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Mössbauer effect studies of $R\mathrm{Fe}_{11}\mathrm{Ti}$ and $R\mathrm{Fe}_{11}\mathrm{TiH}$ ($R = \mathrm{Y, Gd, Er}$)

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Abstract

The Mössbauer spectra of ferromagnetic $R\mathrm{Fe}_{11}\mathrm{Ti}$ and $R\mathrm{Fe}_{11}\mathrm{TiH}_x$ ($R = \mathrm{Y, Gd, Er}$, $x = 0, 1$) have been investigated in the temperature range 20–300 K and analysed in terms of a new model which allows a better fit of the spectra using less constraints than previously reported analyses. In addition to the dependence of magnetic hyperfine field and isomer shift on the number of Ti nearest-neighbours (NN) of the Fe atoms, this new model also considers the effect of the average interatomic distances between Fe atoms on the 8i, 8f and 8j crystallographic sites. Magnetic hyperfine fields were found to decrease with the average interatomic distances for Fe atoms on the same sites and with the same number of iron NN. This decrease was however lower than that due to the presence of one additional titanium NN. Furthermore the present model distinguishes the 8f from the 8j sites on the basis of the relative areas of the corresponding sextets. It leads to higher average magnetic hyperfine fields and isomer shifts for the 8f site as compared to the 8j sites which may be understood on the basis of electronic charge transfer between the rare-earth and Fe atoms. The dependence of hyperfine parameters on the number of titanium NN and on hydrogenation is similar to those previously reported.

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Keywords: $R\mathrm{Fe}_{11}\mathrm{Ti}$; Metal hydride; Mössbauer spectroscopy

1. Introduction

The recent investigation on permanent magnets with high Curie temperature, high magnetization saturation and uniaxial magnetic anisotropy mainly concerns 4f–3d intermetallic compounds. The appropriate combination of these elements can lead to both high magnetization and high coercivity and thus to a strong hard magnet. $R\mathrm{Fe}_{11}$ Ti intermetallics ($R =$ rare-earth metal) [1–8] belong to this type of compounds offering good magnetic properties, ferromagnetic with Curie temperatures, T_c, higher than 480 K, and being attractive from an economic point of view due to the high Fe/R ratio. The $\mathrm{RFe}_{11}\mathrm{Ti}$ compounds crystallize in the tetragonal ThMn_{12}—type crystal structure, $I4/mmm$ space group. The R atom occupies the 2a sites, Fe atoms occupy three crystallographic nonequivalent sites, 8f, 8j and 8i and Ti randomly replaces one of the Fe atoms on the 8i site [5]. In general, insertion of light elements, such as hydrogen, nitrogen or carbon into the lattice of these materials has a dramatic and beneficial effect upon the magnetic properties [2–4]. When inserted, hydrogen fully enters into the octahedral 2b site [6].

The highest T_c in this series of compounds, 608 K, is observed for $\mathrm{GdFe}_{11}\mathrm{Ti}$. In the case of nonmagnetic R, such as Y, the magnetic properties are only due to the Fe sublattice. The easy magnetic direction in $\mathrm{YFe}_{11}\mathrm{Ti}$ and $\mathrm{GdFe}_{11}\mathrm{Ti}$ is parallel to the c-axis in the whole temperature range. $\mathrm{ErFe}_{11}\mathrm{Ti}$ exhibits a spin reorientation transition [9,10] with the Fe moments deviating from the c-axis direction and becoming canted below 50 K. The insertion of one H atom per $\mathrm{RFe}_{11}\mathrm{Ti}$ formula unit produces a significant increase in T_c, 58, 53 and 56 K for $\mathrm{YFe}_{11}\mathrm{Ti}$, $\mathrm{GdFe}_{11}\mathrm{Ti}$ and $\mathrm{ErFe}_{11}\mathrm{Ti}$, respectively [4]. In the case of $\mathrm{ErFe}_{11}\mathrm{TiH}$ a decrease in spin reorientation temperature from 50 to app. 40 K has been observed [9,10]. H atoms were found to decrease the density of states (DOS) at the Fermi level but the change of local DOS at different

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crystallographic sites is probably not the same [6]. Hydrogen also induces a significant modification in the crystal electric-field gradient on the rare-earth site. The increase of the electric-field gradient at the Gd site in $GdFe_{11}TiH$ has been demonstrated by ^{155}Gd Mössbauer spectroscopy [11].

As extensively shown in the Refs. [10–17] Mössbauer spectroscopy is an important tool in the investigation of $RFe_{11}Ti$ and $RFe_{11}TiH$ ($R =$ Y, Gd and Er). Mössbauer spectra of these compounds are complex and the best fits have been achieved by a model considering different contributions for Fe atoms on different crystallographic sites and with a different number of Fe nearest-neighbours (NN) [10,12–14]. This model had already been successfully applied to the spectra of other $ThMn_{12}$-type intermetallics such as AFe_xM_{12-x} with $A =$ U, R and $M =$ Mo, V, Al [15,16]. The contribution to the spectra of $RFe_{11}Ti$ from Fe on each site consists, in the magnetically ordered state, of a sum of sextets, $8f_i$, $8j_i$ and $8i_i$, where i may be 0, 1, 2, 3 and 4 depending on the number of titanium NN. The relative areas of these sextets are given by a binomial distribution based on the random occupation of 25% of the 8i sites by Ti. Hence, the 8i site is represented by five sextets and the 8f and 8j sites by four sextets. A total of 16 sextets should therefore be used to analyse the Mössbauer spectra, although if one ignores those with relative areas lower than 2.5% only nine are actually used [12,14]. However for the title compounds this model, hereafter referred to as the nine-sextets model, has lead to excessively large values of the line widths (0.6–1 mm/s) [12] or, if the values of the line widths were fixed and kept in the range of 0.3–0.35 mm/s, to fits of the experimental data which were not very good particularly in the ±4 mm/s velocity range [14]. For the $RFe_{11}Ti$ which have a spin-reorientation transition an improvement of the fitting model was suggested for the spectra taken in the temperature range where the Fe moments are canted away form the c-axis [10].

A different model was proposed to improve the quality of these fits as well as the consistency of the resulting parameters by considering the Fe–Fe interatomic distances, $d_{Fe\text{–}Fe}$, which may be different for Fe atoms on the same crystallographic site and with the same number of titanium NN [17]. In the present paper this model is successfully applied for the first time to $YFe_{11}Ti$, $GdFe_{11}Ti$ and their hydrides. The influence of H incorporation on the Mössbauer hyperfine parameters and thus on the magnetic properties of the Fe sublattices is also discussed.

2. Experimental details

All the intermetallic samples were prepared as previously described [12]. In the X-ray diffractograms of the $RFe_{11}TiH_x$ ($R =$ Y, Gd, Er; $x = 0, 1$) samples in addition to the peaks of the main $ThMn_{12}$—type phase, weak diffraction peaks corresponding to the strongest peaks of α-Fe were also observed.

The ^{57}Fe Mössbauer spectra were taken between 20 and 295 K with a conventional constant acceleration spectrometer and a ^{57}Co source in a Rh matrix. The absorber was prepared by grinding the sample to 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-Fe foil at room temperature. The isomer shift values are given relative to α-Fe at 295 K. The spectra were analyzed by least-squares fits of the experimental Mössbauer line using the Lorentzian approximation. An impurity contribution of 1–2% of α-Fe phase was included in all data refinements.

3. Results and discussion

The Mössbauer spectra of $RFe_{11}Ti$ compounds and their hydrides are very similar, therefore only the spectra for $R =$ Er are shown (Fig. 2). The number of NN and the corresponding interatomic distances for all the occupied crystallographic sites in the title compounds are summarized in Table 1. There are different 8i–8i and different 8i–8j interatomic distances. In the former case one of the interatomic distances is shorter than the remaining four while in the latter case there are two shorter and two larger interatomic distances. Therefore, assuming a statistical distribution of Ti on the 8i sites the sextets attributed to Fe on these sites with one, two, three and four titanium NN as well as on the 8j sites with one and three titanium NN split into two subsextets each (Fig. 1), corresponding to different average $d_{Fe\text{–}Fe}$. In the same way the sextet assigned to Fe on the 8j site with two titanium NN splits into three subsextets with equal intensities. A total of 24 sextets are thus obtained: 10 for 8i, nine for 8j and five for 8f sites (Fig. 1). In the hydride samples the same approach may be used because hydrogenation retains the crystal structure of the parent compounds changing only the unit-cell volume by app. 1%. The relative areas of sextets from different contributions are shown in Fig. 1.

In order to fit the Mössbauer spectra of $RFe_{11}Ti$ and $RFe_{11}TiH$ our calculation was restricted to the sextets derived from Fe positions with 0, 1, 2 and 3 titanium NN, skipping 5 sextets, which have negligible intensities. Furthermore, Fe on the same crystallographic site and with the same number of titanium NN whose total contribution to the spectra is less than 10% were considered as giving rise to single sextets even if they were split in sets corresponding to different $d_{Fe\text{–}Fe}$. Finally, only 14 Zeeman sextets (Fig. 1) were considered in the refinement of $RFe_{11}Ti$ and the corresponding hydride spectra [17]. Peaks of all the Zeeman sextets were assumed to have equal linewidths in the range 0.29–0.35 mm/s and the area ratio 1:2:3 for lines 3,4 and 2,5 and 1,6 of each sextet (Fig. 2).

3.1. Hyperfine parameters on the 8f, 8j and 8i sites

The temperature dependence of the estimated magnetic hyperfine fields H_{eff} for all nonequivalent Fe sites in all