MÖSSBAUER SIX-LINE SPECTRA POSITION ANALYSIS FOR Fe^{57} IN METALLIC IRON

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The formulae for evaluating the parameters of magnetically split Mössbauer six-line spectra with quadrupole splitting from measured line positions are derived. Some special cases are considered and the suitability of the centre of gravity rule for the shift determination as well as the case of the internal magnetic field measurement from the distance of the outermost lines of the Mössbauer sextet are discussed. From the measured spectra of metallic iron the ratio of magnitudes of the nuclear magnetic moments for Fe^{57} $|\mu_1/\mu_0| = 1{\cdot}701 \pm 0{\cdot}008$ is derived by means of the proposed method. Further, the internal magnetic field intensity at the Fe^{57} nucleus in metallic iron $H_i = (329{\cdot}4 \pm 1{\cdot}2)$ kOe and other quantities are determined.

1. INTRODUCTION

Measurements of the Mössbauer velocity spectra provide the dependence of the gamma ray counting rate on the relative velocity between the source and the absorber or the scatterer. One of the requirements for an interpretation of these spectra is to find quantities characterizing the positions and splittings of pertinent nuclear levels, from which other parameters, e.g. structure characteristics, can be derived.

There are two ways of elaborating the velocity spectra:

1. to analyze the measured spectrum as a whole,
2. to determine the parameters of individual lines and to obtain the information needed by subsequent evaluation. Considering the difficulty of the former it is advantageous to use the latter in the case when shifts and splittings of the lines are needed.

In this paper a method is presented for evaluating the parameters of the Mössbauer six-line spectra from the measured positions of the individual lines. The solution for the general case and for some special cases is performed and the evaluation of further quantities is shown.

The suggested method is illustrated on examples of measurements of the velocity spectra for different forms of metallic iron and compared with the least squares analysis of the spectrum as a whole. Mössbauer spectra in the transmission arrangement are taken as examples; the suggested method, however, can also be used for scattering measurements.

The results obtained, particularly the ratio of magnitudes of the magnetic moments $|\mu_1/\mu_0|$ of the first excited and ground nuclear states of Fe^{57} and the internal field intensity H_i at the Fe^{57} nuclei in metallic iron, are compared with the published values.

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2. FORMULATION OF THE PROBLEM

The Mössbauer spectrum corresponding to the magnetic dipolar transition between the levels with nuclear spins $I = \frac{3}{2} \rightarrow I = \frac{1}{2}$ (e.g. in the isotopes Fe^{57} and Sn^{119}) in the case when the source or the absorber is placed in the magnetic field has the well-known form of a six-line pattern [1, 2]. Without loss of generality we can suppose below that this sextet has its origin in the absorption of the monoenergetic source radiation with energy E_s in the absorber with Zeeman split nuclear levels. An example of a typical spectrum (computed with arbitrary chosen parameters) is given in Fig. 1.

On the assumption of the simultaneous presence of magnetic splitting and of electric quadrupole splitting in the axial symmetric field the energies of the transitions 1 to 6 according to the designation in Fig. 2 [2, 3] are

$$\begin{aligned}
E_{a1} &= E_\gamma + \Delta E_a + \varepsilon - \tfrac{1}{2}g_0 - \tfrac{3}{2}g_1 \\
E_{a2} &= E_\gamma + \Delta E_a - \varepsilon - \tfrac{1}{2}g_0 - \tfrac{1}{2}g_1 \\
E_{a3} &= E_\gamma + \Delta E_a - \varepsilon - \tfrac{1}{2}g_0 + \tfrac{1}{2}g_1 \\
E_{a4} &= E_\gamma + \Delta E_a - \varepsilon + \tfrac{1}{2}g_0 - \tfrac{1}{2}g_1 \\
E_{a5} &= E_\gamma + \Delta E_a - \varepsilon + \tfrac{1}{2}g_0 + \tfrac{1}{2}g_1 \\
E_{a6} &= E_\gamma + \Delta E_a + \varepsilon + \tfrac{1}{2}g_0 + \tfrac{3}{2}g_1
\end{aligned} \tag{2.1}$$

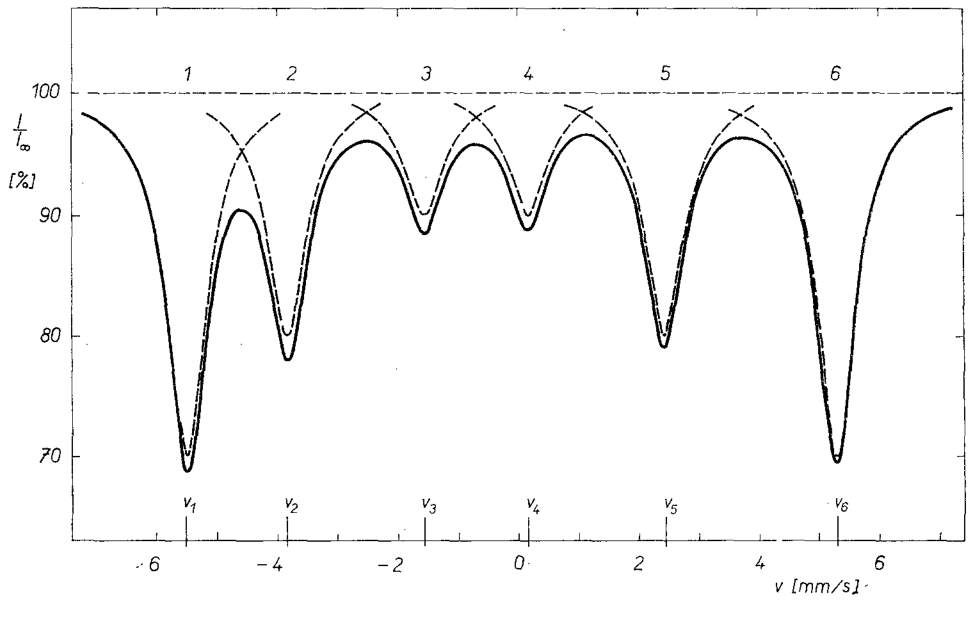

Fig. 1. Computed Mössbauer sextet with Lorentz line shape with the line widths $\Gamma = 0{\cdot}8$ mm s^{-1} and intensity ratio 3 : 2 : 1.

The dashed curve denotes the particular absorption lines. The parameters of the spectrum are $\Delta E = -0{\cdot}4$ mm s^{-1}, $\varepsilon = 0{\cdot}3$ mm s^{-1}, $g_0 = 4{\cdot}0$ mm s^{-1} and $g_0/g_1 = 1{\cdot}77$. v — relative velocity between source and absorber, I/I_∞ — counting rate relative to that for $v \rightarrow \infty$.

where $E_\gamma = E_1 - E_0$ is the energy difference of the levels in a free nucleus; ΔE_a is the difference of the level shifts in the absorber resulting from the interaction between the nucleus and the electron density at the nucleus;

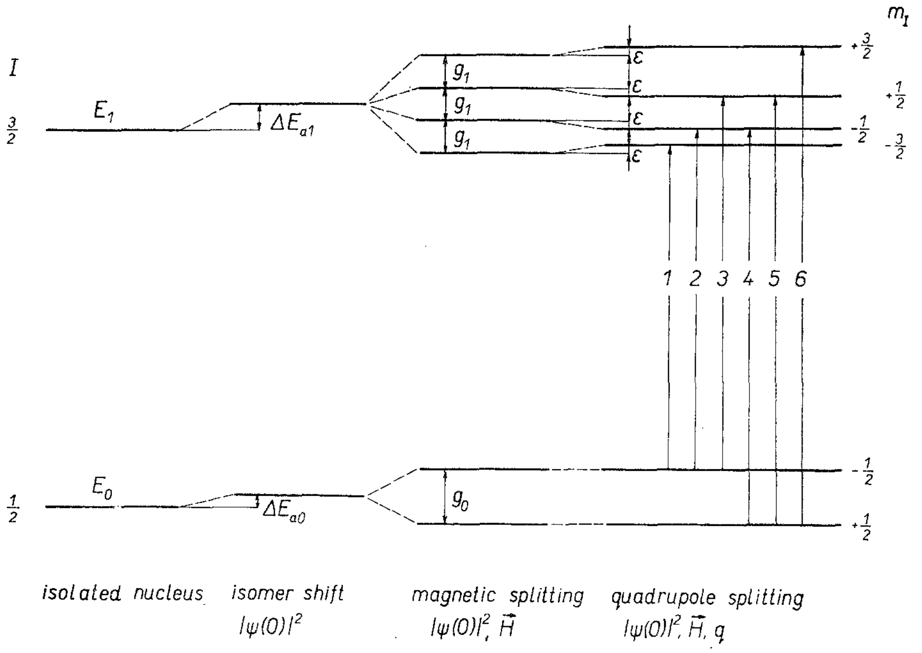

Fig. 2. Splittings and shifts of the nuclear levels in different fields and transitions between the sublevels. The notation of transitions corresponds to Fig. 1. I — nuclear spin, m_I — nuclear magnetic quantum number. For other parameters see text.

$$\varepsilon = \text{const.}\; q \,.\, Q \tag{2.2}$$

is the quadrupole splitting in the case of axial symmetric electric field gradient with the axial component q (Q is the nuclear quadrupole moment) [2, 3];

$$\begin{aligned} g_0 &= |\mu_0|\, H_i/I_0 \\ g_1 &= |\mu_1|\, H_i/I_1 \end{aligned} \tag{2.3}$$

are the magnitudes of the ground and excited level splittings, μ_0, μ_1 being the nuclear magnetic moments, I_0, I_1 the nuclear spins; and

$$\boldsymbol{H}_i = \boldsymbol{H}_0 + \boldsymbol{H}_e \tag{2.4}$$

is the magnetic field intensity at the nucleus, composed of the effective field $\boldsymbol{H}_0$ (proportional to the domain magnetization) and the additive contribution of the external magnetic field $\boldsymbol{H}_e$ [4, 5, 9].

Let us consider also the level shifts in the radiation source

$$E_s = E_\gamma + \varDelta E_s \,. \tag{2.5}$$

and designate the resulting isomer shift [6]

$$\varDelta E_i = \varDelta E_a - \varDelta E_s = \text{const.}\,(|\psi_{oa}|^2 - |\psi_{os}|^2) \tag{2.6}$$

($|\psi_{oa}|^2$ and $|\psi_{os}|^2$ are the electron densities at the nucleus of the absorber and the source, respectively). Considering the thermal shift as the consequence of the second-order Doppler effect $\varDelta E_t$ [7, 8] we obtain the total shift

$$\varDelta E = \varDelta E_i + \varDelta E_t$$

The velocities v_1 to v_6 in the Mössbauer spectrum corresponding to the transitions 1 to 6 (Fig. 1) according to (2.1) have the values

$$\begin{aligned} v_1 &= \varDelta E + \varepsilon - \tfrac{1}{2}g_0 - \tfrac{3}{2}g_1 \\ v_2 &= \varDelta E - \varepsilon - \tfrac{1}{2}g_0 - \tfrac{1}{2}g_1 \\ v_3 &= \varDelta E - \varepsilon - \tfrac{1}{2}g_0 + \tfrac{1}{2}g_1 \\ v_4 &= \varDelta E - \varepsilon + \tfrac{1}{2}g_0 - \tfrac{1}{2}g_1 \\ v_5 &= \varDelta E - \varepsilon + \tfrac{1}{2}g_0 + \tfrac{1}{2}g_1 \\ v_6 &= \varDelta E + \varepsilon + \tfrac{1}{2}g_0 + \tfrac{3}{2}g_1 \end{aligned} \tag{2.8}$$

the quantities $\varDelta E$, ε, g_0 and g_1 being as usual expressed in velocity units.

The purpose of the analysis is to determine the quantities on the right side of the system of equations (2.8) from the measured velocities v_1 to v_6. To find the most probable solution of this overdetermined system the precision of measurements of the starting quantities has to be taken into consideration.

3. GENERAL SOLUTION OF THE PROBLEM

Let us suppose that the velocities v_1 to v_6 are determined with the errors $\delta(v_1)$ to $\delta(v_6)$ and let us seek the solution of the system (2.8) with the unknown quantities $\varDelta E$, ε, g_0 and g_1 for these quantities to have the least possible errors.

To simplify the system (2.8) we can adapt it by introducing new quantities s and d for the sums of the line positions and their differences, respectively,

$$\begin{aligned} s_1 &= v_6 + v_1 & d_1 &= v_6 - v_1 \\ s_2 &= v_5 + v_2 & d_2 &= v_5 - v_2 \\ s_3 &= v_4 + v_3 & d_3 &= v_4 - v_3 \,. \end{aligned} \tag{3.1}$$

Thus the system (2.8) falls into two independent systems

$$
\begin{aligned}
&(3.2), (3.3) \qquad & s_1 &= 2(\Delta E + \varepsilon) \qquad & d_1 &= g_0 + 3g_1 \\
& & s_2 &= 2(\Delta E - \varepsilon) & d_2 &= g_0 + g_1 \\
& & s_3 &= 2(\Delta E - \varepsilon) & d_3 &= g_0 - g_1 \,.
\end{aligned}
$$

We designate the errors of the new quantities by

$$
\begin{aligned}
(3.4) \qquad \delta_1 &= \delta(s_1) = \delta(d_1) = \sqrt{[\delta^2(v_1) + \delta^2(v_6)]} \\
\delta_2 &= \delta(s_2) = \delta(d_2) = \sqrt{[\delta^2(v_2) + \delta^2(v_5)]} \\
\delta_3 &= \delta(s_3) = \delta(d_3) = \sqrt{[\delta^2(v_3) + \delta^2(v_4)]} \,.
\end{aligned}
$$

The general solution of the system of the type (3.2), (3.3) is found in the Appendix. By substituting the pertinent coefficients of the system (3.2) into Eq. (A 9) and into the cyclic permuted relations we obtain the coefficients of the solution

$$
\begin{aligned}
(3.5) \qquad \Delta E &= a_1 s_1 + a_2 s_2 + a_3 s_3 \\
\varepsilon &= b_1 s_1 + b_2 s_2 + b_3 s_3
\end{aligned}
$$

in the form

$$
\begin{aligned}
(3.6) \qquad a_1 &= b_1 = \tfrac{1}{4} \\
a_2 &= -b_2 = \tfrac{1}{4}\delta_3^2/(\delta_2^2 + \delta_3^2) \\
a_3 &= -b_3 = \tfrac{1}{4}\delta_2^2/(\delta_2^2 + \delta_3^2) \,.
\end{aligned}
$$

Similarly, by substituting the coefficients of the system (3.3) into Eq. (A 9) and into the cyclic permuted relations we get the coefficients of the solution

$$
\begin{aligned}
(3.7) \qquad g_0 &= a'_1 d_1 + a'_2 d_2 + a'_3 d_3 \\
g_1 &= b'_1 d_1 + b'_2 d_2 + b'_3 d_3
\end{aligned}
$$

in the form

$$
\begin{aligned}
(3.8) \qquad a'_1 &= \frac{1}{2}\,\frac{2\delta_2^2 - \delta_3^2}{\delta_1^2 + 4\delta_2^2 + \delta_3^2} \qquad & b'_1 &= \frac{1}{2}\,\frac{2\delta_2^2 + \delta_3^2}{\delta_1^2 + 4\delta_2^2 + \delta_3^2} \\
a'_2 &= \frac{1}{2}\,\frac{\delta_1^2 + 3\delta_3^2}{\delta_1^2 + 4\delta_2^2 + \delta_3^2} & b'_2 &= \frac{1}{2}\,\frac{\delta_1^2 - \delta_3^2}{\delta_1^2 + 4\delta_2^2 + \delta_3^2} \\
a'_3 &= \frac{1}{2}\,\frac{\delta_1^2 + 6\delta_2^2}{\delta_1^2 + 4\delta_2^2 + \delta_3^2} & b'_3 &= -\frac{1}{2}\,\frac{\delta_1^2 + 2\delta_2^2}{\delta_1^2 + 4\delta_2^2 + \delta_3^2}
\end{aligned}
$$

The resulting errors of the found quantities ΔE, ε, g_0 and g_1 can be obtained by sub-

Tab.

Coefficients of the linear combinations (3.5) and

Case	Number of lines	$\frac{1}{\delta_1^2}:\frac{1}{\delta_2^2}:\frac{1}{\delta_3^2}$	$a_1 =$ $= b_1$	$a_2 =$ $= -b_2$	$a_3 =$ $= -b_3$
H_i randomly oriented	6	3 : 2 : 1	$\frac{1}{4}$	$\frac{1}{6}$	$\frac{1}{12}$
H_i perpendicular to the direction of observation	6	3 : 4 : 1	$\frac{1}{4}$	$\frac{1}{5}$	$\frac{1}{20}$
H_i generally oriented	6	3 : n : 1	$\frac{1}{4}$	$\frac{n}{4(n+1)}$	$\frac{1}{4(n+1)}$
H_i along the direction of observation	4	3 : 0 : 1	$\frac{1}{4}$	0	$\frac{1}{4}$
outer lines1)	4	3 : n : 0	$\frac{1}{4}$	$\frac{1}{4}$	0
inner lines2)	4	0 : n : 1	0	—3)	—3)

1) e.g. in the case of unresolved inner lines of the sextet.

2) e.g. in the case of small scope of velocity scale.

3) system undetermined; ΔE, ε cannot be estimated.

stituting the coefficients into relations of the type (A4). Then we get

$$\delta^2(\Delta E) = \delta^2(\varepsilon) = \frac{\delta_1^2\delta_2^2 + \delta_2^2\delta_3^2 + \delta_3^2\delta_1^2}{16(\delta_2^2 + \delta_3^2)} \tag{3.9}$$

$$\delta^2(g_0) = \frac{\delta_1^2\delta_2^2 + 9\delta_2^2\delta_3^2 + \delta_3^2\delta_1^2}{4(\delta_1^2 + 4\delta_2^2 + \delta_3^2)}$$

$$\delta^2(g_1) = \frac{\delta_1^2\delta_2^2 + \delta_2^2\delta_3^2 + \delta_3^2\delta_1^2}{4(\delta_1^2 + 4\delta_2^2 + \delta_3^2)}\,.$$

In the case when one of the pairs of lines did not appear or was not measured – which can happen in some cases, as we shall see in Sec. 4 – one of the equations drops out of the systems (3.2) and (3.3) and the unambiguous solution in this case can be obtained either directly or according to the Appendix as the limiting case of the general solution for $\delta_i \to \infty$, the index i designating the equation dropping out of the system.

1

(3.7) and the resulting errors (3.9) for particular cases.

a'_1	a'_2	a'_3	b'_1	b'_2	b'_3	$\frac{\delta^2(\Delta E)}{\delta^2}$	$\frac{\delta^2(g_0)}{\delta^2}$	$\frac{\delta^2(g_1)}{\delta^2}$
0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{10}$	$-\frac{1}{10}$	$-\frac{1}{5}$	$\frac{1}{24}$	$\frac{3}{8}$	$\frac{3}{40}$
$-\frac{3}{28}$	$\frac{5}{7}$	$\frac{11}{28}$	$\frac{9}{28}$	$-\frac{1}{7}$	$-\frac{5}{28}$	$\frac{1}{30}$	$\frac{2}{7}$	$\frac{1}{14}$
$\frac{3(2-n)}{8(n+3)}$	$\frac{5n}{4(n+3)}$	$\frac{n+18}{8(n+3)}$	$\frac{3(2+n)}{8(n+3)}$	$\frac{-n}{4(n+3)}$	$\frac{-(n+6)}{8(n+3)}$	$\frac{n+4}{48(n+1)}$	$\frac{n+28}{16(n+3)}$	$\frac{n+4}{16(n+3)}$
$\frac{1}{4}$	0	$\frac{3}{4}$	$\frac{1}{4}$	0	$-\frac{1}{4}$	$\frac{1}{12}$	$\frac{7}{12}$	$\frac{1}{12}$
$-\frac{1}{2}$	$\frac{3}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{n+3}{48n}$	$\frac{n+9}{12n}$	$\frac{n+3}{12n}$
0	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	– 3)	$\frac{n+1}{4n}$	$\frac{n+1}{4n}$

4. SOLUTION IN SOME SPECIAL CASES

a) Six-line spectrum of the thin absorber

In this case the areas of the absorption lines are in the proportion $3 : n : 1 : 1 : n : 3$ [2, 9], n depending on the relative orientation of the direction of observation and of the vector $\boldsymbol{H}_i$. In the case of observation along the $\boldsymbol{H}_i$, $n = 0$, for the perpendicular direction $n = 4$ and in the most frequent case of the isotropic distributions of $\boldsymbol{H}_i$ in multidomain material $n = 2$. In the case when the line widths in the spectrum are equal, the relative depths of the absorption minima are also in the given proportions. Therefore, these proportions hold for the weights of the determination of their positions that are proportional to the reciprocal of the squares of position errors. For the errors δ_1, δ_2 and δ_3 it holds in this case that

$$1/\delta_1^2 : 1/\delta_2^2 : 1/\delta_3^2 = 3 : n : 1 \tag{4.1}$$

i.e. when the error $\delta = \delta_3$ is taken as the basis

$$\delta_1^2 = \tfrac{1}{3}\delta^2\,, \quad \delta_2^2 = \frac{1}{n}\,\delta^2\,, \quad \delta_3^2 = \delta^2\,. \tag{4.2}$$

By substituting this into Eq. (3.6) and (3.8) we obtain the coefficients of linear combinations (3.5) and (3.7), respectively, that are given in Table 1, together with the resulting errors according to (3.9).

In the most frequent case when $n = 2$, by substituting this value into Eq. (3.5), (3.7) we obtain

$$(4.3) \qquad \begin{aligned} \Delta E &= \tfrac{1}{12}(3s_1 + 2s_2 + s_3) & \qquad \varepsilon &= \tfrac{1}{12}(3s_1 - 2s_2 - s_3) \\ g_0 &= \tfrac{1}{2}(d_2 + d_3) & g_1 &= \tfrac{1}{10}(3d_1 - d \ - 2d_3)\,. \end{aligned}$$

The relation for ΔE expresses the well-known centre of gravity rule [2, 9] for the shift determination. As can be seen from relation (4.3), this rule does not give the best value for ΔE in the general case. In our case the resulting errors according to (3.9) have the values

$$(4.4) \qquad \delta^2(\Delta E) = \delta^2(\varepsilon) = \tfrac{1}{24}\delta^2\,, \quad \delta^2(g_0) = \tfrac{3}{8}\delta^2\,, \quad \delta^2(g_1) = \tfrac{3}{40}\delta^2\,.$$

The coefficients according to (3.6), (3.8) and the resulting errors (3.9) for some important cases are also summarized in Tab. 1.

b) Four lines in the spectrum

This case takes place when observing in the direction along the internal magnetic field $\boldsymbol{H}_i$, where the lines corresponding to the transitions with $\Delta m_I = 0$ (see Fig. 2) vanish, i.e. $n = 0$ in Eq. (4.1) and in the subsequent relations. As will be mentioned in the Appendix, the solution of the problem in this case is unambiguous and can be achieved either by the limiting transition $\delta_2 \to \infty$, i.e. $n \to 0$ (see Eq. (4.2)), or by the solution of systems (3.2) and (3.3) for given s_1, s_3 and d_1, d_3, respectively.

In the case when the measurements of particular points in the velocity spectrum – compared with the depth of the least intensive absorption lines 3, 4 (Fig. 1) – exhibit a considerable statistical error, it can happen that these lines become practically indistinguishable and hence the values of s_3 and d_3 cannot be determined. Similarly, in the case when the scope of the velocity scale is not sufficiently large for the highest velocities v_1 and v_6, the values of s_1 and d_1 cannot be determined. In both cases, the systems (3.2) and (3.3) are solved analogically to the above-mentioned case when $n = 0$.

For these three cases that occur in practice the coefficients according to Eqs. (3.6) and (3.8) and the errors according to (3.9) are given in Tab. 1 as well.

c) Evaluation of H_i and $|\mu\ /\mu_0|$

The magnitude of the internal magnetic field H_i determined by Eq. (2.3) and the ratio of magnitudes of the nuclear magnetic moments of the ground and excited states $|\mu_1/\mu_0|$ cannot be obtained directly by solving the system (2.8). The evaluation of these quantities is described in this section.

For the determination of H_i from Eq. (2.3) we must know the coefficient of proportionality between the splitting of the nuclear levels and H_i, i.e. some linear combination of the magnetic moment magnitudes $|\mu_0|$ and $|\mu_1|$. As the value of μ_0 is known from other measurements (e.g. from the NMR) it is advantageous for the absolute determination of H_i to use the first equation from (2.3).

For the relative evaluation of H_i it is sufficient to know an arbitrary linear combination of the quantities $|\mu_0|$ and $|\mu_1|$. This can be obtained by means of a suitable etalon with known H_i, e.g. of the pure metallic iron in the case of the Fe^{57} nucleus. With regard to relations (3.3), the most advantageous seems to be the measurement of

$$d_1 = g_0 + 3g_1 = \text{const. } H_i \tag{4.5}$$

i.e. of the difference of the positions (distance) of the outermost absorption minima in the spectrum [11]. These minima are frequently intensive (i.e. δ_1 is small) and their distance d_1 is great, i.e. the relative error of the determination of H_i becomes the minimum value δ_1/d_1. This absolute minimum of the error of determined H_i is necessarily lower than the relative error of both the values g_0 and g_1 evaluated from Eq. (3.7).

On the other hand, for the determination of the quantity $|\mu_1/\mu_0|$ according to the relation [9]

$$\left|\frac{\mu_1}{\mu_0}\right| = \frac{I_1}{I_0} \cdot \frac{g_1}{g_0} = \frac{3g_1}{g_0} \tag{4.6}$$

which follows from Eq. (2.3), we can achieve minimum error of the ratio g_0/g_1 with minimum errors of the quantities g_0, g_1 by substituting the solution (3.7) and the solutions in special cases according to Sec. 4, respectively, into Eq. (4.6).

5. ANALYSIS OF THE METALLIC IRON SPECTRA

By means of the cam-driven Mössbauer spectrometer that will be described in another paper the velocity spectra of different metallic iron samples were measured at room temperature. The source of the 14·4 keV gamma rays was Co^{57} in Pt [10]. The positions of individual minima were determined from the corresponding pairs of equally deep lines by means of the least squares method [11]. These measurements were evaluated by means of the method derived in Sec. 3; the values of the starting and final parameters are summarized in Tab. 2, together with the weighted mean values of the quantities ΔE, ε, g_0 and g_1.

For the sake of comparison the first spectrum from Tab. 2 was evaluated also as a whole by means of the least squares method. The results of this evaluation – compared with the first method this is about one order more exacting as regards time – are given in Tab. 2. The smoothed curves drawn through the measured points are presented in Fig. 3. We can see that the results of both evaluating methods are in good agreement.

Tab. 2

Results of metallic iron spectra measurements and their elaboration. Dimensions of the quantities are in mm s^{-1}; values of measured quantities are not corrected for the geometry of measurement and the cam rise.

Material	v_1	v_2	v_3	v_4	v_5	v_6	$-s_1$ d_1	$-s_2$ d_2	$-s_3$ d_3	ΔE	ε	g_0	g_1	g_0/g_1
Technical pure Fe (AREMA) unannealed	−5·632 ±21	−3·404 ±25	−1·226 ±31	0·531 ±31	2·712 ±22	4·974 ±20	0·658 10·606 ±29	0·692 6·116 ±33	0·695 1·757 ±44	−0·338 ±10	0·009 ±10	3·939 ±27	2·217 ±13	
Electrodeposited Fe unannealed	−5·648 ±28	−3·374 ±33	−1·187 ±30	0·594 ±39	2·762 ±29	5·002 ±28	0·646 10·650 ±40	0·612 6·136 ±44	0·593 1·781 ±49	−0·312 ±13	−0·011 ±13	3·968 ±32	2·220 ±16	
Electrodeposited Fe annealed	−5·618 ±26	−3·358 ±19	−1·194 ±29	0·502 ±24	2·748 ±19	4·972 ±24	0·646 10·590 ±35	0·610 6·106 ±27	0·692 1·696 ±38	−0·321 ±10	−0·002 ±10	3·901 ±23	2·224 ±13	
Ferrite in carbon steel tempered	−5·612 ±30	−3·358 ±28	−1·179 ±31	0·480 ±29	2·774 ±23	4·972 ±33	0·640 10·584 ±45	0·584 6·132 ±36	0·699 1·659 ±42	−0·318 ±13	−0·002 ±13	3·895 ±28	2·231 ±15	
weighted mean value										−0·324 ±6	0·000 ±6	3·921 ±13	2·223 ±7	1·764 ±8
Technical pure Fe (AREMA) unannealed[1])	−5·630	−3·423	−1·199	0·504	2·728	4·969	0·661 10·599	0·695 6·152	0·695 1·704	−0·339 ±14	0·009 ±14	3·928 ±10		1·766 ±7

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[1]) Analysis of the same spectrum as in the first row as a whole by means of the least squares method (for comparison). The values v_1 to v_6 and s_1, s_2, s_3, d_1, d_2, d_3 are already smoothed and fit precisely together with the values of ΔE, ε, g_0 and g_1.

From the resulting values in Tab. 2 we obtain for the ratio of the magnetic splittings $g_0/g_1 = 1{\cdot}764 \pm 0{\cdot}008$, i.e. according to (4.6) the quantity $|\mu_1/\mu_0| = 1{\cdot}701 \pm 0{\cdot}008$. When taking the value $\mu_0 = (0{\cdot}09024 \pm 0{\cdot}00007)\, \mu_n$ [12, 13] (μ_n is the nuclear magneton) for the ground state magnetic moment of Fe^{57} we obtain $|\mu_1| = (0{\cdot}1535 \pm \pm\, 0{\cdot}0007)\, \mu_n$. According to the first equation from (2.3) by using the constants from [14] and the value of $E_\gamma = (14.39 \pm 0.01)$ keV [13], we get the internal field intensity

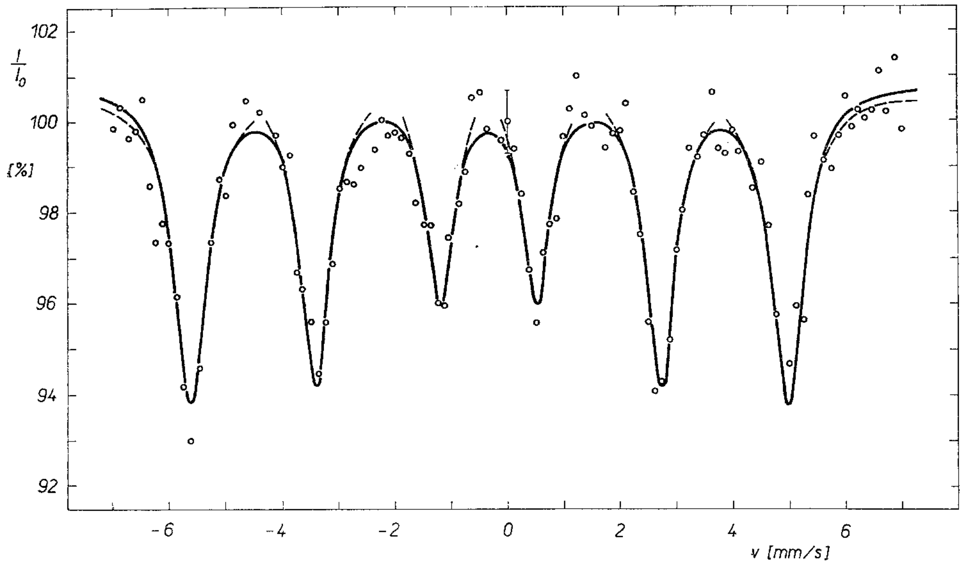

Fig. 3. The Mössbauer spectrum of metallic technical pure iron (AREMA) evaluated by means of the least squares method as a whole (full line) and as line pairs (dashed line). v — relative velocity between source and absorber, I/I_0 — counting rate relative to that for $v = 0$.

at the iron nucleus $H_i = (329{\cdot}4 \pm 1{\cdot}2)$ kOe. The coefficient of proportionality between the internal field intensity and the distance of the outermost lines in the spectrum according to Eqs. (2.3) and (4.8) is

$$(5.1) \qquad \frac{H_i}{d_1} = \frac{1}{2(|\mu_0| + |\mu_1|)} = (31{\cdot}24 \pm 0{\cdot}10)\,\text{kOe/mm s}^{-1}\,.$$

From Tab. 2 it can also be seen that in the limits of errors the quadrupole splitting is zero, in agreement with the cubic symmetry of the metallic α-iron lattice.

The given results except of H_i are not influenced by the correction for the geometry of measurements and the cam rise; this slight correction, that is of the same magnitude in all our cases (-0.41 %), has been made for the final values of H_i only.

Furthermore, a series of measurements of the outer sections of velocity spectra was carried out and by means of the above-mentioned method (on the assumption of equally deep outermost absorption lines) the distance of their minima d'_1 was derived (the dash means the correction for the geometry of measurements and the cam rise). The results of these measurements are summarized in Tab. 3. As can be seen from the weighted mean values, the unannealed electrodeposited iron exhibits a higher value of d'_1, i.e. of H_i. The relevant values of d'_1 were therefore not taken into account in further evaluation and the question of the origin of this higher value of H_i will be the subject of another study.

Tab. 3

Results of measurements of distances between the outermost lines in the metallic iron spectra. Values d'_1 are corrected for the geometry of measurement and the cam rise.

Material	d'_1 [mm s^{-1}]	$\delta(d'_1)$ [mm s^{-1}]	$\overline{d'_1}$ 1) [mm s^{-1}]	$\delta'(\overline{d'_1})$ [mm s^{-1}]
Technical pure Fe (AREMA), annealed	10·586	0·045		
Technical pure Fe, unannealed	10·562	0·029		
ditto	10·602	0·037		
Ferrite in carbon steel, tempered	10·549	0·034		
ditto	10·542	0·035		
ditto	10·540	0·045		
Electrodeposited Fe, annealed	10·546	0·035		
ditto	10·588	0·033	10·564	0·013
Electrodeposited Fe, unannealed	10·580	0·026		
ditto	10·601	0·016		
ditto	10·606	0·039		
ditto	10·590	0·040		
ditto	10·614	0·040		
ditto	10·589	0·018	10·594	0·010

1) weighted mean values.

From the first group of measurements shown in Tab. 3, the value $H_i/d'_1 = (31{\cdot}18 \pm 0{\cdot}13)$ kOe/mm s^{-1} is also obtained which is in good agreement with the above-mentioned value obtained from the measured nuclear moments.

The results of our measurements are given in Tab. 4 in comparison with the results compiled from the literature. We can see that, especially in view of the relative simplicity of elaborating these not very precise starting measurements, the obtained values are in good agreement with the quoted ones.

Tab. 4

Comparison of measured quantities for Fe^{57} from different sources. Unless otherwise stated, the measurements were done for metallic iron at room temperature.

Source	g_0/g_1	$\lvert\mu_1/\mu_0\rvert$	$\lvert\mu_1/\mu_n\rvert$	H_i [kOe]	d [mm s^{-1}]
Hanna et al. [1]	1·78[1] ±5	1·69[1] ±2	0·153 ±4	333 ±10	10·65[1]
Kistner, Sunyar [2]	1·77[2] ±2	1·69[1] ±2			
Nagle et al. [15]				333[1]	10·64[3]
Shirane et al. [16]				334[1] ±2	10·67 ±8
Booth, Violet [17]	1·75[1] ±1	1·72[4] ±1			
Nikolajev et al. [18]	1·78[5] ±15	1·69[1] ±15			
Benedek, Armstrong [19]				330·5[6]	
Preston et al. [9]	1·750[1] ±4	1·715[7] ±4	0·1549 ±13	330 ±3	
Perlow et al. [5]	1·7508 ±15	1·7135[8] ±15			
Muir et al. [11][9]	1·76[1]	1·71[1]	0·154		
Present paper	1·764 ±8	1·701 ±8	0·1535 ±7	329·4 ±1·2	10·564 ±13

[1] recalculated value.
[2] measured for Fe_2O_3.
[3] without correction for geometry.
[4] measured at 80°K.
[5] measured for $FeSn_2$.
[6] measured by the NMR method.
[7] mean value of measurements from 4 to 913°K.
[8] measured for metallic Co.
[9] critical values.

6. CONCLUSION

The position analysis of Mössbauer six-line spectra of the transition $I = \frac{3}{2} \rightarrow I = \frac{1}{2}$ was made from the point of view of the precision of measurements to eliminate their incidental errors. We considered neither the way of obtaining the starting positions of the lines nor the influence of systematic errors. The results were derived on the assumption of the presence of both magnetic and quadrupole splittings for a more general case and for some special cases.

From the above analysis it follows that it is advantageous to calculate the parameters of such spectra from the line positions according to the equations derived in Sec. 3; then the errors of parameters are smallest. In the special cases (see Sec. 4) we can use the coefficients given in Tab. 1. For more complicated Mössbauer spectra than in these examples, the shape of which has been calculated under less special conditions (see e.g. [20, 21]), it is most convenient to use either the general formulae from Sec. 3 or the first method mentioned in the Introduction, their use depending on whether the spectrum is well resolved and the line positions can be described by Eq. (2.8).

The values of the parameters ΔE, ε, g_0 and g_1 (or some of these) are quite normally evaluated from Mössbauer measurements. According to the Introduction they are obtained either by the least squares analysis of the whole spectrum, which is more demanding as regards computing technique (e.g. [5, 9]), or by means of a second method similar to that proposed above. However, the calculations are either not described or they are made without respect to the precision of the starting quantities (cf. [1, 2, 16]). The present paper is an attempt to give a precision analysis of this problem.

The validity of our conclusions was proved for metallic iron spectra. The elaboration of the measurements by means of the proposed method showed that, on the very general assumptions, a position analysis of six-line velocity spectra can be performed with good results by a relatively simple method. A programme for the MINSK-22 computer was prepared which quickly gives the values of ΔE, ε, g_0 and g_1 and their errors from measured line positions $v_1 \pm \delta(v_1)$ etc. according to Eqs. (3.1) and (3.4) to (3·9). These equations are very convenient for practical purposes due to their explicit form.

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APPENDIX

We are seeking the solution of the system of equations

$$\begin{aligned} x_1 &= \alpha_1 y + \beta_1 z \\ x_2 &= \alpha_2 y + \beta_2 z \\ x_3 &= \alpha_3 y + \beta_3 z \end{aligned} \tag{A 1}$$

for unknown y, z, where the values of x_1, x_2, x_3 are loaded with the errors $\delta_1, \delta_2, \delta_3$. The condition demands that the values of y, z have minimum possible error.

The assumed solution can be expressed in the form of a linear combination

$$y = a_1 x_1 + a_2 x_2 + a_3 x_3 \tag{A 2}$$

with the conditions

$$\begin{aligned} \alpha_1 a_1 + \alpha_2 a_2 + \alpha_3 a_3 &= 1 \\ \beta_1 a_1 + \beta_2 a_2 + \beta_3 a_3 &= 0 \end{aligned} \tag{A 3}$$

and similarly for z.

The condition for minimum error of y is

$$\delta^2 y = a_1^2\delta_1^2 + a_2^2\delta_2^2 + a_3^2\delta_3^2 = \min. \tag{A 4}$$

This, together with the conditions (A 3) (when solving the problem with the Lagrange method of uncertain coefficients λ, μ), leads to the system of equations for the unknown $a_1, a_2, a_3, \lambda, \mu$

$$\begin{array}{ccccccl} 2a_1\delta_1^2 & & & + & \alpha_1\lambda + \beta_1\mu & = 0 \\ & 2a_2\delta_2^2 & & + & \alpha_2\lambda + \beta_2\mu & = 0 \\ & & 2a_3\delta_3^2 & + & \alpha_3\lambda + \beta_3\mu & = 0 \\ \alpha_1 a_1 + & \alpha_2 a_2 + & \alpha_3 a_3 & & & = 1 \\ \beta_1 a_1 + & \beta_2 a_2 + & \beta_3 a_3 & & & = 0\,. \end{array} \tag{A 5}$$

When assigning $(i, j = 1, 2, 3)$

$$\varDelta_{ij} = \begin{vmatrix} \alpha_i & \alpha_j \\ \beta_i & \beta_j \end{vmatrix} \tag{A 6}$$

the determinant of the system (A 5) can be expressed in the form

$$D = 2(\delta_1^2\varDelta_{23}^2 + \delta_2^2\varDelta_{31}^2 + \delta_3^2\varDelta_{12}^2) \tag{A 7}$$

and the conjugated determinants in relation to the unknown a_1, a_2, a_3 in the form

$$D_1 = 2(\beta_2\delta_3^2\varDelta_{12} - \beta_3\delta_2^2\varDelta_{31}) \tag{A 8}$$

and similarly for D_2, D_3 by cyclic permutation.

The solution for a_1 is therefore

$$a_1 = \frac{\beta_2\delta_3^2\varDelta_{12} - \beta_3\delta_2^2\varDelta_{31}}{\delta_1^2\varDelta_{23}^2 + \delta_2^2\varDelta_{31}^2 + \delta_3^2\varDelta_{12}^2} \tag{A 9}$$

and similarly for a_2, a_3 by cyclic permutation. A similar solution can be found for the unknown z.

The value of the error δy can be obtained by substituting a_1 from Eq. (A 9) and from the equations for a_2, a_3 into Eq. (A 4), and similarly for δz.

The solution of the system of equations

$$x_1 = \alpha_1 y + \beta_1 z \qquad \text{(A 10)}$$
$$x_2 = \alpha_2 y + \beta_2 z$$

for the unknown coefficients a_1, a_2 in the linear combination

$$y = a_1 x_1 + a_2 x_2 \qquad \text{(A 11)}$$

has the form

$$a_1 = \beta_2 / \Delta_{12} \,, \quad a_2 = -\beta_1 / \Delta_{12} \qquad \text{(A 12)}$$

which is the limit case of the solution (A 9) for $\delta_3 \to \infty$.

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