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Simultaneous Analysis of Several Mössbauer Spectra

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A method based on a simultaneous fit of several Mössbauer spectra from a series of measurements is compared with the one based on an independent analysis of each spectrum. Three different algorithms, namely a least squares iteration procedure, a Gauss–Seidel function minimization and a genetic algorithm based method are applied and discussed. The conclusions drawn are supported by a simulated and a measured spectra analysis.

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1. Introduction

An analysis of the Mössbauer spectra composed of some overlapping subspectra having similar hyperfine parameters is not an easy task. In case of a lack of any additional information concerning the spectral parameters and relations between them, a fitting procedure is not unique, and the interpretation of the obtained results can be sometimes doubtful, all the more so since some different sets of the hyperfine parameters give fits of a similar quality. In such case, an intrinsic consistency of spectral parameters obtained from the series of measurements as a function of an external parameter, e.g. temperature, composition or magnetic field, can be taken as a test for the correctness of the fitting procedure. The results obtained from the whole series should reflect the foreseen influence of the external parameter on each spectrum separately, as well as the relationship between the experimental parameters predicted by a theory.

A method based on a simultaneous analysis of several spectra from the series of measurements is proposed and tested on: (a) two series of simulated spectra with significantly different statistical quality, (b) a series of the spectra measured at ¹¹⁹Sn nuclei on Sn-doped CoSb₃ skutterudite, (c) a series of the spectra measured at ⁵⁷Fe nuclei on Fe_{1-x}Ti_x Fe-rich alloys and (d) a series of the ⁵⁷Fe-site spectra recorded on a σ -FeV sample. It has been shown that an assumption that some spectral parameters are common for all fitted spectra, some of them are in-

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dependent and some follow the predicted or assumed functional dependence on an external parameter, enables one to fit the series of measurements in a more unique way.

2. Estimation of fit quality

In the case of a single spectrum the quality of the fit is generally estimated as the weighted squared deviations sum [1]. It follows a χ^2 -distribution with the assumption that the stochastic errors have normal distribution:

$$\chi^{2} = \frac{1}{n - N_{\rm S}} \sum_{i} \frac{[y_{i} - y(v_{i})]^{2}}{\sigma_{i}^{2}},\tag{1}$$

where y_i represents the *i*-th measured value, $y(v_i)$ is the corresponding calculated value for the velocity v_i , σ_i^2 is the variance associated with the *i*-th point ($\sigma_i^2 = y_i$ in the case of the Poisson distribution), *n* stands for the total number of measured points and $N_{\rm S}$ is the number of degrees of freedom ($N_{\rm S}$ describes the total number of free parameters used in the model).

The quality of the multispectral fit should not be described just by the sum of χ_j^2 -values because some spectral parameters are common for several spectra and their influence on each spectrum must not necessarily be the same. Additionally, some quantities may not be fitted as free parameters, but calculated from the assumed functional dependence, so the parameters describing this dependence should be used instead. Because of these restrictions, a formula for the total χ^2 -value, χ_T^2 is proposed

$$\chi_{\rm T}^2 = \frac{1}{\sum_j n_j - N_{\rm M}} \sum_j \sum_i \frac{[y_{ji} - y(v_{ji})]^2}{\sigma_{ji}^2},\tag{2}$$

where index j counts the number of the spectra fitted simultaneously, and i stands for the summation within a single j-th spectrum. $N_{\rm M}$ describes the total number of free parameters used in the model.

Let us assume that one has to fit N spectra, the *j*-th of them is described by the set of parameters: $(c_1, \ldots, c_i, \ldots, c_{n_c}, e_{j1}, \ldots, e_{ji}, \ldots, e_{jn_e}, d_{j1}, \ldots, d_{ji_i}, \ldots, d_{jn_d})$ where c_i stands for the *i*-th parameter common for all fitted spectra and e_{ji} describes the *i*-th parameter characteristic of a single *j*-th spectrum. Finally, d_{ji} is also treated as a characteristic parameter, but its functional dependence on the external parameter x_j is known

$$d_{ji} = f_i(x_j, p_{i1}, \dots, p_{ik}, \dots, p_{in_f}).$$
(3)

 p_{ik} stands for the k-th parameter of the function f_i .

The total number of parameters describing the single spectrum, $N_{\rm S}$ is equal to $n_c + n_e + n_d$ and to $N \cdot N_{\rm S}$ for the whole series. In the case of the multispectral fit, one has to find only $N_{\rm M} = n_c + N \cdot n_e + n_d \cdot n_f$ independent values, much less than for N single fits. In this case the set of p parameters is calculated instead of the d one.

In the set of single fits, the dependence between the set of *i*-th fitted parameters d_{ji} and the external parameter x_j should be found separately in the next

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step of analysis. This can be achieved by a regression or any other similar method. The situation is schematically presented in Fig. 1a. Multispectral fit provides a direct calculation of f_i and p_i , but one has to pay for this with an increased total squared deviation sum (Fig. 1b).



Fig. 1. Scheme of the series measuremets analysis for (a) the parameters fitted separately and (b) the same parameters fitted simultaneously. Thick vertical lines stand for χ^2 values obtained for each spectrum, dashed lines stand for dependences of χ^2 on external parameter. In (c) a comparison between minimization of squared deviation sums in a single and a multispectral fit is presented.

On the other hand, finding f_i and p_{ik} with both methods is based on the minimization of squared deviation sums (SDS): between measured points and fitted spectra for multispectral fit, $\chi^2_{\rm T}$, and, additionally, between d_{ij} parameters and functional dependence f_i for a set of single fits (Fig. 1c):

$$SDS = \sum_{j} \chi_{j \min}^{2} + \sum_{j} [f_{i}(x_{j}) - d_{ji}]^{2}.$$
(4)

Assuming in the first approximation the χ_j^2 dependence on d_j is parabolic

$$\chi_j^2(d_{ji}) = \chi_{j\min}^2 + (\Delta d_{ji})^2, \tag{5}$$

where Δd_{ji} is the distance from the d_{ji} calculated for $\chi^2_{j\min}$ in a single fit, the minimization process relates to the same functional dependences in both methods. From this point of view, these methods are equivalent and should lead to similar results.

Unfortunately, the real function $\chi_j^2(d_{ji})$ is not smooth, specially for low signal-to-noise ratios (SNR), and a high possibility of finding local minimum instead of the global one occurs. Moreover, multidimensional function χ_j^2 can possess several shallow minima, each of them described by a different set of the hyperfine

parameters, and only one of them corresponds to the "true values" describing the fitted spectrum. Applying foreseen dependences between parameters just during the fitting procedure enables, reasonably early, rejection of accidental and not acceptable values of the parameters.

3. Fitting methods

Fitting of the single spectrum can be carried out with the least squares method described in [2]. There are standard computer programs available for this procedure. In order to fit several spectra simultaneously, one can, in principle, directly use the same fitting algorithm as for the single spectrum with the restriction to the estimation of the fit quality as mentioned above. However, a total number of fitted parameters in the multispectral fit is greater than in the single one and the computer program should have the capability of working with large-enough sets of data.

One of disadvantages of the least squares methods is the necessity of knowing values of starting parameters for the fitting procedure. These parameters are often taken from the "rule of thumb" and may not lead to the convergence of iterations for poorly resolved spectra, in particular. Moreover, minimization process can lead to an unacceptable minimum, as it was mentioned above. For that reason minimization of $\chi^2_{\rm T}$ based on the Gauss–Seidel method was tested [3], as well as a finding the minimum with a program based on genetic algorithms [4]. The former permits a wider range of starting parameters in calculations, the latter enables, additionally, localization of the global minimum of the investigated function, not only the local one.

4. Calculations for simulated spectra

The fitting procedures described above were tested on two sets of six simulated Mössbauer spectra with a different statistical quality. They are presented in Figs. 2 and 3 at the top of each figure. Each spectrum consists of two components: a single line and a small doublet, with very similar spectral parameters (see Table). Additionally, a linear dependence of some chosen spectral parameters and external parameter x_j was assumed to hold ($x_j = j$ for the simplicity). All spectra have been simulated with a statistical noise. For the first series of the spectra the SNR value was high and equal to 45, whereas the second series was characterized by a poor statistics with SNR = 4.5.

Each set of data was fitted with four independent methods:

1. All spectra were fitted independently with the least squares iteration method. No assumption regarding their hyperfine parameters was made, starting values of the fitted parameters were the same for all spectra. The differences between the starting and the true values were smaller than 0.01 mm/s, the relative amounts of the subspectra were started from the value of 0.5. Each spectrum was described by 8 independent parameters (48 independent parameters for all the spectra).

TABLE

The hyperfine parameters assumed for simulated spectra. Parameter x changes from 1 to 6.

	Subspectrum 1	Subspectrum 2
abundance [%]	60	40
line width $[mm/s]$	0.30 + 0.01x	0.30 + 0.02x
isomer shift [mm/s]	0.01x	0.005x
quadrupole splitting $[mm/s]$	_	0.10 + 0.01x



Fig. 2. ⁵⁷Fe-site Mössbauer spectra simulated for SNR = 45. Solid lines represent the best fits obtained with method 4. External parameter values, x, are indicated. The spectrum without statistical noise (solid line) and its components (dashed lines) for external parameter equal to 1 are shown at the top of the figure. Fig. 3. The same as in Fig. 2 but for SNR = 4.5.

- 2. All spectra were analyzed simultaneously. Line widths, quadrupole splittings and isomer shifts were assumed to be external parameter dependent. The relative amounts of the subspectra were kept constant and common for all cases. Starting values for the parameters and the fitting procedure were similar like those in method 1. All the spectra were described by 24 independent parameters.
- 3. All assumptions were identical like in method 2, except the fitting procedure. The Gauss–Seidel method for finding the minimum of multidimensional $\chi^2_{\rm T}$

function was used.

4. Minimization of $\chi^2_{\rm T}$ was obtained by the genetic algorithm based method. This method was succesfully applied in the analysis of the single Mössbauer spectra having Lorentzian line shapes [5, 6]. For the multispectral fit, proposed here, the individual related to one series of the fitted spectra was described by 24 parameters. 2000 individuals were used for calculations with a mutation probability p = 0.001. The fitness of each series was calculated as proportional to the inverse of $\chi^2_{\rm T}$.

4.1. Results for the first series (SNR = 45)

As can be clearly seen in Fig. 4, the parameters describing the line position on the velocity scale (IS, QS) and the line widths (G) could have been fitted with similar quality independently of the fitting method. Also the dependences of the parameters on x_j were found correctly. A larger difference between the assumed and the obtained values were, however, obtained for abundances of the subspectra, the largest being in the case of methods 1 and 2, whereas methods 3 and 4 have given much better agreement.

4.2. Results for the second series (SNR = 4.5)

Fitting results of the Mössbauer spectra with the low SNR value are presented in Fig. 5. A failure of method 1 is obvious in this case. Also the values obtained with method 2 are unsatisfactory (this is caused by a poor statistical quality of the spectra that results in finding a deeper local minima of χ_j^2 , even for the starting parameters very similar to the correct ones). None of the two methods has supplied a full set of correct fitting parameters, although particular parameters e.g. IS for the single line had the correct values. The fitted parameters obtained with methods 3 and 4 are rather close to the correct values, the differences between them being not larger than for the first series.

The above examples clearly demonstrate that fitting a series of the spectra simultaneously can give better results than fitting the same spectra independently, especially when a proper fitting method has been applied. In other words, methods 3 and 4 fulfilled introduced constraints and provided correct fits even for the low SNR values. Method 2 was found useful, but only for the spectra with the high SNR, while for low SNR it is not resistant against finding the local minima of χ^2 . The results obtained with method 1 cannot be acceptable for both series of measurements (the set of partially correct parameters cannot be regarded as entirely correct). This restricts the least squares iteration methods to the spectra with good-enough statistics.

5. Calculations for Sn-doped CoSb₃

An Sn-doped $CoSb_3$ skutterudite series measurements for various Sn concentrations are a suitable example for a practical application and testing of

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Fig. 4. Spectral parameters for the simulated spectra (SNR = 45). The correct ones are in form of solid lines, and the fitted ones with different methods are marked by circles and dashed lines. x_j — external parameter described in the text, A — abundance, IS — isomer shift, QS — quadrupole splitting, G — line width. Index 1 stands for the singlet, and 2 for the doublet.

the fitting methods. Doping $CoSb_3$ skutterudite with Sn atoms was carried out in order to improve its thermoelectric properties, e.g. by influencing the Seebeck coefficient through changing electron/hole masses. For that purpose one should control positions of Sn atoms in the matrix (in this case there are only two: Sn atoms can be (a) located substitutionally i.e. on the Sb crystallographic posi-



Fig. 5. The same as in Fig. 4 but for SNR = 4.5.

tions, or (b) interstitionally i.e. in a cage). The Mössbauer measurements are well situated for distinguishing between these two positions.

¹¹⁹Sn Mössbauer spectra were recorded in a transmission geometry on powdered samples using a standard spectrometer and a scintillation detector for the γ -rays supplied by a Ba^{119m} SnO₃ source. The room temperature spectra are presented in Fig. 6. They can be decomposed into two subspectra with two sets of the hyperfine parameters different enough to justify the application of the fitting method 2. Additional subspectrum with isomer shift IS ≈ 0 mm/s corresponds to an unknown phase containing Sn atoms. Its abundance is very small (it was



Fig. 6. ¹¹⁹Sn-site Mössbauer spectra of Sn-doped CoSb₃ skutterudite for various tin concentration: (a) 0.5 at%, (b) 1.0 at%, (c) 1.5 at%, (d) 2.0 at%, (e) 2.5 at%. Solid lines represent the best fits with method 2, dashed lines represent subspectra related to different crystallographic tin positions.

Fig. 7. ⁵⁷Fe-site Mössbauer spectra of $Fe_{1-x}Ti_x$ measured at 80 K for various x: (a) x = 0.02, (b) x = 0.05, (c) x = 0.07, (d) x = 0.09, (e) x = 0.11. Solid lines represent the best fits with method 4.

not seen in any X-ray diffraction (XRD) measurements) and for that reason it was neglected in further analysis.

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The analysis was carried out assuming that any differences between the spectra are caused only by different amounts of the (a) and (b) sites, and all other spectral parameters were kept identical for all the spectra in the series.

All the spectra were fitted simultaneously, using the least squares iteration procedure. The hyperfine parameters obtained from the fit enabled decomposition of each spectrum into two subspectra related to the different crystallographic positions of tin. Also abundances of Sn atoms in position (a) or (b) were calculated with a good accuracy. The results are close enough to similar results gained for the NiSbSn skutterudite system. See Ref. [7] for details.

6. Calculations for $Fe_{1-x}Ti_x$ alloys

The fitting of a series measurements on Fe–Ti alloys is another example of the application of the presented methods. The question which should be answered this time is: are titanium atoms distributions in iron matrix random, and, if no, what type of inhomogeneity is observed for this system?

 57 Fe-site Mössbauer spectra, whose examples are shown in Fig. 7, were recorded at 295 K and at 80 K in a transmission geometry using a standard spectrometer and a 57 Co/Rh source for gamma radiation of 14.4 keV energy. The samples were in form of powder, measurements at liquid nitrogen (LN) temperature were carried out with temperature stabilization within 0.1 K.

It was assumed that each spectrum was a superposition of a number of sextets corresponding to various atomic configurations around the probe Fe atoms, in the first two neighbor shells. Composition-dependent changes of spectral parameters i.e. the hyperfine field, H, and the isomer shift, IS, were assumed to be additive, too. The hyperfine field at Fe nuclei having m Ti atoms in the firstneighbor shell (NN) and n ones in the second-neighbor shell (NNN), H(m,n;x)can thus be written as follows:

$$H(m,n;x) = H(0,0;x) - m\Delta H_1 - n\Delta H_2,$$
(6)

where $\Delta H_{1,2}$ stands for a change of H due to one Ti atom situated in NN (index 1) or in NNN (index 2). Similar relationship was assumed to hold for the isomer shift. Such a procedure was successfully used for various Fe-based alloys e.g. [8] and the shifts $\Delta H_{1,2}$ and $\Delta IS_{1,2}$ are in a wide range concentration-independent. However, the critical concentration at which the additivity formula breaks down depends on a foreign element: for Fe–Ti it seems to be valid only for x < 8. In the present fitting procedure the spectra were treated as composed of two parts. A low-field subspectrum observed for x > 8, was accounted for by a doublet, whose hyperfine parameters were calculated separately for each spectrum. A high-field subspectrum in form of a sextet was fitted assuming the $\Delta H_{1,2}$ and $\Delta IS_{1,2}$ are concentration-independent. The H(0,0,x) and I(0,0,x) were assumed to be a linear function of concentration. Only the sextets corresponding to the configurations with m < 3 and n < 3 were taken into account. The starting values of a probability configuration, P(m, n; x) should be close to the nominal one, $P_N(m, n; x)$

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derived from the binomial distribution. The tendency of changes for a given (m, n) configuration should be also similar for all investigated concentrations. Following this idea the probability values were calculated according to the formula

$$P(m, n; x) = P_{\rm N}(m, n; x) + P_{m,n}(x),$$
(7)

where $P_{m,n}(x)$ stands for a polynomial of x describing the correction of the (m, n) configuration probability with respect to its nominal value.



Fig. 8. Probabilities of the atomic configurations, P(m,n) taken into account in the fitting procedure versus Ti-content, x. The P(m,n) values found from the spectra recorded at 80 K are shown as full symbols, those obtained from the spectra measured at 295 K as open symbols, and the solid lines represent the values expected for the random distribution.

In order to be up to the above assumptions all the spectra were fitted simultaneously with common hyperfine parameters and 9 formulae describing $P_{m,n}$ polynomials. The method based on the genetic algorithms as well as the Gauss– Seidel method of $\chi^2_{\rm T}$ minimization were used. This choice of the fitting methods was caused by a high enough degree of complication of the chosen model, where the polynomials of at least 3rd order should be fitted. The knowledge of the best-fit spectral parameters enabled evaluation of the concentration dependent probability of each configuration (m, n) for the two temperatures, independently (Fig. 8), and proved that the distribution was not random, but some configurations were occupied preferentially. See Ref. [9] for details.

7. Calculations for σ -FeV series measurements

Analysing of a set of measurements on σ -FeV alloys is the last example of the application of these methods. The problem which should be solved here is an analysis of a series of 13 Mössbauer spectra measured at different temperatures. The spectra are poorly resolved and most of their parameters are unknown. On the other hand, all these parameters (except two of them) should be identical for all temperatures.

The crystallographic structure of the σ -phase was identified as close-packed tetragonal — space group $D144h - P4_2/mnm$ — with 30 atoms in the unit cell, which are distributed over five crystallographically non-equivalent lattice sites with different occupation numbers (2, 4, 8, 8, and 8, respectively). The sites have rather high coordination numbers (12 to 15) and quite different local symmetry. Non-statistical distribution of the two constituent atoms on the different lattice positions is present.

The Mössbauer spectroscopy belongs to the most suitable methods for investigations of structural properties and magnetic behavior of the Fe-based σ -phase. This stems from its high sensitivity to the hyperfine parameters, which are strongly influenced by the local configuration of NN atoms of the 57 Fe atom probe. A typical Mössbauer spectrum of the σ -phase must be composed of at least five subspectra with various intensities related to the iron occupation of the five inequivalent crystallographic sites. Although the corresponding hyperfine parameters (IS, QS, and H) differ from each other, the differences are comparable or smaller than the typical experimental line widths. Consequently, the spectrum is not well resolved, even below the Curie temperature. Some of the parameters describing the spectrum could have been determined in other experiments (e.g. relative subspectra contributions should be proportional to the Fe concentrations on particular sites determined in the neutron diffraction experiment), but the rest (IS, QS, H, and line widths G) should be obtained from the fitting procedure. The assumption that all the parameters (except average IS and H values) are identical for all the spectra measured at various temperatures can seriously facilitate the fitting procedure and increase the reliability of the fitting results.

Examples of 57 Fe-site Mössbauer spectra are shown in Fig. 9. They were recorded at the range of 4–295 K in a transmission geometry using a standard spectrometer and a 57 Co/Rh source for gamma radiation of 14.4 keV energy. The samples were in form of powder, measurements were carried out with a temperature stabilization within 0.1 K.

Each spectrum can be described with five sets of IS, QS, G and H (the latter only below the Curie temperature). In the analysis of the spectra the QS and G were assumed to be independent of temperature. The average center shift $\langle CS \rangle$ was calculated as the weighted mean over all subspectra. Generally, the center shift consists of two terms CS = IS + SOD, where IS is the isomer shift, which is proportional to the *s*-electron density at the Fe-nucleus, and SOD the second-



Fig. 9. ⁵⁷Fe Mössbauer spectra of σ -Fe₆₀V₄₀ for various temperatures (indicated in the figure). Solid lines represent the best fits to the spectra.

-order Doppler shift, which is related to the atomic mean square displacement and, therefore, is strongly temperature dependent. Assuming that in the first approximation the phonon spectrum can be described by the Debye model, and taking into account that the temperature dependence of IS can be neglected, the temperature dependence of CS can be related to the Debye temperature. The obtained SOD(T) dependences are smooth enough (see Fig. 10) to determine Debye temperature values for different alloy compositions with a good accuracy, which was the main aim of the applying this fitting procedure.



Fig. 10. Second-order Doppler shifts versus temperature for various vanadium concentrations. The extreme center shift $\langle CS \rangle$ curves are indicated in the inset for comparison.

8. Conclusions

It should be clearly noted that the analyses based on the well-known least squares methods are of a great importance and they give good results for recorded spectra. In the case of overlapping subspectra having similar hyperfine parameters, the simultaneous analysis of several Mössbauer spectra with either common parameters or external parameter dependent seems to be very useful. Even for poorly resolved spectra this procedure enables finding values of the parameters as well as dependences between them, a task hardly accessible for single fits. Applying χ^2 minimization methods different than the least squares one makes the minimization procedure less sensitive to the starting values of the parameters and to statistical quality of the spectra. The fitting method enabling localization of the global minimum of $\chi^2_{\rm T}$, independently of the starting parameters, is also worth underlining. The costs one has to pay for such profits are twofold. The first one is connected with a sort of the problem to be solved: for more complicated or unusual measurements, dedicated computer programs should be prepared. The second one is due to the fact that calculations based on method 3 or 4 are time consuming and convergence is rather slow. For method 4 an acceleration of calculations can be achieved by using parallel search genetic algorithms [10, 11] or, by applying more advanced versions of them.

The simultaneous analysis should be, however, applied very carefully, more particularly since one has to know the kind of dependences on external parameter. There is a danger that new information will be lost when the dependence has not been correctly chosen. Sometimes it is enough (and more safely) to assume a type of monotonicity for the dependence only and to resign from an analytical formula. This allows one to check the kind of the dependence first, and then apply it to the fitting procedure in the next step.

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