

Substitutional effects in RFe_3 intermetallics ($R = Dy, Sm, Y$)

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Abstract

Samples of RFe_3 ($R = Dy, Sm, Y$) were doped with Si, Al and Ti and studied by Mössbauer spectroscopy and X-ray diffraction. Most Mössbauer spectra were analyzed with three sextets, corresponding to the 6c, 3b and 18 h inequivalent lattice sites for iron. A quadrupole split doublet was also present in some spectra, which became dominant for the case of Al substitution. The collapse of the hyperfine magnetic structure is a magnetic effect due to substitutions: the X-ray diffraction patterns yielded a particle size of about 100 nm, thus precluding the occurrence of superparamagnetism in these systems.

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1. Introduction

All RFe_3 compounds ($R =$ rare earth) crystallize in the $PuNi_3$ -type structure, with space group $R\bar{3}m$. The structural and magnetic properties of these systems were studied recently by X-ray diffraction, Mössbauer spectroscopy and magnetic measurements. In particular, investigation of crystal and magnetic properties of Dy–Fe intermetallic compounds proved their ferrimagnetic behavior, localization of Fe magnetic moments and long-range Fe–Fe exchange magnetic interactions [1–4]. As far as $SmFe_3$ is concerned, there were reports on the solid-state amorphization by hydrogenation [5] and studies of mechanical alloying of Sm and Fe [6,7] with the formation of nanoscale structures. Furthermore, YT_3 ($T = Fe, Co, Ni$) compounds are typical itinerant ferromagnets and chemically, excellent hydrogen absorbers [8]. Hydrogen absorption strongly affects their magnetic properties and changes the Mössbauer spectra.

However, the effect of substitutions on the structure and magnetic properties of the RFe_3 compounds is still not explored and makes the subject of our current paper. We

employed several nonmagnetic substitutions such as Si, Al and Ti and investigated the magnetic behavior of these systems using X-ray diffraction (XRD) and Mössbauer spectroscopy. We emphasize the site preference of each type of substitution and study these effects in terms of the hyperfine parameters of the Mössbauer spectra.

2. Experimental

The intermetallics of the type RFe_3 ($R = Dy, Sm, Y$) with Si, Al and Ti substitutions were prepared by melting the components in an arc furnace under protective argon atmosphere. The ingots were turned several times to avoid inhomogeneities and annealed at 950–1050 °C for 10 days. XRD patterns were recorded on a powder diffractometer using the $K_{\alpha 1}$ radiation of a Cu cathode at $\lambda = 1.5404 \text{ \AA}$.

Room temperature transmission Mössbauer measurements were made with a constant acceleration spectrometer. The 25 mCi gamma ray source was ^{57}Co in a Rh matrix, maintained at room temperature. All spectra were analyzed with the NORMOS program.

3. Results and discussion

Fig. 1 (a)–(d) represents the XRD spectra of the $DyFe_3$ compounds, substituted with Al, Si and Ti, respectively.

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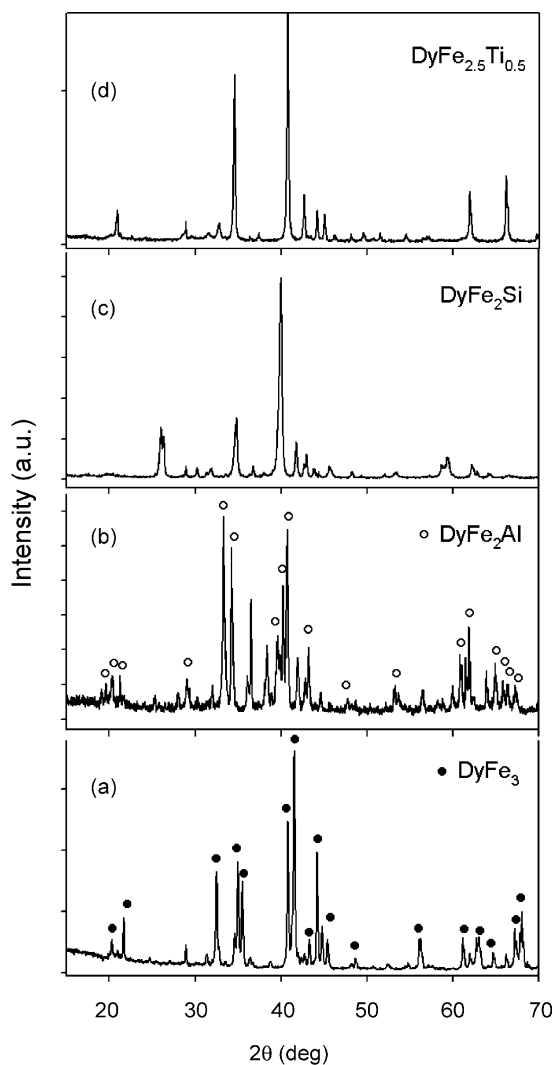


Fig. 1. XRD patterns of (a) DyFe₃; (b) DyFe₂Al; (c) DyFe₂Si; (d) DyFe_{2.5}Ti_{0.5}.

These XRD spectra are also typical for the SmFe₃ and YFe₃ compounds, substituted with Al, Si and Ti elements, respectively. These atoms substitute for Fe atoms in the crystalline structure. We applied the Scherrer formula and derived the particle size from the XRD patterns. The average particle size determined was around 100 nm. As it will be discussed in the Mössbauer section of this paper, these large particle sizes cannot be associated with the occurrence of superparamagnetic effects in these systems.

Fig. 2 (a)–(d) shows the room temperature transmission Mössbauer spectra of DyFe₃ and its substitutions with Al, Si and Ti, respectively. The values of the fitted hyperfine parameters are given in Table 1. The spectrum of DyFe₃ was fitted with three sextets, with hyperfine magnetic field values of 22.5, 21.4 and 21.0 T. These fields were assigned to the 6c, 3b and 18 h crystallographic sites based on the number of Fe nearest neighbors (6 NN, 9 NN and 7 NN) and distances between neighbors. DyFe₂Si was fitted with three sextets, corresponding to the 6c, 3b and 18 h sites

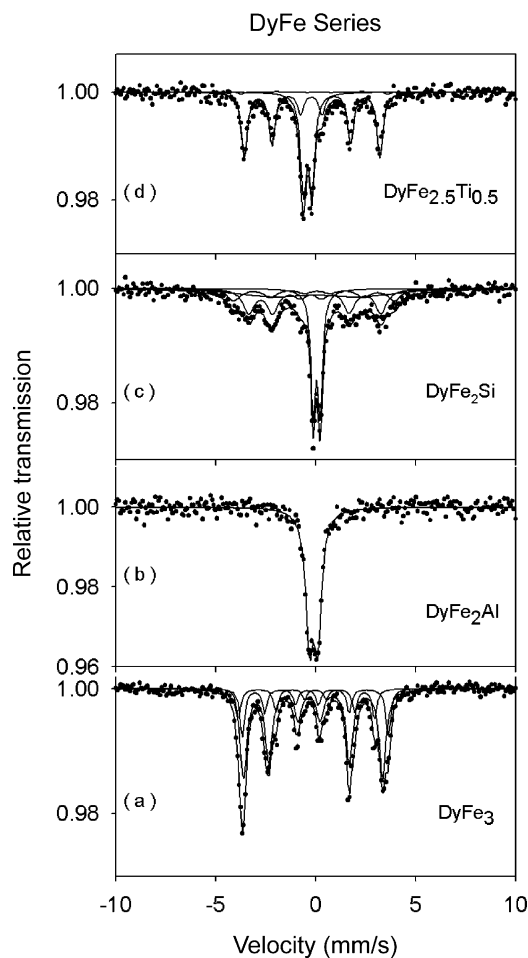


Fig. 2. Mössbauer spectra of (a) DyFe₃; (b) DyFe₂Al; (c) DyFe₂Si; (d) DyFe_{2.5}Ti_{0.5}.

and a quadrupole split doublet. The marked decrease of the population of site 3b compared to the same site in DyFe₃ indicates that Si substitutions prefer the 3b crystallographic sites. Along the same idea, in DyFe₂Al only the quadrupole split doublet is present, suggesting that in this compound Al substitutes for Fe in all positions,

Table 1
Mössbauer fit parameters for DyFe₃ series

| Sample | H_{hf} (T) | IS (mm/s) | QS (mm/s) | Rel. areas (%) | Site assign- ment | |
|---------------------------------------|------------------------|--------------|--------------|-------------------|----------------------|----|
| DyFe ₃ | 22.5 | -0.04 | 0.1 | 20.3 | 6c | |
| | 21.4 | -0.13 | 0.26 | 64.6 | 3b | |
| | 21.0 | -0.15 | -0.19 | 15.1 | 18 h | |
| DyFe ₂ Al | | 0.01 | 0.41 | 100 | Paramagnetic | |
| | DyFe ₂ Si | 24.9 | -0.09 | -0.14 | 15.8 | 6c |
| | | 20.8 | 0.10 | -0.01 | 23.7 | 3b |
| DyFe _{2.5} Ti _{0.5} | 20.5 | -0.03 | 0.20 | 31.7 | 18 h | |
| | | 0.15 | 0.35 | 28.8 | Paramagnetic | |
| | 22.7 | 0.15 | -0.25 | 0.8 | 6c | |
| | 21.0 | -0.09 | 0.04 | 59.1 | 3b | |
| | | -0.29 | 0.42 | 40.1 | Paramagnetic | |
| Errors: | +0.2 | +0.01 | +0.01 | +0.4 | | |

IS is the isomer shift relative to α -Fe and QS is the quadrupole shift.

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