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Abstract. The Mössbauer spectrum of β-FeSi$_2$ consists of four lines originating from two quadrupole doublets corresponding to two different local environments of iron. Measurements in external magnetic fields, and numerical analysis support the idea that the first and third lines belong to a doublet. This doublet has a negative quadrupole splitting while the other two lines form a doublet with a positive quadrupole splitting. The model of two doublets and randomness of the electric field gradient tensor axes fails at fields larger than about 6 T. The quadrupole splittings as well as the effective internal field show non-trivial linear variation with the intensity of the external magnetic field.

1. Introduction

FeSi$_2$ is an example of a substance interesting in both applied and basic research. Semiconducting β-FeSi$_2$ with a direct gap of approximately 0.85 eV (Dimitriadis *et al* 1990) has potential optoelectronic applications. Doped β-FeSi$_2$ reveals a high efficiency as regards changing heat into electric energy (Kojima *et al* 1984). Thin layers of FeSi$_2$ with various crystallographic forms have been obtained and can be integrated into well developed Si technology (Radermacher *et al* 1991, Desimoni *et al* 1993).

β-FeSi$_2$ crystallizes in an orthorhombic structure with a primitive cell containing as many as 48 atoms (Dusausoy *et al* 1971). The iron atoms are located in two different Fe sites, both surrounded by eight Si atoms forming distorted cubes; see figure 1. The Mössbauer spectrum of β-FeSi$_2$ consists of four narrow, overlapping lines with approximately equal intensities (Wandji *et al* 1971, Blaauw *et al* 1973, Kondo *et al* 1994, Szymański *et al* 1996a). Let us label these lines with the numbers 1 to 4, corresponding to their positions on the increasing velocity scale of the spectrum. Obviously, there are three ways of forming two doublets from four lines: 1–2, 1–3 and 1–4, where *k–l* means that lines *k* and *l* belong to the first doublet while the remaining lines belong to the second one.

The problem of determination of the hyperfine structure must start from the correct assignment of the lines to the doublets, and this was discussed for the first time by Wandji *et al* (1971). On the basis of point charge calculations of the electric field gradient (EFG) they argued that it is the 1–3 combination which is realized. As was pointed out by Wandji *et al* (1971), the 1–2 combination 'would correspond to very weak quadrupole effects, which is not realistic for compounds having an important lattice contribution'. Next, a number of

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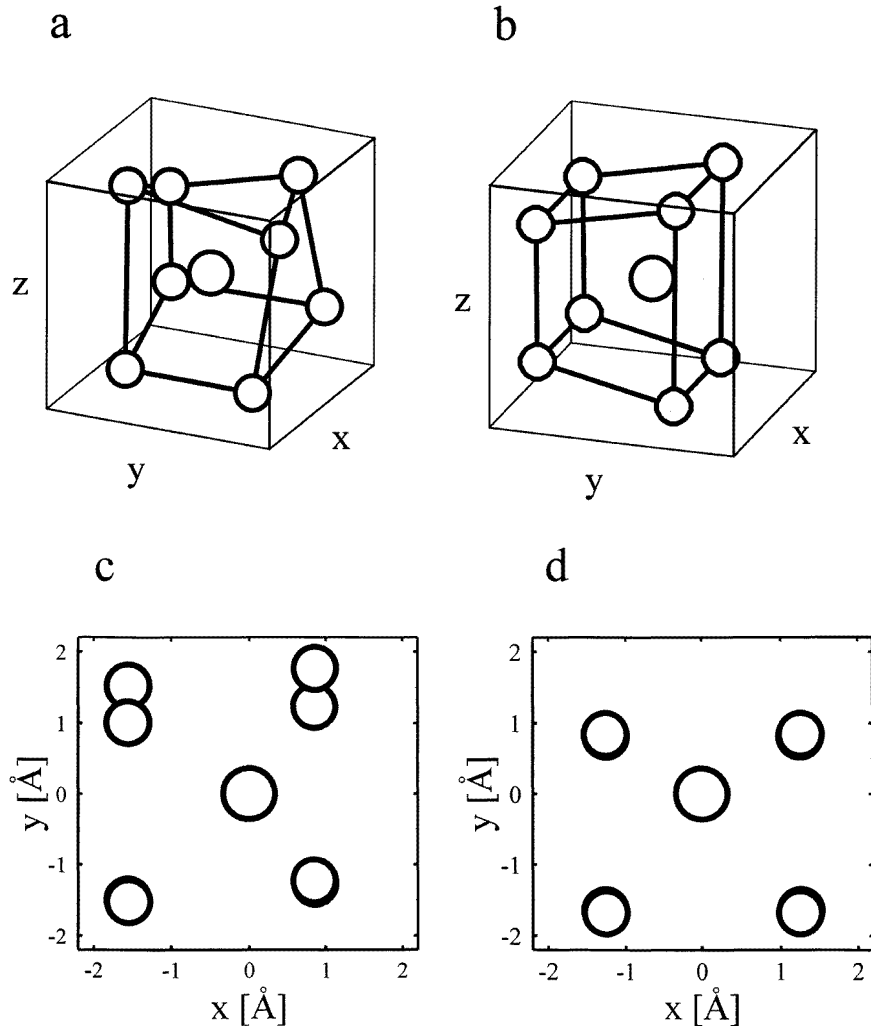
Figure 1. (a), (b) The local surroundings of an iron atom, located in the centre of the box, and the projections (c)–(h). The left- and right-hand panels of the figures correspond to two different iron sites in β-FeSi$_2$ (Dusausoy *et al* 1971).

groups followed this interpretation and tried to confirm it either by making more precise point charge EFG calculations (Blaauw *et al* 1973) or via electronic structure calculations.

It is hard to find any simple qualitative arguments which would support one particular model. The reason for this is that the nearest neighbourhood of two inequivalent iron sites—see figure 1 (Dusausoy *et al* 1971)—varies geometrically in a way which prevents the making of unambiguous predictions concerning the differences in the values of the hyperfine parameters. Also, the structure as a whole is so complicated that there exist no reliable band-structure calculations which would be of help in this respect. For example, the relativistic LMTO calculations showing the difference between the electron charge densities at two inequivalent iron sites to be equal to 0.17 au (Christensen 1990, Fanciuli *et al* 1995) indicate the validity of the 1–4 combination. However, more recent LCAO SCF cluster
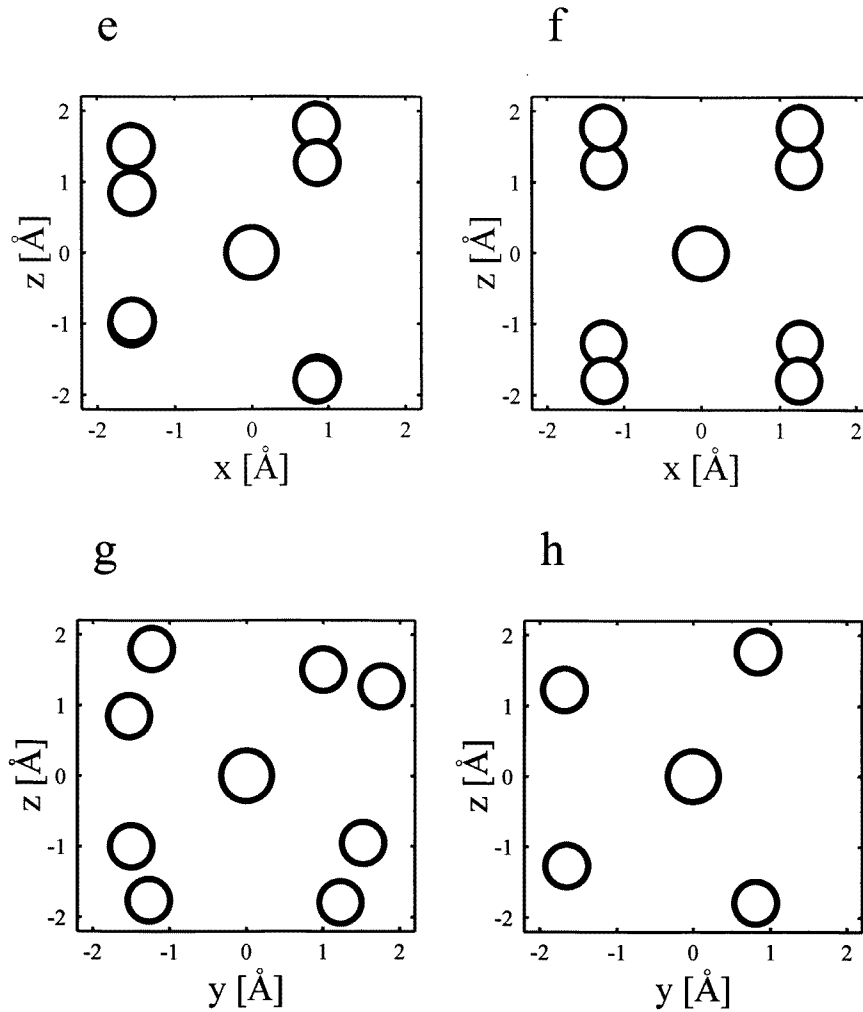
Figure 1. (Continued)

calculations give the difference as 0.65 au (Kondo and Hasaka 1995) and point to the 1–3 combination as being the correct one. Therefore it is now crucial to carry out experiments which will clarify the situation.

Advanced technology allows one to obtain thin single-crystal layers of β-FeSi$_2$. Conversion-electron Mössbauer measurements performed on such layers showed a change of the line intensities with the sample orientation (Fanciuli *et al* 1995). After applying non-standard, refined numerical analysis of the line sharpening, Fanciuli *et al* (1995) demonstrated that the 'hitherto accepted quadrupole couplings of lines 1–3 and 2–4 are inconsistent with the theoretical angular dependence of the intensity ratio'. The authors' conclusion was that the 1–4 combination is realized with positive quadrupole splitting of the doublet corresponding to the first and fourth lines, while the remaining lines form another doublet with a positive QS. This experimental result thus supports the results of LMTO calculations (Christensen 1990, Fanciuli *et al* 1995).

Searching for a clear-cut interpretation, we have recently performed measurements with ^{57}Co implanted into β-FeSi$_2$. One of the results of this experiment was the demonstration that Co enters into both sites of the iron with a slight preference for one of them (Szymański *et al* 1996b). Because the degree of preference was small, it was again impossible to decide which possibility is realized in nature: 1–3 or 1–4.

We show below that the problem of hyperfine structure determination can be solved by measurements in an external magnetic field, and the results of such measurements are presented.

2. Samples and preliminary Mössbauer experiments

A full sample characterization was presented by Szymański *et al* (1996a). X-ray diffraction patterns showed that the crystal structure was identical to that presented by Dusausoy *et al* (1971). Some traces of FeSi phase were also found in the sample. The sample for use in the room temperature Mössbauer measurement was prepared by homogeneous distribution of powder on a few pieces of Scotch tape, resulting in a total thickness of 4.8 mg of sample per cm^2. The sample for use in the 200 K measurements was prepared by mixing β-FeSi$_2$ powder with boron nitride powder and pressing the mixture between two plastic discs forming the container. The thickness was 10 mg cm^{-2} of β-FeSi$_2$.

The Mössbauer measurements were performed in constant-acceleration mode. ^{57}Co in a Rh matrix was used as the source.

The Mössbauer spectrum measured without an external field at room temperature is shown in figure 2(a). The width of the Lorentzian lines for the spectrum shown in figure 2(a) was found to be equal to 0.23(1) mm s^{-1}. The contribution of the 3% of FeSi phase present in our sample (Szymański *et al* 1996a) is shown by the almost flat lines above the ones representing the doublets.

3. In-field measurements

One measurement was performed at room temperature in a field produced by a permanent magnet. The field was parallel to the direction of the unpolarized γ-radiation. To demonstrate the homogeneity of the field and the lack of any stray field acting on the source, we have measured the spectrum of the K$_4$Fe(CN)$_6\cdot$3H$_2$O, known, single-line Mössbauer standard; see figure 2(b). From the fitted function, which was a single Zeeman sextet with a linewidth of 0.24(1) mm s^{-1}, we obtained $B = 1.03(2)$ T, which agrees within 10% with a direct measurement performed using a Hall probe.

A polycrystalline, sintered β-FeSi$_2$ sample reveals diamagnetic behaviour (Birkholz and Frühauf 1969), while recent measurements on single crystals revealed quite small, positive susceptibility (Arushanov *et al* 1996). Our measurements show that the susceptibility of the sample under investigation changes sign at about 280 K (Szymański *et al* 1996a). Thus the magnetic torque acting on the powder grains must be negligible and not able to reorient them. Thus the orientations of the crystallographic directions may be regarded as random.

The spectrum of β-FeSi$_2$ measured in the external field (figure 2(c)) consists of overlapped peaks, and differs substantially from the spectrum measured without a field (figure 2(a)). The spectrum was fitted with a sum of functions which are exact solutions for the hyperfine levels of the ^{57}Fe nucleus exposed to an EFG and a magnetic field (Blaes *et al* 1985). The functions are analytical averages over the angles between the directions of the magnetic field and the EFG axes (which is equivalent to the assumption of an isotropic
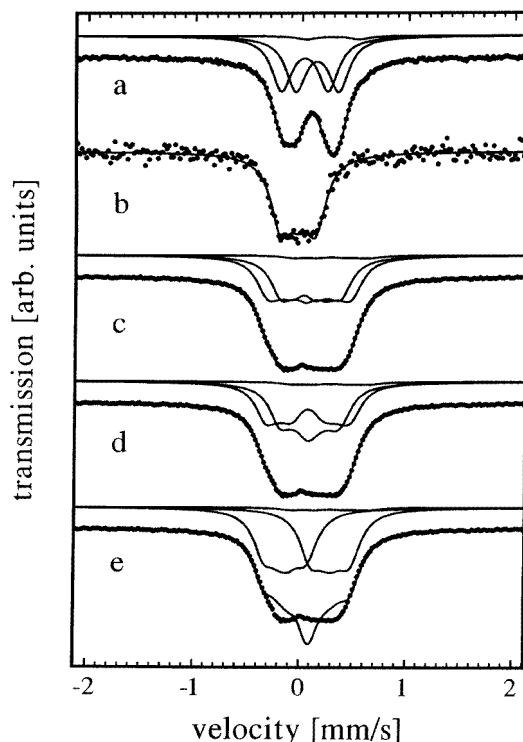
Figure 2. (a) The Mössbauer spectrum of β-FeSi$_2$ measured without an external field. The fitted spectra consist of 1–3 and 2–4 quadrupole doublets, and traces of the FeSi phase. (b) The spectrum of K$_4$Fe(CN)$_6 \cdot$3H$_2$O measured in the field of the permanent magnet. (c) The spectrum of β-FeSi$_2$ measured in the external field and fitted with the 1–3 combination. The signs of the QS were chosen so as to show the worst agreement of the fitted function with the spectrum. (d) The spectrum of β-FeSi$_2$ measured in the external field fitted with the 1–4 possibility. The signs of the QS were chosen so as to show the best agreement of the fitted function with the spectrum. (e) The spectrum fitted with the 1–2 combination.

Table 1. The parameters of the functions fitted to the spectrum measured in a field of about 1 T. The isomer shifts relative to (the isomer shift of) α-Fe at room temperature, and the absolute values of the quadrupole splittings were determined in a zero-field experiment.

IS$_1$ (mm s^{-1})	QS$_1$ (mm s^{-1})	η_1	IS$_2$ (mm s^{-1})	QS$_2$ (mm s^{-1})	η_2	χ^2	Figure	Notation in the text
0.024	−0.439	0.1	0.141	0.403	0.3	1.5	1(c)	1–3
0.074	0.538	0.1	0.092	0.304	0.0	1.6	1(d)	1–4
−0.128	0.135	0.0	0.293	0.099	0.4	110.0	1(e)	1–2

distribution of directions of the EFG axes with respect to the magnetic field direction). The isomer shift (IS) and the modulus of the quadrupole splitting (QS) were determined from the measurement without the field and were kept constant; only the asymmetry parameters of the EFG were varied during the fits. The asymmetry parameter η of the EFG was defined in the usual way as $\eta = (\varphi_{xx} - \varphi_{yy})/\varphi_{zz}$, $|\varphi_{zz}| > |\varphi_{xx}|, |\varphi_{yy}|$ and $\varphi_{ij} = \partial^2\varphi/\partial_i\partial_j$, where φ denotes the Coulomb potential. Because of the equal population of the two iron sites, it

was assumed that the areas under the curves representing the two doublets of interest are the same. Because the shape of the spectrum in the magnetic field depends on the sign of the EFG, one has to test both cases. There are two local environments, and thus four different combinations of the signs of the QSs. We have performed fits for all combinations of signs. The results may be summarized as follows. The 1–3 combination shows much better agreement than the 1–4 one: the χ^2-value for the worst fit with the 1–3 combination was smaller than χ^2 for the best fit with the 1–4 possibility; see table 1. These two extreme cases are hardly distinguishable, as illustrated in figures 2(c) and 2(d). For each possibility, 1–3 or 1–4, four fits with different combinations of signs of the QSs showed similar qualities of fits. It was thus not possible to determine the signs of the QSs from this measurement.

The agreement of the fitted function for the 1–2 combination with the experimental data was very poor: χ^2 was over 100 times larger than in the cases of the two former combinations; see figure 2(e) and table 1. This test confirmed the conclusion of Wandji *et al* (1971) and the experimental evidence of Fanciuli *et al* (1995) that the 1–2 possibility is not realized in nature.

Table 2. The parameters of the fitted function with the first and third lines forming a doublet with a negative QS, and the second and fourth lines forming a doublet with a positive QS (columns 2 to 6). Also given are the ratios of the appropriate χ^2-values for other signs of the QSs (columns 7–9) as well as for the 1–4 combination (columns 10–13). $(+-k\,l)$ stands for the ratio $\chi^2_{(+-kl)}/\chi^2_{(-+13)}$, where $\chi^2_{(+-mn)}$ is the χ^2-value for the fit in which lines m and n form a doublet with a positive QS value (subscript $+$) and the two remaining lines form a doublet with a negative QS value (subscript $-$). We also list the isomer shifts determined in the zero-field experiment, for the 1–3 combination: $IS_1 = 0.056$ mm s^{-1}, $IS_2 = 0.191$ mm s^{-1}; and for the 1–4 combination: $IS_1 = 0.116$ mm s^{-1}, $IS_2 = 0.130$ mm s^{-1}.

B_{appl} (T)	B_{int} (T)	QS_1 (mm s^{-1})	η_1	QS_2 (mm s^{-1})	η_2	(++13)	(+−13)	(−−13)	(++14)	(+−14)	(−+14)	(−−14)
0	0	−0.44	—	0.41	—	—	—	—	—	—	—	—
2	1.84	−0.43	0.8	0.43	0.6	1.1	1.1	1.1	1.7	1.6	1.7	1.7
4.5	4.17	−0.49	1.0	0.46	1.0	1.0	1.0	1.0	1.7	1.7	1.7	1.7
6	5.63	−0.57	0.3	0.54	0.4	2.0	2.3	1.6	1.6	1.8	1.4	1.6
8.5	8.07	−0.68	0.3	0.69	0.2	1.3	1.4	1.3	1.2	1.2	1.2	1.2

Other measurements were performed in external fields of 2, 4.5, 6, and 8.5 T parallel to the unpolarized γ-radiation, with the sample maintained at the temperature 200 K. The experimental set-up used was described elsewhere (Greneche *et al* 1990). The spectra are shown in figure 3. We tried to fit the spectrum in a similar way to that used for the field 1.03 T. From an additional measurement at 200 K, and in the absence of the magnetic field, we obtained $IS_1 = 0.056(3)$, $IS_2 = 0.191(3)$, $|QS_1| = 0.440(5)$ and $|QS_2| = 0.412(5)$ (in units of mm s^{-1}, in terms of the 1–3 combination), in agreement with reported values (Blaauw *et al* 1973). However, the situation turned out to be more complicated: in higher external fields we had to conclude that the external magnetic field must induce a change of the EFG, so it would not be possible to perform reasonable fits with IS and QS values which corresponded to the zero-field values. The hyperfine magnetic field acting on the ^{57}Fe nucleus was also different from the applied field; see column 2 of table 2. Treating the next hyperfine-magnetic-field and QS values as free parameters (the ISs were again determined in a zero-field experiment), we checked that the only possibility which produced reasonable fits was the 1–3 combination with well defined signs of the QS: a positive QS for a doublet with a larger IS and a negative QS for a doublet with a smaller IS. This turned out to be so
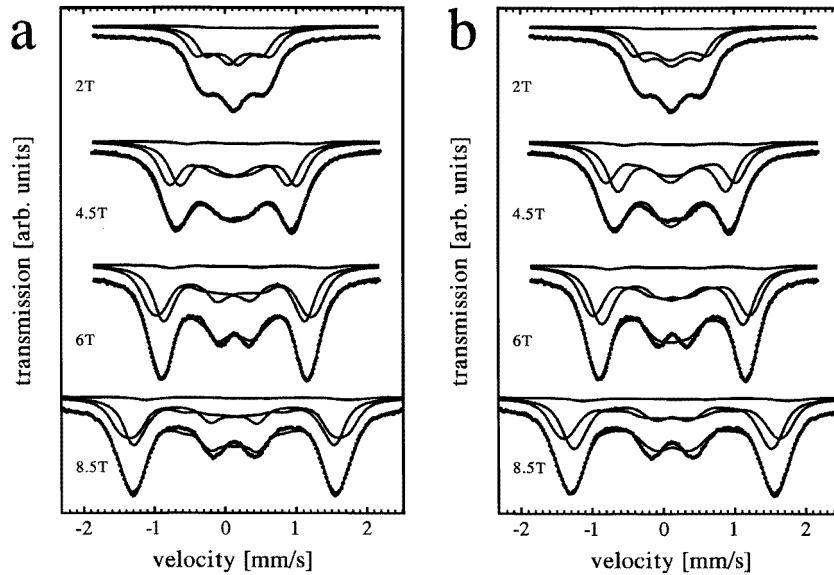
Figure 3. Mössbauer spectra of β-FeSi₂ measured in various external fields at 200 K, and the best results of the fits: (a) one doublet formed with peaks 1 and 3 with a negative QS, and the second one with a positive QS; and (b) one doublet formed with peaks 1 and 4 with a positive QS and the second one with a negative QS, according to Fanciuli *et al* (1995).

for all values of the applied field. The fitted spectra, together with subspectra, are shown in figure 3(a). All other fits, like 1–3 with other combinations of signs of the EFG, or 1–4 for any combination of signs, produced much worse fits. For comparison, results of the fits which stem from the interpretation of Fanciuli *et al* (1995) are shown in figure 3(b). In table 2 the ratios of the appropriate χ^2-values are given as well as the parameters of the fitted functions. The main discrepancy observed at $B = 8.5$ T shows up in the central part of the spectra. The theoretical curve has there only one broad maximum, instead of the observed two peaks. Assuming that the field-induced changes of the QSs and internal magnetic field are linear with the applied field, we find that

$$\frac{\partial QS_1}{\partial B} = -0.022(5) \text{ mm s}^{-1} \text{ T}^{-1} \tag{1}$$

$$\frac{\partial QS_2}{\partial B} = 0.026(5) \text{ mm s}^{-1} \text{ T}^{-1} \tag{2}$$

$$\frac{\partial B_{int}}{\partial B} = 0.95(2). \tag{3}$$

The field dependence of the asymmetry parameter—see table 2—is not well defined, especially in the light of the fact that the fitted spectra do not reproduce the experimental ones well at the highest fields.

At first, it would seem that we would gain a better understanding of the results if standard analysis for the determination of the hyperfine-magnetic-field distribution were applied. Indeed, the spectrum measured in a field of 8.5 T is symmetrical and composed of four broad peaks, and this resembles the situation for a material in an external longitudinal field in which a hyperfine-magnetic-field distribution is present. This type of analysis is, however, dangerous for two reasons. Firstly, the ratio of the QS to the magnetic splitting,

called R in the literature (Le Caer and Dubois 1984), is equal in this case to 1.2, and is too large for one to derive unambiguous information about the true shape of the hyperfine-field distribution. Secondly, in the case of randomly oriented powder in an external field, one deals with a distribution of hyperfine parameters due to the EFG-axis orientation with respect to the magnetic field direction. Having assumed an additional magnetic field distribution, one arrives at the problem of a two-dimensional distribution. Because two inequivalent iron sites are present in β-FeSi$_2$, and for each one a two-dimensional distribution should be applied, the whole problem becomes extremely complicated.

4. Discussion and conclusions

The central results of the present work are hard to reconcile with the recent spectral interpretation given by Fanciuli *et al* (1995). In contrast to their assumption that the asymmetry parameter is close to zero, our results indicate that the asymmetry parameters may have values remarkably different from zero; see table 2. Also the choice of the 1–4 combination may be questioned: an apparent disagreement between the calculated and measured intensities can be seen in figure 3 of Fanciuli *et al* (1995).

Looking at our data, we need to explain why the results of the fits for a stronger field are not as good as in the case of the fields of 1.03 T and 2 T. Moreover, the absolute disagreement increases with increasing value of the applied field. Two main reasons can be postulated.

(i) As the magnetic field induces changes of the EFG, the distribution of the principal directions of the tensor can no longer be isotropic, and thus the assumption of isotropic distribution of the EFG direction fails. A possible mechanism for the QS changes may be the field-induced lattice distortion. Indeed, the possibility of an influence of the external field on the crystal structure has already been mooted in the literature (Asamitsu *et al* 1996, Araujo 1996). However, in the case of β-FeSi$_2$, such an interpretation is only speculation. Further experiments are needed in order to clarify this point, as well as to work out a quantitative interpretation of the results given by equations (1)–(3).

(ii) One may also consider the influence of the stray field, approximately equal to 0.2 T, which was found at the source (Greneche *et al* 1990). One can easily show that while this field could worsen χ^2, the effective-field value, B_{int}, is insensitive to the stray field.

Our measurements show that the spectra measured at weak fields can be fitted with the procedure described by Blaes *et al* (1985), with QS and IS values determined in a zero-field experiment. The 1–3 combination gives, as a rule, better agreement than the 1–4 one. As expected, in this field intensity region, the fitting procedure produces results in perfect agreement with zero-field measurements. At higher external magnetic fields, the 1–3 combination again gives the best fits in all of the cases investigated. This time, however, the method is sensitive enough to allow for a unique determination of the signs of the QS. We were able to prove that a doublet with a negative quadrupole splitting is formed from peaks No 1 and No 3 while peaks No 2 and No 4 form a doublet with a positive quadrupole splitting. This interpretation agrees with recent electronic structure calculations, in which the difference of the charge densities at two iron sites corresponds to the difference of the isomer shifts (Kondo and Hasaka 1995).

It is remarkable that we observe that, at the highest field of 8.5 T, both models show deficiencies, the origin of which needs further study. Nevertheless, our experiment clearly shows that one can hardly advocate the 1–4 combination, while the 1–3 one explains the data well at least in fields up to 6 T.

As was explained in the introduction, standard Mössbauer spectra measured without an external magnetic field are identical for the 1–4 and 1–3 combinations. Thus the problem of correct doublet assignment is not critical in such experiments. If, however, single crystals are used, or an external field is applied, or polarized resonant radiation is used, the doublet assignment plays an important role in the determination of the shape of the Mössbauer spectra.

We hope that our work has illuminated some methodological aspects of this problem, and that it makes a substantial step towards producing a better explanation of the situation for β-FeSi₂. Because of the aforementioned importance of this semiconductor, we believe that precise band-structure calculations will soon be available; they can then be compared with existing experimental data.

Acknowledgment

References

Araujo M A N 1996 *J. Phys.: Condens. Matter* **8** 6911
Arushanov E, Respaud M, Broto J M, Kloc C, Leotin J and Bucher E 1996 *Phys. Rev.* B **53** 5108
Asamitsu A, Mositomo Y, Tomioka Y, Arima T and Tokura Y 1996 *Nature* **373** 407
Birkholz U and Frühauf A 1961 *Phys. Status Solidi* **34** K181
Blaauw C, Van der Woude F and Sawatzky G A 1973 *J. Phys. C: Solid State Phys.* **6** 2371
Blaes N, Fisher H and Gonser U 1985 *Nucl. Instrum. Methods* B **9** 201
Christensen N E 1990 *Phys. Rev.* B **42** 7148
Desimoni J, Bernas H, Behar M, Lin X W, Washburn J and Liliental-Weber Z 1993 *Appl. Phys. Lett.* **62** 306
Dimitriadis C A, Werner J H, Logothetidis S, Stutzmann M, Weber J and Nesper R 1990 *J. Appl. Phys.* **68** 1726
Dusausoy P Y, Protas J, Wandji R and Roques B 1971 *Acta Crystallogr.* B **27** 1209
Fanciuli M, Rosenblad C, Weyer G, Svane A and Christensen N E 1995 *Phys. Rev. Lett.* **75** 1642
Greneche J M, Linares J and Varret F 1990 *J. Phys.: Condens. Matter* **2** 4243
Kojima T, Okamoto M and Nishida I 1984 *Proc. 5th Int. Conf. on Thermoelectric Energy Conversion (Arlington, TX)* p 56
Kondo S and Hasaka M 1995 *J. Phys.: Condens. Matter* **7** 2123
Kondo S, Hasaka M, Morimura T and Miyajima Y 1994 *Physica* B **198** 332
Le Caer G and Dubois J M 1984 *Nucl. Instrum. Methods* B **5** 25
Radermacher K, Mantil K, Dieker C and Lüth H 1991 *Appl. Phys. Lett.* **59** 2145
Szymański K, Baas J, Dobrzyński L and Satuła D 1996a *Physica* B **225** 111
Szymański K, Dobrzyński L, Andrejczuk A, Chrenowicz R, Vantomme A, Degrote S and Langouche G 1996b *J. Phys.: Condens. Matter* **8** 5317
Wandji R, Le Corre C, Genin J M and Roques B 1971 *Phys. Status Solidi* b **45** K123