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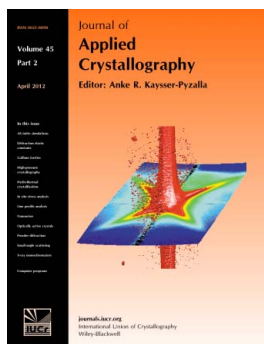
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MossA: a program for analyzing energy-domain Mössbauer spectra from conventional and synchrotron sources

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The program *MossA* provides a straightforward approach to the fitting of ^{57}Fe conventional and synchrotron energy-domain Mössbauer spectra. Sites can be defined simply by mouse clicks and hyperfine parameters can be constrained to constant values, within specific ranges, and can be coupled linearly between different subspectra. The program includes a full transmission integral fit with Lorentzian line shape (conventional source) or Lorentzian-squared line shape (synchrotron source). The fitting process is graphically displayed in real time while fitting and can be interrupted at any time. Gaussian-shaped quadrupole splitting distributions for analyzing nonmagnetic amorphous materials are included. *MossA* is designed especially for the rapid and comprehensive analysis of complex Mössbauer spectra, made possible by its native graphical user input.

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1. Introduction

Mössbauer spectroscopy is a unique tool for sampling spin states, oxidation states and coordination of specific elements. It is used particularly frequently in the earth sciences, because of the ease of obtaining structural information and the oxidation state of iron in rocks and minerals. The Mössbauer milliprobe technique (McCammon, 1994) has enabled an evaluation of the spin and oxidation state of iron in materials relevant to the Earth's interior up to pressures of the Earth's core (e.g. McCammon *et al.*, 2008). However, detailed analysis of compounds with different iron environments or a mixture of different phases containing iron can be challenging owing to the ambiguity of possible fitting models. The outcome of the fitting procedure can depend strongly on the input of the initial parameters of the distribution of sites. Therefore complex spectra need to be evaluated visually before fitting in order to define the initial parameters, and the progress of the fit should ideally be tracked while fitting in order to allow intervention if the solution becomes physically improbable. However, most recently described Mössbauer analysis programs (e.g. Azevedo *et al.*, 1997; Brand, 1995; Grosse, 1993; Hjøllum & Madsen, 2009; Kent, 1998; Lagarec & Rancourt, 1992; Žák, 2006) are founded on a text-based input of initial parameters, which makes fitting of complex spectra challenging or even impossible. Additionally the commonly used Gauss–Newton and Levenberg–Marquardt least-squares methods do not search for the global minimum but only for local minima, which may be biased by the choice of initial parameters in the fitting model.

We present the *MATLAB*-based (The MathWorks Inc., Natick, MA, USA) Mössbauer fitting program *MossA*, which overcomes these difficulties in the analysis of complicated spectra. Through its clear graphical user interface (GUI) and straightforward procedures for handling data and exporting parameters and fitted spectra, it is easy to analyze complex Mössbauer spectra even for users that are new to Mössbauer spectroscopy.

2. Theory

The experimental Mössbauer spectrum is described by the transmission integral, which is essentially a sum of the nonresonant

background and a convolution of the source emission line $N(E, \nu)$ and the absorber response $\exp[-t\sigma(E)]$:

$$C(\nu) = N_0 \exp(-\mu_0 t') \left[(1 - f_s) + \int_{-\infty}^{+\infty} N(E, \nu) \exp[-t\sigma(E)] dE \right], \quad (1)$$

where N_0 is the number of quanta emitted by the source, μ_0 is the mass absorption coefficient, t' is the absorber thickness, f_s is the recoilless fraction of the source and t is the effective absorber thickness. The source line $N(E, \nu)$ and the resonant cross section $\sigma(E)$ are defined by a Lorentzian curve as given by the Breit–Wigner equation:

$$I(E) = \frac{\Gamma/(2\pi)}{(E - E_0)^2 + (\Gamma/2)^2}, \quad (2)$$

where Γ is the full width at half-maximum (FWHM) and E_0 is the center of the distribution.

For thin absorbers with $t \ll 1$, the transmission integral can be expanded in a series. Using the first two terms of the expansion yields

$$C(\nu) = N_0 \exp(-\mu_0 t') \left\{ 1 - f_s \frac{t}{2} \frac{\Gamma^2}{[E_0(\nu/c) - \Delta E] + \Gamma^2} \right\}. \quad (3)$$

This is a linear combination of two Lorentzian line shapes, which can be described by a Lorentzian line with the FWHM being the sum of the source and the absorber FWHM. This thin absorber approximation is frequently used in Mössbauer spectroscopic analysis because of the ease in computation.

New advances in Mössbauer synchrotron technology have made it possible to obtain Mössbauer spectra in the energy domain with the aid of nuclear Bragg reflection, the so-called synchrotron Mössbauer source (Smirnov *et al.*, 1997). This process leads to a slightly different source line shape, however, which because of the physics of the process is a normalized squared Lorentzian (Smirnov *et al.*, 2011):

$$I(E) = \pi \Gamma \left[\frac{\Gamma/(2\pi)}{(E - E_0)^2 + (\Gamma/2)^2} \right]^2. \quad (4)$$

Table 1

Quantitative results of fitting an Fe_7C_3 Mössbauer spectrum measured at 1 GPa in a diamond anvil cell at beamline ID18, ESRF.

CS: center shift with respect to $\alpha\text{-Fe}$; QS: quadrupole splitting; BHF: magnetic hyperfine splitting; a_{23} : intensity ratio of the second and fifth line to the third and fourth line of the sextet.

| Site | CS (mm s^{-1}) | FWHM (mm s^{-1}) | Intensity (%) | QS (mm s^{-1}) | BHF (T) | a_{23} |
|------|------------------------------|--------------------------------|------------------|------------------------------|------------|----------|
| 1 | 0.156 (5) | 0.55 (1) | 42.9 (2) | -0.125 (8) | 22.5 (3) | 1.90 (6) |
| 2 | 0.135 (3) | 0.351 (7) | 42.9 (2) | 0.305 (5) | 16.00(2) | 1.69 (4) |
| 3 | 0.195 (9) | 0.35 (2) | 14.3 (1) | -0.06 (2) | 19.40(6) | 2.5 (3) |

Synchrotron Mössbauer experiments in the energy domain are characterized by very high absorption (typically of the order of 50%) and by the lack of nonresonant background. The high absorption makes it absolutely necessary to use the transmission integral; however, most of the current software packages for analyzing Mössbauer spectra lack the capability for fitting these spectra. With *MossA* it is possible to fit data using the full transmission integral with either source line shape. A further characteristic of the synchrotron Mössbauer source is that radiation is linearly polarized. In the case of powder samples with random crystallite orientation, Mössbauer spectra are unchanged from those collected with an unpolarized source. However in the case of single crystals or powder samples with preferred orientation, the component area ratios of quadrupole doublets and of magnetic sextets will change. This effect can be accounted for by allowing component area ratios to vary, which is implemented in *MossA*.

3. Program features

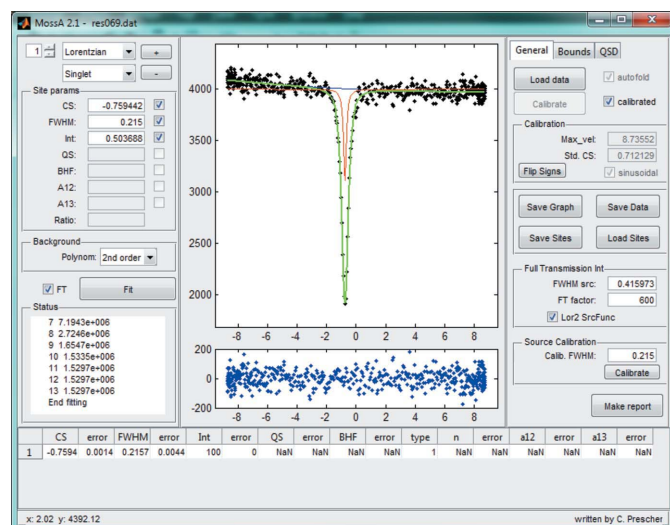
MossA is based on the *MATLAB* programming language, and uses its native GUI library and the *Optimization Toolbox*. *MossA* is capable of fitting Lorentzian, Gaussian, pseudo-Voigt and Lorentzian-squared absorber line shapes. The available subspectra are singlets, doublets and sextets. These subspectra are defined visually by two mouse clicks for singlets and three mouse clicks for doublets and sextets. In order to more precisely define specific parameters, values can be edited after adding the subspectrum. The parameters (center

shift, FWHM, quadrupole splitting, magnetic hyperfine splitting) can be kept constant or can be constrained to fall within specific ranges in their search space during fitting. This can be useful when fitting overlapping subspectra, for example, to constrain a subspectrum to have a specific center shift range. Spectra of samples with preferential orientation or single crystals can be treated empirically by fitting the component area ratios of doublets or sextets. Furthermore, it is possible to linearly couple two parameters (including component area ratios) from the same or different subspectra. One application of this feature is when information about site occupancy from crystallography or crystal chemistry is available, which constrains the abundance relationships between the different sites of a phase. If the Lamb-Mössbauer factor can be assumed to be the same for all of the sites, the fit can be constrained to fix the area ratios between different subspectra according to a specific factor inferred from crystallography.

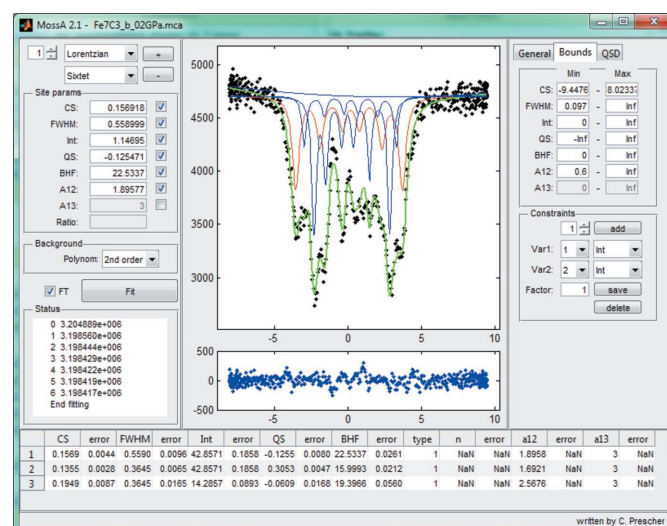
The analysis of Mössbauer spectra measured from amorphous samples can be challenging, even in the absence of magnetic hyperfine splitting. Because of the different environments of the Mössbauer active isotope, there is a significant line broadening and there can be a coupling of center shift and quadrupole splitting. One mathematical model for this coupling was introduced by Rancourt & Ping (1991) as a quadrupole splitting distribution (QSD). An interface for fitting such distributions is included in the program *MossA*. Sites with QSD can be combined with normal sites in a fit and also used in combination with the full transmission integral.

The trust-region reflective method of the *Matlab* optimization toolbox is used as minimization algorithm. This method is more stable than the commonly used finite-difference least-squares procedure since it is more likely to detect global minima. The progress and direction of the fitting can be seen in the graphics window during the fitting process. If the fitting approaches a local minimum that is physically improbable, the user has the option to stop the fitting process at any time.

The program is especially suited for analyzing synchrotron Mössbauer source data. The program features include a sinusoidal baseline, a squared Lorentzian source function for the full transmission

**Figure 1**

Calibration of the FWHM of a Lorentzian-squared source line. A second-order polynomial is automatically calculated to account for curvature in the baseline.

**Figure 2**

User interface during the fitting process. The example spectrum shown is for a full transmission integral fit to Fe_7C_3 (measured in a diamond anvil cell at 1 GPa) with three sextets, each with the component area ratio A_{13} fixed to 3 and the intensities of the first and second sextets constrained to be equal as required by crystallographic constraints. Results of the fit are shown in Table 1.

integral and one-mouse-click calibration of the FWHM of the source function.

The fitted parameters can be either copied directly to a spreadsheet or saved as a plain text file. Graphical output formats include *.Fig (*MATLAB* editable plot file) or any other common picture format. For distributing and discussing with colleagues, the report option is most suitable as it presents the graphical data and fitted parameters in a PDF file.

4. Example workflow

The first step for sample analysis is to calibrate the velocity scale of the transducer by analyzing an α -Fe calibration spectrum. *MossA* has a tool to obtain the best fit values for the relative shift and the maximum of the velocity scale. After calibration, the values are saved in program memory. The next step is to estimate the FWHM of the source function by calibrating a single line absorber (Fig. 1). Next the data file is loaded and the possible sites are defined by clicking the mouse at appropriate places in the graphics window (Fig. 2). If the initial estimates are satisfactory, the fitting process can be started. The progress of the fit is shown in the graphics window, where the χ^2 value is displayed as a measure of the goodness of fit. Depending on the outcome of the fitting, additional sites can be added, the background model can be changed, and parameters can be constrained or coupled. When the fitting process is completed satisfactorily, all parameters can be copied and pasted into a spreadsheet, and the fit can be saved as numerical values for plotting with the user's preferred plot software or directly output in one of the common image formats from the *MossA* program.

5. Distribution

The Program *MossA* and its documentation can be obtained at <http://www.clemensprescher.com/> under Programs/MossA after registra-

tion. To run the program it is not necessary to have a *MATLAB* license; only the *MATLAB* runtime component is needed, which will be delivered with the program executable. *MossA* runs under Windows, MacOS X and Linux.

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References

- Azevedo, M. M. P., Rogalski, M. S. & Sousa, J. B. (1997). *Meas. Sci. Technol.* **8**, 941–946.
- Brand, R. A. (1995). *Normos-90 Mössbauer Fitting Program Package*. Angewandte Physik, Universität Duisburg, Germany.
- Grosse, G. (1993). *PC-Mos II*. Version 1.0. Fast ComTec, Oberhaching, Germany.
- Hjølsum, J. & Madsen, M. B. (2009). arXiv:0912.0449v1 [physics.comput-ph]. <http://arxiv.org/abs/0912.0449>.
- Kent, T. A. (1998). *WMOSS*. Version 2.5. WEB Research Co., Minneapolis, MN, USA.
- Lagarec, K. & Rancourt, D. A. (1992). *Recoil – Mössbauer Spectral Analysis Software for Windows*. Department of Physics, University of Ottawa, Ontario, Canada.
- McCammon, C. A. (1994). *Hyperfine Interact.* **92**, 1235–1239.
- McCammon, C. A., Kantor, I., Narygina, O., Rouquette, J., Ponkratz, U., Sergueev, I., Mezouar, M., Prakapenka, V. & Dubrovinsky, L. (2008). *Nat. Geosci.* **1**, 684–687.
- Rancourt, D. G. & Ping, J. Y. (1991). *Nucl. Instrum. Methods Phys. Res. Sect. B*, **58**, 85–97.
- Smirnov, G. V., van Bärck, U., Chumakov, A. I., Baron, A. Q. R. & Ruffer, R. (1997). *Phys. Rev. B*, **55**, 5811–5815.
- Smirnov, G. V., Chumakov, A. I., Potapkin, V. B., Ruffer, R. & Popov, S. L. (2011). *Phys. Rev. A*, **48**, 53851.
- Žák, T. & Jirásková, Y. (2006). *Surf. Interface Anal.* **38**, 710–714.