

Contents

1	Introduction	1
2	Parameter	2
3	The measurements	4
4	Ambiguity	5
4.1	Shallow χ^2 -minimum	7
4.2	Powder spectrum	7
4.3	Polarized source	9
5	Xray msd-tensor	12
6	Bull et al. msd-tensor	13
7	Conclusion	14

1 Introduction

The PhD-student James Bull of Craig Tennant did the accurate Mossbauer measurements on a single crystal of Ferrous ammonium sulphate hexahydrate (This crystal is now in the KFKI Lab - Zoltan Nemeth). The spectra were evaluated utilising the intensity tensor formalism introduced first by Zimmermann [1] and in parallel with the Mossbauer routine of effi. The comparison was always difficult, since the Mossbauer routine does not know intensities, areas and line broadenings by thickness effects. To have the orientation of the tensors (msd and EFG) in the crystal in the language of the computer program MOSREF of Craig and the Mossbauer routine in effi took some time.

The PhD-work has been published [5]. There it is written: "We believe that we have obtained, possibly for the first time, an unambiguous solution to the ambiguous" monoclinic case where the Mossbauer nucleus does not sit on a 2-fold axis."

One aim was the comparison of the X-ray-determined atomic-displacement parameters (ADPs) for the iron nucleus with the msd-tensor determined from Mossbauer measurements.

The authors state: The msd-tensor differ considerably from the values

of the X-ray measurement.

The Zimmermann procedure is labour-intensive. The areas of the quadrupole lines are fitted spectrum by spectrum. Thickness correction is done iteratively. Error propagation is a problem, such that the inspection of a manifold of solutions compatible within error limits is almost impossible.

The simultaneous fit of the tensors directly to the measurements without approximations which need corrections in a further procedure (the convolution integral is always included) makes it easy to explore possible manifolds. Such manifolds are indeed discovered. It turned out that all measurements on a cone of a 2π circle cannot fix the parameter space to a point but an infinite number of solutions is left.

The measurement parallel to the axis of the cone fixes the parameter space to a point, but the χ^2 surface is so shallow at least in one direction (as a result of the still large error of spectra with 10^6 counts), that further measurements are necessary. The hope was and is that the polarized source fixes the problem.

2 Parameter

Ferrous ammonium sulphate hexahydrate (FAS) crystallizes in the monoclinic space group P 21/c with two crystallographically equivalent Fe-sites related by a rotation π (C_2) about the unique axis, b. b shall be the z-axis of a cartesian coordinate system attached to the unit cell with axes (a, b, c). c is chosen to be the y-axis. The second rank tensors attached to the two equivalent sites of the unit cell differ from the the sign of the xz and yz elements. So there are 4 possibilities to attach 2 tensors to one crystal site. Since always the signal of both sites is measured, the experiment can decide only between two possibilities.

The EFG-tensor and the anisotropic msd-tensor effect the Mossbauer spectrum. Lets fix the EFG-tensor

$$(V) = V_{zz} \cdot R(\omega) \begin{pmatrix} -\frac{1}{2}(1 - \eta) & & \\ & -\frac{1}{2}(1 + \eta) & \\ & & 1 \end{pmatrix} R^{-1}(\omega) \quad (1)$$

to site 1. The rotation matrix $R(\omega)$ at site 1 with Euler angle $\omega =$

(ϕ, θ, ψ) changes to $\omega = (\phi + \pi, \theta, \psi - \pi)$ at site 2.

The Lamb-Mossbauer factor $f(\mathbf{k})$ at site 1 in the direction \mathbf{k}

$$f(\mathbf{k}) = e^{-\mathbf{k} \cdot \langle \mathbf{X}^2 \rangle \cdot \mathbf{k}^\dagger} \quad (2)$$

is calculated from the symmetric msd-tensor $\langle \mathbf{X}^2 \rangle$

$$\langle \mathbf{X}^2 \rangle = \begin{pmatrix} X2_{xx} & X2_{xy} & X2_{xz} \\ & X2_{yy} & X2_{yz} \\ & & X2_{zz} \end{pmatrix} \quad (3)$$

at site 2 the elements $X2_{xz}, X2_{yz}$ are replaced by $-X2_{xz}, -X2_{yz}$. From X-ray structure the msd-tensor is attached to a site characterized by the positions of the atoms from which the EFG-tensor at that site can be calculated [2]. Mossbauer measurements directly decide which of the two msd-tensors belongs to the EFG-tensor assigned to site 1.

The matrix of the msd-tensor is split into a sum of three matrices ($\underline{1} :=$ unit matrix).

$$= \frac{1}{3} \text{Tr}(\langle \mathbf{X}^2 \rangle) \cdot \underline{1} + \begin{pmatrix} XX & X2_{xy} & 0 \\ & YY & 0 \\ & & ZZ \end{pmatrix} + \begin{pmatrix} 0 & 0 & X2_{xz} \\ & 0 & X2_{yz} \\ & & 0 \end{pmatrix} \quad (4)$$

The two matrices with offdiagonal elements are diagonalized by rotation matrices D with Euler angles $\omega_i = (\phi_i, \theta_i, \psi_i)$.

$$= \frac{1}{3} \text{Tr}(\langle \mathbf{X}^2 \rangle) + dx2 \cdot D(\omega_1) \begin{pmatrix} -\frac{1}{2}(1 - \eta) & & \\ & -\frac{1}{2}(1 + \eta) & \\ & & 1 \end{pmatrix} D^\dagger(\omega_1) \quad (5)$$

$$+ dsx2 \cdot D(\omega_2) \begin{pmatrix} 0 & & \\ & -1 & \\ & & 1 \end{pmatrix} D^\dagger(\omega_2)$$

The 6 msd-parameter are now expressed by the trace $\text{Tr}(\langle \mathbf{X}^2 \rangle)$, η , $dx2$, $dsx2$, and the two Euler angles $\omega_1 = (\phi_1, 90, 0)$ and $\omega_2 = (\phi_2, 45, 90)$ which depend on the two angles ϕ_1 and ϕ_2 . The tensor with the prefactor $dx2$ has the symmetry C_{2z} , the symmetry of the crystal and is the same for both sites. $dsx2$ has opposite signs for the two sites related by

the C_{2z} -rotation.

The 5 parameters of the traceless EFG-tensor and the 6 parameters of the msd-tensor are listed in Table 1. There are two further parameters which turned out to be necessary to fit the spectra. These are the widths of the two absorption lines of the quadrupole spectra which are somewhat broadened. This broadening is expected to be relaxation broadening as observed for other Fe^{2+} -compounds. The broadening of the quadrupole lines of ferrous fluosilicate was identified as relaxation broadening by D.C. Price [3]. In the fast relaxation limit the lineshape is Lorentzian and different for the two absorption lines, so that there are two further parameters: Lw_L and Lw_H , for the low and high velocity line.

EFG:	V_{zz}	η	ϕ	θ	ψ	
msd:	$\langle \mathbf{X}^2 \rangle$	$dx2$	η_{msd}	ϕ_1	$dsx2$	ϕ_2
Line-width:	Lw_L	Lw_H				

Table 1: The parameters of the EFG- and msd-tensors. V_{zz} can be replaced by the quadrupole splitting carrying the sign. $\langle \mathbf{X}^2 \rangle$ is replaced by the isotropic part of the f-factor $f_{isotrop} = exp(-\langle \mathbf{X}^2 \rangle / 3)$

3 The measurements

FAS crystallizes as flat plates containing the $(\bar{2}01)$ plane of the crystal. The crystal is rotated in steps of 20° about an axis perpendicular to the $(\bar{2}01)$ plane and inclining an angle 45° with gamma beam, which then traces out a right (circular) cone in the crystal. The period of 2π requires 18 measurements with the step width of 20° .

The background fraction was carefully determined using a 0.25mm Cu filter in 45° orientation giving a thickness $d=0.354$ mm which absorbs the 14.4keV completely ($I(d)/I(0) \approx 10^{-13}$). With the attenuation coefficients $\mu(122keV) = 2.676cm^{-1}$ and $\mu(136keV) = 2.230cm^{-1}$ the intensity ratios are $I(d)/I(0) = 0.9096$ for 122keV(90.6%) and $I(d)/I(0) = 0.9241$ for 136keV(9.4%). The ratio of both high energy γ together ($I(d)/I(0) = 0.094 \times 0.9241 + 0.906 \times 0.9096 = 0.911$) is needed to correct the number of counts N_{Cu} with the filter to $N_H = N_{Cu}/0.911$, the number of high energy γ of the source which are responsible for the background of nonresonant γ 's in the 14.4keV energy window. The

ratio of N_H divided by the counts without filter gives the background fraction determined to be `bg_fraction=0.0831`.

For the measurement number 19, γ -direction perpendicular to the $(\bar{2}01)$ plane, the `bg_fraction` has not been explicitly measured.

The measurement of a powder absorber should show the Goldanskii-Karjagin effect, a small asymmetry of the quadrupol doublet. A powder absorber of 0.25mm thickness was measured also in 45° orientation (the angle is not far from the magic angle $\delta = 54.7^\circ$ of $\cos\delta=1/\sqrt{3}$). The background fraction of this measurement is also not known.

4 Ambiguity

When starting the simultaneous fits of the 18 spectra on the cone no line broadening was introduced. The spectra could not be fitted with natural linewidth ($\Gamma = 0.097mm^{-1}$) and a `bg_fraction=0.083`. An excellent fit of $\chi^2 = 1.03$ over all spectra was obtained with a much larger `bg_fraction` of 0.23. Allowing for line broadening changes the situation and an even slightly better fit ($\chi^2 = 1.012$) is obtained using the measured `bg_fraction=0.083`.

The fit for the 18 spectra at any fixed pair (η , `dx2`) runs into a minimum of the same (within numerical uncertainty) value of $\chi^2=1.012$. For 3 values of `dx2` the fit parameters are listed in Table 2. The parameter set

<code>dx2</code>	ϕ	θ	ψ	$f_{isotrop}$	η_{msd}	ϕ_1	<code>dsx2</code>	ϕ_2	Lw_L	Lw_H
-0.13	131.3	80.8	-14.8	0.284	1.072	84.1	-0.132	-92.5	0.056	0.051
-0.20	131.3	80.6	-14.9	0.272	0.112	109.7	-0.092	-79.5	0.056	0.053
-1.00	131.5	79.9	-16.1	0.219	-0.035	132.8	-0.069	-75.2	0.056	0.053

Table 2: The 10 fit parameters (`dx2` and $\eta = 0.8$ are fixed) of the 18 spectra on the cone at the same minimum value of $\chi^2 = 1.012$.

for the unphysically large value `dx2=-1.0` is also listed. The χ^2 -valley in direction of `dx2` is indeed absolutely flat (χ^2 always reaches 1.012 and we have an infinite number of solutions).

As next step the spectrum measured perpendicular to the crystal plate (number 19) has been taken into consideration. The χ^2 -values with `bg_fraction=0.083` (black curve) and when fitting the `bg_fraction` (red curve) are shown in Fig. 1. The 18 cone-spectra are fitted with the η -value fixed to 0.8 and the value of `dx2` to values between -0.20 and

-0.13 and 10 fit parameters, the orientation of the EFG-tensor(3), 5 msd-parameters and the two linewidths (see Table 1). V_{zz} is not a fit parameter any more as the well defined quadrupole splitting fixes this value by the value of η .

At each minimum (specified by η and $dx2$) the spectrum perpendicular to the plate of the crystal is fitted with one parameter, the `bg_fraction`. The χ^2 -value and the `bg_fraction` are plotted in red color in Fig. 1. Over the whole range ($-0.2 \leq dx2 \leq -0.13$) the value of χ^2 is less than 1.040. This figure clearly demonstrates the necessity of the determination of the `bg_fraction`. The black line shows the values of χ^2 if the `bg_fraction`=0.083 is fixed to the value of the 18 spectra on the cone.

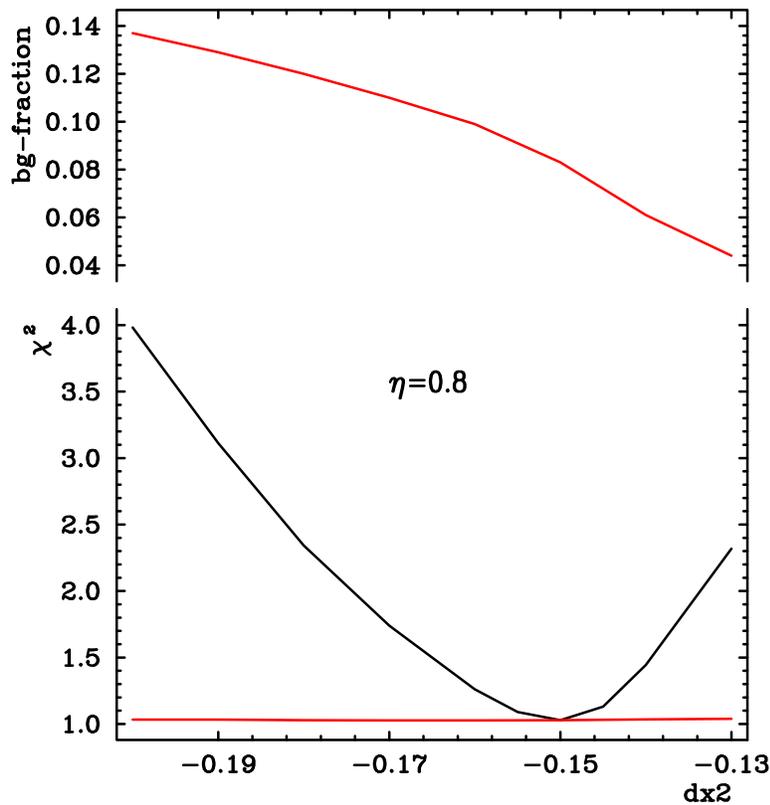


Figure 1: χ^2 and `bg_fraction` of the spectrum with the γ -direction perpendicular to the crystal plate is plotted versus `dx2`. Red curve: `bg_fraction` fitted; Black: `bg_fraction`=0.083. All other parameters (see Table 2) are determined by the fit of the 18 spectra on the cone.

4.1 Shallow χ^2 -minimum

Now let's stay on the minimum at $dx_2=-0.15$, which is a minimum of all 19 spectra if the $bg_fraction=0.083$ is also true for spectrum number 19 (perpendicular to the crystal plate), and vary the η -value. The result is shown in Fig. 2.

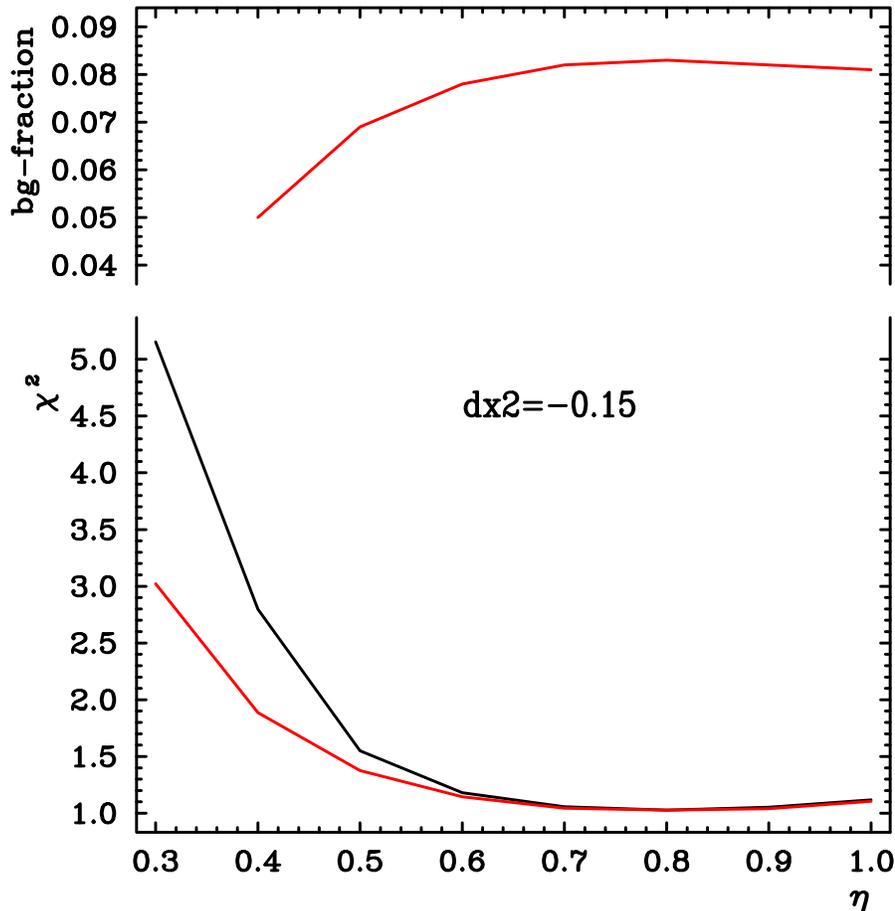


Figure 2: χ^2 and $bg_fraction$ of the spectrum with the γ -direction perpendicular to the crystal plate plotted versus η . Red curve: $bg_fraction$ fitted; Black: $bg_fraction=0.083$. All other parameters are determined by the fit of the 18 spectra on the cone.

In the range $0.7 \leq \eta \leq 1.0$ the χ^2 -value is close to 1 so that with the information contained in all 19 spectra no further restriction of the parameter is possible.

4.2 Powder spectrum

The powder spectrum was measured with an old source (1mCi, original 10mCi) so that the f-factor (reduced by selfabsorption) and the linewidth are unknown. The background fraction of this measurement

(several years ago) is also not known. This gives 4 parameters, 2 for the lineshape(Lorentz- and Gauss-broadening: Voigt-profile), the f-factor and background. Since the absorption lines are not polarized and the linewidths are fixed from the fit of the 18 spectra, there are only two further parameters to be fitted: the effective thickness of the absorber and the intensity ratio of the two quadrupole lines, which should be different but close to 1 caused by the Goldanskii-Karyagin effect.

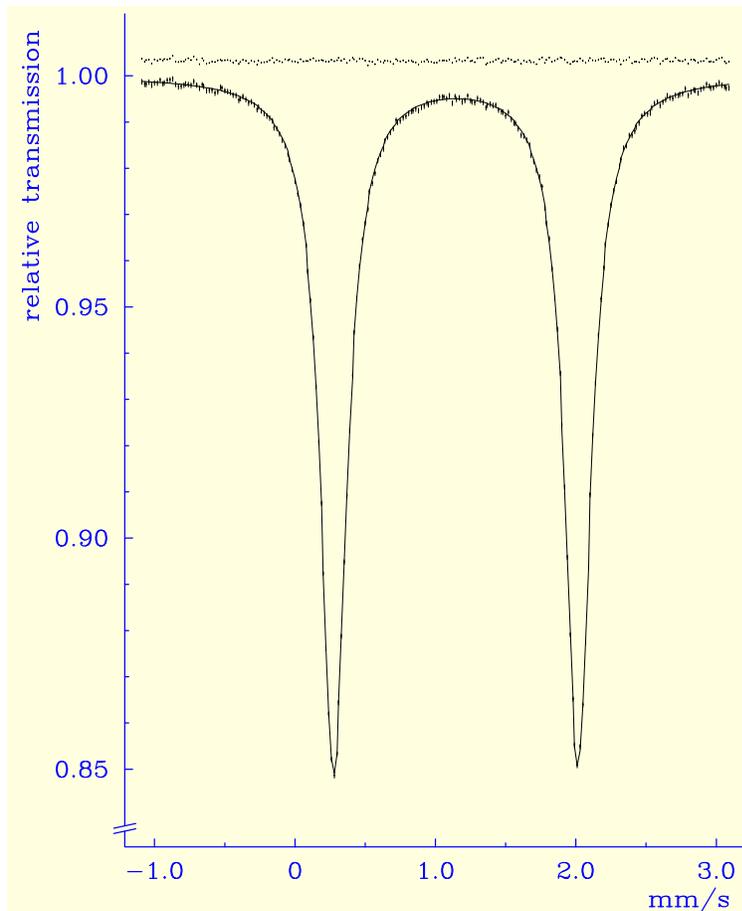


Figure 3: A section (-1 to 3 mm/s) of the powder spectrum in order to visualize the small intensity ratio of 1.014. Since the line widths of the left line is a bit broader (from the fit of the 18 spectra on the cone) the difference of the depths of the absorption line is less enhanced.

The effective f-factor of the old source is expected to be not larger than 0.7 so that the bg fraction is set to 0.100. The fit of the powder spectrum with the parameter of FAS -averaging over the sphere- has no free parameter (apart from nonlinearity parameter and the counts of the baseline) and gives $\chi^2=1.038$, a perfect fit.

bg_fraction:	0.083	0.100	0.125	0.150	0.165	0.175
f_source:	0.69	0.70	0.71	0.72	0.73	0.74
L_broadening:	0.122	0.122	0.121	0.119	0.118	0.116
mg/cm2xf:	2.124	2.149	2.177	2.207	2.212	2.237
left/right_ratio:	1.0146	1.0144	1.0142	1.0142	1.0142	1.0142

Table 3: The parameter bg_fraction is fixed. Gauss-broadening is very close to zero in all cases and is not listed. $\chi^2 = 1.010$ does not depend on the parameter set. The width of the source is $(1 + L_broadening)\Gamma_{natural}$

The powder absorber was 0.25mm in thickness at 45° . The density of the crystal would give a thickness $1.637/0.222*0.25*\sqrt{2}=2.61$ which has to be compared with 2.149 mg/cm2xf (0.222mm thickness of the crystal). The density of the powder is then by a factor 0.82 smaller than the density of the crystal (reasonable? It would have been better to weight the powder).

Leaving the point $\eta = 0.8$ and $dx2=-0.15$ by varying η between 0.7 and 1.0 does not change the χ^2 -value, so that the powder spectrum does not restrict the η -range.

4.3 Polarized source

At the point $dx2=-0.15$ and $\chi^2 = 0.8$ several parameters have been introduced for the magnetized source in order to obtain a reasonable fit. First of all the selfabsorption routine for the simplest case of a δ -distribution at a depth of $d-\mu$ iron has been included in the program. A field distribution consisting of 5 magnetic fields $B, B \pm dB, B \pm 2dB$ with independent weights and a Gauss-broadening for the pairs 1/6, 2/5 and 3/4 are together 9 parameters for 4 spectra. In addition a deviation from exact orientation is allowed, a common angle $d\omega = 4.4^\circ$ of several degrees between the 0-position of the absorber and magnetic field direction and a small angle $d\theta \leq 5.0^\circ$ between the foil of the source and the γ -direction (the angle always fitted to $15 - 20^\circ$ without selfabsorption).

The Gauss-broadening (1.00 gives a linewidth of 0.230 instead of $2 \cdot \Gamma_n = 0.194$) are 1.01, 0.57, 0.47 for pairs 1/6, 2/5 and 3/4, respectively. The field distribution is asymmetric. The weights are 0.003, 0.009, 0.637, 0.230, 0.120 for $B+(-2dB, -dB, 0, dB, 2dB)$, respectively with $B=329.4$ and $dB=3.2$. The fit shown in Figure 4 is absolutely not pleasurable. The value of $d-\mu = 5.99$ (all ^{57}Co is at a depth of about 6μ) suggests that the

source was used from the wrong side (I controlled this together with Zoltan). If the wrong side is true, the δ -distribution is well justified! The deviations shown on the top of the spectra have an antisymmetric shape. This means that the nonlinearity of the drive is well fitted by the six nonlinearity parameter. The reason for the poor fits is the unknown field distribution of the partly polarized iron foil (similar to the situation at DESY). Nevertheless, one can ask for a trend with $\eta = 0.7$ to 1.0 as parameter. Figure 4 shows already the best fit of the η series. The parameter $d\omega$, $d-\mu$, and bg_fraction are fitted for each η -value.

η	0.7	0.8	0.9	1.0
$d\omega$	4.44	2.82	1.41	0.21
$d-\mu$	5.99	5.93	5.89	5.88
bg_fraction*	0.165	0.168	0.170	0.174
χ^2	1.916	1.987	2.135	2.342

Table 4: The bg_fraction are very similar for the 4 spectra, the fit values and the experimental values for N_u/N as well. Therefore only one number - the average bg_fraction* - is listed.

The trend of χ^2 -values as shown in Table 4 point to the lowest η -value. But the large misfits (the large χ^2) classify this trend as very weak. The Lamb-Mossbauer factor of 0.8 from [4] leads to large bg_fractions as compared to the experimental values for N_{Ni}/N between 0.134 to 0.144. The attenuation by the Ni-filter should be about $0.140/0.170=0.82$ to have the fitted bg_fractions of the right size.

This attenuation requires a Ni-foil of about 0.8mm thickness ($Ni \mu(122keV) = 3.03cm^{-1}$, $\mu(136keV) = 2.52cm^{-1}$). The thickness of the Ni-foil was not measured - this can be done. May be another difficulty will arise by this knowledge.

Inspection of the outer line of the 4 spectra shows that with increasing angle the theory calculates too low intensity for these lines. Enlarging the allpol.eps file, this trend is clearly visible.

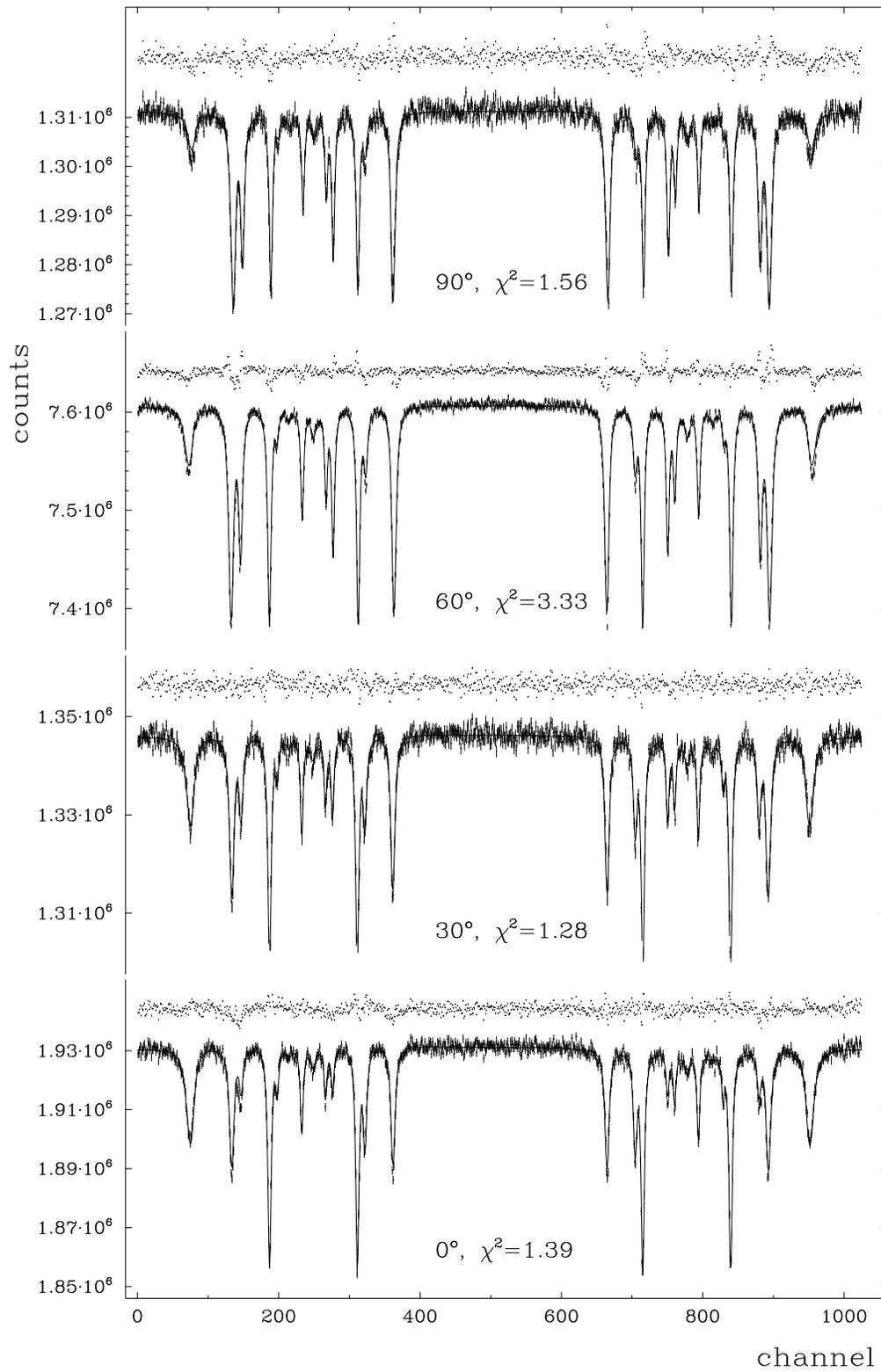


Figure 4: The angle $\phi = 0^\circ, 30^\circ, 60^\circ, 90^\circ$ is between the magnetic field direction of the source and the mirror plane of the FAS-absorber perpendicular to the $(\bar{2}01)$ plane. The spectra are calculated with the parameter fitted to the 18 spectra on the cone with $dx2=-0.15$ and $\eta = 0.7$.

5 Xray msd-tensor

The msd-tensor obtained from X-ray structure measurements multiplied by the square of the 14.4keV- wave number is taken from the combined X-ray ^{57}Fe Mossbauer single crystal study of Bull et al. [5]. The dimensionless matrix

$$\langle k^2 \mathbf{X}^2 \rangle = \begin{pmatrix} 0.96075 & 0.02790 & -0.06703 \\ 0.02790 & 0.75009 & -0.04855 \\ -0.067034 & -0.04855 & 0.91014 \end{pmatrix} \quad (6)$$

is decomposed according to eq.5: $dx_2 = -0.1272$, $\eta_{msd} = 0.4264$, $\phi_1 = 82.58^\circ$, $dsx_2 = -0.08277$, $\phi_2 = 144.08^\circ$. Only ϕ_2 really differs from the values of Table 2.

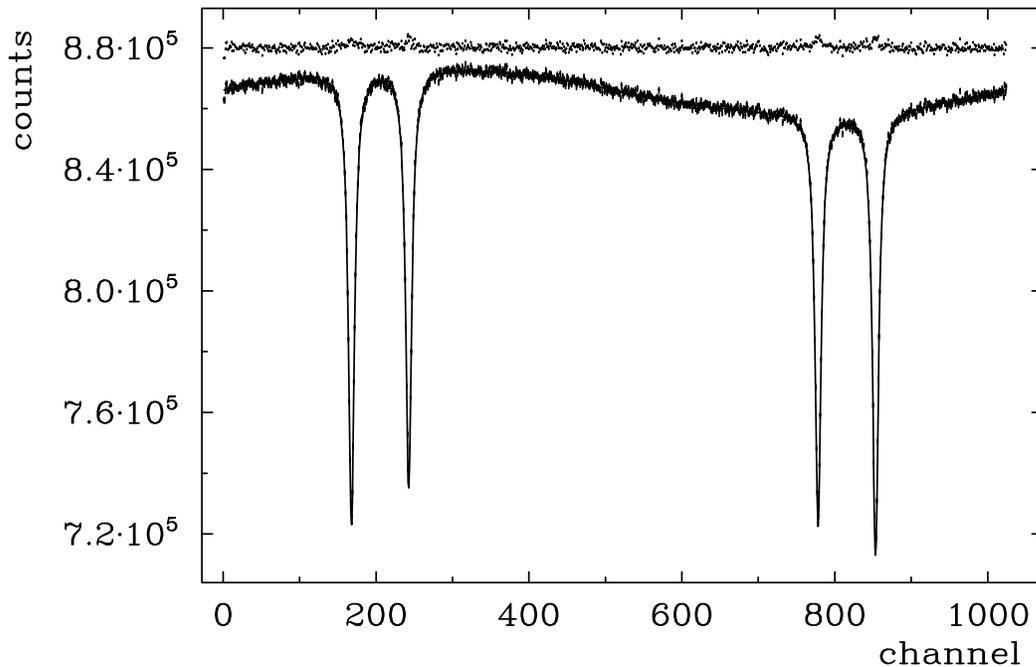


Figure 5: The fit of the EFG-tensor(3, η_{00} fixed), the 2 line widths and $f_{isotrop}$ (1) (= 6 parameters) with msd-tensor elements as obtained from X-ray measurements (except for the trace) the χ^2 -value for spectra 1-19 is not too bad: $\chi^2(1-19) = 1.14$. Spectrum number 13 (this figure) has the largest deviation from theory: $\chi^2 = 1.419$. The deviation is only visible plotting the difference shown on the top of the figure

The dependency of χ^2 on the Euler angle ϕ_2 is weak. Varying ϕ_2 between 0 and 360° χ^2 varies between 1.136 and 1.184, see red curve in Fig.6. The variation looks much more significant if χ^2 is close to 1 (black curve), the solution $dx_2 = -0.15/\eta = 0.8$. The red curve has two minima, the second one at 270° agrees with the minimum of the black

curve. It would be interesting to see the curve $\chi^2(\phi_2)$ of the fit to the X-ray data.

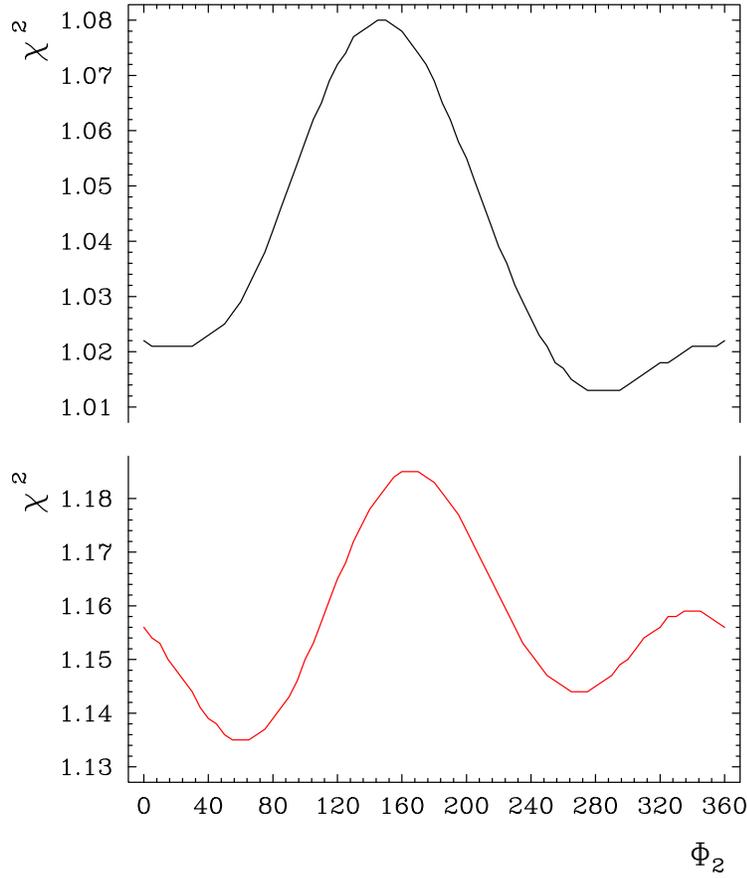


Figure 6: χ^2 -values dependent on the angle ϕ_2 for spectra 1-19 at the point $dx_2=-0.15$ and $\eta = 0.8$

6 Bull et al. msd-tensor

The msd tensor published by Bull et al. [5] is the dimensionless matrix

$$\langle k^2 \mathbf{X}^2 \rangle = \begin{pmatrix} 1.218 & -0.019 & -0.395 \\ -0.019 & 0.956 & 0.286 \\ -0.395 & 0.286 & 1.171 \end{pmatrix} \quad (7)$$

which is decomposed according to eq.5:

$$dx_2 = -0.160, \eta_{msd} = 0.302, \phi_1 = 94.13^\circ, dsx_2 = -0.487, \phi_2 = 215.9^\circ.$$

The local intensity tensor \mathbf{P} is proportional to the Efg-tensor of one site.

$$\langle P \rangle = \begin{pmatrix} 0.0004 & -0.1788 & -0.001 \\ -0.1788 & -0.0781 & -0.094 \\ -0 - 0.001 & -0.094 & 1.171 \end{pmatrix} \quad (8)$$

η and the Euler angle of the EFG-Tensor are obtained from \mathbf{P} . $\eta = 0.5199$, $\phi = 126.7^\circ$, $\theta = 76.69^\circ$, $\psi = 213.98^\circ$

The simulation of the 19 spectra gives a $\chi^2 = 2.152$ which is larger than the X-Ray solution with a fitted EFG with $\eta = 0.8$ fixed.

The local anisotropy $ds^2 = -0.487$ due to molecular vibrations (high frequency) is much larger than the Debye part ($ds^2 = -0.160$). This is an unreasonable result.

7 Conclusion

All discussed parameter sets are based on Fig 1, on the assumption that the bg_fraction of spectrum 19 is 0.083. If Craig cannot confirm this value, it can still be measured with the original crystal (in Budapest/Zoltan).

The powder spectrum can also be repeated to make sure the excellent agreement found.

The source seems to be used from the wrong side. We can measure with both sides and look for the difference. Some information about the diffusion profile could be gained.

The best would be to run the polarimeter in order to have a well defined magnetization of the source. A high quality fit of the 4 spectra is a challenge.

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