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LETTER TO THE EDITOR

Determination of the hyperfine parameters of α -FeSi₂ by angle dependent Mössbauer spectroscopy on single crystals

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Abstract

The hyperfine parameters of the metallic disilicide phase α -FeSi₂ at room temperature are determined with high accuracy by conversion electron Mössbauer spectroscopy measurements on a single crystal. It is found that there are two well defined iron environments with different electron densities (isomer shifts 0.202 and 0.257 mm s⁻¹, respectively) and different electric field gradients. Both quadrupole splittings are negative (−0.382 and −0.730 mm s⁻¹, respectively) and the site occupation for both sites is different.

Iron disilicide exists in two stable modifications, the room temperature phase β -FeSi₂ which is orthorhombic and the high temperature phase α -FeSi₂ which is tetragonal. Both phases show very interesting properties for potential applications in thermoelectrics, photovoltaics and optoelectronics. For phase analysis on bulk material and on thin layers, conversion electron Mössbauer spectroscopy (CEMS) is a very suitable method due to its high sensitivity to the atomic and electronic environment of the Mössbauer probe nuclide ⁵⁷Fe. Prerequisite for such investigations is the exact knowledge of the hyperfine parameters of the different phases. In case of these non-magnetic silicides these are the isomer shifts δ , quadrupole splittings Δ by value and sign, the line widths Γ and the occupation of each iron site A_i .

While for β -FeSi₂ the situation is clear due to CEMS investigations on a single crystal grown by chemical vapour transport [1] it is quite different for α -FeSi₂. There are several measurements on polycrystalline powder samples. In [2] the Mössbauer spectrum is described as being very complex due to the presence of a large number of Fe vacancies. A distribution of quadrupole splittings coupled to a distribution in the isomer shift is expected. At room temperature, the average values were determined as $\delta = 0.20$ mm s⁻¹ (here and in the following given relative to α -Fe) and $\Delta = 0.55$ mm s⁻¹. In another powder study, the difficulty to interpret the spectrum in a simple way was addressed [3]. The best fit was achieved with two quadrupole doublets with $\delta = 0.23$ and 0.26 mm s⁻¹ and $\Delta = 0.47$ and 0.73 mm s⁻¹. In [4] an investigation on a thin (4 nm) single-crystalline sample grown by molecular beam epitaxy was reported. The obtained CEM spectrum was fitted with four quadrupole doublets taking into consideration different coordination spheres of the Fe sublattices. The isomer shifts range

from 0.06 to 0.42 mm s⁻¹ while the quadrupole splittings range from 0.04 to 0.70 mm s⁻¹. The authors actually remark that the spectrum may be affected by the interfaces but they do not mention the orientation of the crystalline layer with regard to the direction of the exciting gamma radiation, which may influence the pattern of Mössbauer spectra very strongly. In [5] α -FeSi₂ was prepared by ion beam synthesis. Mössbauer spectra were evaluated according to [3] with different areas for both doublets. The two subspectra were assigned to iron atoms with and without vacancies as nearest neighbours. However, there was no declaration of which doublet belongs to which environment. So far, there exist conflicting views about the hyperfine parameters of α -FeSi₂. Most frequently, the values of [3] were used successfully for phase analysis. One way to obtain reliable values is measurements on single crystals. In this letter we report such measurements.

Single crystals of α -FeSi₂ were obtained by a chemical transport reaction in closed silica ampoules (14 cm length, 1.4 cm diameter) starting from a mixture of ⁵⁷Fe and Fe (5N purity) and Si (6N purity) as source materials with a composition of 375 mg ⁵⁷Fe_{0.40}Fe_{0.60}Si_{1.9} and 100 mg I₂ as the transport medium. The chemical vapour transport was performed in a horizontal configuration [6, 7] and proceeded from the source at a temperature of 1050 °C to the crystallization zone kept at 900 °C for 480 h. Quadratic platelets with an edge length of about 1.5 mm and a thickness of about 0.2 mm were obtained. The orientation of the single crystal was determined by the x-ray Laue back-scattering method. Figure 1 shows the crystal used for the measurements, where the [001] direction is perpendicular to the surface and the edges are parallel to [100] and [010] directions. The measured lattice constants of $a = 0.2703$ nm and $c = 0.5154$ nm are significantly larger than that taken from the JCPDS files ($a = 0.2693$ nm, $c = 0.5136$ nm). From the phase diagram of the Fe–Si system it is known that a homogeneity region exists for the α -FeSi₂ phase. The lattice constants will increase with decreasing iron content [8]. The iron to silicon ratio in the single crystal was determined by energy dispersive x-ray detection to be 1:2.21 indicating about 9.4% iron vacancies, which is consistent with the measured increased lattice constants.

CEMS measurements were performed at room temperature with a ⁵⁷Co(Rh) source with nominally 3.7 GBq. The source was moved by a standard constant-acceleration drive. The conversion electrons were detected by a proportional gas flow counter with a mixture of He and 5% CH₄ as counting gas. The single crystal was tilted by several angles with respect to the direction of the exciting gamma radiation. It was both tilted with regard to the main c -axis (polar angle β) and rotated around the c -axis (azimuthal angle γ).

In a Mössbauer spectrum, the intensities of both lines of a quadrupole doublet are equal for polycrystalline materials (excluding the Goldanskii–Karyagin effect). If single crystals are investigated the intensity ratio between the lines depends on the angle between the direction of the electric field gradient at the site of the nucleus and the propagation direction of the exciting γ -radiation. The intensity ratio of the two lines $I(1)$ and $I(2)$ of the quadrupole doublet can be calculated as a function of the angles β and γ according to [9]:

$$\frac{I(1)}{I(2)} = \frac{(1 + \delta^2/3)(1 + \cos^2 \beta) + \frac{4}{3}\delta^2 \sin^2 \beta + (2\delta/\sqrt{3}) \sin^2 \beta \cos 2\gamma}{(\delta^2 + \frac{1}{3})(1 + \cos^2 \beta) + \frac{4}{3} \sin^2 \beta - (2\delta/\sqrt{3}) \sin^2 \beta \cos 2\gamma} \quad (1)$$

with

$$\delta = \frac{\eta}{\sqrt{3}(1 + \sqrt{1 + \eta^2/3})} \quad (2)$$

and the asymmetry parameter

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}. \quad (3)$$

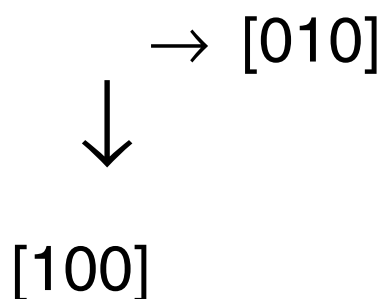
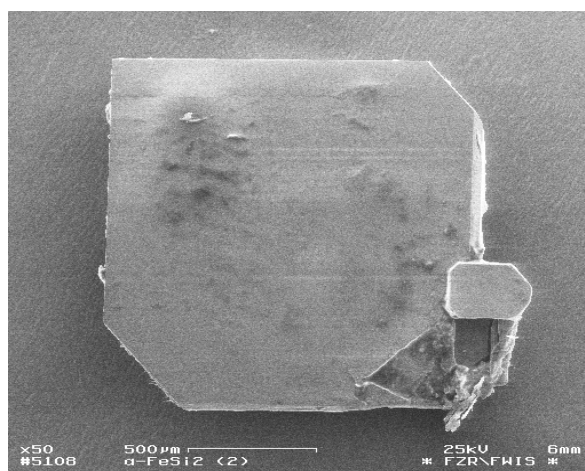


Figure 1. α -FeSi₂ single crystal (secondary electron microscopic image).

V_{xx} , V_{yy} and V_{zz} denote the principal components of the diagonalized electric field gradient in the x , y and z -direction, respectively. Assuming axial symmetry ($\eta = 0$) the relative line intensities are 3:1 for $\beta = 0^\circ$ and 3:5 for $\beta = 90^\circ$. For $\eta \neq 0$ and $\gamma \neq 0$ the line intensities will deviate: the differences between them will become smaller.

The obtained spectra were evaluated with the NORMOS least squares computer program [10]. Figure 2 shows the CEM spectra collected for different crystal orientations. It becomes apparent that tilting with regard to the c -axis changes the spectrum dramatically while rotating around the c -axis (displayed for one example) has no effect. The best fit for all spectra was obtained by assuming four single lines (not more and not less). Due to their intensity variations as a function of the orientation they could unambiguously be combined as quadrupole doublets, namely line 1 to 4 and 2 to 3, respectively. To fit these results with the intensities calculated according to (1) is only possible if negative signs are assumed for each quadrupole splitting. In figure 3, the intensity ratios obtained in this manner are compared with the calculated ones while the calculated hyperfine parameters are given in table 1.

The results given above can be explained as follows: although the tetragonal unit cell possesses only one iron position there are two clearly distinct iron environments with different electron densities and different electric field gradients. The reason for this must be the large number of iron vacancies. However, there is not a statistic distribution of these vacancies,

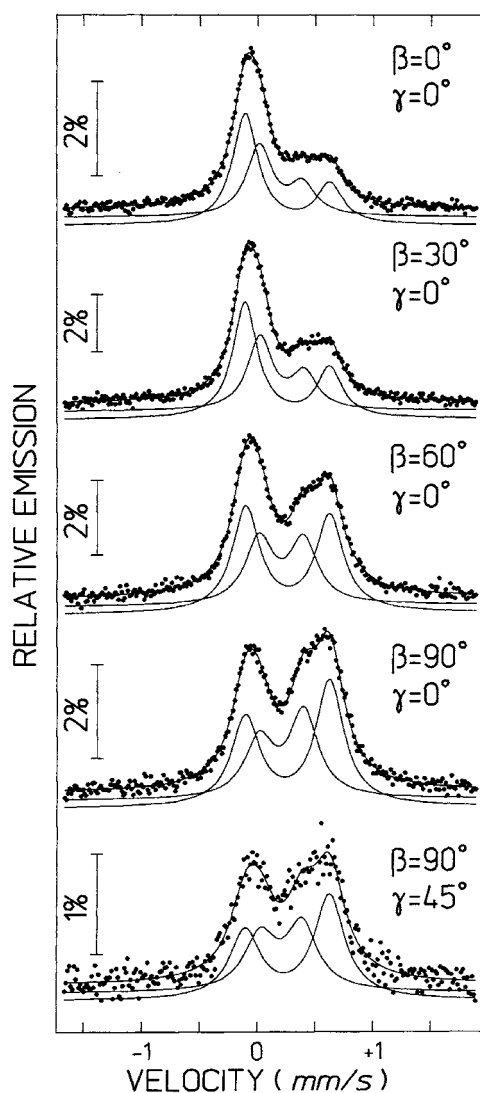


Figure 2. CEM spectra of the α -FeSi₂ single crystal taken in different crystal orientations. The two subspectra are displayed at the bottom of each spectrum.

Table 1. Hyperfine parameters of α -FeSi₂ as determined of a single crystal. (Values in brackets denote the uncertainties of the last digits.)

Site	δ (mm s ⁻¹)	Δ (mm s ⁻¹)	Γ (mm s ⁻¹)	A (%)
FeI	0.202(2)	-0.382(6)	0.279(18)	40.5(7)
FeII	0.257(2)	-0.730(2)	0.279(18)	59.5(7)

since this would produce a distribution of the hyperfine parameters as predicted in [4]. The occupation of the iron sites is different. Considering the number of vacancies, doublet I can be assigned to iron atoms without vacancies in the neighbourhood while doublet II can be assigned to iron atoms with one vacancy in the neighbourhood. This can be concluded from a

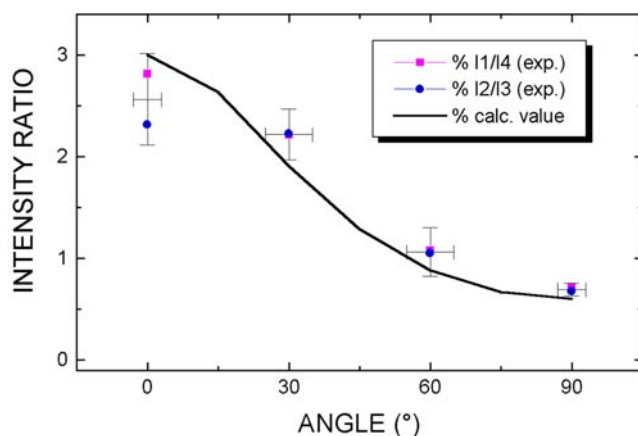


Figure 3. Intensity ratio of both lines of the quadrupole doublets at different crystal orientations as measured (dots) and as calculated according to equations (1). The lines are numbered with increasing isomer shift from $I1$ to $I4$.

simple geometric consideration. The nearest neighbour environment for every iron site is equal and consists of silicon atoms without any vacancies. The next neighbour after that will be an iron place. Considering only the iron sublattice, a cube of $10 \times 10 \times 10$ unit cells contains 94 iron vacancies and 906 iron atoms. Generally, each vacancy has six iron atoms as next nearest neighbours. Thus 94 vacancies influence the electric field distribution of 564 neighbour atoms, which corresponds to a fraction of 62.3%. Taking into account all simplifications and possible uncertainties this value is in sufficient accordance with the measured site occupation.

The main direction of both electric field gradients is parallel and axially symmetric to the long c -axis of the unit cell. The negative sign indicates an oblate (flattened) nucleus and a respective electron density distribution in the c -direction. The negative sign could not be found in the previous measurements on polycrystalline powder samples. In this case the intensity ratio between the two lines of the quadrupole doublet is 1 and thus the shape of the spectrum is independent of the sign.

In conclusion, we have determined with high accuracy the hyperfine parameters of α -FeSi₂. There are two well defined iron environments with different electron densities and different electric field gradients. Both quadrupole splittings are negative and the site occupation for both sites is different.

References

- [1] Reuther H, Behr G, Dobler M and Teresiak A 1998 *Hyperfine Interact.* C **3** 385
- [2] Blaauw C, van der Woude F and Sawatzky G A 1973 *J. Phys. C: Solid State Phys.* **6** 2371
- [3] Helgason Ó and Sigfusson T I 1989 *Hyperfine Interact.* **45** 415
- [4] Fanciulli M, Rosenblad C, Weyer G, von Känel H and Onda N 1996 *Thin Solid Films* **275** 8
- [5] Dobler M 1998 *Thesis FZR-Report* 214 TU Dresden
- [6] Behr G, Werner J, Weise G, Heinrich A, Burkov A and Gladun C 1997 *Phys. Status Solidi* a **160** 549
- [7] Behr G 2000 *Crystal growth Semiconducting Silicides (Springer Series in Materials Science, Vol. 39)* ed V E Borisenko (Berlin: Springer) p 137
- [8] Villars P and Calverd L D (eds) 1996 *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* vol 3 (Materials Park: Materials Information Society) p 3378
- [9] Barb D 1980 *Grundlagen und Anwendungen der Mössbauerspektroskopie* (Berlin: Akademie)
- [10] Brand R A, 1987 *Nucl. Instrum. Methods B* **28** 398