

Effect of the substitution of Ti for Y on structural properties and hyperfine interactions in $Y_{1-x}Ti_xFe_2$ compounds

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Abstract Room temperature ^{57}Fe Mössbauer spectroscopy and X-ray diffraction measurements are reported for a series of $Y_{1-x}Ti_xFe_2$ polycrystalline samples. Our research shows that except for $x = 0$ and $x = 1$, the samples are a mixture of two C15 and C14 pseudobinary Laves phases. Some Ti atoms occupy the crystallographic positions 8a characteristic of the Y atoms in the cubic C15 structure while the rest of them form the hexagonal C14 phase. However, the lattice constant dependencies on concentration x suggest the occurrence of Y atoms in the positions 4f characteristic of Ti atoms in the hexagonal C14 structure. The partial substitution of Ti atoms for Y atoms is responsible for the HMF changes in the cubic phase. Contrary to the situation taking place in the $Zr_{1-x}Ti_xFe_2$ compounds, magnetic arrangement in the pseudobinary hexagonal phases is not observed at room temperature.

Key words hyperfine interactions • Mössbauer effect • quasibinary Laves phase • $Y_{1-x}Ti_xFe_2$

Introduction

Systems of the $(T_{1-x}T'_x)Fe_2$ -type (where $T = Y, Nb, Ti$ and $T' = Sc, Zr$) have been extensively investigated. In many such pseudobinary systems interesting magnetic and structural properties were observed [6, 8, 11].

In the cubic C15 YFe_2 phase ($MgCu_2$ -type, space group $Fd\bar{3}m$) Fe atoms (16d positions) create a sublattice of corner sharing regular tetrahedrons (see Fig. 1a). Six Fe atoms and six Y (8a positions) atoms surround each Fe atom composing its nearest neighbourhood. The Y atoms create a sublattice of the diamond type. These two sublattices penetrate each other.

In the hexagonal C14 $TiFe_2$ phase ($MgZn_2$ -type, space group $P6_3/mmc$) Fe atoms create a sublattice of regular tetrahedrons linked alternately by apexes (2a positions) or by their bases (6h positions). In this structure the population ratio of 6h and 2a sites is 3:1. The Ti atoms create a sublattice of the wurcrite type.

The compound YFe_2 is a ferrimagnet ($T_C = 542$ K) with a saturation magnetization of $2.9\mu_B$ per formula unit [5]. More detailed theoretical study [7] and experimental neutron diffraction investigations [9] have shown that all Fe atoms have a magnetic moment of about $1.66(8)\mu_B$ and there is an antiparallel induced magnetic moment at Y sites of about $-0.45(4)\mu_B$. This moment is a result of the hybridization of 3d Fe and 4d Y bands [7].

The Laves phase $TiFe_2$ is an antiferromagnet ($T_N = 285$ K [3]). From the neutron diffraction investigations [11], it is known that the magnetic moments of $1.2(1)\mu_B$ (at 10 K) of the Fe 6h atoms in the layers perpendicular to the c-axis are ferromagnetically aligned along this axis while the coupling between adjacent layers is antiferromagnetic. Fe atoms at the 2a sites lying midway between the two

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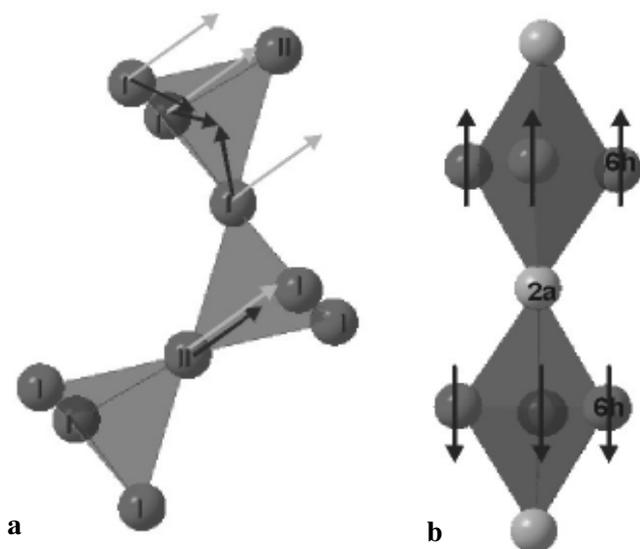


Fig. 1. Magnetic arrangement of: a – YFe_2 . The light arrows indicate direction of easy magnetization axis; the dark arrows indicate direction of local EGF; b – TiFe_2 . The arrows represent magnetic arrangement.

adjacent antiferromagnetically coupled planes are paramagnetic, because the molecular fields from the 6h sites are cancelled (see Fig. 1b).

In the C15 structure, all Fe atoms have local $\bar{3}m$ symmetry with a three-fold axis in the $\langle 111 \rangle$ direction which possesses axial symmetry of the electric field gradient EFG. For the pure YFe_2 intermetallic an easy axis of magnetization has the same direction. In the magnetically ordered state the local magnetic field makes two possible angles: $70^\circ 32'$ and 0° with the principal axis of the EFG. This determines two distinct types of magnetically nonequivalent Fe positions called I and II, respectively, with a population ratio of 3:1. This arrangement is schematically shown in Fig. 1a.

The purpose of our study is to examine the effect of the substitution of Ti for Y on structural properties and hyperfine interactions in $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ compounds.

Experimental

The intermetallic compounds $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ were prepared by arc melting appropriate stoichiometric amounts of the

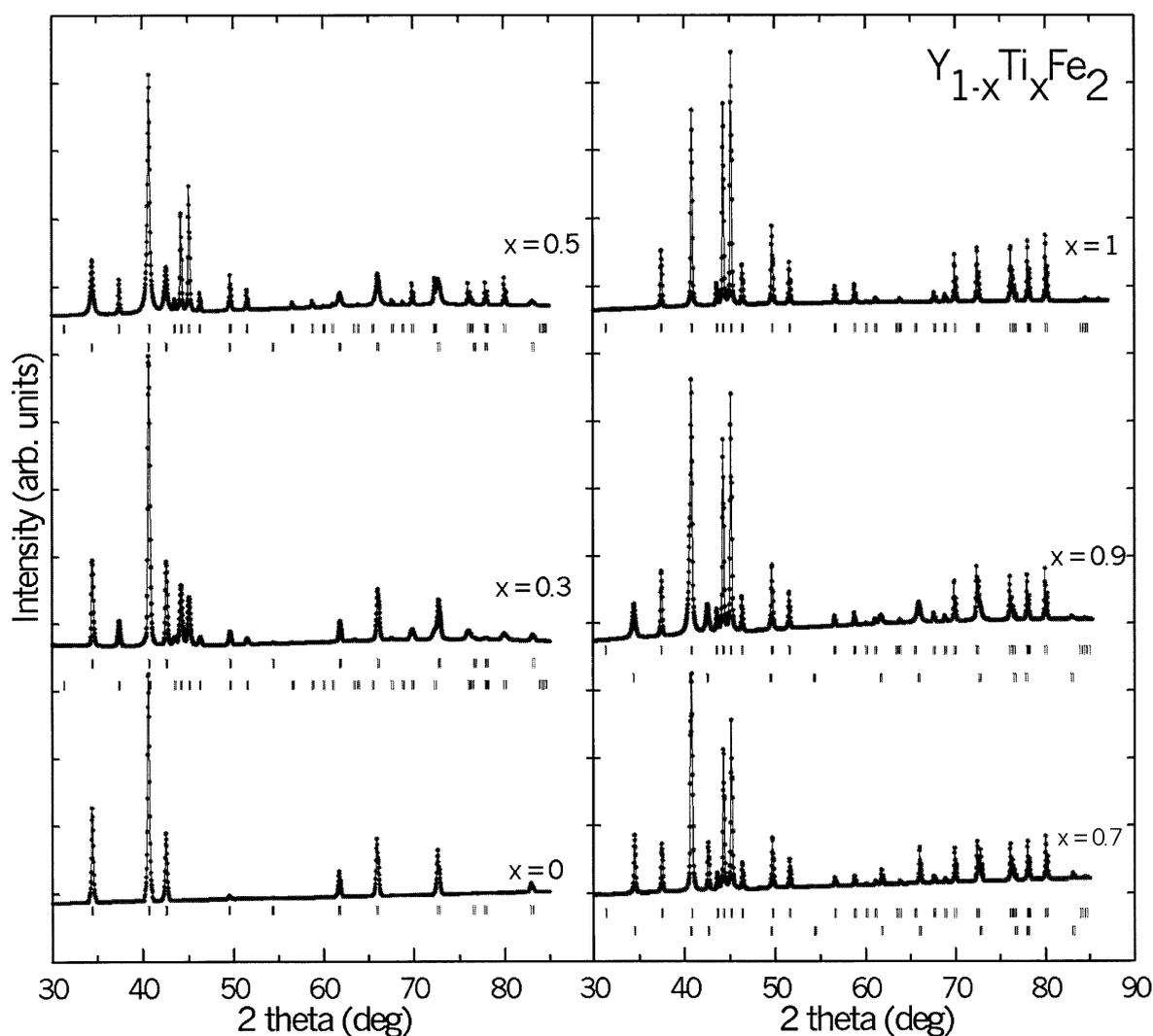


Fig. 2. XRD patterns of some selected samples of the $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ compounds. Short vertical marks below the diffraction pattern indicate the calculated Bragg position for the cubic and hexagonal phases.

elements of 99.99% purity under an inert argon atmosphere. Phase analysis was carried out by means of X-ray powder diffraction with $\text{Cu K}\alpha$ radiation. The scans were realized in the range from 30° to 90° (2θ). The Mössbauer spectra of powder samples were recorded using a constant acceleration spectrometer at room temperature with a $^{57}\text{Co}(\text{Rh})$ source. The Mössbauer spectra were fitted using the least-squares procedure, where the quadrupole interaction is treated as a perturbation to the hyperfine field. The diffraction patterns were refined by the FULLPROF Rietveld refinement program [10].

Results and discussion

The X-ray diffraction patterns representative of $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ series are shown in Fig. 2 and indicate that the compound for $x = 0$ (YFe_2) crystallizes in the cubic C15 structure and TiFe_2 has the hexagonal C14 structure. Bragg reflections characteristic of both phases occur in the pseudobinary samples for $0.1 \geq x \geq 0.9$. The increase of titanium concentration causes a growth of the hexagonal phase content in the investigated samples. The cubic phase content in the investigated samples is shown in Fig. 3. Up to $x \leq 0.7$, a small excess of this phase occurs in comparison to the titanium stoichiometric content. For $x > 0.7$, the contributions of both phases are exactly compatible with the elemental composition of samples. This fact suggests the replacement of Y atoms (atomic radii: 1.81 Å) by smaller Ti atoms (1.47 Å) in the C15 phase at a low concentration of titanium which leads to the contraction of elementary units. The remaining part of Ti atoms forms the hexagonal C14 phase which appears already in the sample with $x = 0.1$. Figure 4 shows the lattice constant parameters as a function of Ti concentration for both types of crystal structures. In these dependencies two different regions are visible. For $x \leq 0.7$, the lattice constant parameters decrease much faster than those for $x > 0.7$. It seems to be in accordance with the phase contributions dependence on the Ti concentration x . The decrease of lattice constants of the C14 phase indicates that this phase is pseudobinary, too. Probably, some Ti sites in the hexagonal phase are occupied

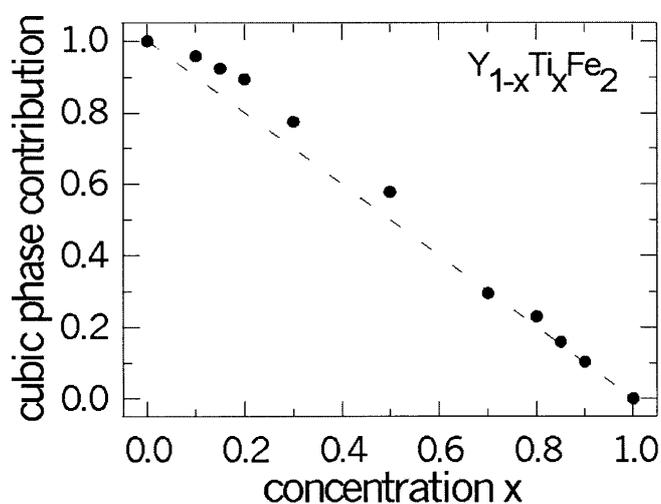


Fig. 3. The cubic phase contribution in the investigated $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ compounds estimated from the Mössbauer spectra.

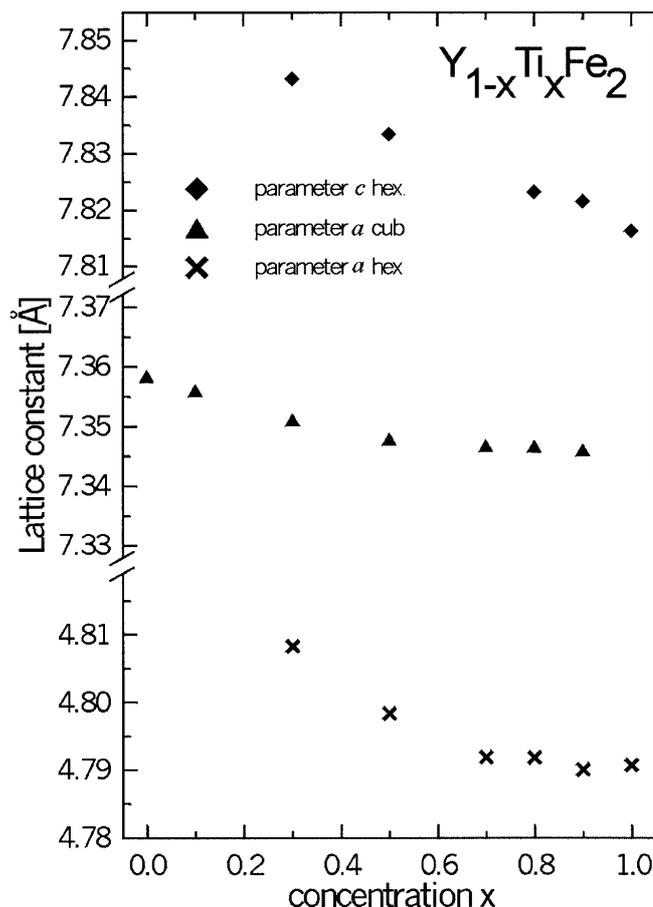


Fig. 4. The lattice parameters values vs. the concentration x in the $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ phases from XRD.

by Y atoms in spite of their size incompatibility. However, in the high Ti concentration range such substitution is very small. From the HFM dependencies on the concentration x , it may be concluded that Ti atoms do not locate at the Fe sites in the cubic phase. From our earlier investigations [4], it is known that the replacement of one Fe atom in NN of ^{57}Fe nuclear probe by another atom decreases HMF at least by about 1.5 T.

Figure 5 presents the typical Mössbauer spectra of $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ recorded at room temperature. The pattern corresponding to $x = 0$ consists of two sextets related to two magnetically nonequivalent positions of ^{57}Fe probes in the cubic structure. The supplementary component appears in the pseudobinary samples ($x \geq 0.1$). This component is related to the hexagonal phase and is described by the Mössbauer's doublet. Hence, it can be concluded that this phase is nonmagnetic in the whole range of x under examination.

From the dependence of hyperfine magnetic fields (HMF) shown in Fig. 6, it can be seen that the HMF decreases with increasing of concentration x in the quasi-binary samples. The decrease by about 0.4 T in the whole of range of concentration is observed. The decrease of the hyperfine field value can be explained by the elementary cell decrease. An analogous dependence for the hyperfine magnetic field on ^{57}Fe measured by the NMR method is observed in the high pressure experiment [2]. Possible explanation of this concentration dependence is as follows.

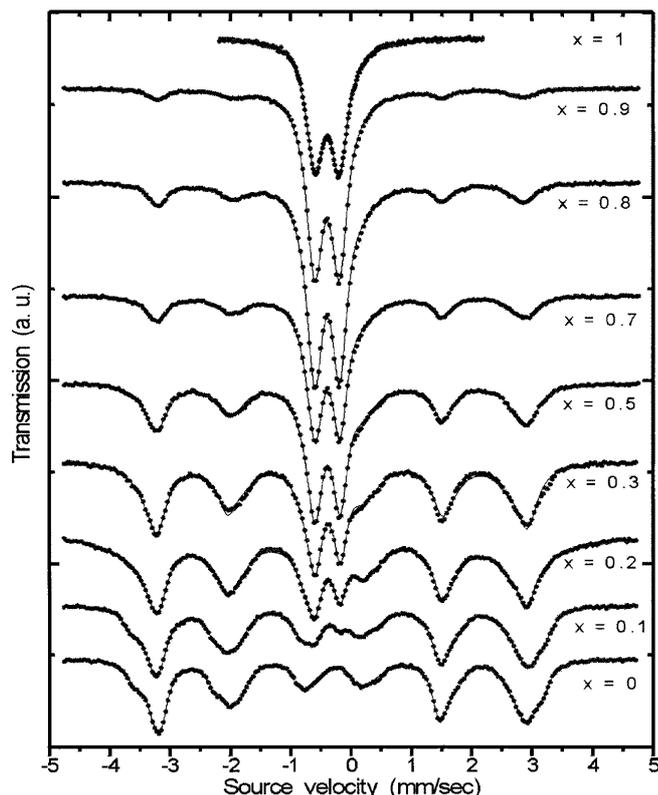


Fig. 5. The selected ^{57}Fe Mössbauer spectra for the $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ intermetallic compound.

The theoretical calculations [1] for the pseudobinary systems, which are the weak itinerant electron ferromagnets, show that the crystallographic lattice contraction leads to broadening of the $3d$ Fe bands. Additionally, the Ti atoms entering the cubic C15 lattice introduce one d -type electron more than the Y atoms. These two factors change the net spin at Fermi level and the Fe magnetic moment decreases. As a result, the HMF on ^{57}Fe also diminishes. Broadening of $3d$ Fe band in the investigated system is confirmed by the change of the IS value observed in the cubic phase which changes with the concentration x from -0.09 mm s^{-1} for $x = 0$ to -0.11 mm s^{-1} for $x = 0.9$. Then, the Fe $3d$ band

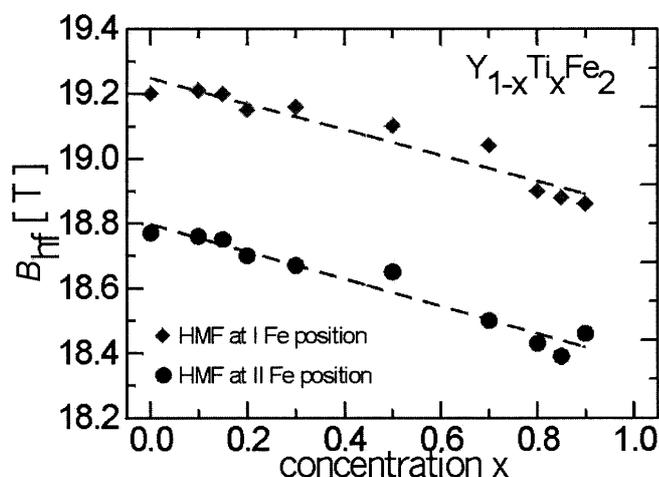


Fig. 6. The hyperfine magnetic field values vs. the Ti concentration x in the $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$.

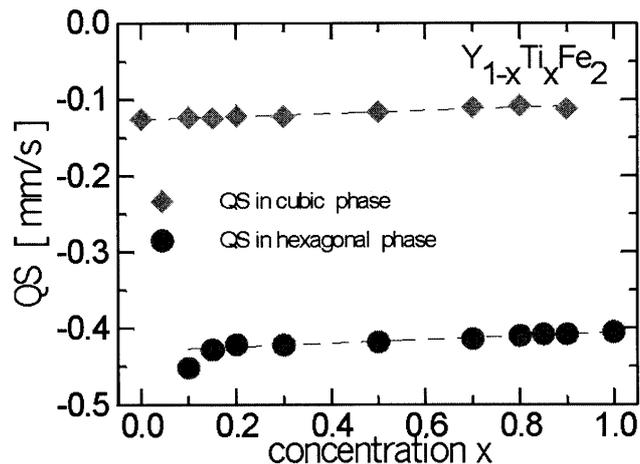


Fig. 7. The quadrupole shift and splitting values vs. the Ti concentration in the $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ Laves phase compounds.

becomes larger, the degree of its states localization decreases. Consequently, the shielding of $3s$ Fe electrons by the $3d$ Fe electrons becomes weaker and the s charge density on ^{57}Fe nuclei increases.

The difference of values B_I and B_{II} related to the respective sites in the YFe_2 can be fully explained by different dipole contributions [3].

From the analysis of the relevant Mössbauer spectra, the values of quadrupole shifts $\epsilon_{OI} = \text{QS}(3\cos^2\theta - 1)/2$ in the cubic phase, where $\text{QS} = e^2qQ/4$ can be obtained. The quadrupole shift ϵ_{OII} for $\theta = 0^\circ$ is equal to three times as much as ϵ_{OI} for $\theta = 70^\circ 32'$ with the opposite sign (see Introduction). The QS values as a function of Ti concentration are given in Fig. 7. The QS values are close to -0.11 mm/s and -0.40 mm/s in the cubic and hexagonal phases, respectively. The absolute values of QS decrease insignificantly with the concentration x in both phases. This suggests that the substitution of Ti for Y almost does not disturb the Fe local symmetry in both phases.

Summary

The studies carried out in this paper show that in the pseudobinary compounds of $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ -type coexistence of cubic and hexagonal phases is observed in the whole of range of concentration x . The substitution of Ti atoms for Y atoms in these compounds occurs only to a small extent.

In the $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ compounds, the values of the internal magnetic fields measured on the ^{57}Fe nuclei at 16d sites in the C15 lattice decrease insignificantly with the concentration x . The internal magnetic fields were not observed for the Fe 6h and 2a lattice sites related to the C14 hexagonal structure contrary to the situation taking place in the $\text{Zr}_{1-x}\text{Ti}_x\text{Fe}_2$ series [11]. This shows that the presence of Y atoms in the pseudobinary hexagonal phase $\text{Y}_{1-x}\text{Ti}_x\text{Fe}_2$ samples does not influence on the increase of T_N above room temperature.

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