

^{57}Fe Mössbauer effect studies of $\text{ErFe}_{11}\text{Ti}$ and $\text{ErFe}_{11}\text{TiH}$ compounds

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Abstract Ferromagnetic compounds $\text{ErFe}_{11}\text{TiH}_x$ ($x = 0, 1$) have been investigated by ^{57}Fe Mössbauer spectroscopy in the temperature range 20–300 K. Mössbauer spectra were analyzed in terms of a model which takes into account the local environment of Fe atoms on three crystallographic sites (8f, 8j and 8i) and an influence of the random distribution of titanium on the 8i site. The 14 sextets with different intensities have been considered. The temperature dependencies of hyperfine interaction parameters and subspectra contributions were derived from experimental spectra. The hyperfine fields and the isomer shift increasing upon hydrogenation are discussed in terms of the hydrogen-induced Wigner-Seitz unit cell expansion and the *s*-electrons transfer from Fe atoms to the adjacent hydrogen atoms.

Key words rare earth • iron compounds • metal hydrides • Mössbauer spectroscopy

Introduction

RFe_{11}Ti ($\text{R} = \text{rare earth metal}$) systems are interesting ferromagnetic compounds [2] which attract attention for their large magnetization, high Curie temperatures and pronounced uniaxial magnetic anisotropy [8]. These magnetic properties can be improved by hydrogen, nitrogen or carbon absorption [9]. High concentration of the cheap iron metal in these compounds is worth of emphasizing if they are used as a material for permanent magnets in the future. This class of material is also interesting from the fundamental point of view (for review see Ref. [10]). Both $\text{ErFe}_{11}\text{Ti}$ and $\text{ErFe}_{11}\text{TiH}$ are ferromagnets at temperatures 515 and 563 K, respectively. They also exhibit spin reorientation transitions at 50 and 41 K, respectively [7]. RFe_{11}Ti compounds crystallize in the tetragonal ThMn_{12} -type crystal structure, which belongs to the $I4/mmm$ space group. There are 26 atoms (two molecules) per unit cell. Rare earth atoms (R) occupy 2(a) (in Wyckoff notation) sites, iron occupies three crystallographic inequivalent sites, i.e. the 8f, 8i, and 8j sites. It has been established that titanium randomly replaces one fourth of iron at the 8i site, whereas hydrogen, if present, fully enters into the octahedral 2b (0, 0, 1/2) site.

$\text{ErFe}_{11}\text{Ti}$ intermetallic compound has been a subject of many different investigations [5, 7] including a ^{57}Fe Mössbauer technique [1, 3]. Initially, the low temperature Mössbauer spectra of $\text{ErFe}_{11}\text{Ti}$ were fitted by three Zeeman sextets, which are associated with the three non-equivalent Fe atom crystal sites in $I4/mmm$ lattice [12]. However, due to the partial occupation of the 8i sites by titanium atoms, the Fe atoms are subjected to different atomic and magnetic environments caused by the various numbers of Ti atoms present in the Fe neighbourhood. In such a case,

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each of the three sextets must be additionally divided into subsextets, $8f_n$, $8j_n$ and $8i_n$, where $n = 0, 1, 2, 3$ which corresponds to iron atoms with zero, one, two and three titanium in the nearest neighbourhood. The intensities of these subsextets are proportional to the probability, $P_m(k)$, of finding k Ti atoms in a set of (m) 8i nearest neighbour positions of a considered Fe crystal site. The probabilities $P_m(k)$ are calculated from a binomial distribution law [1]:

$$(1) \quad P_m(k) = \frac{m!}{k!(m-k)!} p^k (1-p)^{m-k}$$

where p is the relative fraction of Ti atoms in the 8i site and k varies in step of one to m .

Taking into account the six 8i nearest neighbours for the 8i sites, five for 8j and five for the 8f site one should consider at least 16 subspectra for appropriate analysis of the experimental Mössbauer spectra. However, in earlier papers the Mössbauer spectra of analogous compounds $\text{CeFe}_{11}\text{Ti}$ [6], and YFe_{11}Ti [11] were adjusted with the model of nine Zeeman sextets. It means that for each Fe position the three types of neighbourhood have been considered with zero, one and two Ti atoms in NN, respectively. This approximation was reasonable because nine sextets covered almost 93.5% of the total spectra, expected for 16 sextets.

In this paper the Mössbauer spectra of $\text{ErFe}_{11}\text{Ti}$ and $\text{ErFe}_{11}\text{TiH}$ hydride are analyzed in terms of the crystallographic structure, and site occupancy as a function of temperature in the range of 20–300 K. The main aim of our studies was to evaluate the contribution of hydrogen atoms to the global magnetic properties and its influence on the magnetic contributions associated with each of the three Fe sites.

Experimental

The ^{57}Fe spectra were taken with a conventional constant acceleration spectrometer. The γ radiation source was ^{57}Co in an Rh matrix. The absorber was prepared by grinding the sample to a fine powder with MgO to ensure a constant surface density with an optimal thickness of 9-mg Fe cm^{-2} . The velocity scale was calibrated with a metallic α -iron foil at room temperature. The isomer shift values are given relative to α -Fe at $T = 295$ K. The spectra were analyzed by the least-squares fits of the experimental Mössbauer line using the Lorentzian approximation. The isomer shift, IS, and magnetic hyperfine field, H_{hf} , parameters have been obtained.

Results and discussion

Mössbauer spectra registered at room temperature for $\text{ErFe}_{11}\text{Ti}$ and its hydride $\text{ErFe}_{11}\text{TiH}$ are shown in Fig. 1. The attempts to describe the Mössbauer spectra with nine sextets appeared to be unsatisfied in this case. First of all, the temperature dependence of hyperfine parameters obtained was not enough logical and consistent. The estimated average linewidth of the order of 0.7–1 mm/s

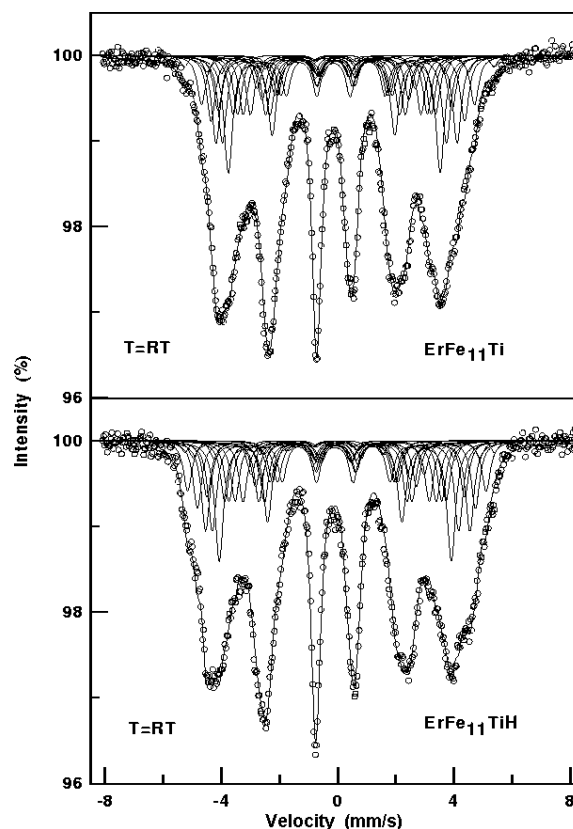


Fig. 1. ^{57}Fe Mössbauer transmission spectra for the $\text{ErFe}_{11}\text{Ti}$ and $\text{ErFe}_{11}\text{TiH}$ ferromagnets at room temperature. The solid lines are fits to the data. Line position of the 14 sextets and their relative intensities are depicted.

were also too high. A fit with nine sextets failed particularly to fit the inner side of the lines at around of ± 4 mm/s. All this indicated that another approximation has to be found and applied. Therefore, to describe the Mössbauer spectra in $\text{ErFe}_{11}\text{Ti}/\text{ErFe}_{11}\text{TiH}$ systems we propose in this paper a more real approach, which will differentiate sites not only with the various number of Ti atoms in NN but also with the different distances between iron atoms. Actually, this new approach is an extension of 16 Zeeman subspectra model [1].

Model

In the $\text{ErFe}_{11}\text{Ti}$ compound (see Table 1) each Fe atom in 8f site has 4 near-neighbour (NN) atoms in 8i, 4 in 8j sites, and 2 in 8f site. Each atom in 8j site has four NN atoms in 8f, two in 8j sites, and four in 8i sites but two of them at a distance of 2.62 Å and the other two at a distance of 2.75 Å. The Fe in 8i site has four NN in 8i site at a distance of 3.05 Å and one atom at 2.75 Å. Taking into account different distances and statistical distribution of the Ti in 8i sites, the 8i sites with 1, 2, 3 and 4 Ti atoms and 8j site with 1 and 3 Ti atoms in the NN split into two subsextets each. The 8j site with 2 Ti atoms in the near-neighbour splits into three subsextets with equal intensities. This model gives 24 sextets all together: 10 sextets for 8i positions, 9 sextets for 8j and 5 for 8f sites (see Table 2). In the hydride samples this approach is the same because hydrogenation retains the crystal structure of the parent

Table 1. Crystal lattice sites and their nearest neighbourhood in the ThMn₁₂ structure. The Wigner-Seitz unit cell volumes for the 8f, 8j and 8i sites in the ErFe₁₁Ti and ErFe₁₁TiH compounds.

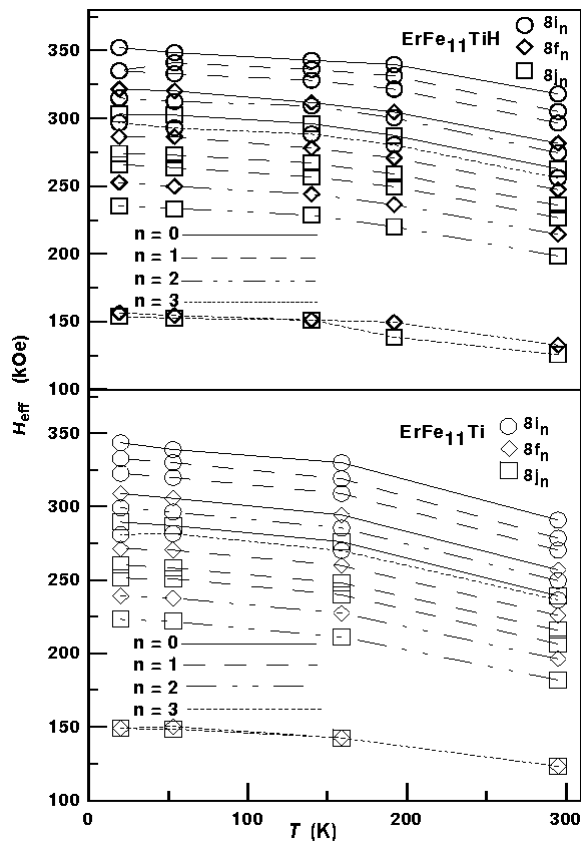
Site	Er, 2a	Fe, 8f	Ti/Fe, 8i	Fe, 8j	H, 2b	Total near neighbours	Iron near neighbours	V_{w-s} (Å ³) ErFe ₁₁ Ti	V_{w-s} (Å ³) ErFe ₁₁ TiH
Er, 2a	0	8	4	8	2	20, 22	17	28.27	28.40
Fe, 8f	2	2	4	4	0	12	9	11.27	11.35
Ti/Fe, 8i	1	4	5	4	0	14	11.75	12.75	12.84
Fe, 8j	2	4	4	2	1	12, 13	9	11.64	11.72
H, 2b	2	0	0	4	0	6	4	–	1.48

Table 2. Relative contribution of various crystal lattice sites in the ⁵⁷Fe Mössbauer spectra of RFe₁₁Ti-type crystal structure compounds.

	Average Fe-Fe distances (Å)	Total NN number	Intensity (%)	Sextet importance
0 Ti	8i	13	6.47	yes
	8f	10	11.51	yes
	8j	10	11.51	yes
1 Ti	8i ₁	12	2.16	yes
	8i ₁	12	8.63	yes
	8f ₁	9	15.34	yes
	8j ₁	9	7.67	yes
	8j ₁	9	7.67	yes
2 Ti	8i ₂	11	2.88	
	8i ₂	11	4.31	yes
	8f ₂	8	7.67	yes
	8j ₂	8	2.56	
	8j ₂	8	2.56	yes
3 Ti	8i ₃	10	0.96	
	8i ₃	10	1.44	yes
	8f ₃	7	1.70	yes
	8j ₃	7	0.85	
	8j ₃	7	0.85	yes
4 Ti	8i ₄	9	0.1	no
	8i ₄	9	0.3	no
	8f ₄	6	0.12	no
	8j ₄	6	0.12	no
5 Ti	8i ₅	8	0.03	no

compound changing the cell volume only by about 1%. To fit the Mössbauer spectra of ErFe₁₁Ti and ErFe₁₁TiH compounds we however, restricted our calculations to the lines derived from iron positions with 0, 1, 2, and 3 Ti atoms in NN. We skip 5 lines, which have negligible intensities. We also neglected the fine splitting for those positions whose total contribution to the spectra is less than 10% (see Table 2). Finally, we worked with 14 Zeeman sextets for ErFe₁₁Ti and its hydride. We have assumed all Zeeman sextets have an area in the ratio 1:2:3 for 3, 4 and 2, 5 and 1, 6 lines, respectively with an equal linewidth of 0.35 mm/s. The different subspectra considered in the fit are presented as solid lines below the respective total spectrum in Fig. 1. The assignment of the 8i, 8f and 8j sextets is based on their relative intensities and the number of Fe atoms in NN. The largest average hyperfine field is expected for 8i site because it has the largest number of iron atoms in the near

neighbourhood (11.75 on average). The sequence of the average hyperfine fields for 8j and 8f sites was controversial up to now because the 8j and 8f sites have the same (9) number of adjacent Fe atoms (see Table 1). The assignment based on the average Fe-Fe distances [4] has predicted the $H_{eff}(8j) > H_{eff}(8f)$ sequence whereas the assignment based on the relationship between an isomer shift and the Wigner-Seitz cell volume in the CeFe₁₁Ti [6] suggests that the hyperfine fields follow the sequence $H_{eff}(8f) > H_{eff}(8j)$. In these models the same number of the sextets with equal intensities were assumed for both sites. In our approach, distinguishing between 8j and 8f sextets is much clear-cut because their relative intensities appear to be different. Finally, we have found that the sequence $H_{eff}(8f) > H_{eff}(8j)$ is to be fulfilled for both compounds.

**Fig. 2.** The temperature dependence of hyperfine fields for 14 Mössbauer subspectra with various numbers of n Ti atoms in NN for the ErFe₁₁Ti and its hydride.

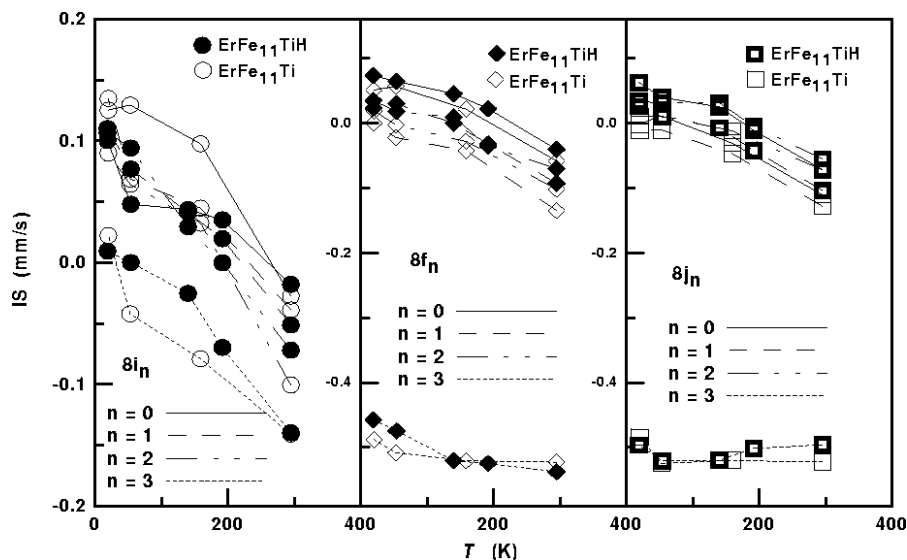


Fig. 3. Isomer shift as a function of temperature for 14 Zeeman sextets describing the Mössbauer spectra in $\text{ErFe}_{11}\text{Ti}$ and its hydride phase.

Results

The results of the best least-squares fits to these spectra are presented as solid lines superimposed on the experimental points in Fig. 1. As is shown, a fit with 14 sextets is excellent; the corresponding hyperfine parameters, H_{eff} and IS, adjusted during the fitting procedure are shown in Figs. 2 and 3 as a function of temperature. Their average values are displayed in Fig. 4. The temperature dependence of the site weighted average hyperfine fields show a similar Brillouin-type behaviour. As it is seen in Fig. 3, the increasing of the titanium atom numbers in NN over $n = 2$ decreases the isomer shift values dramatically. It is particularly visible for 8f and 8j positions. In turn, the hydrogen, as is seen in Fig. 4, increases the average isomer shift in the 8j and 8f sites by about 0.04 mm/s, whereas for 8i position the changes of the isomer shift upon hydrogenation are negligible. The observed changes of the isomer shift can be in the easiest way accounted for by the increase of the Wigner-Seitz unit cell volumes of Fe induced by hydrogen (see Table 1). It is a rule that a larger isomer shift corresponds to a larger Wigner-Seitz volume. The increase of the isomer shift on the Fe (8j) and Fe (8f) nuclei can reflect the decrease of the s -electron density on these positions caused by the volume effect. But in this light the negligible change in the Fe (8i) isomer shift upon hydrogenation is not understandable. According to the data in Table 1, the W-S cell volume increases for 8i site like for the 8f and 8j positions in the hydride sample. Therefore, we are expecting to observe the same changes of isomer shift value in all three positions. The lack of measurable changes of an isomer shift in 8i position inclines us to propose another phenomenon connected with hydrogen. One should remember that apart from the unit cell expansion (Wigner-Seitz unit volume increasing) hydrogen atoms can donate their electrons to the iron sd -bands or can depopulate them as well [9, 14]. We suggest that the observed changes of the isomer shift in 8j and 8f sites are rather the results of the local transfer of the s -electrons from the iron atom to the hydrogen atoms than as the results of volume effects. Neutron diffraction studies [13] show that hydrogen atoms occupy 2b site in the ThMn_{12} structure. There are four iron atoms in 8j sites in ab plane,

which surround a hydrogen atom at a distance of 1.86 Å. The larger interatomic distances of H atoms are to Fe (8f) atoms (3.24 Å) and Fe (8i) atoms (3.7 Å). The short bonds between 8j (Fe) and interstitial hydrogen facilitate strong hybridization and an increase of the isomer shift on the Fe (8j) nuclei. The largest interatomic distances of H atoms are to Fe (8i) atoms (3.78 Å) that is why it does not experience the hydrogen insertion to the lattice keeping its isomer shift unchanged. Of course, we cannot rule out the lattice volume

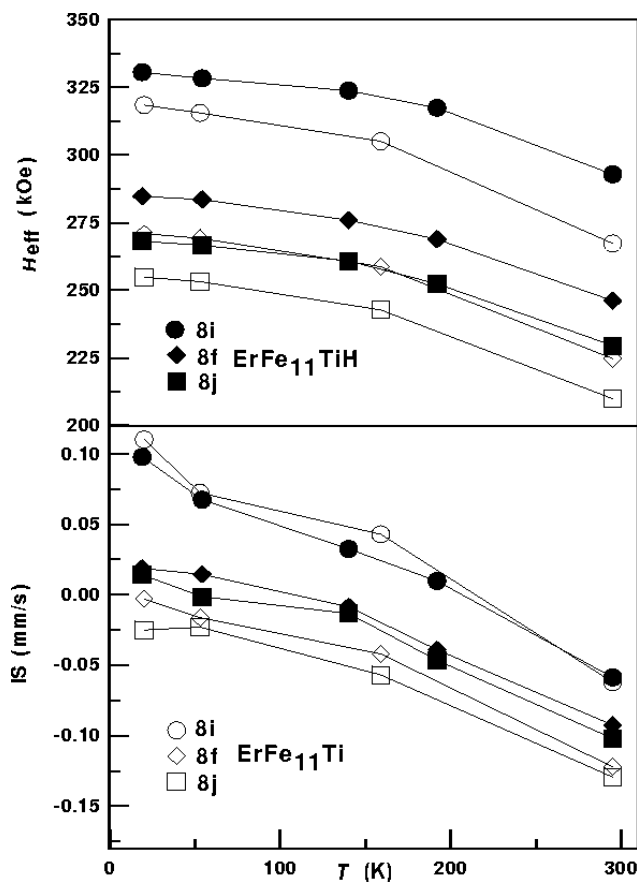


Fig. 4. The temperature dependence of the weighted average hyperfine magnetic field and an averaged isomer shift for different crystal sites of the $\text{ErFe}_{11}\text{Ti}$ and $\text{ErFe}_{11}\text{TiH}$.

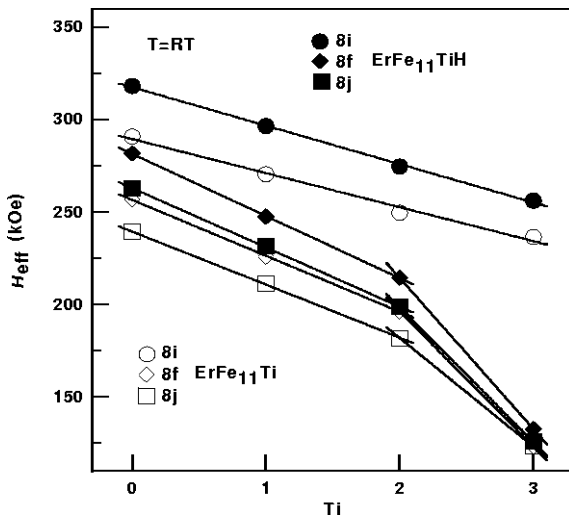


Fig. 5. The weighted average hyperfine magnetic field as a function of the number of Ti atoms in NN experienced by Fe atom in three non-equivalent crystal sites 8f, 8j, and 8i in the ErFe₁₁Ti and ErFe₁₁TiH compounds.

effects from our attention as well. Probably, what we observed in the isomer shift in the ErFe₁₁TiH hydride is the sum of at least two mentioned above different phenomena.

The average hyperfine fields (Fig. 4) for all iron sites in the ErFe₁₁TiH hydride are about 20 kOe larger than in the ErFe₁₁Ti alloy. These increases can be justified by the lattice expansion due to H atom insertion, thus increasing the average Fe-Fe distances with a consequent re-enforcement of Fe-Fe exchange interactions upon hydrogenation. The increase of the interatomic distances by hydrogen insertion leads to a narrowing of the 3d-bands and to the strengthening of the 3d-3d-exchange interaction.

Fig. 5 shows the average hyperfine fields H_m for the three Fe sites as a function of the number of Ti neighbours. For the considered cases, H_m obey a simple linear relationship $H_m(n) = H_{m0} - n \Delta H$ ($n = 1, 2, 3$) where $\Delta H = 20$ kOe/Ti atom for 8i sites and $\Delta H = 30$ kOe/Ti atom for sites 8f and 8j with ($0 < n < 2$). The contributions from the nearest neighbours to the hyperfine field experienced by the Fe nuclei are additive in both studied compounds. For 8j and 8f sites with 3 Ti atoms in NN the hyperfine field changes are much serious and reach the values of 50–70 kOe.

It is worth of mentioning that the spin reorientation transitions observed in the magnetization measurements [7, 10] are not visible in our Mössbauer investigations. At temperatures where the spin orientation transition was reported, the Mössbauer parameters, in the frame of experimental accuracy, show not any spectacular changes. We are not convinced that the anomalies of an isomer shift of the 8i-like sites observed in Fig. 3 in the low temperatures region, are related to a spin-reorientation phenomenon. We would rather expect such anomalies on the hyperfine field vs. temperature curves. Unfortunately, they are absent (see Fig. 2).

Conclusions

This paper presents a new extension of the model of Mössbauer spectrum for RFe₁₁Ti-type compounds, which

take into account not only the number of Fe atoms in near neighbourhood but also the different distances between atoms. This new model allows distinguishing the 8f and 8j sites much easier, and brings more details for the titanium near neighbour effect. Titanium atom statistical distribution over the 8i sites in RFe₁₁Ti crystal lattice reduces the hyperfine magnetic fields and isomer shift. Upon hydrogenation, the isomer shift and hyperfine fields increase again due probably to the unit cell volume increasing or due to the decreasing of the s-electron density on some iron positions with hydrogen insertion.

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References

1. Bara JJ, Bogacz BF, Pędziwiatr AT, Wielgosz R (2000) Hyperfine interaction and crystal site occupancies in RTiFe_{11-x}Co_x (R = Y, Dy and Er) as seen by Mössbauer spectroscopy. *J Alloys Compd* 307:45–50
2. Fujii H, Sun H (1995) Interstitially modified intermetallics of rare earth and 3D elements. In: Buschow KHJ (eds) *Handbook of magnetic materials*, 9th ed. Elsevier, Amsterdam, pp 304–334
3. Hu B, Li H, Coey JM (1989) An ⁵⁷Fe Mössbauer study of rare-earth intermetallic compounds R(Fe₁₁Ti). *Hyperfine Interact* 45:233–240
4. Hu B, Li H, Gavigan JP, Coey JM (1989) Intrinsic magnetic properties of the iron-rich ThMn₁₂-structure alloys RFe₁₁Ti (R = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu). *J Phys-Condens Mater* 1:755–770
5. Isnard O, Guillot M (1998) Investigation of the magnetic properties of ErFe₁₁Ti and ErFe₁₁TiH in high magnetic field. *J Appl Phys* 83:6730–6732
6. Long GJ, Hautot D, Grandjean F, Isnard O, Miragila S (1999) A Mössbauer spectral study of CeFe₁₁Ti and CeFe₁₁TiH. *J Magn Magn Mater* 202:100–106
7. Nikitin SA, Tereshina IS, Skurskij YuW *et al.* (2001) Vlijanie gidrirovaniya na spin-pereorientacjonnoe fazovye perekhody i konstanty magnitnoj anizotropii monokristalov RFe₁₁Ti (R = Lu, Ho, Er). *Fizika Tverdogo Tela* 43:279–288
8. Nikitin SA, Tereshina IS, Verbetsky VC, Salamova AA (2001) Transformations of magnetic phase diagram as a result of insertion of hydrogen and nitrogen atoms in crystalline lattice of RFe₁₁Ti compounds. *J Alloys Compd* 316:46–50
9. Soubeyrou JL, Fruchart D, Isnard O, Miragila S, Tomey E (1995) Role of the (H, C, N) interstitial elements on the magnetic properties of iron-rare earth permanent magnet alloys. *J Alloys Compd* 219:16–24
10. Suski W (1996) The ThMn₁₂-type compounds of rare earths and actinides: structure, magnetic and related properties. In: Gschneidner KA Jr, Eyring L (eds) *Handbook on the physics and chemistry of rare earths*, vol. 22. Elsevier, Amsterdam, pp 143–294
11. Tereshina IS, Gaczyński P, Rusakov VS *et al.* (2001) Magnetic anisotropy and Mössbauer effect studies of YFe₁₁Ti and YFe₁₁TiH. *J Phys-Condens Mater* 13:8161–8170
12. Vagizov FG, Andreev AV, Suski W, Drulis H, Goto T (1993) Structure, magnetic properties and the ⁵⁷Fe Mössbauer effect in the LuFe_{11-x}Al_xTi system. *Physica B* 190:126–130
13. Weihua M, Jinbo Y, Bo C *et al.* (1998) A study on the effect of hydrogen in the compounds with ThMn₁₂-type structure. *J Phys-Condens Mater* 10:2611–2616
14. Zhang B, Bauer HJ, Baier M, Wagner FE, Antonov VE, Antonova TE (1991) ⁵⁷Fe Mössbauer study of the hydrides of Ni-Cu alloys. *J Less-Common Metals* 172/174:343–350