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Mössbauer and X-ray Diffraction Studies of $Zr_{1-x}Ti_xFe_2$ Laves Phase Compounds

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Mössbauer spectroscopy of ^{57}Fe and X-ray diffraction measurements in the $Zr_{1-x}Ti_xFe_2$ phase have been made. Our X-ray diffraction spectra revealed that the samples have the cubic $C15$ crystal structure for low Ti concentration and the hexagonal $C14$ structure for high Ti concentration. In the range of $0.2 \le x \le 0.5$ a mixture of both structures occurs. The investigated compounds are paramagnetic at RT for $x > 0.80$ and magnetic for $x \le 0.8$. In the magnetic samples we found four different values of hyperfine magnetic fields. The presence of two hyperfine magnetic fields in the $C14$ phase suggests magnetic moments on Fe atoms at $2a$ sites. The obtained ε_Q vs. the x dependence indicates the spin canted antiferromagnetic structure in the hexagonal phase in the range of $0.2 \le x \le 0.8$.

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1. Introduction

Our X-ray diffraction (XRD) investigations show that in the quasibinary system of $ZrFe_2$ and $TiFe_2$ with Laves structure the crystal structure changes from the cubic $C15$ type ($MgCu_2$, space group $Fd3m$) to the hexagonal $C14$ type ($MgZn_2$, space group $P6_3/mmc$). In the cubic phase Fe atoms create regular tetrahedrons ($16d$ positions of the $\overline{3}m$ point symmetry) connected via their corners. Six Fe and six Zr atoms surround each Fe atom composing its nearest neighbour (see Fig. 1a). In the hexagonal phase Fe atoms create the sublattice of regular tetrahedrons linked alternately by apexes ($2a$ positions of the $\overline{3}m$ point symmetry) or by their bases ($6h$ positions of the mm point symmetry). In this structure the population ratio of $6h$ and $2a$ sites is equal to 3:1. The number of the nearest neighbours of Fe atoms is identical to that in the $C15$ structure. The difference among the structures is only in local symmetry of the nearest neighbours (see Fig. 1b and c). The compound $ZrFe_2$ is a ferromagnet ($T_C = 630$ K, $M_S(\mathrm{RT}) = 76$ emu/g [1]) in which at the RT all Fe atoms have a magnetic moment of about $1.5\mu_B$. The neutron diffraction measurement results [2] suggest an antiparallel induced magnetic moment at Zr sites of about $-0.3\mu_\mathrm{B}$ as a result of hybridization of $3d$ Fe and $4d$ Zr bands [3]. The Laves phase $\mathrm{TiFe_2}$ is an antiferromagnet ($T_\mathrm{N} = 285$ K [4]). From the neutron diffraction investigations [4] it is known that the magnetic moments of $1.4(1)\mu_\mathrm{B}$ (at 4 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 adjacent antiferromagnetically coupled planes do not carry any ordered moment, because the molecular fields from the $6h$ sites are cancelled.

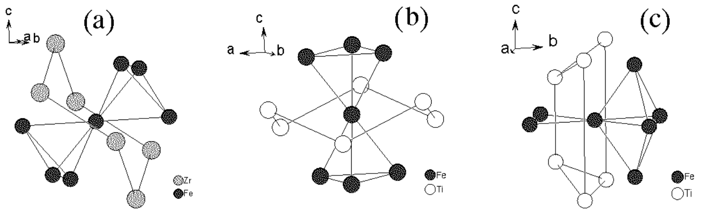

Fig. 1. The nearest neighbours of Fe atom at: (a) I or II site in the $C15$ structure, (b) $6h$, and (c) $2a$ site of the $C14$ structure.

In the $C15$ structure all Fe atoms have local $\bar{3}m$ symmetry with a three-fold axis along one of [111] directions. For the pure $\mathrm{ZrFe_2}$ intermetallic an easy magnetization axis has the same direction. In the presence of a magnetic field the principal axis of the electric field gradient (EFG) makes two possible angles with that axis, of $70°32'$ and $0°$. This determines two distinct types of magnetically nonequivalent Fe positions called I and II, respectively, with a population ratio of 3:1.

In the $C14$ lattice the principal axes of the local EFGs for $6h$ sites are perpendicular to the c axis being simultaneously an easy magnetization axis. In the case of $2a$ sites relevant axes overlap.

In the quasibinary $(\mathrm{Zr}_{1-x}\mathrm{Ti}_x)\mathrm{Fe}_2$ Laves phase compounds the situation is more complicated. It is known [5] that in the $C14$ phase the thermal fluctuations of the $6h$ Fe moments give rise to a dynamical molecular field upon $2a$ sites at a temperature close to T_N, which causes strong spin fluctuations and an arising magnetic moment at these sites. It is possible that the spatial disorder in these phases resulting from Zr replacement with Ti atoms and phases interaction may have a similar effect on the magnetic structure. Also easy magnetization axes may change their directions [6] which gives a wide range of possible angles θ between these vectors and the principal axes of EFG. This fact is reflected in the relevant Mössbauer spectra through different observed values of quadrupole shifts $\varepsilon_Q = \mathrm{QS}(3\cos^2\theta - 1)/2$. To obtain a better understanding of the magnetic property and the nature of ferromagnetism–antiferromagnetism transition in this quasibinary system, we have carried out studies using the Mössbauer effect (ME) over the whole concentration.

2. Experimental

The quasibinary $Zr_{1-x}Ti_xFe_2$ compounds in the polycrystalline form were produced by arc furnace melting of appropriate stoichiometric amounts of zirconium, titanium, and iron of 4N purity, in argon atmosphere. To avoid inhomogeneities the samples were remelted a few times. The crystal structure of produced samples was examined by means of a diffractometer with Cu K_α radiation at $\Theta-2\Theta$ geometry. The ^{57}Fe Mössbauer spectra of the powdered samples were measured at RT using a constant acceleration spectrometer in a transmission mode with the ^{57}Co/Rh source. From the data on crystal structures and XRD results we could accept a two-site model for the single-phase range and a four-site model for the mixed phase range. Each fitted sextet has fixed the relative line intensities $3:2:1:1:2:3$ characteristic of polycrystal materials. For both phases the sextet intensity ratio ($6h$ sites/$2a$ sites or I sites/II sites) was fixed as 3:1. All the other parameters were set free in the fitting processes.

3. Results and discussion

The samples under discussion formed the quasibinary Laves phases in which Ti atoms replaced a part of Zr atoms, therefore the produced phases could crystallize forming a cubic or hexagonal crystal lattice. Such a replacement is strongly suggested both by atomic sizes of the Ti and Zr atoms (1.46 and 1.60 Å, respectively) and their chemical similarity (Pauling electronegativities: 1.3 and 1.2, respectively). Another possibility is the formation of a mixture of both above-mentioned structures in one sample. Powder X-ray diffractograms were made for each sample, confirming a single phase of the $C15$ structure in the samples with Ti content less than 0.15 and a single phase of the $C14$ structure in the probes with Ti content over 0.6 at.%. Powder patterns in a range of the Ti concentration of $0.2 < x < 0.6$ show the coexistence of both phases. The analysis of intensities of some carefully chosen diffraction lines, representative for the respective crystal structures, allow us to estimate relative contribution of the hexagonal $C14$ phase for the samples in investigation. The correspondent dependence, given in Fig. 2, exhibits progressive increasing of the $C14$ phase contribution with increasing Ti concentration in the region of the mixed phases. Figure 3 presents the lattice constants dependences on Ti concentrations for both observed crystal structures. About 2% decrease in the cubic cell dimension in the $C15$ phase occurrence range is related to the partial substitution of Zr atoms by smaller Ti atoms without structure transformation. Similarly, the replacement of greater Zr atoms by Ti atoms in the hexagonal structure leads to about 3% decrease in the a and c parameters. Only minor deviations from Vegard's law are observed for both structures individually. The a and c values for pure $TiFe_2$ are consistent with the results of [4]. The samples in investigation reveal different behaviour in various ranges of concentration. For $x \leq 0.15$ Ti atoms are dissolved in the Zr sublattice of the cubic structure of $ZrFe_2$ in the form

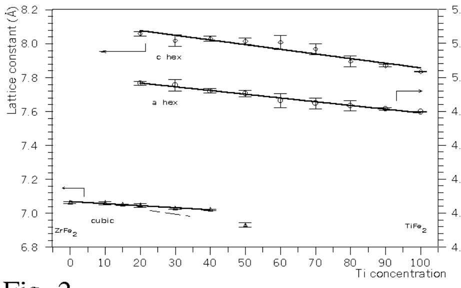

Fig. 2

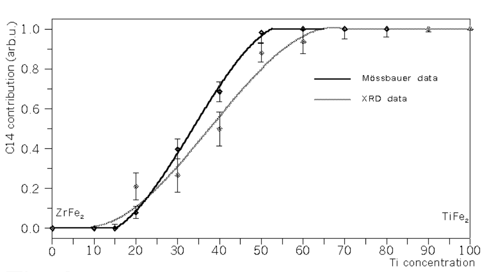

Fig. 3

Fig. 2. The lattice constant values vs. the Ti concentration x in the $Zr_{1-x}Ti_xFe_2$ phases from XRD.

Fig. 3. The hexagonal $C14$ phase contributions in the investigated $Zr_{1-x}Ti_xFe_2$ compounds estimated from the XRD measurements and the Mössbauer spectra.

of solid solutions. For $x \geq 0.6$ exchange of roles occurs and the $C14$ phase serves as solvent for Zr atoms. In the range of $0.2 < x < 0.6$ we have to do with a kind of a mixture.

The results of hyperfine interactions parameters are given in Figs. 4–6. For the Ti concentration of $0 \leq x \leq 0.5$ there are two hyperfine magnetic fields on ^{57}Fe of the values about 200 and 185 kGs (see Fig. 4). On the basis of their practical independence of the sample composition and analysis of the sextet intensities related to them we could ascribe these values to I and II sites, respectively. The observed difference of H between these two types of sites in the cubic phase can be explained by the so-called pseudodipolar anisotropic interaction [6]. The term "pseudodipolar" stands for the effective anisotropic contribution to the ^{57}Fe hyperfine magnetic field, which exceeds significantly the amount of the classical dipole–dipole interaction. This can be caused by overlapping p-orbitals and/or by an interaction involving not completely quenched orbital moments on the Fe atoms. For the Ti content of $0.2 \leq x \leq 0.5$ two additional internal magnetic fields appeared, the values of which amount to about 50 and 15 kGs. They occur up to $x \leq 0.8$ and change hardly with the increasing Ti concentration. As earlier, taking into account the magnitudes of these fields and the relevant sextet intensities, we assigned them to ^{57}Fe atoms at $6h$ and $2a$ positions in the hexagonal phase. For $x \geq 0.90$ the lack of hyperfine magnetic field results, of course, from paramagnetic character of the samples. Preservation of four well-determined hyperfine magnetic field values in the mixed phase range allows for the statement that in this range we have to do with the mixture of two well-separated $C15$ and $C14$ phases at least in the micro-scale. On the basis of the above-discussed accepted model attributing the specific fields to the appropriate crystal phases we estimated relative contribution of the $C14$ phase in the investigated samples as the function of Ti concentration. This contribution corresponds to the ratio of intensities of sextets related to two low and two high H components in the Mössbauer spectra, respec-

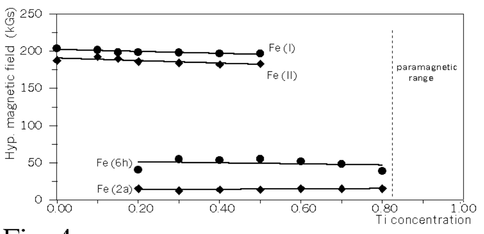

Fig. 4

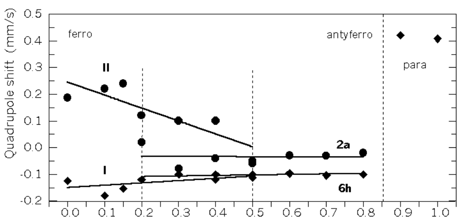

Fig. 5

Fig. 4. The hyperfine magnetic field values versus Ti concentration x.

Fig. 5. The quadrupole splitting QS or the quadrupole shift ε_Q values versus the Ti concentration x.

tively. The result of such estimation is given in Fig. 2. It can be seen in this figure that both Mössbauer spectroscopy (MS) and XRD methods give very similar dependences of the $C14$ phase contribution in the investigated samples. The QS or ε_Q values (in the magnetic range) as a function of the Ti concentration are given in Fig. 5. In the paramagnetic state QS values are close to 0.40 mm/s. In the light of this result and the $C14$ structure symmetry described above, we can draw a conclusion that in spite of different local symmetries of the $2a$ and $6h$ sites, QS at these both positions have the same value within the limits of measurement errors. Similarly for the $ZrFe_2$ compound we have measured QS in a temperature above T_C and we have obtained the value of about 0.42 mm/s [7]. A noticeable difference of values and opposite signs of ε_Q at I and II sites observed in the pure cubic phase range occurs due to different θ angles for these positions (see Sec. 1). The same signs and very closed values of ε_Q for two types of sites in the mixed and pure hexagonal phases range can be explained as follows. As a result of the $C15$ and $C14$ phases interaction, the latter becomes a spin canted antiferromagnetic with $6h$ Fe spins only slightly deflected from the c axis. This causes an appearance of small magnetic moments at $2a$ sites lying in the plane perpendicular to the c axis. These moments give the above-mentioned hyperfine field $H \cong 15$ kGs. Simultaneously, in such a situation the respective θ angles are the same for both sites and equal approximately to 90°.

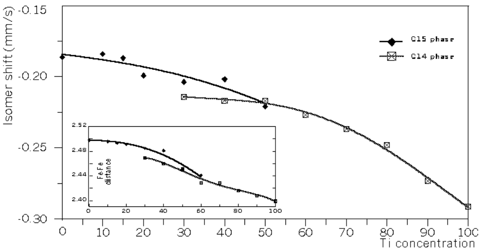

Fig. 6. Mean values of the isomer shift IS and Fe–Fe distance (the inset) versus the Ti concentration x.

For each x value the IS values of ^{57}Fe at both types of sites in the $C15$ and at both types of Fe positions in the $C14$ structure are the same within the experimental error limits. Thus only the mean IS values dependence vs. x is shown in Fig. 6. IS value changes almost monotonically from –0.18 mm/s for pure $ZrFe_2$ to IS $= -0.29$ mm/s for pure $TiFe_2$. In the ^{57}Fe probe case the s electron density increases on the nucleus. The possible explanations of this dependence are as follows. Firstly, the density of the $4s$ conduction electrons may increase directly due to the decrease in the nearest neighbour distances (see Fig. 6). Secondly, the density of the inner $3s$ electrons may increase as a result of the weaker shielding of these electrons by the $3d$ Fe electrons. It is known [8] that when $4d$ transition atoms are substituted by $3d$ atoms in the quasibinary Laves AFe_2 compound, hybridization between the $3d$ Fe bands and the respective d bands of the A atom becomes stronger. Then the width of the Fe $3d$ band becomes larger and the degree of the states localization decreases in such a band.

4. Conclusions

The ME and XRD measurements indicate the coexistence of the ferromagnetic $C15$ phase and the canted antiferromagnetic $C14$ phase for $0.2 \leq x \leq 0$ in the $Zr_{1-x}Ti_xFe_2$ system. It seems that in the mixed phases range the coupling between the ferromagnetic and antiferromagnetic components is considerably weaker than those within each of these components. This allows us to preserve the canted antiferromagnetic structure of the hexagonal phase. In order to explain the mean IS dependence on x it is necessary to include the effects related to the mixing of $3d$ Fe bands and d bands of A atom. Furthermore, there is a strong correlation between the IS values and the distances from ^{57}Fe atom probes to their nearest neighbours in the lattice.

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