An Interactive Package for Mössbauer Spectra Analysis: SPECFIT - PC

Florin-Dan Barb and Martin Weiss

Research Institute for Informatics
8-10 Averescu Avenue,
71316 Bucharest
ROMANIA

Monica Sorescu

"Politehnica" University of Bucharest
313 Splaiul Independentei,
77206 Bucharest
ROMANIA

Dan Sorescu

Institute for Atomic Physics
235, Oteteleseanu str.,
76900 Bucharest
ROMANIA

Abstract: SPECFIT-PC is an interactive package on personal computers for Mössbauer spectra fitting by a sum of Lorentzian or Gaussian functions. SPECFIT-PC implements a modified Gauss-Newton algorithm and includes a spectra calibration task. All functions are performed by means of a command language and predefined command sequences can be used.

Florin Dan Barb received the M.Sc. degree in Electrical Engineering from the Polytechnical Institute of Bucharest in 1989. He joined the staff of the Research Institute for Informatics in Bucharest in 1990. His research interests are mainly placed in the area of model reduction and reduced order control with emphasis on sampled-data systems. He is currently preparing a doctoral thesis in control engineering at the Faculty of Technical Mathematics and Informatics, Delft University of Technology.

Martin Weiss was born in 1966. His studies were in Control Engineering at the Polytechnical Institute of Bucharest. Since graduation in 1990, he has worked at the Research Institute for Informatics in Bucharest, where his main research work has been carried out in the field of optimal control for discrete, hybrid systems and infinite-dimensional systems. He prepares now a doctoral thesis in control engineering at the Mathematics Institute, University of Groningen.

Monica Sorescu was born in Cluj, Romania in 1963. She received the M.Sc. degree in Solid State Physics at the University of Bucharest, Romania in 1986 and the Ph.D degree in Mössbauer spectroscopy at the Institute of Atomic Physics Bucharest,Romania in 1992. At present, she has a faculty position at the "POLITEHNICA" University of Bucharest, Department of Physics. In 1990 and 1991 she was a visiting research fellow at the University of Saarbrücken ,F.R.Germany and at the Institute " Jozef Stefan" in Ljubljana, Slovenia. She is through a research scholarship at the Oklahoma State University, USA. Dr.Monica Sorescu's main fields of interest are Mossbauer spectroscopy applied to the study of magnetic, thermal and crystallization properties of materials, computer simulation of the responses of materials subject to high-frequency perturbations and numerical algorithms in applied physics.

Dan Sorescu was born in Pitesti, Romania in 1962. He received the M.Sc. degree in Laser Physics at the University of Bucharest, Romania in 1987 and is under Ph.D contract with the Institute of Atomic Physics, Bucharest. At present, he holds a scientific researcher position at the Institute of Opto-Electronics, Bucharest-Magurele. He is through a research scholarship at the Oklahoma State University, USA. Mr.Dan Sorescu's main fields of interest are laser-induced chemical reactions, laser processing of materials, computer-aided optimization of the properties of magneto-optical materials and magneto- optical storage devices.

1. Introduction

In order to renounce expensive mainframes in Mössbauer spectra fitting, a specific package that runs satisfactorily on the same personal computer used to read-out the data from the spectrometer is required. SPECFIT-PC implements a recently developed modified Gauss-Newton algorithm [1] for the least-squares determination of non-linear parameters, which only requires several square matrices for computation, with the dimension

given by the number of parameters to be determined.

SPECFIT-PC makes use of a powerful package of portable FORTRAN routines-BIMASC [2], which implements the latest advances in numerical algorithms using the highest quality numerical software available and takes advantage of the multiple graphical facilities provided by the powerful engineering graphics processor DISPLAY [3].

SPECFIT-PC runs on IBM-PC/AT compatible personal computers, having 1Mbyte RAM available, mathematical co-processor, hard disk and MS-DOS version 3.3 or next versions. The package can execute Mössbauer curve fitting for maximum 1,024 channels and 64 parameters, the computations being carried out in double precision. All functions are performed by means of a command language and the SPECFIT-PC environment offers the possibility of using predefined command sequences [4].

2. Data Structure and SPECFIT-PC Command Language

SPECFIT-PC deals with various data types organized in data files on hard disk, conforming to a predefined format. The basic data management operations are performed through the standard operating system-offered editing and file operation utilities. Files' identification is possible by a file description of the form:

filename: filetype (1)

where filename is a string of maximum 6 characters and filetype is a 3-character string. There are four basic data filetypes, namely. INP for experimental data files, .INI for parameter files, .SPF for indirect command files and .DIS for files holding graphics processed by DISPLAY.

The SPECFIT-PC command language gives evidence about the nature of the user- computer interaction during the Mössbauer spectra fitting process. The general format of a SPECFIT-PC command line is:

operation [filename [:filenature [/switch...]]] (2)

where "operation" is a string yielded by the following vocabulary:

V_1 = {FILE,SAVE,LOAD,TYPE, MODF, CALB, PLOT,WORK,EXIT, QUIT, HELP, PAUSE, EDIT,INFO,DEMO},

"filenature" is a 4-character string from the couple:

V_2 = {DATA,COND}

and the multiple switches specify some problem parameters or user options, having maximum 40 characters.

In order to avoid an on-end entering of long command lines and to develop a conversational working mode for all the implemented commands, the SPECFIT-PC environment makes it possible that predefined command sequences be used during the "eye-fitting" step.

3. Mössbauer Spectra Analysis with SPECFIT-PC

A Mössbauer spectrum results from recording detector counts,y, at different channels,x, on n data pairs and is usually assumed to consist of Lorentzian peaks and a parabolic baseline. The isomer shift, electric quadrupole and magnetic dipole hyperfine interactions [5] are responsible for the formation of singlets,doublets and sextets in the Mössbauer spectra:

$$Y(x) = B(x) + P(x) \tag{3}$$

where $B(x) = B_1 + B_2x + B_3x^2$ (4)

and

$$P(x) = \sum_{i=1}^{n_I} P_I^i(x;H_I^i,W_I^i,C_I^i) + \sum_{j=1}^{n_{II}} P_{II}^j(x;H_{II}^j,W_{II}^j,C_{II}^j) + \sum_{k=1}^{n_{VI}} P_{VI}^k(x;H_{16},H_{25},H_{34},W_{16},W_{25},W_{34},C_6,D_{61},D_{62},\varepsilon) \tag{5}$$

The number of singlets (n_I), doublets (n_{II}) and sextets (n_{VI}), as well as the peak heights (H), peak widths (W), distances between peaks (D) and centers of the component patterns (C) allow further testing of the assumed theoretical models

of structures and properties of the studied material and provide quantitative information on the hyperfine interactions present in the sample.

The most convenient measure unit for expressing the hyperfine parameters to be determined by Mössbauer spectra fitting is millimeters per second. However, for most of the Mössbauer spectrometers the one-by-one correspondence between channels and mm/s is not perfectly linear and a cubic dependence can be satisfactorily assumed. Provided that the CALB command is invoked, SPECFIT-PC performs the calibration of the Mössbauer spectra, relative to α-Fe, hematite or another absorber chosen by the user.The screen MEASURE facility of DISPLAY is used for locating the positions of the six peaks in the spectrum of the sample used for calibration. The four coefficients of the cubic dependence are the least squares solution determined by a QR decomposition [6]. As an example, the four calibration coefficients (A) determined for an α -Fe absorber, whose Mössbauer spectrum has been recorded on 256 channels, used for calibrating the $\pm$ 7.5 mm/s velocity range are listed in Table I.

Table I

Calibration coefficients for α – Fe absorber

A_0	-11.28875994
A_1	3.25331847 E-002
A_2	5.63393219 E-005
A_3	-7.59321392 E-008

At the stage of initial parameter selection (the "eye-fitting" step), SPECFIT-PC allows screen plot for the experimental data, the "eye-fitted" curve and all component subspectra, as well as parameter modifying (provided that the MODF command is invoked) followed by replot and calculus of the "goodness" parameter X^2 [7]:

$$X^2 = \left(\sum_{i=1}^{n} \left[y(x_i) - y_i \right]^2 / y_i \right) / (n-m) \qquad (6)$$

If X^2 is not close to unity, the "eye-fitting" has to be resumed by choosing another set for the initial values of the parameters. The "eye-fitting" step provides approximate values for the parameters to be determined, which are the input values for the least squares fitting.

The least squares fitting is the most important part of parameter determination. At this stage (provided that the WORK command is invoked), SPECFIT-PC solves an optimization problem, using a modified Gauss-Newton algorithm [1] for the least squares determination of nonlinear parameters.This method offers the certainty of convergence and high convergence speed, thus scoring well within the small memory size of personal computers.

The equation determining the unknown parameters $C_1,...,C_m$ by means of a least-squares approach:

$$\min \sum_{i=1}^{n} \left[Y(x_i) - y_i \right]^2 / y_i = \min \sum_{i=1}^{n} Y \left[(x_i; C_1,...,C_m) - y_i \right]^2 / y_i \qquad (7)$$

can be written, using the notations:

$$y = \left[\sqrt{y_1}, \sqrt{y_2}, ..., \sqrt{y_n} \right]^T; \quad C = \left[C_1, C_2, ..., C_m \right]^T;$$

$$Y(C) = \left[Y(x_i;C)/\sqrt{y_1}, Y(x_2;C)/\sqrt{y_2}, ..., y(x_n;C)/\sqrt{y_n} \right] \qquad (8)$$

in the equivalent form:

$$\min (Y(C)-y)^T (Y(C)-y) = \min f(C)^T f(C) \qquad (9)$$

Assuming $f(C) = AC + b$, here follows:

$$f(C)^T f(C) = (AC+b)^T (AC+b) = C^T A^T AC + 2b^T AC + b^T b \qquad (10)$$

and

$$\nabla \left[f(C)^T f(C) \right] = 2A^T AC + 2A^T b \qquad (11)$$

The solution to equation (9) is then obtained by solving the system with a linear equation:

$$A^T AC^* = -A^T b \qquad (12)$$

For a nonlinear F(C), during the k^{th} iteration, the first-order Taylor expansion of f(C) at C^k may be written as:

$$f(C) \approx f(C^k) + A(C^k)(C-C^k) \qquad (13)$$

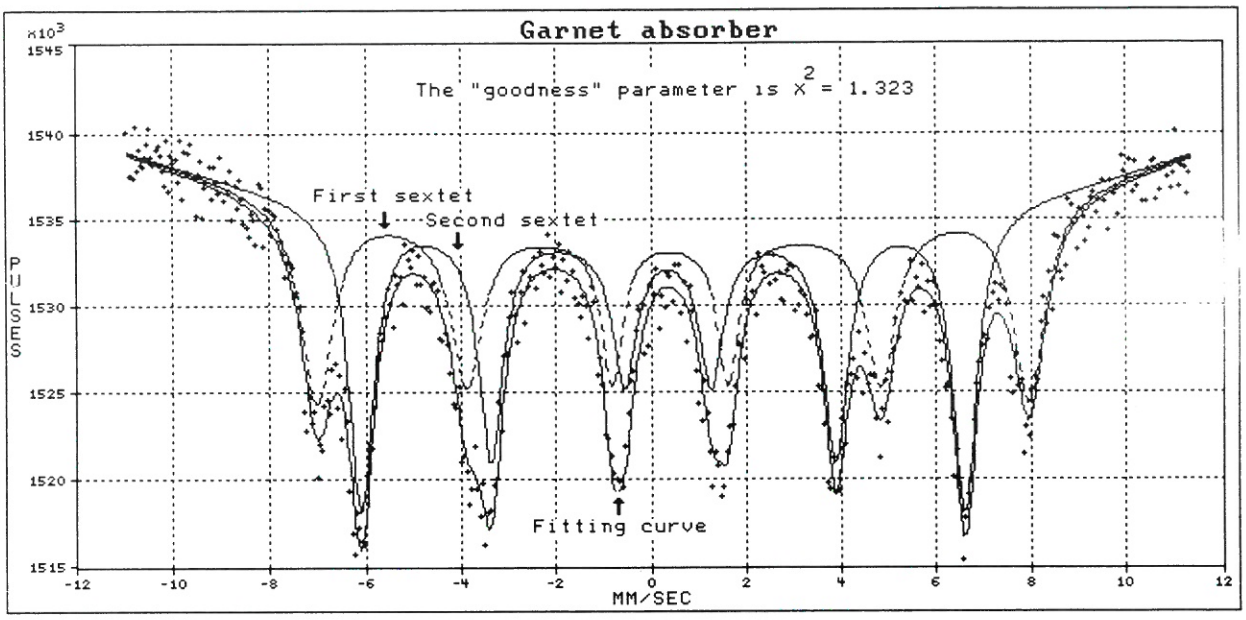

Figure 1. Mössbauer spectrum, fitted curve and component subspectra for polycrystalline $Y_{2.4}Gd_{0.6}Fe_{4.25}Al_{0.75}O_{12}$.
Least squares fitting has been carried out in the assumption of Lorentzian lineshapes.

so that the solution to the linear least-squares problem:

$$\min [\, f(C^k) + A(C^k)P^k \,]^T [\, f(C^k) + A(C^k)P^k], \quad P^k = C - C^k \tag{14}$$

is found by solving the simultaneous linear equations:

$$A(C^k)^T A(C^k)P^k = - A(C^k)^T f(C^k) \tag{15}$$

the new value of C being:

$$C^{k+1} = C^k + P^k \tag{16}$$

The modification of the Gauss-Newton algorithm, as implemented in SPECFIT [4] lies in using P^k as a linear search direction:

$$C^{k+1} = C^k + \lambda P^k \tag{17}$$

with λ determined by minimizing $f(C^k)^T f(C^k)$ and using the expression:

$$P^k = -A(C^k)^T f(C^k) \tag{18}$$

whenever $\mathrm{Det}A(C^k)^T A(C^k) = 0$, so that the steepest descent method is used for this iteration.

4. Applications

The SPECFIT package testing on different types of Mössbauer spectra produced satisfactory results, if taking into account the fact that the quality of the fitted spectra equalized that attained by a mainframe computer. A typical running time of about 10 minutes was necessary in order to reach the saturation values of the parameters after 3 iterations for a hematite six-line spectrum, provided a good "eye-fitting" had been obtained.

Figure 1 shows the room temperature Mössbauer spectrum, fitted curve and component subspectra for polycrystalline $Y_{2.4}Gd_{0.6}Fe_{4.25}Al_{0.75}O_{12}$ double- substituted yttrium iron garnet. The spectrum was analysed in the assumption of Lorentzian lineshapes and could mainly be resolved by considering two sextets, corresponding to the octahedral [a] and tetrahedral (d) sublattices [8]. The values of the parabolic baseline coefficients and hyperfine parameters are listed in Table II, as obtained from the test-run output. The determined values of the

hyperfine parameters furnished new conclusions on the dependence of the magnetic hyperfine fields with respect to the sample composition.

Table II

Parabolic baseline coefficients and hyperfine parameters of the Mössbauer spectrum in Figure 1

Number of fitted parameters is 23	
Baseline coefficients	: B_1 = 1533986.877 : B_2 = -28.076 : B_3 = 39.159
First sextet	
Peak heights	: H_{16} = -8438.300 : H_{25} = -9274.495 : H_{34} = -11734.309
Peak widths	: W_{16} = 2.685 E-001 : W_{25} = 3.797 E-001 : W_{34} = 4.091 E-001 : C_6 = 4.073 E-001
Peak center Distance from center to peak 3	: D_{61} = -7.482 : D_{62} = 3.132
Separation between peaks 1 & 2 Quadrupole shift	: EPS = -3.327 E-002
Second sextet	
Peak heights	: H_{16} = -8404.257 : H_{25} = -13237.198 : H_{34} = -17290.052
Peak widths	: W_{16} = 3.069 E-001 : W_{25} = 3.053 E-001 : W_{34} = 3.097 E-001 : C_6 = 2.718 E-001
Peak center Distance from center to peak 3	: D_{61} = -6.339 : D_{62} = 2.715
Separation between peaks 1 & 2 Quadrupole shift	: EPS = 5.475 E-002

The package modularity let other functions available for the resonance lineshape. Indeed, when analysing the Mössbauer spectra of amorphous ferromagnetic alloys, Gaussian lineshapes should be used. Figure 2 shows the room temperature Mössbauer spectra of $Fe_{81}B_{13.5}Si_{3.5}C_2$ amorphous system in the as-received state (a) and after multipulse excimer laser irradiation (b,c,d) [9]. Beside the effective hyperfine magnetic field determination, SPECFIT-PC allowed the evaluation of the areal intensity ratio of the second to the first lines of the Mössbauer spectra.The determined values of the relative intensity I_{21} (Table III) made it possible to study the corresponding changes in spin texture and magnetic anisotropy as a function of the number of applied laser pulses.

Table III

Relative intensity of the second to the first line of the Mössbauer spectra in Figure 2

Number of laser pulses	Areal intensity ratio $I_{21} = A_2/A_1$
0	1.10
25	0.21
50	0.34
75	0.38

On these grounds, the SPECFIT-PC interactive package for Mössbauer spectra fitting with personal computers turns out to be a powerful tool for the analysis of the information obtainable from the Mössbauer spectroscopy investigations.

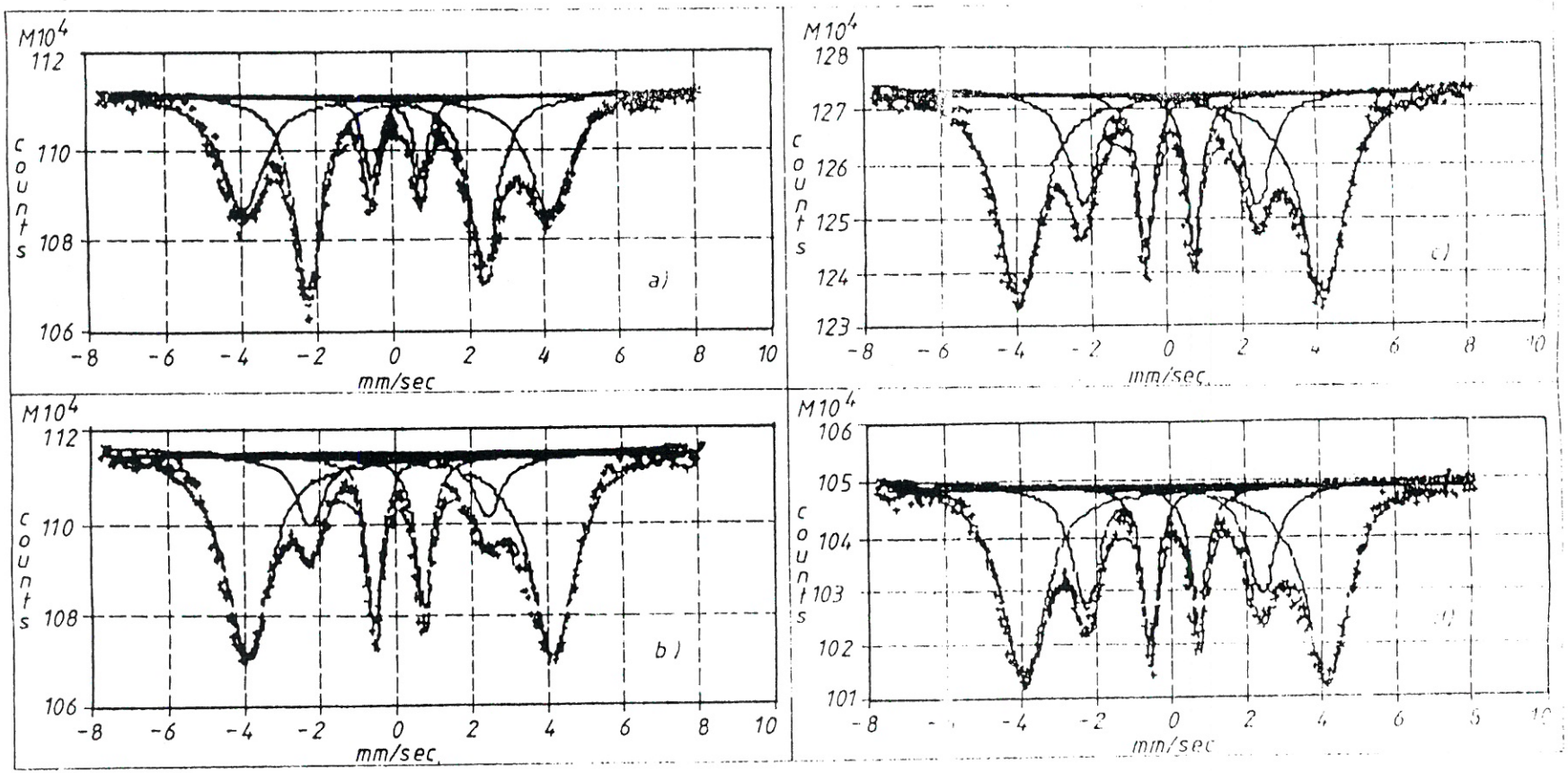

Figure 2. Mössbauer spectra, fitted curves and component subspectra for $Fe_{82}B_{13.5}Si_{3.5}C_2$ amorphous ferromagnetic alloy: a) in the as-received state, b), c) and d): after excimer laser irradiation ($\lambda = 248$ mm) with 25.50 and 75 laser pulses per spot, respectively. Least squares fitting has been performed in the assumption of Gaussian lineshapes.

REFERENCES

1. MEI , Z. and MORRIS JR.,J.W., NUCL. INSTRUM.METHODS B47 1990,181.
2. VARGA, A., BIMASC - **A Package of FORTRAN Routines for Analysis, Design and Simulation of Control Systems**, ICI Report , TR- 10.89,1989.
3. NETOIU,O., **DISPLAY-An Engineering Graphics Processor**, Reference Manual, Version 5.1,ICI Report , 1991.
4. BARB,F.D., NETOIU,O., SORESCU, M. and WEISS,M., Proceedings of the International AMSE Conference "Signals & Systems", Warsaw, July 15-17,1991, COMPUTER PHYS.COMMUN., Vol.2, pp.125-132.
5. BARB,F.D., in Gründlagen und Anwendungen der Mössbauer-spektroskopie, Ch.4, AKADEMIE VERLAG, Berlin 1980.
6. DONGARA,J.J., MOLER,C.B., BUNCH, T.R. and STEWART,G.W., **LINPACK - User's Guide**, Ch.9 SIAM, Philadelphia, PA., 1979.
7. LONGWORTH,G., in G.J.Long (Ed.) Mössbauer Spectroscopy Applied to Inorganic Chemistry, Vol.1, PLENUM, New York, 1984, p.43.
8. BARB,F.D., DIAMANDESCU,L., PUFLEA, R., SORESCU,M. and TARINA, D., MATERIALS LETT., 12, 1-2, 1991, pp. 109-111.
9. SORESCU,D.,SORESCU,M., HENING, A.,MIHAILESCU,I.N.and BARB,F.D., to be published.