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On the preferential location of Co in β -FeSi₂

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Abstract. Results of Mössbauer measurements on ⁵⁷Co-implanted β -FeSi₂ are reported. It is demonstrated that Co atoms are mobile during applied annealing. Co enters into both possible sites of iron with a slight preference for one of them. Because of this weak preferential occupancy of iron sites, two models can explain the Mössbauer spectrum equally well.

1. Introduction

FeSi₂ forms a stable low-temperature orthorhombic phase and the unit cell consists of 48 atoms [1]. Iron atoms are located in two non-equivalent sites. One of these, called Fe_I, is surrounded by eight Si atoms, forming a distorted cube with Fe_I–Si distances ranging from 2.34 to 2.39 Å. In the second type of site, called Fe_{II}, iron is surrounded by a more distorted cube formed by Si atoms, and the Fe_{II}–Si distances vary from 2.33 to 2.44 Å.

The Mössbauer spectrum of β -FeSi₂ can be satisfactorily fitted with four Lorentzian lines of nearly equal intensities and widths [2–5]. In [2–5] it was assumed that the first and third lines form one doublet, which will call Fe_{1,3}, while the second and fourth lines form a second doublet, called Fe_{2,4} (the peaks were numbered according to increasing velocity in the Mössbauer absorption spectrum). The problem of assigning doublets to crystallographic sites of iron was discussed in [2] where, on the basis of point charge calculations of electric field gradients (EFG) it was concluded that Fe_{1,3} corresponds to Fe_I. This conclusion was also confirmed by recent calculations of electron density [6]. An opposite opinion was presented in [3]. Their point charge calculations of EFG and crystal-field model have led to the assignment of Fe_{1,3} to Fe_{II} sites.

However, the problem of correspondence between the site and the pair of peaks forming a doublet is even more complicated. The spectra of β -FeSi₂ may be fitted assuming that the first and fourth lines form one doublet while the second and third form the second doublet. Hence we have two possibilities of ‘forming doublets’ and two possibilities of assigning a given doublet to the Fe_I site. From the experimental point of view, one has first to decide which lines are forming doublets.

In the case of four lines which differ from each other in their position only, the spectrum composed of Fe_{1,3} and F_{2,4} is identical with that composed of Fe_{1,4} and F_{2,3} (we shall call these two choices of doublets model 1 and model 2, respectively). If, however, the occupation of the Fe_I site was different from that of the Fe_{II} site or if the linewidths for these sites were different, careful analysis of Mössbauer spectra should indicate which of the two models is correct. We tried to perform such an analysis on the samples described in

[5] but the first results have shown that some further experiments will be needed to obtain a unique answer.

Recently, it was reported that Co introduced into β -FeSi₂ locates preferentially in one of the non-equivalent sites of Fe [4]. In [4] it was stated that, for a Co concentration from 1 to 3 at.%, almost all cobalt atoms occupy the Fe_{II} site (in table 3 of [4], one can find that the Co concentration in site II is over 140 times larger than in site I). This conclusion has been drawn from the change in intensities of the doublets when Fe was substituted by Co. If such a strong site preference exists, one has a unique possibility of checking which of the two models is true. Namely, radioactive ⁵⁷Co, doped into β -FeSi₂, should decay to excited ⁵⁷Co and emit resonant radiation which could be observed by the Mössbauer effect. Thus, using ⁵⁷Co implanted into β -FeSi₂ as a source, one should observe the Mössbauer spectrum of iron located in Fe_{II} sites.

In this paper we report the results of such an experiment. The paper is organized as follows. First, characterization of the material used for implantation is presented. The parameters of the Mössbauer absorption spectra are of particular importance here. Next, the conditions of implantation, thermal treatments and results of Mössbauer source experiments are presented. It is demonstrated that the Co atoms were mobile during annealing. We discuss the results obtained in the light of recent experiments.

2. Sample characterization

Stoichiometric amounts of 99.95% pure iron (Ubichem) and 99.999% pure Si (Institute of Electronic Technology, Warsaw) were arc melted and remelted a few times in a high-purity argon atmosphere. The loss of mass was 0.02%. Some of the sample was powdered and annealed with the remaining (bulky) pieces, in an evacuated quartz tube for 8 h at 1100 °C, for 141 h at 700 °C and then cooled at a rate of 5.3 °C h⁻¹. The powdered sample was used for chemical analysis and x-ray diffraction, and the bulk sample for optical microscopy and magnetic measurements [5]. The chemical analysis revealed 33.24(7) at.% Fe.

Mössbauer measurements were carried out in transmission-geometry constant-acceleration mode. ⁵⁷Co in a Cr matrix was used as a source. Two independent measurements were performed for an absorber thickness of 4.5 mg of powder per cm². The temperature of the sample and transducer was 298 °C and was stabilized with an accuracy of 0.3 K to avoid any systematic shifts of the measured parameters and to ensure constant working conditions of the apparatus. A calibration spectrum of an iron foil was recorded before and after each measurement. Three other measurements were performed at room temperature with ⁵⁷Co in a Rh matrix and with sample thicknesses of 4.5 and 2.1 mg cm⁻². Analysis of the spectra was performed by using the transmission integral [7]. The doublets used had equal intensities and linewidths. The isomer shift (IS) and quadrupole splitting (QS) of the first doublet are 0.141(3) mm s⁻¹ and 0.403(4) mm s⁻¹, respectively and for the second doublet 0.024(3) mm s⁻¹ and 0.439(2) mm s⁻¹, respectively ($T = 298$ K; IS relative to α -Fe). These results agree with previous reports of 0.13 mm s⁻¹, 0.40 mm s⁻¹, 0.01 and 0.42 mm s⁻¹ [3], 0.15 mm s⁻¹, 0.41 mm s⁻¹, 0.01 mm s⁻¹ and 0.43 mm s⁻¹ and 0.41 mm s⁻¹ [2], 0.137 mm s⁻¹, 0.406 mm s⁻¹, 0.019 mm s⁻¹ and 0.440 mm s⁻¹ [4], respectively.

Because x-ray diffraction and energy-dispersive microanalysis revealed traces of the FeSi phase [5], we introduced a third doublet corresponding to this phase with the IS and QS parameters given in [8]. IS and QS for the FeSi phase were fixed and only its intensity was varied during the fitting. From the fits we could infer that 3(1)% of Fe forms the FeSi phase.

3. Implantation

⁵⁷Co implantation was performed at the Instituut voor Kern- en Stralingsfysika, Katholieke Universiteit, Leuven. 67% of 95 keV ions and 33% of 18 keV ions were implanted with the intention of obtaining a homogeneous distribution at a depth of approximately 700 Å. Implantation was performed at room temperature on a flat surface of β -FeSi₂ with dimensions 3 mm × 7 mm × 1 mm. The activity of the source was determined to be 2.2 μ Ci.

4. Thermal treatments and Mössbauer source experiments

After implantation, a quick Mössbauer measurement was performed with a ⁵⁷Fe foil absorber. The sample was subsequently annealed twice, and the Mössbauer spectra were measured (see table 1) after each thermal treatment. Mössbauer spectra measured in emission experiments correspond to the spectra of absorption experiments except for the fact that the velocity axes are reversed. In figure 1, each curve consists of two spectra of FeSi₂ located at the positions of the two inner absorption lines of iron. Figure 1(c) shows two spectra of β -FeSi₂, located at about +1 and −1 mm s^{−1}, which correspond to the reversed spectra given in the literature [2–5].

Table 1. Annealing conditions and Mössbauer absorbers used after each annealing run.

Annealing run No	Annealing conditions	Mössbauer run No	Mössbauer absorbers	Corresponding figure
1	1 h, 973 K	1	⁵⁷ Fe foil	1(a)
		2	⁵⁷ Fe foil	1(b)
2	4.5 h, 973 K	3	⁵⁷ Fe foil	1(c)
		4	⁵⁷ Fe in Pd	2(a)
3	1 h, 1183 K	5	⁵⁷ Fe in Pd	2(b), 2(c) and 2(d)

Next, longer and more precise Mössbauer measurements with a Pd foil containing 0.98 at.% ⁵⁷Fe and with a thickness of about 7.5 μ m were performed. The IS of the absorption line of this absorber, relative to α -Fe, was found to be 0.178(1) mm s^{−1}, in excellent agreement with the reported value of 0.177(2) [9]. The linewidth measured with a source in a Rh matrix was 0.23(1) mm s^{−1}. The spectra measured with the Pd(⁵⁷Fe) absorber are shown in figure 2(a) and 2(b). The spectra from figure 1(c) and 2(a) were measured using different absorbers after the same annealing run 2 (see table 1).

To make a comparison of the ISs for experiments with different absorbers in emission and absorption experiments, we rescaled all measured values of ISs in such a way that they correspond to the spectrum measured with an FeSi₂ absorber. The IS is given relative to α -Fe. The results can be summarized as follows. The spectrum of the as-implanted sample is nearly symmetric (figure 1(a)) and consists of two broad peaks with a width of 0.55(1) mm s^{−1}. The mean QS and IS are large, equal to 0.74(5) mm s^{−1} and 0.14(1) mm s^{−1}, respectively. After the first anneal, both values decrease to 0.47(5) mm s^{−1} and 0.10(1) mm s^{−1}, respectively, and the spectrum becomes asymmetric (figure 1(b)). Three further anneals cause further but much smaller decreases in both values. After the final annealing stage (figure 2(b)), the mean IS and QS are equal to 0.44(5) mm s^{−1} and

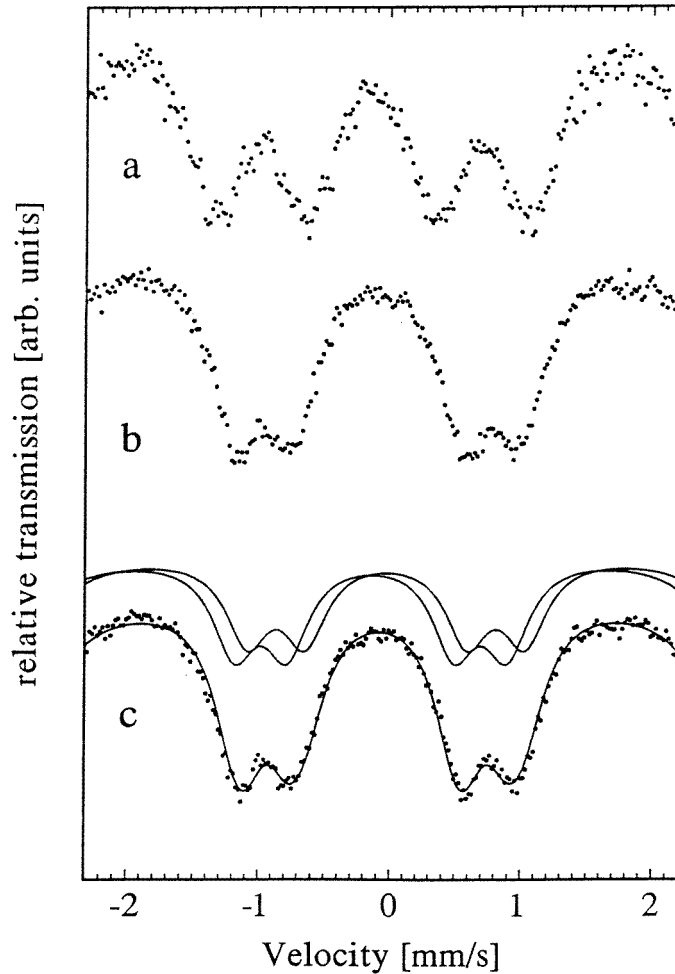


Figure 1. Emission spectra of β -FeSi₂ measured with a ^{57}Fe foil (a) after implantation, (b) after the first annealing (1 h at 973 K) and (c) after the second annealing (4.5 h at 973 K).

0.088(5) mm s⁻¹, respectively.

To show changes in the spectra caused by probing hyperfine fields by implanted ^{57}Co we performed a few fits in which the parameters of two Lorentzian doublets were fixed and corresponded to the values in the spectrum of bulk β -FeSi₂ measured in absorption experiments (given in section 2). The common width of Lorentzian lines and the relative intensities of the doublets were the only free parameters in the fits. In figures 1(c), 2(a) and 2(b), one can see that the spectra of the annealed samples may be fitted with two doublets with a small preference (relative intensity of about 54%) of that which was referred to as Fe_{1,3}. This result is in conflict with the conclusion of [4] where nearly 100% preference of Fe_{1,3} was deduced. We have considered the model (see figure 2(d)) in which the preference given in [4] was assumed. The assumptions about strong preference remains, however, in conflict with experimental data for any choice of two peaks as a doublet. This follows from apparent asymmetry of the two experimental peaks in the spectrum shown in figures 2(b)

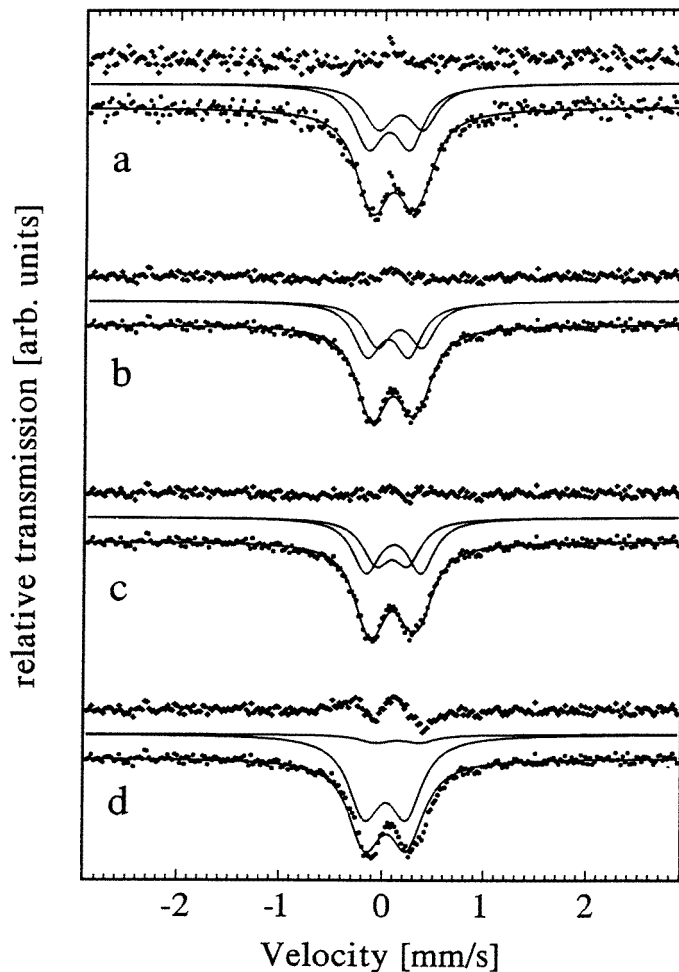


Figure 2. Emission spectra of β -FeSi₂ measured with a Pd foil doped with ⁵⁷Fe. Results of fits of model 1 to the spectra (a) after the second anneal and (b) after the third anneal. (c) Spectra after the third anneal fitted with model 2. (d) Spectra after the third anneal when a strong Co occupation preference is assumed. Above each spectrum the difference between the experimental points and the solid curve is shown.

and 2(c) and which excludes the possibility of fitting the spectrum with one doublet only.

Because of the weak preference of occupation of Fe_I and Fe_{II} sites by implanted Co, it was still not possible to judge which of the two models, model 1 or model 2 is correct. Indeed, in figure 2(c) we show the same spectrum as in figure 2(b) fitted with model 2. The differences in χ^2 -values are small but indicate a preference of model 2. We have also tested the influence of the fraction of FeSi phase on the results of the analysis. A third doublet corresponding to the FeSi phase with fixed parameters was introduced. The IS values of the doublets of the main spectrum were fixed and their intensities and QSs were allowed to vary. We have found that, up to the presumed concentration of 5.3% FeSi, model 2 gives a smaller value of χ^2 . The amount of FeSi phase estimated from absorption Mössbauer spectra amounts to 3(1)% and agrees with a less accurate susceptibility estimation of the

content of this phase of between 0.4 and 5.6% [5].

5. Diffusion of radioactive probe atoms in the sample

One could suspect that the lack of preference of Co substitution may result from too short an annealing time or too low a temperature. Because the Fe–Fe distance is large, Co atoms may not have sufficient time to find energetically better positions. Thus we have performed an experiment which demonstrates that ^{57}Co atoms in the annealing run 3 (1 h at 1183 K) do actually change their positions.

The intensity of the radiation emitted from the implanted sample depends on the depth from which it is emitted; low-energy components are attenuated more strongly than are high-energy components. Because the attenuation of the 122 keV radiation can be neglected, by measuring the change in the ratio of the intensity of the 14.4 keV line to the intensity of the 122 keV line it is possible to estimate the change in the average depth at which the ^{57}Co layer is located.

The measurements were performed with the use of a solid state gamma detector (HPGe; 9 mm; effective depth, 7 mm). The energy resolution was 500 eV at 14 keV, and 700 eV at 122 keV. A 4096-channel spectrum in the energy range 0–140 keV was collected in the same conditions before and after annealing. From the intensities of the 122 keV line measured before and after annealing it was inferred that the total amount of ^{57}Co in the sample remains constant within the experimental accuracy. The relative intensity measurements are more precise than the absolute data. Therefore the ratio of the integrated intensity of the 14.4 keV peak to the integrated intensity of the 122 eV peak has been measured. It was found that the relative intensity of the 14.4 keV radiation decreased after a 1 h anneal at 1183 K by 0.848(50).

Let us now estimate the change in the effective depth of the ^{57}Co layer. The intensity of the 14.4 keV radiation emitted by ^{57}Fe atoms passing through a layer of $\beta\text{-FeSi}_2$ with thickness x decreases owing to electronic and resonant absorption. Assuming that the thickness x of the layer is small, one can write [7]

$$I(x) = I_0(1 - f) + f \exp\left[-\frac{1}{2}\tau(x)\right] \exp(-\mu x) \quad (1)$$

where f denotes the recoilless fraction, $\tau(x)$ is the thickness parameter and μ is the electronic linear absorption coefficient. If it is assumed that the concentration of ^{57}Co atoms decreases exponentially with increasing distance x from the surface, the intensity of emitted radiation is equal to

$$N(d) = \int_0^\infty I(x) \frac{N_0}{d} \exp\left(-\frac{x}{d}\right) dx \quad (2)$$

where N_0 is the total number of ^{57}Co atoms and d their effective penetration depth. If the distributions before and after annealing are assumed to be exponential, the intensity ratio measured in the experiment is equal to

$$\frac{I_b}{I_a} = \frac{N(d_b)}{N(d_a)} \quad (3)$$

where d_b and d_a are the effective penetration depths of Co before and after annealing, respectively. For numerical determination of the relation between d_b and d_a from equation (3), we have used $f = 0.87$ and $\mu = 187.3 \text{ cm}^{-1}$. Because the spectrum of $\beta\text{-FeSi}_2$ consists of four partially overlapping lines, the parameter τ was estimated for two limiting cases: when the spectrum consists of four separated lines and when the pair of

lines overlaps with the other. With these assumptions the attenuation coefficient for resonant radiation was estimated to have a value between 160 and 320 cm⁻¹. Solving equation (3) we have found that $d_a - d_b = 7 \pm 3$ and 6 ± 2 μm , respectively, for the two limiting cases. This means that a 1 h anneal at 1183 K results in an increase in the effective depths by micrometres. The estimation is dependent on the assumption about the Co depth profile distribution; so the results must be treated as an estimation of the order of magnitude only.

We have also tried to estimate the probable diffusion depth from some diffusion coefficients. Namely, from Fick's law of diffusion, one can estimate the average distance r traversed by an atom in a time t when the sample is at a temperature T [11]:

$$r \approx \sqrt{D(T)t} = \sqrt{D_0 \exp\left(-\frac{Q}{RT}\right) t} \quad (4)$$

where D_0 and Q are diffusion coefficients, and R is the gas content. Although neither D_0 nor Q is known, they can be estimated from the correlation between the aforementioned parameters at the melting temperature and the type of bonding and the structure of compound. From figure 2.13 in [10], one can estimate that for BCC transition metals the values of Q/RT_m and $D(T_m)$, where T_m is the melting temperature, are in the range 4.7×10^{-13} – 2.9×10^{-11} m² s⁻¹ and 16–20, respectively. Taking T_m for FeSi₂ as 1220 °C [11], one obtains, from equation (4), $r = 3$ – 40 μm . For more covalent groups of compounds such as metal carbides, Q/RT_m and $D(T_m)$ are equal to 1.3×10^{-12} – 4.9×10^{-11} m² s⁻¹ and 22–26, respectively, and the estimated r is reduced to 2–23 μm . However, we have recently learnt that, while the diffusion of iron in, for example Fe₈₂Si₁₈ alloy is fast, the diffusion of iron in FeSi at $T = 1379$ °C is very slow; D is smaller than 10^{-14} m² s⁻¹ [12]. This pushes the limits of r to about 10 Å! We conclude that, without making direct measurements on FeSi₂, one can hardly carry out any sensible estimation of r from the diffusion data and equation (4).

6. Discussion and conclusions

The Mössbauer spectra measured right after implantation of the sample have an increased IS and QS. This shows that the structure of the bulk sample is strongly disturbed in the vicinity of ⁵⁷Co centres. There are few mechanisms which can cause such a disturbance. Radiation damage and microstrains usually cause an increase in QS and the line broadening. The local formation of other than β -FeSi₂ phases, such as amorphous FeSi₂, FeSi and α -FeSi₂, are also possible. All of these have larger QS and IS values than does β -FeSi₂. The reported QS and IS are 0.95 mm s⁻¹ and 0.20 mm s⁻¹ for amorphous FeSi₂ [13], and 0.495(3) mm s⁻¹ and 0.283(3) mm s⁻¹ for FeSi [8]. Average parameters of QS and IS for α -FeSi₂, estimated from figure 4 of [3], are 0.55(1) mm s⁻¹ and 0.21(1) mm s⁻¹, respectively. Thus we conclude that all these phases may be formed locally and enhance QS and IS values to the observed values of 0.74(5) mm s⁻¹ and 0.14(1) mm s⁻¹, respectively.

Radiation defects and locally created phases other than β -FeSi₂ are nearly completely removed already after the first anneal. Subsequent anneals do not produce any substantial changes in the spectrum which may be fitted by two doublets with parameters corresponding to the β -FeSi₂ phase. The decrease in the intensity of the 14.4 keV line shows that ⁵⁷Co atoms were mobile during the anneal and passed an average distance of the order of a micrometre.

If there was preferential occupation of one of the Fe sites by Co, we should have observed domination of one of the subspectra. However, this is not the case. The preference

exists, but is small—not larger than 55:45. In the light of the above results we cannot support the conclusion of Kondo *et al* [4] that nearly all Co atoms enter selectively into Fe_{II} sites. It seems likely that their result would be disturbed, for example, by small inclusions of α -FeSi₂ and FeSi phases.

The small occupation preference of Co atoms and the limited statistics of our measurements do not allow a unique assignment of which lines belong to which doublet. Both possible models show similar values for the occupational factors and both are producing fits of similar quality. Very recently the problem of assigning the lines to the doublets was discussed in [14] where CEMS measurements were performed on a β -FeSi₂ layer 750 nm thick with different orientations. The material was grown by MBE on a Si(001) substrate. The results strongly favour model 2, i.e. the doublets Fe_{1,4} and Fe_{2,3}, and exclude model 1. Whether this is also true for the bulk material will hopefully be cleared up in our planned experiment with ⁵⁷Co implanted into high-quality material with negligibly small content of FeSi and α -FeSi₂ phases.

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