

High-Pressure Mössbauer Studies of Magnetism in ScFe_2 and $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ Laves Phases

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We report on ^{57}Fe -Mössbauer studies of the magnetic properties in ScFe_2 and $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ performed as a function of pressure and temperature. Both systems crystallize in the $C14$ -type Laves phase structure with two different Fe sites 6h and 2a. The ferromagnetic properties of ScFe_2 ($T_C = 540$ K at ambient pressure) change around 30 GPa to antiferromagnetic order of the 6h sites with non-magnetic 2a sites. The ordering temperature is lowered to $T_N = 300$ K at 51 GPa. This pressure-dependent behaviour of ScFe_2 resembles that observed within the $\text{Sc}_{1-x}\text{Ti}_x\text{Fe}_2$ series as a function of x . In ferromagnetic $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ we observe, as a function of temperature and of pressure, an abrupt high-moment to low-moment transition of the Fe band moments of the 6h sites, accompanied by a rearrangement of the spin directions. In both systems the decrease in the Fe moments is accompanied by a strong increase in the volume coefficient of the isomer shift, originating from a reduced s -electron shielding capability of the d -electrons in the low-moment state.

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1. Introduction

The hexagonal $C14$ -type Laves phase system $\text{Sc}_{1-x}\text{Ti}_x\text{Fe}_2$ exhibits, as a function of x , different forms of $3d$ band magnetism, e.g. ferromagnetism (fm) in ScFe_2 ($T_C = 540$ K) with relatively large Fe band moments and antiferromag-

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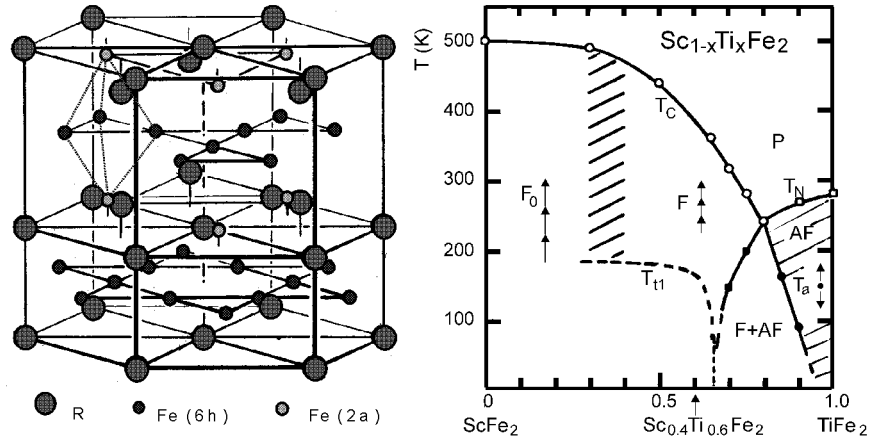


Fig. 1. Left: Crystallographic structure of $C14$ RFe_2 Laves phases and right: magnetic phase diagram of the $C14$ Laves phase system $Sc_{1-x}Ti_xFe_{1.95}$ [2].

netism (afm) in $TiFe_2$ ($T_N = 285$ K) with smaller moments (6h sites) or vanishing moments (2a sites) [1, 2]. Within the $Sc_{1-x}Ti_xFe_2$ series this different behaviour leads to a complex magnetic phase diagram [2] (see Fig. 1). Since the substitution of Sc by Ti is accompanied with a reduction of the lattice parameter, high pressure should lead to a similar magnetic behaviour as observed in the $Sc_{1-x}Ti_xFe_2$ series. In the present ^{57}Fe -Mössbauer study of $ScFe_2$ and $Sc_{0.4}Ti_{0.6}Fe_2$ at high pressure we observed indeed similar sequences of magnetic phases as in the $Sc_{1-x}Ti_xFe_2$ series as a function of x .

2. Experimental

The polycrystalline $ScFe_2$ and $Sc_{0.4}Ti_{0.6}Fe_2$ samples were prepared by arc melting of appropriate quantities of constituents in argon atmosphere using iron enriched to 30% with ^{57}Fe . X-ray diffraction (XRD) patterns proved the single phase quality of the samples. High pressure was applied to the samples in a diamond-anvil cell. The pressure was determined by ruby fluorescence. Details are described in Refs. [3, 4], where high-pressure studies of RFe_2 Laves phases with nuclear forward scattering (NFS) of synchrotron radiation are presented. The pressure dependence of the lattice parameters of the samples were determined by energy-dispersive XRD at the beamline F3 at HASYLAB (DESY, Hamburg) [5]. The ^{57}Fe -Mössbauer spectra were taken with a $^{57}CoRh$ point source. The Mössbauer absorbers enriched with ^{57}Fe had the effective thickness t up to 10. To take into account the thickness effect, the fitting program based on transmission integral was used. The simultaneous fit procedure, which allowed to constraint selected parameters to the same values within a series of spectra (measured, for instance, as a function of temperature), was applied. Details of the fitting procedure are described elsewhere [6, 7].

3. Results and discussion

3.1. Magnetic properties of ScFe_2 at high pressures

Two series of high-pressure Mössbauer measurements were performed on ScFe_2 , one up to 51 GPa and the other one up to 72 GPa. Mössbauer spectra from the second series of measurements, performed at 300 K and 78 K and various pressures, are shown in Fig. 2. The spectra at ambient pressure were fitted with two subspectra and with fixed intensity ratio to 3:1 corresponding to the ratio of 6h and 2a sites in $C14$ -type structure (see Fig. 1). The fit revealed hyperfine fields B_{eff} of 180 kGs and 177 kGs for the 6h and 2a sites, respectively, at 300 K and equal hyperfine fields of 197 kGs for both sites at 78 K. In these fits an identical value of electric quadrupole interaction, $\Delta E_Q = -0.40$ mm/s, but different angles $\beta_{6h} = 90^\circ$ and $\beta_{2a} = 0^\circ$ between the direction of B_{eff} and the main axes of the electric field gradients for the 6h and 2a sites were assumed. This arrangement of magnetic moments and electric field gradients, the one for the 6h sites additionally with an asymmetry parameter of $\eta = 0.7(1)$, follows from the known structural and magnetic properties of ScFe_2 and has been proven by other Mössbauer studies of the $\text{Sc}_{1-x}\text{Ti}_x\text{Fe}_2$ series [2] and TiFe_2 [8].

The Mössbauer spectra of ScFe_2 at 40 GPa show a drastic change by the appearance of a non-magnetic quadrupole doublet and magnetic sites with smaller hyperfine fields. Due to a broken diamond anvil, there was a larger pressure distri-

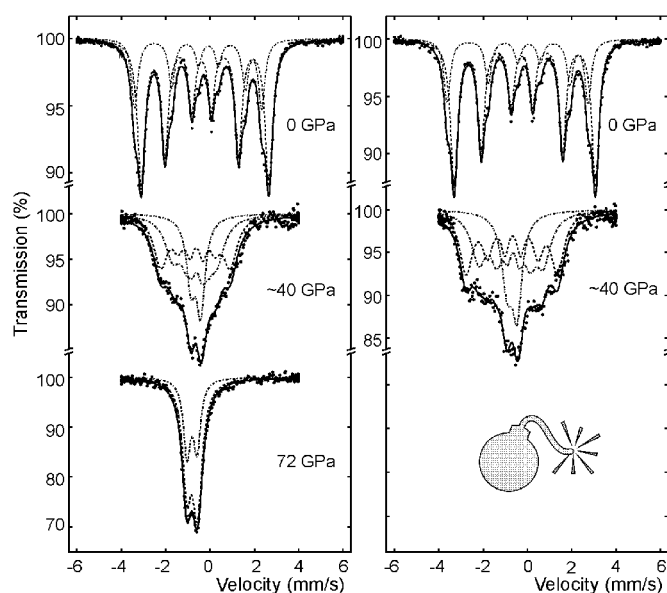


Fig. 2. ^{57}Fe -Mössbauer spectra of ScFe_2 at various pressures at 300 K (left) and at 78 K (right).

bution at the sample and the magnetic sites were fitted by two sites with different hyperfine fields. The spectra of ScFe_2 at 40 GPa resemble those of afm TiFe_2 at low temperature, where the 6h sites are magnetically ordered and the 2a sites are non-magnetic [8]. The quadrupole doublet of the 2a sites exhibits a quadrupole splitting with broadening, probably due to transferred hyperfine fields from neighbouring 6h sites. It should be noted that the magnetic sites could be only fitted with the assumption of a magnetic texture with the axis of magnetization being preferentially oriented along the direction of the γ -rays, which points to a preferred orientation of the crystallographic c -axes along the load axis of the diamond-anvil cell. Additional Mössbauer and NFS spectra of ScFe_2 taken between 26 and 51 GPa indicate that the fm-afm transition occurs around 30 GPa and that the Néel temperature T_N is lowered to 300 K at 51 GPa [3]. The spectrum of ScFe_2 measured at 72 GPa and 300 K (Fig. 2) clearly demonstrates the loss of magnetic order. The resulting quadrupole doublet with a splitting of $(-)$ 0.43 mm/s exhibits again a slight asymmetry, originating from the above-mentioned pressure induced texture of the hexagonal lattice. It was fitted with two asymmetric quadrupole doublets corresponding to the 6h and 2a sites with a fixed intensity ratio of 3:1.

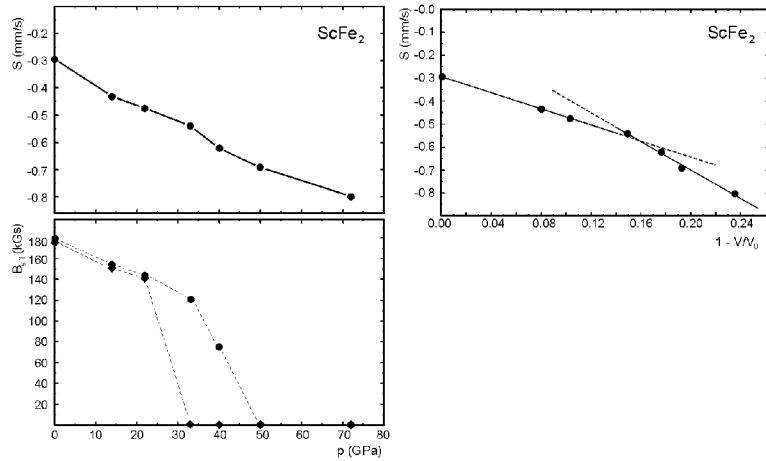


Fig. 3. Left: ^{57}Fe isomer shift S and hyperfine fields B_{eff} in ScFe_2 as a function of pressure (full dots: 6h sites; full diamonds: 2a sites). Right: ^{57}Fe isomer shift in ScFe_2 as a function of the normalized volume.

The pressure dependencies of the isomer shift and magnetic hyperfine fields B_{eff} for the 6h and 2a sites at 300 K are shown in Fig. 3. From the disappearance of the magnetic hyperfine field for the 2a sites around 30 GPa and from comparison with the magnetic phase diagram of the $\text{Sc}_{1-x}\text{Ti}_x\text{Fe}_2$ series (see Fig. 1), we conclude that a transition from fm to afm ordering takes place at that pressure. As in the case of TiFe_2 with $C14$ structure, the Fe atoms at the 2a sites lose their moments, while the Fe moments of the 6h sites are fm coupled within the planes,

but afm coupled between the planes. The large pressure-induced variation of the isomer shift by -0.50 mm/s for 72 GPa will be discussed later together with that observed in $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$. It is interesting to note that the quadrupole interaction for both sites remains almost constant at -0.40 ± 0.08 mm/s for the whole pressure range. This resembles the behaviour observed in TiFe_2 in a smaller pressure range [8]. In contrast to this one observes in the cubic $C15$ systems YFe_2 and LuFe_2 a strong increase in the quadrupole splitting from about -0.35 mm/s at ambient pressure to -0.80 mm/s at 80 GPa [9, 10].

3.2. Magnetic properties of $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ as a function of temperature and pressure

The composition of the $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ sample was chosen to assure a transition between the two fm states (high and low spin state of iron) as a function of temperature. In addition, the sample is close to the boundary between fm and afm order (see Fig. 1).

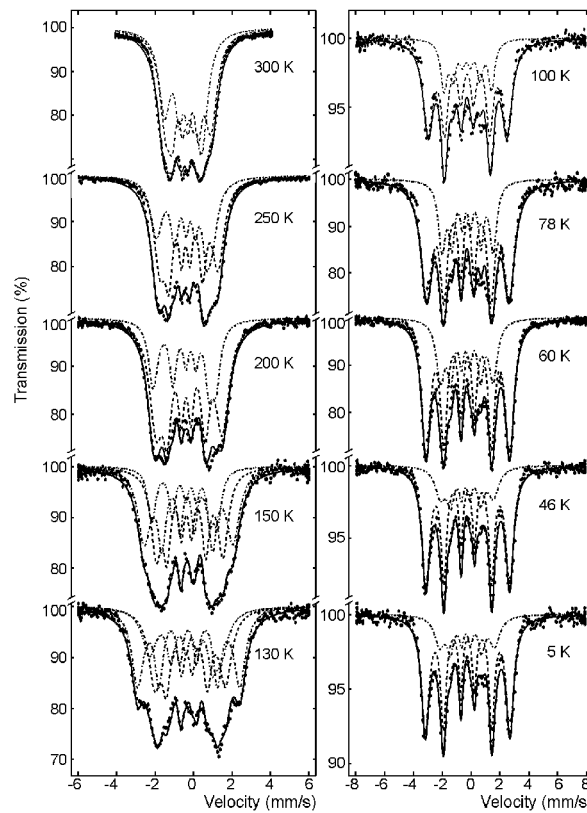


Fig. 4. ^{57}Fe -Mössbauer spectra of $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ at ambient pressure and various temperatures. The subspectra for the 6h- and 2a sites are explained in the text.

Figure 4 shows the Mössbauer spectra of $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ at ambient pressure and various temperatures. Their spectral features change considerably in the temperature region between 100 K and 150 K. The spectra were fitted below 100 K and above 150 K with two subspectra, corresponding to the 6h and 2a sites. In the transition region, the 6h sites were adjusted by two subspectra.

The fitted values for the isomer shift S , the magnetic hyperfine field B_{eff} and for the angle β between B_{eff} and the electric field gradient (EFG) are plotted in Fig. 5. The magnetic hyperfine field of the 6h site exhibits, with decreasing temperature, a sudden increase from 120 kGs to 170 kGs; this change is accompanied by a change in the isomer shifts and the angles β of both sites. A similar change in the hyperfine fields was also observed in a previous study of $\text{Sc}_{0.35}\text{Ti}_{0.65}\text{Fe}_{1.95}$ [2]. From an anomalous decrease in the lattice parameters with increasing temperature, resembling a first-order character of this magnetic phase transition, an Invar-like behaviour of the $\text{Sc}_{1-x}\text{Ti}_x\text{Fe}_2$ system was postulated for higher Ti concentrations [2]. The change in the isomer shift of the 6h site can be also explained by a modified s -electron shielding by the more localized (larger) $3d$ band moments

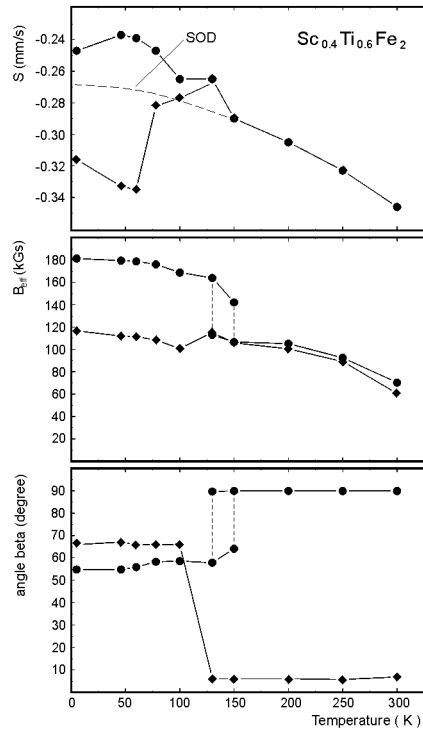


Fig. 5. Temperature dependence of the ^{57}Fe isomer shift S , hyperfine fields B_{eff} , and angles β in $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ at ambient pressure derived from the spectra of Fig. 4 (full dots: 6h sites; full diamonds: 2a sites).

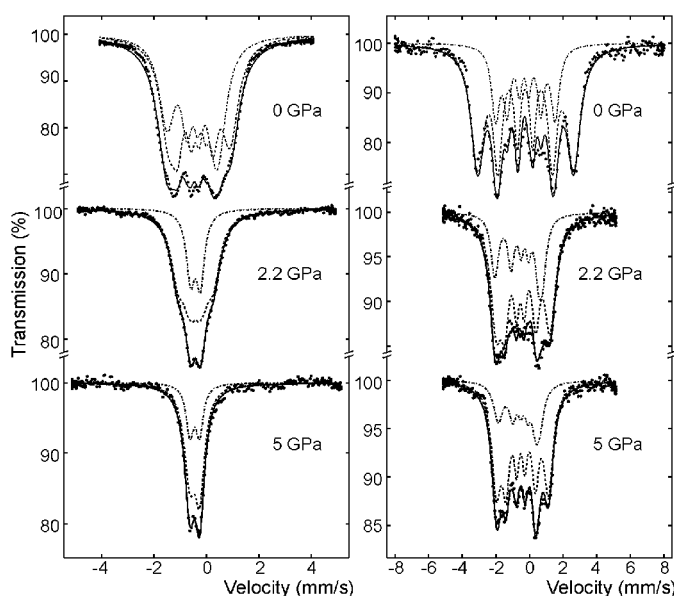


Fig. 6. ^{57}Fe -Mössbauer spectra of $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ at 300 K and various pressures (left) and at 78 K and various pressures (right). The subspectra for the 6h- and 2a sites are explained in the text.

of the 6h sites in comparison to the 2a sites. It should be mentioned that the quadrupole splitting remained unchanged for both sites at -0.35 mm/s, similar to values observed throughout the whole $\text{Sc}_{1-x}\text{Ti}_x\text{Fe}_2$ series [2].

Selected spectra of $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ taken at 300 K and 78 K for different pressures are shown in Fig. 6. The high-pressure spectra exhibit, in comparison to the spectra at ambient pressure, drastic changes in the magnetic properties. The spectrum at 2.2 GPa and 300 K exhibits a magnetically ordered 6h site with $B_{\text{eff}} = 36$ kGs (in comparison to 70 kGs at ambient conditions) and a non-magnetic 2a site with a well-resolved quadrupole splitting of (-0.37) mm/s. It resembles that of afm TiFe_2 at 275 K, near to $T_{\text{N}} = 285$ K [8]. The spectra at 5 GPa and 300 K exhibit a pure quadrupole splitting of (-0.37) mm/s for both sites. This indicates that in $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ at 300 K transitions from fm ordering to afm ordering like in TiFe_2 and further to a paramagnetic state takes place at moderate pressures.

The 78 K spectra of $\text{Sc}_{0.4}\text{Ti}_{0.6}\text{Fe}_2$ (Fig. 6) exhibit, as a function of pressure, the high-moment/low-moment transition for the 6h site observed at ambient pressure as a function of temperature. The corresponding hyperfine field of the 6h sites changes from 176 kGs (0 GPa) abruptly to 98 kGs (2.2 GPa) and 94 kGs (5 GPa). For comparison, the hyperfine field at the 2a site varies continuously from 108 kGs (0 GPa) to 88 kGs (2.2 GPa) and 75 kGs (5 GPa). The change of the magnetic hyperfine field (magnetic moment) of the 6h site is accompanied by a similar change of the angle β as observed above.

*3.3. Pressure/volume dependence of the isomer shifts
in ScFe₂ and Sc_{0.4}Ti_{0.6}Fe₂*

Here we want to discuss the variation of the isomer shifts observed for ScFe₂ and Sc_{0.4}Ti_{0.6}Fe₂ as a function of volume and compare with that observed in other RFe₂ systems. The pressure dependence of the lattice parameters of many RFe₂ systems was measured by Reiß [5]. This information was used to derive, as shown in Fig. 3, the volume dependence of the isomer shift in ScFe₂. There is a characteristic kink in the slope of S versus $(1 - V/V_0)$. From this one derives the volume coefficients $(\partial S/\partial \ln V)_{300\text{ K}} = 1.8(3)$ mm/s for pressures below 30 GPa and $\partial S/\partial \ln V)_{300\text{ K}} = 3.1(3)$ mm/s for pressures above 30 GPa. These values are compared in Table with $(\partial S/\partial \ln V)_{300\text{ K}} = 2.6(8)$ mm/s obtained for Sc_{0.4}Ti_{0.6}Fe₂ in the present study as well as values for TiFe₂ [8] and YFe₂ [6, 9] obtained in previous studies. Comparison with pure iron as well as with Fe diluted in d -metals [11] indicate that volume coefficients up to $(\partial S/\partial \ln V) = 1.9$ mm/s are indicative of a normal compression of s -like conduction electrons. The larger values of $(\partial S/\partial \ln V)_{300\text{ K}}$ up to 3.1 mm/s point, as discussed above for the Sc_{0.4}Ti_{0.6}Fe₂ system, to a change of the $3d$ configuration with a concomitant change in the screening potential. In both ScFe₂ (above 30 GPa) and in Sc_{0.4}Ti_{0.6}Fe₂ we observe a strong reduction of the (averaged) Fe moment with pressure, which is seemingly correlated a delocalization of the $3d$ band electrons, which readily explains the observed larger volume coefficients of the isomer shift.

TABLE

Volume coefficients $(dS/d \ln V)_{300\text{ K}}$ of the ⁵⁷Fe isomer shifts S in ScFe₂ and Sc_{0.4}Ti_{0.6}Fe₂ (present work), in TiFe₂ [8], in YFe₂ [6, 9], and in Fe and dilute systems [11].

| System | $(\frac{\partial S}{\partial \ln V})_{300\text{ K}}$ [mm/s] |
|---|---|
| TiFe ₂ | 1.5(2) |
| Sc _{0.4} Ti _{0.6} Fe ₂ | 2.6(8) |
| ScFe ₂ | 1.8(3) ($p < 30$ GPa) 3.1(3) ($p > 30$ GPa) |
| YFe ₂ | 1.9(3) ($p < 30$ GPa) 2.5(3) ($p > 30$ GPa) |
| ⁵⁷ Fe in Ti | 1.0 |
| ⁵⁷ Fe in W | 1.8 |
| ⁵⁷ Fe in Co | 1.1 |
| ⁵⁷ Fe in Ni | 1.1 |
| α -Fe | 1.4 |

4. Summary and outlook

In conclusion, the present studies of ScFe₂ and Sc_{0.4}Ti_{0.6}Fe₂ demonstrate that the variations of the magnetic properties within the Sc_{1-x}Ti_xFe₂ series can

be reproduced by the application of pressure. A full discussion of the pressure effects in comparison to a substitution of trivalent Sc by tetravalent Ti, which is accompanied also by a change in the number of band electrons, will be given in a forthcoming paper. There we will also present very recent data on the pressure induced changes in magnetic ordering temperatures in ScFe_2 and related RFe_2 systems [12].

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