

# Hyperfine interactions in $(\text{Cr}_{0.99}^{57}\text{Fe}_{0.01})_{3+x}\text{Si}_{1-x}$

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**Abstract.** X-ray diffraction measurements and Mössbauer spectroscopy with external magnetic field were carried out on  $(\text{Cr}_{0.99}^{57}\text{Fe}_{0.01})_{3+x}\text{Si}_{1-x}$  alloys. The Mössbauer spectra for A15 type of structure can be described by superposition of single line S(1) and two doublets D(1) and D(2). The relative ratio of the S(1) and D(2) strongly depends on  $x$ . The nearest neighbours of these components have been identified. It was shown that  $^{57}\text{Fe}$  atoms preferentially locate in Cr positions for  $x \leq 0.0$ , while for  $x > 0.0$  iron atoms are distributed both in Cr and Si positions. It was shown that, in A15 structure, one Cr atom located in the  $^{57}\text{Fe}$  nearest neighbours (n.n.) decreases isomer shift by  $(0.022 \pm 0.002)$  mm/s, while one Si in n.n. increases isomer shift by  $(0.09 \pm 0.01)$  mm/s. The measured Mössbauer spectra of bcc Cr-Si indicate that atoms are randomly distributed and can be well described as superposition of single lines, related to various local environments of  $^{57}\text{Fe}$  atoms.

**Key words:** A15 structure • Cr-Fe-Si alloys • Mössbauer spectroscopy • X-ray diffraction

## Introduction

Transition metal silicides attract a considerable interest due to their unusual mechanical, chemical and magnetic properties [2, 3, 7, 15, 16]. An intermetallic compound  $\text{Cr}_3\text{Si}$  crystallizes in cubic A15 structure ( $Pm\bar{3}n$  space group). Many silicides with A15 structure show superconductivity at relatively high temperatures (e.g.  $\text{V}_3\text{Si}$ ). However,  $\text{Cr}_3\text{Si}$  does not exhibit transition to the superconducting state down to 0.015 K [5]. At the initial stage of the project, we have synthesized  $^{57}\text{Fe}$  doped  $\text{Cr}_3\text{Si}$  with A15 structure. Obtained results, mainly Mössbauer spectra, show a large non-reproducibility. The reason of such a behavior was associated probably with poor control of the Cr concentration due to its strong evaporation during process of melting in an arc furnace. Shape of the Mössbauer spectra strongly depends on the stoichiometry. We have decided to perform detailed studies of the system. In this work the  $(\text{Cr}_{0.99}^{57}\text{Fe}_{0.01})_{3+x}\text{Si}_{1-x}$  ( $x = 0.00, 0.01, 0.04, 0.06$ ) alloys were used to study hyperfine parameters and preferential location of  $^{57}\text{Fe}$  in the alloys. Because of the possibility of presence of other crystallographic phases, three additional samples at concentrations  $x = 0.7, 0.4, -0.2$  were prepared. According to phase diagram of Cr-Si [10], these samples should crystallize in pure bcc, a mixture of bcc and A15, and a mixture of A15 and tetragonal  $\text{Cr}_5\text{Si}_3$  phases, respectively. To the best of our knowledge, there are no reports dedicated to the determination of hyperfine fields and location of  $^{57}\text{Fe}$  in  $\text{Cr}_3\text{Si}$  sites.

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## Experiment

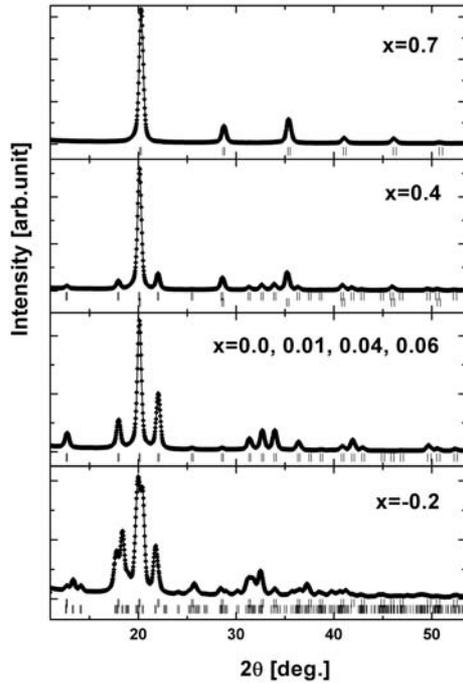
The polycrystalline alloys with formula  $(\text{Cr}_{0.99}^{57}\text{Fe}_{0.01})_{3+x}\text{Si}_{1-x}$  were prepared by melting suitable amounts of pure elements in an arc furnace. Because of strong evaporation of Cr during the melting process, a 1.5% excess of Cr was taken.

Mössbauer spectra were collected with a standard spectrometer, working in constant acceleration mode at room temperature. Measurements in an external magnetic field were performed using an axial permanent magnet with  $B = 1.3$  T. The spectra were analyzed using transmission integral approximation.

X ray measurements were performed on a Super Nova four circle diffractometer from Agilent Technologies, with filtered Mo- $K_\alpha$  radiation.

## Results and discussion

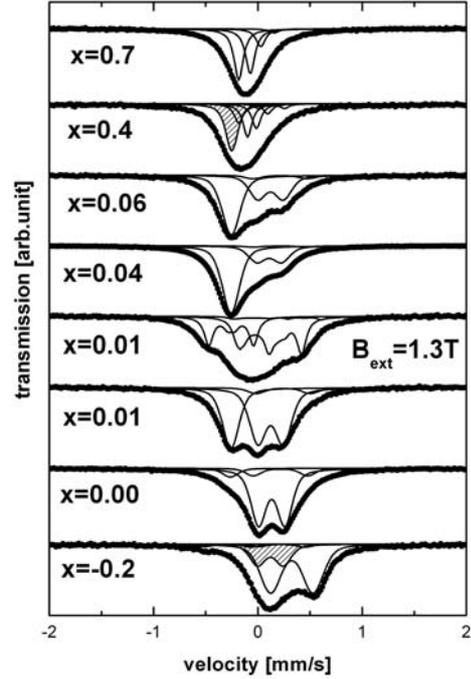
The results of X-ray diffraction show that the sample with  $x = 0.7$  is a single bcc Cr-Si phase, while for  $x = 0.4$  is a mixture of bcc Cr-Si and A15 phases, see Fig. 1. The samples for  $0.00 < x < 0.06$  are a single phase, with A15 type of structure, and the sample with  $x = -0.2$  is a



**Fig. 1.** X-ray diffraction spectra of  $(\text{Cr}_{0.99}^{57}\text{Fe}_{0.01})_{3+x}\text{Si}_{1-x}$ .

**Table 1.** The relative weight contribution and lattice parameters of the observed phases

$x$	Phase	Weight contribution (%)	Lattice parameter (Å)
-0.2	Cr <sub>5</sub> Si <sub>3</sub>	92	$a = 9.160 \pm 0.006$ $b = 4.634 \pm 0.006$
	A15	8	$4.555 \pm 0.006$
0.00	A15	100	$4.555 \pm 0.006$
0.01	A15	100	$4.556 \pm 0.006$
0.04	A15	100	$4.561 \pm 0.006$
0.06	A15	100	$4.556 \pm 0.006$
0.4	CrSi bcc	63.5	$2.876 \pm 0.006$
	A15	36.5	$4.560 \pm 0.006$
0.7	CrSi bcc	100	$2.865 \pm 0.006$



**Fig. 2.** Mössbauer spectra of  $(\text{Cr}_{0.99}^{57}\text{Fe}_{0.01})_{3+x}\text{Si}_{1-x}$  measured at room temperature. In the case two-phases samples  $x = 0.4$  and  $-0.2$  shaded area indicate spectra of  $^{57}\text{Fe}$  located in A15 structure.

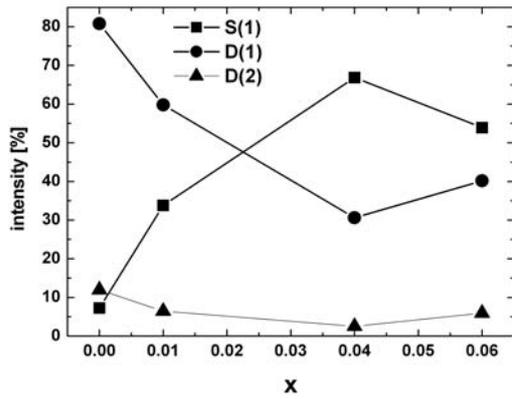
mixture of A15 and a tetragonal Cr<sub>3</sub>Si<sub>5</sub> phase. The lattice parameter of A15 does not depend on  $x$ , see Table 1, and is in good agreement with the data published in [6, 11, 14].

The Mössbauer spectrum for  $x = 0.7$  (pure bcc Cr-Si), see Fig. 2, was analyzed assuming random distribution of atoms in the sites. The shape of spectrum can be described well by superposition of single lines with intensities resulting from the probability of different nearest neighbour (n.n.) configuration. Random distribution of atoms was assumed. The analysis shows that isomer shift IS exhibits a linear dependence on a number of Si atoms in the n.n., according to the relation:

$$(1) \quad \text{IS} = (0.12 \pm 0.01) n - (0.17 \pm 0.01) \text{ mm/s},$$

where  $n$  is the number of n.n. Si atoms.

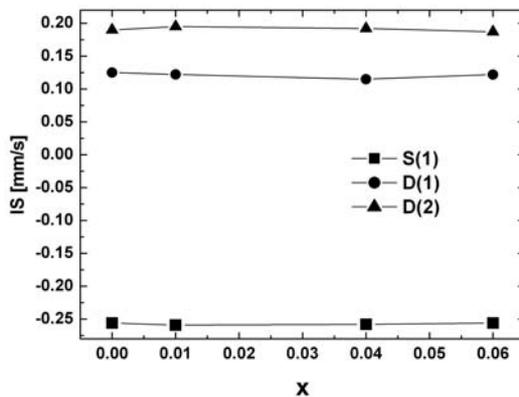
The free parameters of the linear relation can be compared with some already published results. Relation (1) for  $n = 0$  corresponds to the IS observed on  $^{57}\text{Fe}$  in Cr matrix and is in good agreement with the data published in [9]. In the case of Cr-Si alloy, increase of



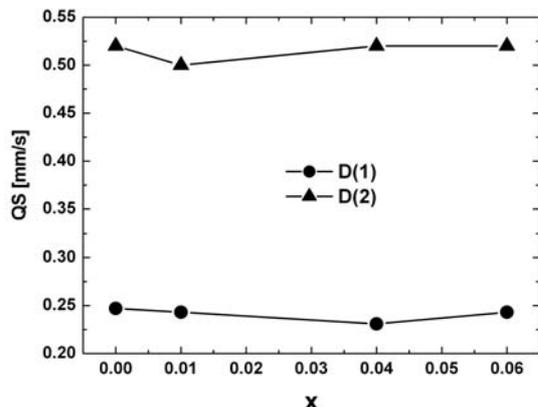
**Fig. 3.** The relative contribution of S(1), D(1) and D(2) used in the description of Mössbauer spectra of A15 structure.

a number of Si atoms in the n.n. is accompanied by the corresponding decrease of the number of Cr atoms in the n.n. One Si atom in the n.n. increases IS by about 0.05 mm/s in the bcc Fe-Si [1, 12, 13] and one Cr atom decreases IS by 0.02 mm/s in the bcc Fe-Cr [1, 8]. Therefore, the expected slope of the linear relation is 0.07 mm/s while the observed value in Eq. (1) for Cr-Si alloy is higher, is equal to  $(0.17 \pm 0.01)$  mm/s.

The Mössbauer spectra of samples with pure A15 structure can be described by a single line S(1) and two doublets D(1) and D(2), see Fig. 2. The intensities of S(1) and D(1) strongly depend on  $x$  (see Fig. 3). For  $x = 0.0$ , the dominant component is doublet D(1), while for  $x > 0.0$ , the intensity of single line increases with  $x$ . The intensity of doublet D(2) does not depend on  $x$ . Also the IS as well as the quadrupole splitting (QS) does not depend on  $x$ , see Figs. 4 and 5. The Mössbauer



**Fig. 4.** Isomer shifts determined for A15 structure.



**Fig. 5.** Quadrupole splitting determined for A15 structure.

**Table 2.** The average values of local isomer shift (IS) and quadrupole splitting (QS) determined from Mössbauer spectra of A15 phase

	S(1)	D(1)	D(2)
IS (mm/s)	$-0.26 \pm 0.01$	$0.13 \pm 0.01$	$0.18 \pm 0.02$
QS (mm/s)		$-0.25 \pm 0.01$	$-0.48 \pm 0.03$

spectrum for the sample with  $x = 0.01$ , measured in external magnetic field  $B = 1.3$  T, was analyzed using the Blaes procedure [4]. The asymmetry parameter  $\eta$  was equal to 0. Fixed parameters, obtained from zero field measurements, were used and the sign of the electric field gradient was determined. The best fit was obtained for the negative values of electric field gradient for both doublets. The mean values of  $^{57}\text{Fe}$  hyperfine fields are presented in Table 2. In the A15 structure the  $^{57}\text{Fe}$  atoms may locate in two different positions, Si sites with 12 Cr atoms as n.n. at a distance of 2.549 Å and Cr sites with 2Cr, 4Si and 8Cr at distances 2.28 Å, 2.549 Å and 2.792 Å, respectively. The surrounding of Si sites has a high symmetry while Cr sites exhibit symmetry axis. One thus concludes that the Mössbauer subspectrum of  $^{57}\text{Fe}$  located in Si sites is a single line while  $^{57}\text{Fe}$  located in Cr sites is described by doublets. Taking into account the values of isomer shift determined for S(1) and D(1) and compositions of nearest surrounding, one Cr in the n.n. of  $^{57}\text{Fe}$  decreases IS by  $(0.022 \pm 0.001)$  mm/s and one Si in the n.n. increases IS by  $(0.082 \pm 0.003)$  mm/s. Obtained value is slightly higher than that observed in Fe-Si alloys [13]. One thus concludes that the influence of Cr atom located in n.n. of  $^{57}\text{Fe}$  on the isomer shift is similar in both bcc and A15 structures.

It was shown in [1, 8] that replacement of Cr atom by iron increases IS by  $(0.022 \pm 0.002)$  mm/s. Observed value of the isomer shift for doublet D(2) is higher by 0.05 mm/s than for D(1). Such a difference can be explained by the replacement of 2 Cr atoms by 2 Fe atoms. Moreover, because there is no subspectrum corresponding to the environment 4Si9Cr1Fe and relative intensity of D(2) is rather high (10% for  $(\text{Cr}_{0.99}\text{Fe}_{0.01})_3\text{Si}$ ), this suggests a possible clustering of  $^{57}\text{Fe}$  atoms in the alloys.

The sample with  $x = 0.4$ , which shows a mixture of bcc Cr-Si and A15, was analyzed using superposition of spectra related to both phases. In the spectrum corresponding to A15 structure two main components, S(1) and D(1), were used. Only intensities of S(1) and D(1) were treated as free parameters. In the case of bcc Cr-Si phase the random distribution of atoms was used. The composition of this phase was estimated using contribution of both phases obtained from X-ray measurements (see Table 1). Assuming that A15 phase is  $\text{Cr}_3\text{Si}$ , the calculated composition of bcc Cr-Si is  $\text{Cr}_{3.63}\text{Si}_{10.27}$ . The spectra of  $^{57}\text{Fe}$  in A15 phase for samples with  $x = 0.4$  are shown in Fig. 2 as shaded fields. The contribution of Mössbauer spectra related to A15 structure is 33% for  $x = 0.4$ . The spectrum corresponding to  $^{57}\text{Fe}$  in A15 phase for the sample with  $x = 0.4$  is mainly a single line, thus  $^{57}\text{Fe}$  preferentially locates in Si sites. In the case of sample with  $x = -0.2$  the measured spectrum was superposition of subspectra corresponding to A15 and tetragonal  $\text{Cr}_5\text{Si}_3$  phases. A15 contribution to the Mössbauer spectrum was analyzed as previously and

the spectrum corresponding to  $\text{Cr}_5\text{Si}_3$  was described by two doublets. In that case the Mössbauer spectrum of A15 structure was described as one doublet. It indicates that the  $^{57}\text{Fe}$  impurities preferentially locate in Cr sites. The determined contribution of Mössbauer spectra connected with A15 structure is 23% for  $x = -0.2$ . These results are fully consistent with  $^{57}\text{Fe}$  location deduced for the samples with pure A15 structure.

## Conclusion

X-ray diffraction and Mössbauer spectroscopy were used to study  $(\text{Cr}_{0.99}\text{Fe}_{0.01})_{3+x}\text{Si}_{1-x}$  ( $x = 0.7, 0.4, 0.00, 0.01, 0.04, 0.06, -0.2$ ) alloys. The analysis shows the presence of bcc Cr-Si, A15 and tetragonal  $\text{Cr}_5\text{Si}_3$  phases in the investigated samples. The lattice parameters of all the observed phases were determined. Local environments of  $^{57}\text{Fe}$  impurity were identified. The shapes of Mössbauer spectra of A15 structure were described by superposition of the component which comes from the  $^{57}\text{Fe}$  located in Si sites (single line) and the component from  $^{57}\text{Fe}$  located in Cr sites (doublets). The analysis of isomer shift of D(1) and D(2) components suggests that doublet D(2) comes from the  $^{57}\text{Fe}$  located in Cr sites surrounded by  $4\text{Si}8\text{Cr}2\text{Fe}$ . Lack of the environment  $4\text{Si}9\text{Cr}1\text{Fe}$  suggests the possibility that part of  $^{57}\text{Fe}$  atoms located in the Cr sites form clusters. The Mössbauer spectra of bcc Cr-Si phase were described well assuming a random distribution of the atoms. The shape of the spectrum was analyzed by superposition of single lines corresponding to the different compositions of  $^{57}\text{Fe}$  nearest surroundings. The shapes of Mössbauer spectra of A15 strongly depend on Si concentration. For sample, at a low Si concentration (Fig. 2,  $x = 0.06$ ),  $^{57}\text{Fe}$  preferentially locates in Si position while for a high Si concentration (Fig. 2,  $x = 0.00$ )  $^{57}\text{Fe}$  preferentially locates in Cr position. Although we show a clear evidence for preferential location of sites, microscopic mechanism remains unclear.

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