

The influence of silicon on hyperfine magnetic fields in $\text{Zr}(\text{Fe}_{1-x}\text{Si}_x)_2$ measured for $x \leq 0.17$
by Mossbauer spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 6473

(<http://iopscience.iop.org/0953-8984/4/30/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:22

Please note that [terms and conditions apply](#).

The influence of silicon on hyperfine magnetic fields in $\text{Zr}(\text{Fe}_{1-x}\text{Si}_x)_2$ measured for $x \leq 0.17$ by Mössbauer spectroscopy

J Sarzyński, M Budzyński, R Wasiewicz and M Wiertel

Institute of Physics, Marie Curie-Skłodowska University, Pl. Marie Curie-Skłodowskiej 1, 20-031 Lublin, Poland

Received 11 November 1991, in final form 21 April 1992

Abstract. Mössbauer (^{57}Fe) spectroscopy has been used to study the Laves phase compounds $\text{Zr}(\text{Fe}_{1-x}\text{Si}_x)_2$ for $x \leq 0.17$. It has been found that the mean values of the hyperfine magnetic field, isomer shift and quadrupole splitting decrease with increasing Si concentration. The dependence of the hyperfine magnetic field on the number of Si atoms as nearest and next-nearest neighbours of ^{57}Fe has been established.

1. Introduction

The specific magnetic behaviour of ferromagnetic iron compounds has been the subject of very extensive investigations. It is well known nowadays that the influence of the substitutional non-magnetic atoms in pseudo-binary iron systems on the hyperfine interaction parameters is undisputed. It was confirmed additionally by our measurements for the cubic Laves phases $\text{Zr}(\text{Fe}_{1-x}\text{Al}_x)_2$ [1]. However, the question which has remained unsolved up to now is which of the two approaches given by the Jaccarino–Walker [2] model and the Van der Kraan [3] model explains the magnetic properties of these compounds. Here, we present our experiments as a contribution to this discussion.

2. Experimental procedure

The samples of $\text{Zr}(\text{Fe}_{1-x}\text{Si}_x)_2$ were prepared by arc melting of high-purity starting materials, under an Ar atmosphere. The samples were remelted several times in order to achieve homogeneity. They were annealed in a vacuum of about 10^{-4} Pa at 850–900 K for 72 h. X-ray powder patterns, observed for all samples, indicated that the samples were single phase with a cubic structure. The lattice constant did not change appreciably with increasing Si concentration. The Mössbauer spectra were recorded at RT with a conventional constant-acceleration spectrometer with a ^{57}Co source in a Cr matrix.

3. Results and discussion

The Mössbauer spectra presented in figure 1 were analysed by means of a standard computer procedure. The number of sextuplets fitted to the experimental spectra changed from two for $x = 0.00$ to six for $0.08 \leq x \leq 0.17$. The linewidth was kept constant for a given x -value. The average half-width Γ of all the absorption lines in the whole range of Si concentrations was equal to about 0.36 mm s^{-1} in comparison with the Γ -value for ^{57}Fe in a Cr matrix of 0.26 mm s^{-1} . The occurrence of two six-line patterns for $x = 0.00$ is connected with the existence of two magnetically inequivalent sites in the iron sublattice in ZrFe_2 . The total intensity ratio observed by us (71:29) differs somewhat from the expected ratio (3:1) for the easy-magnetization axis along the $\langle 111 \rangle$ direction. This divergence may be explained by the change in the easy-magnetization axis from the $\langle 111 \rangle$ direction to the $\langle 100 \rangle$ or $\langle 110 \rangle$ directions, at least locally.

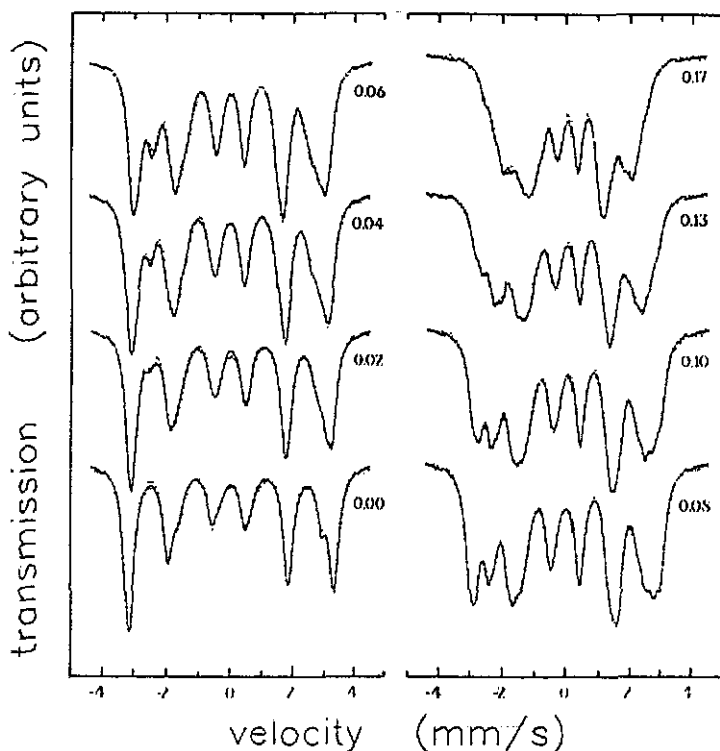


Figure 1. Mössbauer spectra of $\text{Zr}(\text{Fe}_{1-x}\text{Si}_x)_2$ for different x -values.

The mean weighted values of the hyperfine magnetic field B , the isomer shift (IS) and the quadrupole splitting (QS) as functions of the Si concentration are presented in figure 2. The IS scale is given relative to ^{57}Fe in $\alpha\text{-Fe}$. The Si concentration dependences of all parameters exhibit behaviours similar to those observed for $\text{Zr}(\text{Fe}_{1-x}\text{Al}_x)_2$ [1]. B and IS have linear dependences with a change in slope for $x \approx 0.06$. This means that, in this range of x -values, a modification of the electronic structure occurs without a change in crystallographic structure.

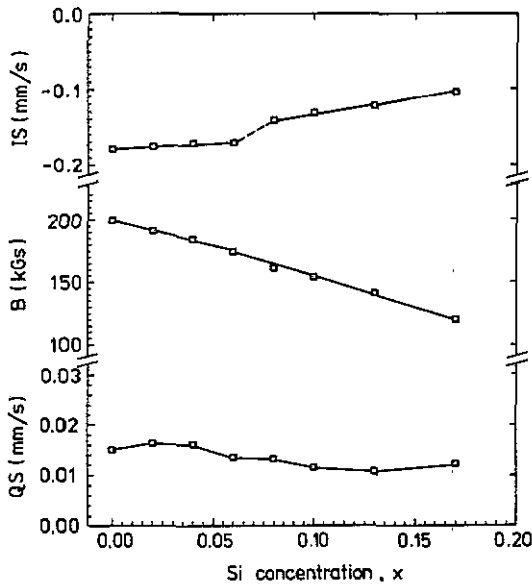


Figure 2. Dependence of mean weighted B , IS and QS values on Si concentration, derived from the Mössbauer spectra.

It is unquestionable that, as in the case of $Zr(Fe_{1-x}Al_x)_2$, the decrease in the hyperfine magnetic field on the ^{57}Fe nuclei is caused by the increasing substitution of magnetic Fe atoms by non-magnetic Si atoms. From the B versus x behaviour (figure 2), one should expect $Zr(Fe_{1-x}Si_x)_2$ to become paramagnetic for Si concentrations up to about $x \simeq 0.35$. This corresponds to the situation where a third of all Fe atoms are substituted by non-magnetic Si atoms.

In the cubic Laves phase structure $ZrFe_2$, the Fe atoms are surrounded by six Fe atoms in their first shell (nearest neighbours (NNS)) and by 12 Fe atoms in their second shell (next-nearest neighbours (NNNS)). The distance of the second-nearest Fe neighbours from the Fe atom is about twice the distance of the first-nearest neighbours. Between six Fe NN atoms and 12 Fe NNN atoms, six Zr atoms are located. The substitution of Fe NN and Fe NNN atoms by non-magnetic Si atoms causes a great variety of ^{57}Fe local environments and some of them can be distinguished as a result of our Mössbauer data.

The dependences of B , IS and QS on Si concentration for all components (sextuplets) are presented in figures 3, 4 and 5, respectively. In figure 3, the full curves join the values of the hyperfine magnetic fields for similar surroundings of ^{57}Fe atom for different compounds. The bifurcation observed below $x \simeq 0.06$ (curves a and a') reflects, in our opinion, the situation for pure $ZrFe_2$, where the Fe atoms are in two magnetically inequivalent sites. This splitting disappears with increasing Si concentration.

Each of the curves in figure 3 corresponds to a different environment of the nuclear ^{57}Fe probes. However, a comparison of the experimental amplitudes of sextuplets from numerical analysis and the binomial distribution data indicates that the attribution of the definite unequivocal configurations of NN and NNN atoms to these curves is impossible, particularly for higher Si concentrations. Therefore, we may only affirm, with great probability, that the configuration of Fe and Si atoms in

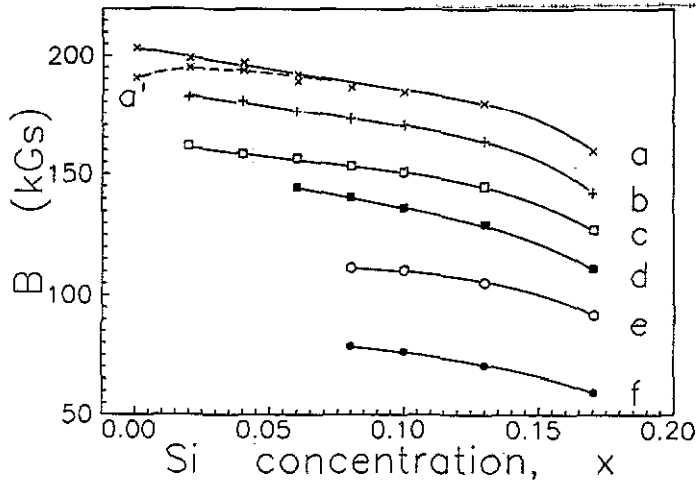


Figure 3. The ^{57}Fe hyperfine magnetic fields in $\text{Zr}(\text{Fe}_{1-x}\text{Si}_x)_2$. The letters on the curves correspond to the descriptions in table 1.

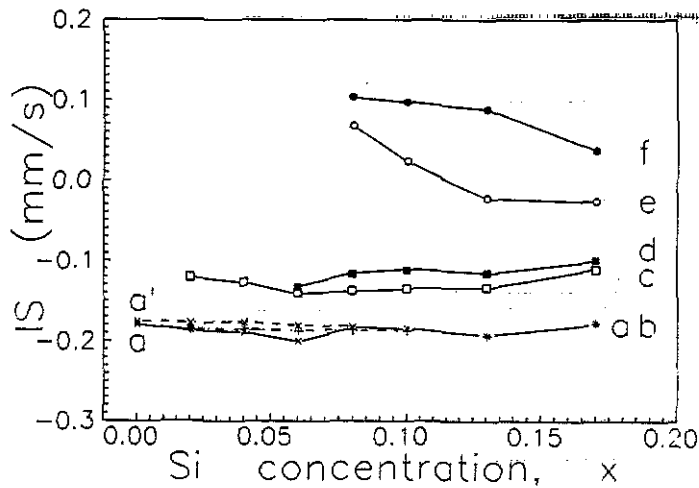


Figure 4. The ^{57}Fe IS values for $\text{Zr}(\text{Fe}_{1-x}\text{Si}_x)_2$.

the NN and NNN shells of ^{57}Fe are those presented in table 1.

The dependence of IS on Si concentration presented in figure 4 seems to confirm such a configuration of atoms. Curves a and b, curves c and d and, to a certain degree, curves e and f form pairs of curves which differ distinctly from each other in their IS values. This difference from one pair to the next pair of curves is caused by the change in electronic structure in the nearest surroundings of the ^{57}Fe atoms. Figure 2 shows that the IS tends to be less negative with increasing Si concentration. This means, recalling that $\delta R/R$ is negative for ^{57}Fe , that the electron density at the ^{57}Fe nucleus decreases with increasing amount of Si. The s-electron density at the nucleus is inevitably influenced by changes in the valence shell structure. It is known that the electronegativity of neighbouring atoms plays an important role in these changes. The electronegativity of silicon is 1.75, whereas the value for iron is

Table 1. The proposed configurations of Fe and Si atoms in the NN and NNN shells of ^{57}Fe atoms, corresponding to curves a-f in figure 3. The underlined configurations provide the largest contribution to the amplitude of hyperfine magnetic field.

Curve in figure 3	Configuration of NN shell	Configuration of NNN shell	
		$x \leq 0.10$	$x \geq 0.13$
a	6Fe	12Fe	12Fe, <u>11Fe + 1Si</u>
b	6Fe	11Fe+1Si	<u>11Fe + 1Si</u> 10Fe+2Si
c	<u>5Fe + 1Si</u> 6Fe	<u>12Fe</u> 10Fe+2Si	<u>11Fe + 1Si, 10Fe+2Si</u> 10Fe+2Si, 9Fe+3Si
d	<u>5Fe + 1Si</u> 6Fe	<u>11Fe + 1Si, 10Fe+2Si</u> 9Fe+3Si	<u>11Fe + 1Si, 10Fe + 2Si</u> 9Fe+3Si 9Fe+3Si
e	4Fe+2Si	12Fe, 11Fe+1Si	12Fe, 11Fe+1Si 10Fe+2Si
f	4Fe+2Si	10Fe+2Si, 9Fe+3Si	10Fe+2Si, 9Fe+3Si 8Fe+4Si

1.65 [4]. Thus, a charge flow off the iron atoms leads to the increment in IS.

Under the assumption of the configuration given in table 1, the divergence between the experimental and theoretical amplitude values remains within the bounds of 20(10)% for $x \leq 0.10$ and 40(10)% for $x \geq 0.13$. The configurations presented for curves e and f are very rough estimations.

The QS value as a function of Si concentration is presented in figure 5. Only curve f is distinctly separated and the bifurcation of curve a, as in the case of the B versus x dependence, is clearly visible.

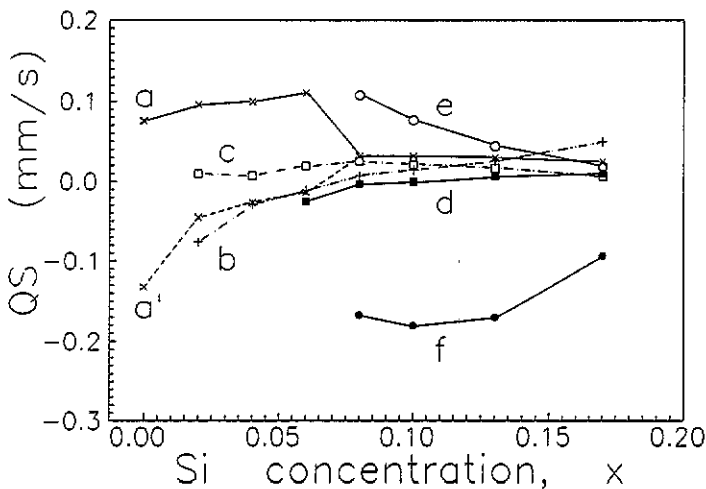


Figure 5. The ^{57}Fe QS values for $Zr(Fe_{1-x}Si_x)_2$.

It can be seen (from figure 2) that the mean value of QS is nearly constant in the whole range of Si concentrations. This means that, on average, the angle ϑ between the V_{zz} -axis and the hyperfine magnetic field vector does not change. The asymmetric charge distribution around the ^{57}Fe atom is observed only for curve f which corresponds to the weakest magnetic fields, i.e. for a large amount of Si atoms in the ^{57}Fe surroundings.

Our results indicate that in $\text{Zr}(\text{Fe}_{1-x}\text{Si}_x)_2$ the concentration dependence of the hyperfine magnetic field cannot be explained by assuming a discontinuous formation of the Fe magnetic moment on the basis of the model of Jaccarino and Walker [2]. In our experiment neither the number of sextuplets required by this model nor the presence of a paramagnetic doublet or a single-line pattern was observed. Our results allow us to conclude that the decrease in ^{57}Fe magnetic moment is stepwise and that the model of Van der Kraan [3] is the better approach for the description of the magnetic properties of these compounds.

The analysis of the curves in figure 3 (see also table 1) allowed us to estimate that the substitution of one Fe NN atom by an Si atom causes a decrease in the hyperfine magnetic field by about $\Delta B_{\text{NN}} \simeq 33.8$ kG. The lack of one Fe NNN atom decreases the field by about $\Delta B_{\text{NNN}} \simeq 16.6$ kG. Thus, $\Delta B_{\text{NN}} \simeq 2 \Delta B_{\text{NNN}} \simeq \frac{1}{6} B_{\text{max}}$, where B_{max} is the highest value of the hyperfine magnetic field (for pure ZrFe_2) equal to about 203 kG. Our ΔB_{NN} -value is in good agreement with the predictions of the Van der Kraan model. The value of ΔB_{NNN} is greater by about 6 kG than that predicted by this model.

Acknowledgment

This work was supported by KBN grant II.1.8/P/04/062.

References

- [1] Sarzyński J, Budzyński M, Wasiewicz R, Spustek H, Tanska-Krupa W and Subotowicz M 1990 *Hyperfine Interact.* 62 273
- [2] Jaccarino V and Walker L R 1965 *Phys. Rev. Lett.* 15 258
- [3] Van der Kraan A M, Gubbens P C M and Buschow K H J 1977 *Proc. Int. Conf. on the Mössbauer Effect* (Bucharest: Documentation Office, Central Institute of Physics) p 121
- [4] Li Z W, Zhou X Z and Morrish A H 1990 *Phys. Rev. B* 13 8617