

## Magnetic and hyperfine interaction in $\text{YbFe}_4\text{Al}_8$ compound

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**Abstract**  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{YbFe}_4\text{Al}_8$  of the tetragonal  $\text{ThMn}_{12}$  structure have been investigated. Mössbauer measurements at the lowest temperatures yield information on the iron population in three crystallographic sites 8f, 8j and 8i available for Fe atoms. The obtained results indicate on the coexistence of magnetically ordered and paramagnetic-like Fe moments within antiferromagnetic phase of  $\text{YbFe}_4\text{Al}_8$ . The MS measurements show that the onset of short range antiferromagnetic interaction in the Fe sublattice takes place at 220 K.

**Key words** Mössbauer effect • rare earth • iron compounds

### Introduction

Magnetic properties of the rare earth compounds of the  $\text{ThMn}_{12}$ -type structure (tetragonal  $I4/mmm$  space group) have caused a considerable interest both from the fundamental point of view as well as potential precursors for hard magnetic materials with high Fe content like  $\text{SmFe}_{10}\text{Si}_2$  (for a review see Ref. [9]). In the  $I4/mmm$  space group, four different sets of equivalent positions 2a, 8f, 8j and 8i (in Wyckoff notation) are available. The rare earth atoms occupy the 2a sites and the transition-metal (Fe) atoms start by occupying a set of 8f sites. A special situation exists for intermetallic compounds of  $\text{RFe}_4\text{Al}_8$  stoichiometry. There are 26 atoms (two molecules) per unit cell. The iron atoms occupy only the 8f sublattice, whereas, the aluminium atoms occupy the 8j and 8i positions. Fe, mixing with the Al atoms with increasing Fe content over four per formula unit, also occupies these positions. The magnetic [1, 2], neutron diffraction [6, 7] and Mössbauer effect [4, 5, 11] measurements have established a complex antiferromagnetic (AF) ordering in the  $\text{RFe}_4\text{Al}_8$  compounds even when the rare earth elements are non-magnetic ( $\text{R} = \text{Y}, \text{Lu}, \text{La}$  and  $\text{Ce}$ ). In this case, antiferromagnetism is determined by Fe-Fe magnetic moment interactions in 8f positions [1]. The transition temperatures  $T_N$  determined from susceptibility measurements are often lower than those determined from the Mössbauer effect [1, 11].

In this report, investigations of the  $^{57}\text{Fe}$  Mössbauer effect in the  $\text{YbFe}_4\text{Al}_8$  compound are presented. Early,  $^{170}\text{Yb}$  Mössbauer studies [2] and  $L_{\text{III}}$  X-ray absorption investigations [8] have indicated that the Yb ions probably carry magnetic moment. However, the examinations of magnetic properties of  $\text{Yb}_{1-x}\text{Sc}_x\text{Fe}_4\text{Al}_8$  alloys [10] have

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shown that this is not the case. The values of effective magnetic moments  $p_{\text{eff}} = 7-8 \mu_B/\text{f.u.}$  measured from the Curie-Weiss law at  $T > 200$  K for various  $x$ , do not depend on composition what indicates that the  $\text{YbFe}_4\text{Al}_8$  compound belongs rather to the group of  $\text{RFe}_4\text{Al}_8$  ( $R = \text{La, Ce, Lu, Y}$ ) compounds, whose magnetic properties are determined only by the iron magnetic moments.

## Experimental

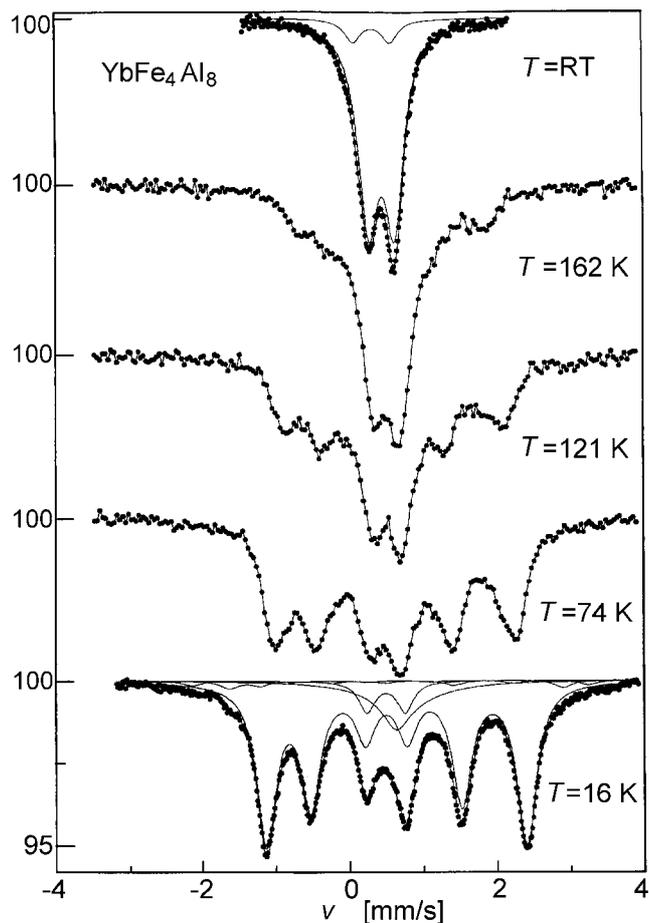
$\text{YbFe}_4\text{Al}_8$  compound has been prepared by melting the elements in stoichiometric quantities 1:4:8 in an arc furnace under protective argon atmosphere. This procedure has been followed by homogenization during 8 weeks at about  $500^\circ\text{C}$  in the unevacuated quartz tube. The powder X-ray diffraction pattern (XRD) shows no traces of impurity phases.

The  $^{57}\text{Fe}$  Mössbauer spectra were taken at temperatures from 16 K to RT with a conventional constant acceleration spectrometer. The source was  $^{57}\text{Co}$  in an Rh matrix. The absorber was prepared by grinding a sample to fine powder and mixed with MgO to ensure constant surface distribution over the absorber container with an optimal thickness of  $9 \text{ mg Fe}/\text{cm}^2$ . The velocity scale calibration and the estimation of isomer shift values have been performed relative to  $\text{Na}_2(\text{NO})\text{Fe}(\text{CN})_5 \cdot 2\text{H}_2\text{O}$ . The spectra were analyzed by the least-squares fits within the Lorentz approximation using BOSSAN program.

## Results and discussion

Mössbauer spectra (MS) registered at various temperatures in the range 16–295 K are shown in Fig. 1. The room temperature MS exhibits an asymmetric quadrupole doublet. More than one doublet were considered to fit this spectrum. The fitting parameters are shown in Table 1. The relative intensity of one of the two doublets is practically constant (about 6%) in the whole temperature range. This line was attributed to the unknown paramagnetic impurity phase whose amount was too small to be detected in XRD analysis.

The Mössbauer spectra at the lowest temperature (16 K) do not correspond to a single unique hyperfine field as one could expect. The spectra can be analyzed as being composed of at least three magnetic subspectra with different hyperfine fields and quadrupole interactions. The interpre-



**Fig. 1.** Mössbauer absorption spectra of  $^{57}\text{Fe}$  at various temperatures in  $\text{YbFe}_4\text{Al}_8$ . The solid line represents a least-squares fit assuming superposition of non-magnetic and magnetic states described in the text.

tation of these Mössbauer spectra is that the Fe atoms not only occupy 8f sites, but probably also 8j and 8i sites normally occupied by the aluminium atoms (see Table 1). This suggestion is supported by the MS results reported for  $\text{YFe}_4\text{Al}_8$  in Ref. [3]. The number of iron ions in  $\text{YFe}_4\text{Al}_8$  in the three sites 8f, 8j and 8i as 3.1, 0.6, 0.3 have been found, respectively. A thorough analysis of the MS of  $\text{YbFe}_4\text{Al}_8$  has shown that one more broadened single line superimposed on a six-line hyperfine field patterns at low temperatures (see bottom pattern in Fig. 1). To get good agreement between the fit and experimental spectra, this line

**Table 1.** Hyperfine parameters estimated from the Mossbauer spectra.\*

$T$ [K]	Sites	$H_{\text{eff}}$ [T]	IS [mm/s]	QS [mm/s]	$t$ [s]	$\Gamma$ [mm/s]	$I$ [%]	Remarks
295	all	–	0.44	0.35	–	0.33	94	doublet
16	8f	11	0.56	0.13	–	0.30	76	sextet
16	–	11	0.72	0.13	$8.8 \times 10^{-1}$	0.30	13	relaxation sextet
16	8j	12.8	0.34	0.25	–	0.30	3	
16	8i	16.3	0.58	–0.21	–	0.30	2	sextet
295	–	–	0.32	0.50	–	0.27	6	sextet
16	–	–	0.48	0.52	–	0.27	6	impurity doublet

\* IS – isomer shift; QS – quadrupole splitting;  $\Gamma$  – line-width;  $H_{\text{eff}}$  – magnetic hyperfine fields.

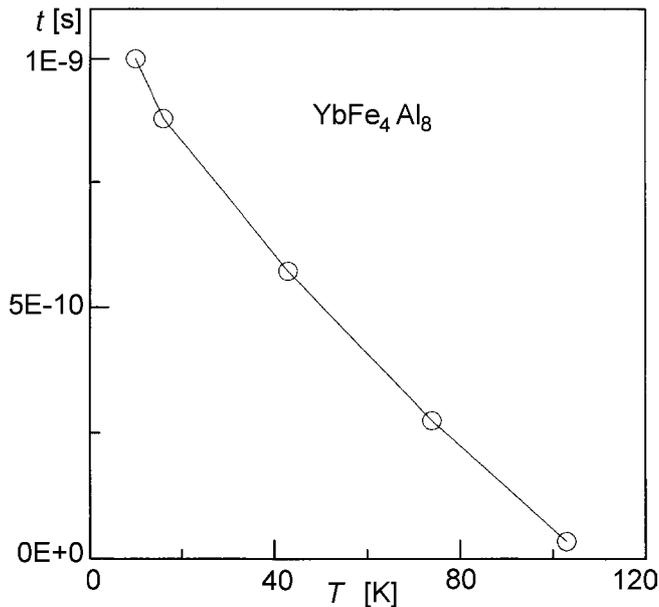


Fig. 2. Temperature dependence of the relaxation time of the frustrated Fe-spin.

must be additionally included. The shape of this line deviates from the Lorentz-like and can be assigned to the Fe moments experienced at partial ordering or rapid relaxation [5]. These effects are most probably due to the distribution of different neighbours nearest to Fe (NN) with a variety of local competing exchange fields which lead to frustration of some Fe 8f moments in the lattice. Using the observed effective hyperfine field, assigned to 8f position we have determined a relaxation time as about  $10^{-9}$  s at 16 K. The relaxation time of these type of Fe sites increases with decreasing temperature as is shown in Fig. 2. The appearance of broad singlet, paramagnetic-like, MS line indicates that at low temperatures coexist regions of fast Fe-spin fluctuations and the regions with just AF ordering. This means that the exchange interactions between some Fe moments and main Fe ordered sublattice are small. It is likely that these Fe moments experience a fast relaxation between the two directions parallel to the

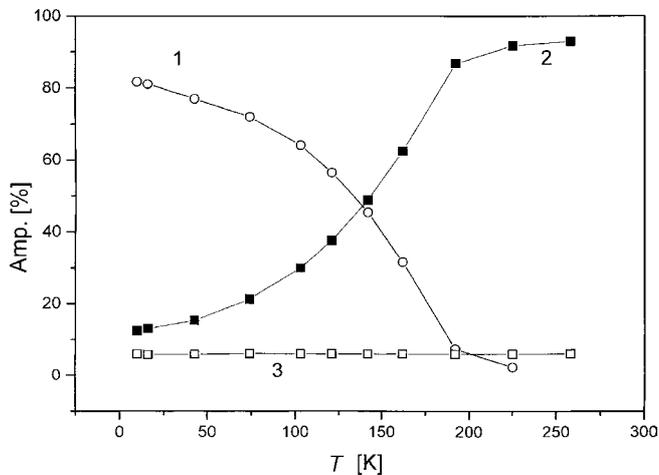


Fig. 3. Relative fraction of the paramagnetic (quadrupole doublet) state (2) and the magnetically ordered (sextet) state (1) as a function of temperature. Open square symbols (3) represent the unknown impurity phase contribution.

antiferromagnetically coupled Fe moments and are responsible for the so-called “relaxation sextet” in the MS of  $\text{YbFe}_4\text{Al}_8$ . This relaxation sextet changes to a paramagnetic doublet at temperatures higher than 100 K.

The interesting temperature dependence of the magnetic sextets has been observed. Their intensities diminish with temperature. Simultaneously, a non-magnetic (paramagnetic-like) doublet ( $IS = 0.44$  mm/s,  $QS = 0.35$  mm/s) appears, whose intensity becomes larger with increasing temperature. In Fig. 3 the relative fraction of paramagnetic and magnetically ordered Fe moments as a function of temperature are presented. Similar features also shows the Y compound [12]. In Fig. 4 the temperature dependence of the magnetic hyperfine field on the dominant site Fe 8f is displayed. These data revealed that the magnetic exchange interaction in  $\text{YbFe}_4\text{Al}_8$  exists, at least within Fe 8f sublattice, until about 220 K.

$\text{RFe}_4\text{Al}_8$  intermetallic compounds are customarily thought as possessing a relatively perfect periodic crystal structure. However, recent studies have indicated that even their single crystals exhibit the deviation from 1:4:8 stoichiometry [11]. It has been found that the differences of 1–2% in the site occupation factors, which are difficult to be detected by X-ray, create random competing Fe-Fe exchange interactions. The observed coexistence of the non-magnetic doublet with the magnetic sextet in MS spectra can be caused by a random distribution of Fe and Al atoms on the 8f and 8j/8i sites. In such a case, in the lattice are created 8f Fe atoms which have only one ( $z = 1$  NN) Fe atom as the nearest neighbour (NN), instead of  $z = 2$  NN's in 8f sites. Simultaneously, there appear Fe atoms in 8j sites, which in turn, will have  $z = 3$  NN instead of  $z = 4$  NN's as is expected for ideal 1:4:8 stoichiometry. All these distorted Fe positions are probably paramagnetic or partly ordered with a very small  $H_{\text{eff}}$  values (partial  $H_{\text{eff}}$  depends on ( $z$ ) value; lower  $z$  smaller  $H_{\text{eff}}$ ). The above mentioned types of behaviour are characteristic of other compounds with composition  $\text{RFe}_4\text{Al}_8$  or close to it [12].

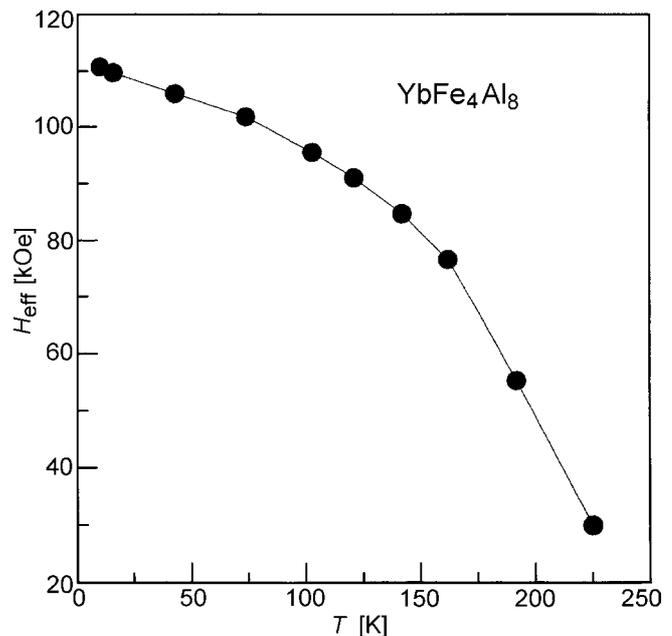


Fig. 4. The effective hyperfine field on the iron Fe 8f atoms as a function of temperature.

## Conclusion

Mössbauer studies of  $\text{YbFe}_4\text{Al}_8$  compound have revealed that its magnetic properties probably are strongly determined by partial disorder within the Fe and Al sublattices. Due to partial disorder, the system is decomposed to the AF and spin fluctuating subsystems which coexist and interact with each other in a wide temperature range.

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