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Line shape of ^{57}Co sources exhibiting self absorption

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Abstract The effect of selfabsorption in Mössbauer sources is studied in detail. Spectra were measured using an old $^{57}Co/Rh$ source of $74\,MBq$ activity with an original activity of ca. $3.7\,GBq$ and a $0.15\,GBq$ $^{57}Co/\alpha - Fe$ source magnetized by an in-plane magnetic field of $0.2\,T$. The $^{57}Co/\alpha - Fe$ source of a thickness of $25\,\mu$ was used both from the active and the inactive side giving cause to very different selfabsorption effects. The absorber was a single crystal of ferrous ammonium sulphate hexahydrate (FAS). Its absorption properties were taken over from a detailed study (Bull et al., Hyperfine Interact. **94**(1–3), 2009; Spiering et al. 2016). FAS (space group P21/c) crystallizes as flat plates containing the ($\bar{2}$01) plane. The γ-direction was orthogonal to the crystal plate. The ^{57}Co atoms of the $^{57}Co/Rh$ source were assumed to be homogeneously distributed over a $6\,\mu$ thick Rh foil and to follow a one dimensional diffusion profile in the $25\,\mu$ Fe-foil. The diffusion length was fitted to $10\,\mu$. The theory follows the Blume-Kistner equations for forward scattering (Blume and Kistner, Phys. Rev. **171**, 417, 1968) by integrating over the source sampled up to 128 layers.

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1 Introduction

So far the effect of selfabsorption getting important with the age of the single line source or in case of ^{57}Co diffused in α-iron for a polarized 6 line source has not been factored in calculations of the lineshape and the density matrices of the emission lines. The work of Odeurs and Hoy [4] lead Rusanov et al. [5] to a detailed discussion of the effect of selfabsorption and the observed linewidth of $^{57}Co/Rh$ sources in general. The measured linewidth of a transmission experiment of a Rh foil from an old (about 20 times the half life) $^{57}Co/Rh$ Mössbauer source was in good agreement with their calculations. They calculated an increase of the line width of a source of typical dimension to be about 0.0004 mm/(s mCi) due to self-absorption broadening.

The emission lines distorted by selfabsorption are not only subject to a broadening but also the shape of the lines are not any more Lorentzian. The absorption of resonant radiation reduces the f-factor of the source and moreover changes the meaning of the background fraction needed for the determination of the f-factor of the absorber. The situation is even worse for measurements with a polarized source of $^{57}Co/\alpha-Fe$. The natural abundance of ^{57}Fe of 0.0214 gives for 1μ of iron foil an effective thickness of 0.465·f. The f-factor of polycrystalline iron foils was measured in the temperature range of 4.2K up to 400K by W. Sturhahn and A. Chumakov [6]. The value at RT is f=0.80 such that the effective thickness of 1μ iron becomes $t_{eff} = 0.372$. If the diffusion depth is large enough emission lines will be absorbed dependent on their polarization and intensity. The overlap regions where the polarization is weak give rise to appreciable distortion of the shape of the whole spectrum.

We present 3 measurements. The one with a single line of a former $3.7 GBq$ source ties up the discussion of Rusanov et al. [5]. The two measurements with a polarized α-Fe foil as a source provide a good test of the theory since the thickness reaches a value of 25·0.372=9.3 for the activity on the surface in case of the inactive side towards the absorber.

The absorber was a single crystal of ferrous ammonium sulphate hexahydrate (FAS) which absorption properties were taken over from a detailed single crystal study [1, 2]. FAS (space group P21/c) crystallizes as flat plates containing the $(\overline{2}01)$ plane and the C_2 symmetry axis. A series of 19 measurements of different directions of a single crystal of $0.600 mm$ thickness was published by Bull et al. [1]. They determined the electric field gradient tensor (EFG) and mean squared displacement tensor (MSD) of the two equivalent sites per unit cell related by the 2-fold axis. The evaluation of the 19 spectra used the method introduced in the eighties by R. Zimmerman and R. Doerfler [7, 8].

This series was repeated with a thinner crystal of $0.222 mm$. These measurements now have been simultaneously fitted with the program package EFFI [9]. The result obtained has a shallow χ^2 minimum which allows for η values of the EFG from $0.6 \leq \eta \leq 0.9$ [2].

This manifold, however, has the property, that the density matrices of the two transitions in the γ-direction orthonormal to the crystal plate within the error is independent of η. Therefore it seemed to be useful to repeat the old measurement of T.C. Gibb [10] from 1975 with a polarized source in order to test the polarization of the FAS-crystal. W.C. Tennant kindly ceded the single crystal used for these measurements. Very soon we became aware of the selfabsorption problem and started further measurements including those mentioned above.

2 Theoretical considerations

2.1 The effective Lamb-Mössbauer factor of the source

The density matrix $\rho_s(E)$ of the source is the sum of Lorentzians multiplied by transition matrices r_α of the resonance lines at energy E_α:

$$\rho_s(E) = \frac{2}{\Gamma\pi} \sum_\alpha \frac{1}{2} r_\alpha \cdot \frac{(\Gamma/2)^2}{(E - E_\alpha)^2 + (\Gamma/2)^2} \tag{1}$$

$$1 = Tr \int_{-\infty}^{\infty} \rho_s(E) dE$$

The total intensity, the trace of the sum over all Lorentzians, is normalized to 1. Γ is the natural linewidth. The radiation travels through a material of refraction index $\mathbf{n}(E)$

$$\mathbf{n}(E) = \underline{1} - \frac{\sigma f(\mathbf{k})}{2k} \sum_j N_j \sum_i R_i^j \cdot \frac{\Gamma/2}{E - E_i^j + i\Gamma/2} \tag{2}$$

and changes $\rho_s(E)$ from position 0 to a depth z to:

$$\rho(E, z) = e^{i\mathbf{n}kz} \rho_s(E) e^{-i\mathbf{n}^\dagger kz} \tag{3}$$

$\underline{1}$ is the unit 2x2 matrix, σ the cross section, $f(\mathbf{k})$ the Lamb-Mössbauer factor in direction of wave vektor $\mathbf{k}$, N_j the density of nuclei of type j and R_i^j the transition matrix belonging to energy E_i^j. In case of absorption by the ^{57}Fe-ground states in the source material the R_i^j are the r_α of one of the indices α. For a single line source the intensity at z=d and energy E_0 reduces to

$$Tr(\rho(E, z)) = \frac{\Gamma/2\pi}{(E - E_0)^2 + (\Gamma/2)^2} e^{-\sigma f(\mathbf{k}) Nd \frac{(\Gamma/2)^2}{(E-E_0)^2+(\Gamma/2)^2}} \tag{4}$$

Apart from the electronic absorption factor $exp(-\mu_e z)$ which will be included later (4) is the starting point of the calculations of Rusanov et al. [5].

Several simplifications for the selfabsorption of a ^{57}Co in α-iron and Rh-matrix are introduced. First of all the f-factor is taken to be isotropic. The profile of the distribution of the ^{57}Co diffused into the Rh-matrix is simplified to a uniform distribution (as in [5]) and in the α-iron foil to 1-dimensional diffusion profile (see Section 2.2). The integrations will be approximated by summations over up to 128 integration points.

The Lamb-Mössbauer factor f for the source function $\rho(E, z)$ appears to be reduced by the fact that the resonance part f of radiation is absorbed more strongly than the non-resonant part (1-f) which is only attenuated by electronic absorption $exp(-\mu_e \cdot z)$. I_r shall denote the fraction of resonant and I_{nr} of non-resonant γ's. If the sum runs over n layers of

equal thickness $\delta = d/n$ with a density N_l of ^{57}Co atoms, such that $\sum_l N_l \cdot \delta$ is the total number of ^{57}Co per unit area, the fractions are

$$I_r = \sum_{l=1}^{n} e^{-\mu_e \cdot l \cdot \delta} \int_{-\infty}^{\infty} Tr(\rho(E, N_l, l \cdot \delta)) dE \tag{5}$$

$$I_{nr} = \sum_{l=1}^{n} N_l e^{-\mu_e \cdot l \cdot \delta} \bigg/ \sum_{l=1}^{n} N_l$$

The effective Lamb-Mössbauer factor of the source is given by the ratio

$$f_{eff}^s = \frac{f \cdot I_r}{f \cdot I_r + (1 - f) \cdot I_{nr}} \tag{6}$$

2.2 Concentration profile of ^{57}Co in the $\alpha-Fe$ foil

The preparation of the source by diffusion of the Co atoms deposited on the surface leads to a diffusion profile with decreasing concentration. The solution for the 1-dimensional problem of the situation of a fixed number of atoms N/area deposited at the surface (of infinite extension), which diffuse into the bulk for some time t is given by Fick's law

$$c(z, t) = \frac{1}{\sqrt{\pi Dt}} exp\left(-\frac{z^2}{4Dt}\right) \tag{7}$$

$$1 = \int_{0}^{\infty} c(x, t) dx$$

The length $2\sqrt{Dt}$ is called the diffusion length (dependent on time t), which will be a fit parameter. The density N_l is then given by the function

$$N_l = c(z = l\delta, t) \cdot \sum_{l=1}^{n} N_l \tag{8}$$

2.3 The decrease of the absorption effect in the spectrum

Instead of the density matrix (1) for the source the matrix obtained factoring in selfabsorption (see (5))

$$\rho_s(E) = \sum_{l=1}^{n} e^{-\mu_e \cdot l \cdot \delta} \rho(E, N_l, l \cdot \delta) \tag{9}$$

is used for the calculation of an absorption spectrum. In order to determine the effective thickness of the absorber the background fraction bg has to be known, that is the number C_B of counts produced by the 122 keV and 136 keV radiation in the discriminator window while the 14.4 keV quanta are completely blocked by a thin metal-foil devided by the total number of counts (C_B is corrected for the electronic absorption by the metal foil). If C_M^s denotes the 14.4 keV Mössbauer quanta leaving the source the counts of the baseline are the sum:

$$C_{base} = C_B + C_M^s \tag{10}$$

C_M^s are related to the number of Mössbauer quanta C_M in the γ-direction inside the source by the fractions I_r and I_{nr}:

$$C_M^s = I_r f C_M + I_{nr}(1-f)C_M, \qquad (11)$$

The effect of the absorption spectrum is reduced by the fraction f of resonant γ-radiation and the background C_B. The reduction factor $r_{resonant}$ becomes inserting (6):

$$bg = \frac{C_B}{C_B + C_M^s} \qquad (12)$$

$$r_{resonant} = f_{eff} \cdot (1 - bg)$$

The code of the fit program shall handle two f-factors, the f-factor of the source matrix and f_{eff}, which is calculated from the reduction factor.

The usual definition of the reduction factor by f instead f_{eff} together with the measured background fraction bg leads to large misfit values [11] of the spectrum.

3 Experimental

A well defined absorber is an essential prerequisite for the determination of the parameter of a source. Single line absorbers from powder samples do not exhibit texture effects and can therefore be easily prepared. But it seems that such a sample still has to be found as for the ("single") absorption line of hydrated sodium ferrocyanide ($Na_4Fe(CN)_6 \cdot 10H_2O$) a small quadrupole splitting was reported [12]. The quadrupole split spectrum of a single crystal of sodium nitroprusside dihydrate ($Na_2[Fe(CN)_5NO] \cdot 2H_2O$) was used as a standard [13].

Here we use the single crystal of ferrous ammonium sulphate hexahydrate (FAS). FAS crystallizes from aqueous solution most frequently as flat plates containing the $(\bar{2}01)$ plane of the crystal. Since it is also very stable it may be suitable for a standard absorber. From the fit of 19 orientation of a FAS single crystal of $0.222\,mm$ thickness [2] the Lamb-Mössbauer $f_{\perp(\bar{2}01)}(RT) = 0.283 \pm 0.002$ and transition matrices ρ_L, ρ_H of the polarized low and high velocity lines have been determined.

$$\rho_L = \begin{pmatrix} 0.644 & 0.152 \\ 0.152 & 0.644 \end{pmatrix} \quad \rho_H = \mathbf{1} - \rho_L \qquad (13)$$

The errors of the matrix elements are of the same size as the error of the f-factor. Since the crystal could only be adjusted by eye the Euler angles for the orientation have been allowed to vary by few degrees minimizing χ^2.

The measurement with the single line source of $74\,MBq$ activity was done using a conventional Mössbauer spectrometer in Mainz with the source moving in constant acceleration mode. The polarized $^{57}Co/\alpha-Fe$ source was fixed between 2 permanent magnets and the FAS-absorber was moving in sinus mode. These measurements done in Budapest took several weeks and in the case of the inactive side directed to the absorber even almost 3 months.

4 Results

4.1 Old 74 MBq source

The spectrum of Fig. 1 has been evaluated in two ways. The conventional method allows for an effective Lamb-Mössbauer factor and a broadened Lorentz curve. This gives $f_{eff} =$
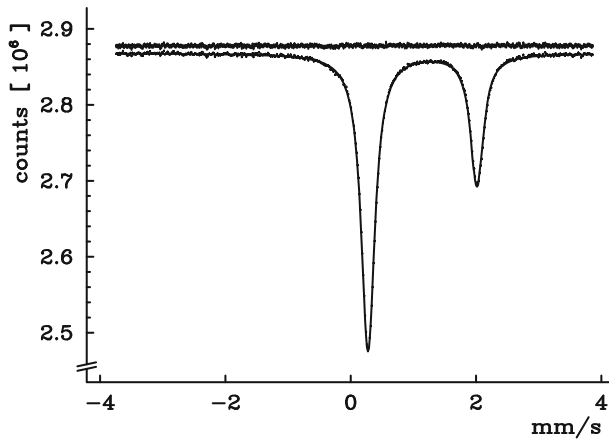
Fig. 1 Single crystal absorption spectrum of FAS with the $(\bar{2}01)$ plane oriented orthogonal to the γ-direction measured with a $74\,MBq$ $^{57}Co/Rh$ of original activity of ca. $3.7\,GBq$. The χ^2-values are 0.997 and 1.009 for a conventional fit with a Gauss-distribution ($\sigma = 0.582\,\Gamma$) of broadened Lorentzians $\Gamma_f = 1.362\,\Gamma$ and a value of 0.685 as effective f-factor of the source and a parameter free fit (concerning the shape and intensity) with the theory of selfabsorption, respectively.

0.690, $\Gamma_f = 1.45 \cdot \Gamma$ and $\chi^2 = 1.073$. If the shape of the absorption lines is fitted with a Gauss distribution ($\sigma = 0.582\,\Gamma$) of broadened Lorentzians $\Gamma_f = 1.362\,\Gamma$ the least squares value improves to $\chi^2 = 0.997$ and $f_{eff} = 0.685$ gets a bit smaller. The misfit [11] value of 0.0004 compared to misfit=0.074 (about factor 200) tells that the latter one is a significant better fit.

The fit with selfabsorption ends up with $\chi^2 = 1.089$. The reduction factors are Ir=0.612, Inr=0.852 and $f_{eff} = 0.683$ close to the value above. These values are obtained optimizing the effective thickness of the ^{57}Fe in the ground state to $0.380/\mu$ which is larger than the value given in the work of Rusanov et al. [5] and corresponds to a thickness of 6μ and an activ area of $4\,mm$ in diameter (compared to 7μ and $5\,mm$). The χ^2 can be improved to $\chi^2 = 1.009$ (Ir=0.614, $f_{eff} = 0.684$) taking into acount an intrinsic source line width by a Gauss distribution $\sigma = 0.38 \pm 0.03\,\Gamma$. This intrinsic width is the so-called source environmental broadening, because atoms in different locations have slightly different environments. The Gauss distribution corresponds to an increase of the half width interpreted by a Lorentzian shape of $\Gamma_s = 1.046 \cdot \Gamma = 0.1015\,mm/s$. From the plot LINEWIDTH,mm/s versus SPECIFIC ACTIVITY,mCi/mm^2 in CYCLOTRON [14] a much higher intrinsic linewidth of ca $\Gamma = 0.108\,mm/s$ is expected, if the whole activity is referred to the surface of $4\,mm$ in diameter. If the assumption of a homogeneous distribution ^{57}Co in the source foil is approximately reached, the specific activity per volume would be the more reliable measure. The data sheet of an actual $1.85\,GBq$ Rh-source [14] guarantees an emission efficiency for $14.4\,keV$ photons 0.84. Taking into account the Al-window of 30μ thickness with an attenuation of 0.926 the attenuation inside the Rh-matrix is 0.84/0.926=0.907 which corresponds to a homogeneous distribution over a thickness of $3.6\,\mu$ about half of the thickness of $7\,\mu$ given for the source foil.

In view of the number of ca 3 million counts and an effect of 14% the fits (see Fig. 1) can be considered as perfect, which means that the lineshape of the source in the velocity range of $\pm 4\,mm/s$ is well described by the Gauss distribution of broadened Lorentzians as
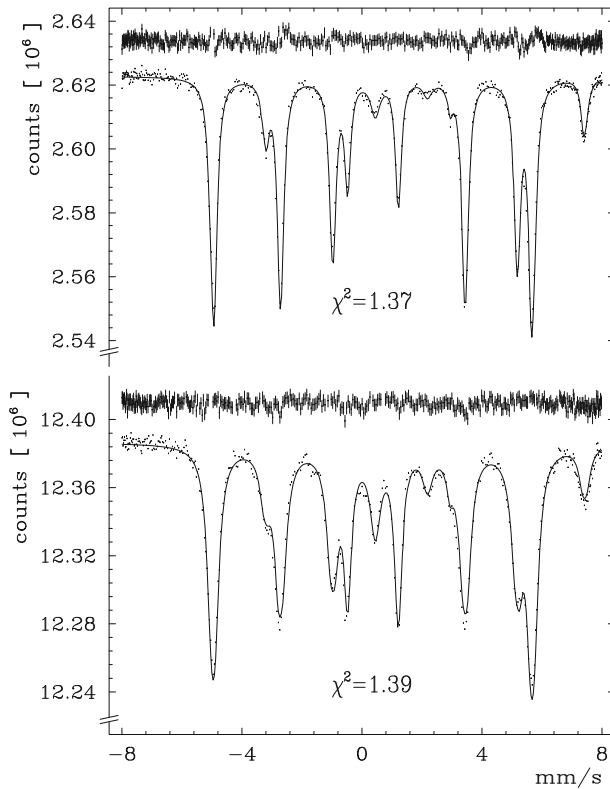
Fig. 2 Single crystal absorption spectrum of FAS with the $(\bar{2}01)$ plane oriented orthogonal to the γ-direction measured with a $0.15\,GBq$ $^{57}Co/\alpha - Fe$ source in an applied field 0f $0.2\,T$ in the plane of the foil of 25μ thickness. The magnetic field is parallel to the C_2 symmetry axis of the crystal. The upper spectrum ($\chi^2 = 1.37$) is measured with the active side of the source directed to the absorber, the lower one ($\chi^2 = 1.39$) with the inactive side giving rise to a strong selfabsorption effect. Observe the huge change in relative intensities, even reversing the ratios.

well as by the selfabsorption calculation approximated by a homogeneous distribution of the ^{57}Co atoms over the whole volume of the source foil.

4.2 $^{57}Co/\alpha-Fe$ source

The natural abundance of ^{57}Fe determines the effective thickness of $\alpha-Fe$ to be $0.372/\mu$. Here we calculated with a 1-dimensional distribution function dependent on one parameter, the diffusion length. If an $\alpha-Fe$ foil would be well defined, the spectra in Fig. 2 need only this common parameter to be fitted. However, an iron foil does not show natural line widths because of small magnetic field distributions, i.e. surface and bulk fields are different.

The fit to the spectra with a $0.2\,T$ magnetic field applied parallel to the foil improves ca $\delta\chi^2 = 0.25$ by a field distribution, which consist of a central field in line with the external field (fraction 0.80) and two fields larger by $0.7\,T$ at angles $\pm 7^o$ in the plane of the foil (fraction 0.1 each).

Although $\chi^2 = 1.0$ cound not be reached, there is no reason to mistrust the code for the calculation of the selfabsorption effect. There are many reasons which may be responsible

for the larger χ^2-value. The large measuring times of up to 3 month to obtain 4 million or even 12 million counts require a very stable equipment. The theory uses only natural linewidts. The distribution of hyperfine fields in the applied field of the 2 permanent magnets is an uncertainty. The homogeneity of the applied field is also not guaranteed.

The source has a small fraction, 0.034, of ^{57}Co atoms which remains on the surface as an oxide and emits a broad single line ($\Gamma_s = 1.58\Gamma$) which gives the doublet with an isomer shift of 1.284 mm/s and the quadrupole splitting (1.739 mm/s) of FAS. This fraction does not experience selfabsorption and therefore its relative intensity increases if the inactive side of the source is directed to the FAS-absorber (see Fig. 2 lower spectrum).

5 Conclusion

So far the selfabsorption of ageing single line sources in general and magnetically split $^{57}Co/\alpha-Fe$ sources was not included in the code of Mössbauer fit programs enabling the calculation of the properties of absorbers without any ad hoc fit parameters as line broadenings and effective Lamb-Mössbauer factors of the source.

The measurement with the old $3.7GBq$ source is encouraging. The conventional fit with broadened emission lines as well as the rigorous calculation of the selfabsorption gives the lineshape and the effect of the single crystal absorption spectrum of FAS to almost the same accuracy. The implementation of the age of the source as a parameter defining the accurate source function does not seem to be unrealistic if a homogeneous distribution over the volume of the source matrix (Rh,...) could be guaranteed.

The measurement of FAS single crystal with the $^{57}Co/\alpha-Fe$ source polarized by an magnetic field of ca $0.2\,T$ proves the accuracy of the implemented code in case of a polarized source and absorber. Even the strong selfabsorption using the inactive side of the $25\,\mu$-foil leading to large shifts of the relative intensities is well reproduced.

This excellent agreement recommends the FAS single crystal as a standard to be used to determine the properties of a source and also of the equipment concerning linebroadening by vibrations and geometry effects. The advantage of the FAS absorber are the two different lines of the quadrupole split spectrum of an intensity ratio of 1.809 which provides two thicknesses in one measurement.

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