 1 0) and (2 0 0/1 0 1) and fits (solid line) according eqn. (1) resulting in values for the exponent β.

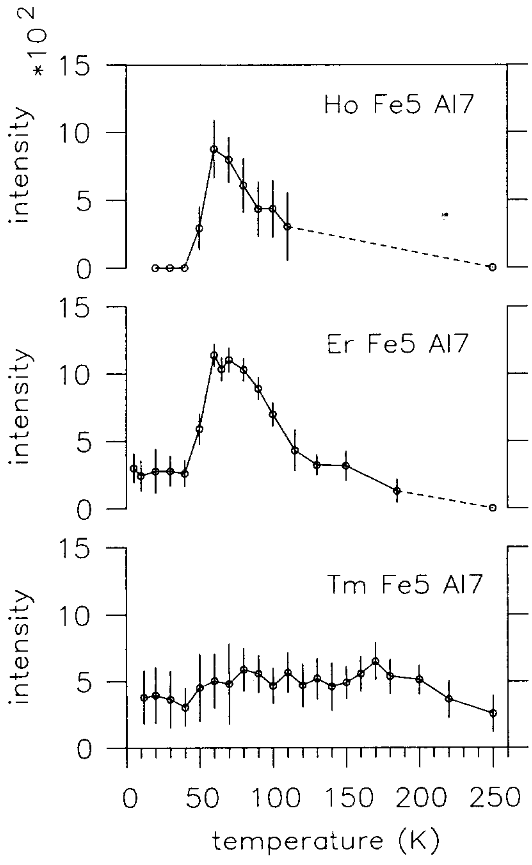

Fig. 5. Temperature dependence of the diffuse magnetic scattering intensity underneath the (2 0 0/1 0 1) peak of $HoFe_5Al_7$ (top) $ErFe_5Al_7$ (middle) and $TmFe_5Al_7$ (bottom).

Magnetic diffuse scattering gives a hint that there is no statistical Fe/Al distribution on 8j and that iron clusters are formed to establish short range order already at higher temperatures. This can be seen by the temperature dependence of the diffuse scattering in $HoFe_5Al_7$ and $ErFe_5Al_7$ (Fig. 5). The onset of short range order above 200 K corresponds to the Curie temperatures given by Felner *et al.* [2] according to magnetometric and Mössbauer experiments. Following the neutron diffraction experiments, we define the Curie temperatures of $HoFe_5Al_7$ and $ErFe_5Al_7$ to be the onset of long range ferrimagnetic order at 61 K and 62 K, respectively (see Fig. 4 and Table 1).

The transition to long range magnetic order in $TbFe_5Al_7$, $DyFe_5Al_7$ and $TmFe_5Al_7$ differs from a normal phase transition of Brillouin like behaviour as to be expected from a paramagnetic state. The observed linear or parabolic enhancements of the magnetic intensities (Fig. 4) point to spin frozen states well above the Curie temperatures. These findings are consistent with the results of susceptibility and Mössbauer measurements on similar compounds by Felner *et al.* [2,3], suggesting spin glass structures in the iron sublattices. Nevertheless, the physical understanding of the temperature behaviour observed here with neutrons is very different for the various rare earth compounds (Figs. 4 and 5) and needs still more experimental effort. At present, we are performing magnetization and Mössbauer measurements on the same sample material that was used for this neutron diffraction study in order to have a reliable basis for combining magnetization, Mössbauer and neutron results.

Acknowledgments

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