Non-linearity correction of the velocity scale of a Mössbauer spectrum

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Motivation

Calibration of the velocity scale of a Mössbauer spectrum is the first step when starting measurements of unknown samples. The spectrum of an α-Fe foil fixes 6 or 12 velocities on the channel scale for single-branch (saw tooth) or mirror (triangular and sinusoidal) mode, respectively. In case of good linearity of the transducer, the set-point velocity value can be assigned to each channel or, more precisely, to the beginning and the end of each channel. Some kind of correction becomes necessary if there is a significant non-linearity between the set-point and actual values of the velocity, a situation occurring in most Mössbauer spectrometers. Neglecting this correction results in an incorrect velocity assignment to a channel which, during spectrum evaluation, distorts the χ2 surface and, therefore, the step-down algorithms for fitting. We present an approach to the evaluation of calibration spectra by which the non-linearity of the spectrometer can be determined and used for correction of the velocity scale in further experiments.

Experimental approach

The linearity of the driving unit is never perfect. In a routine way, it can be only checked by the Mössbauer effect itself by "known" positions of the resonance lines. The most reliable line positions for α-Fe at 298 K were determined in 1971 by Violet and Pipkorn using the Moiré fringe technique [1]. Line positions of other reference materials like α-Fe_2O_3 are secondary and possibly also based on extrapolation so that they should not be used for nonlinearity correction. Nevertheless, the respective number of fixed velocities can be increased from 6 or 12 to 15 or 30 for single-branch or mirror mode if a hyperfine-split ^{57}Co(α-Fe) rather than a single-line ^{57}Co(Rh) source is used with the α-Fe absorber. The test experiments were performed on a WissEl spectrometer using an α-Fe absorber of 25.5 μm thickness.

Correction function for non-linearity

The drive velocity is approximated with a Fourier series:

$$v(t) = -v_{max}\frac{4}{\pi^2}\left(\cos\omega t + \frac{\cos 3\omega t}{3^2} + \frac{\cos 5\omega t}{5^2}\ldots\right) \qquad (1)$$

$$dv(k) = \sum_i \delta a_i \cos(\omega_i k) + \delta \boldsymbol{b_i} \sin(\omega_i k) \qquad \delta \boldsymbol{b_i}:\ \textit{phase shift}$$

$$\omega \cdot 512 = \pi/2,\ \ k = 1-2048 \qquad \omega_i = (2i-1)\cdot\omega,\ \ i\cdot\omega,\ \ i\cdot\omega/2$$

Approximation of the triangular velocity function with a Fourier series

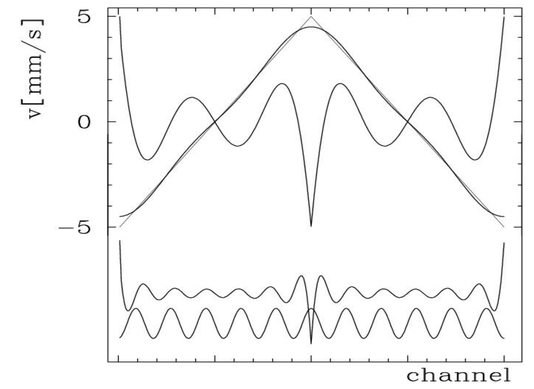

Fig. 1: The triangular function *v(k)*, the velocity (-5 mm/s < *v* < 5 mm/s) versus channel *k* which linearly depends on time *t* is plotted for one period together with the approximate Fourier series of Eq. 1 up to the second term of 3ω. The difference between the triangle and the approximation is super-elevated by a factor of 10. The accuracy around zero velocity defined by *dv* =10mm/s is about 1.4 %. The two lower curves are the deviation for the series up to 11ω and the function -cos(11ω k). Around *v* = 0 the deviations are in phase with the cosine function and specify an accuracy of 0.15 %.

Line intensities, texture and line widths

Theoretical spectra were calculated with the convolution transmission integral formalism accounting for polarization and texture both in source and absorber. Therefore not only the line positions but also the line intensities and the line shapes contain information on the non-linearity of the drive. The texture functions were expanded by spherical harmonics leading to 5 coefficients and the spectra belonging to all possible directions of the hyperfine field were numerically averaged over a sphere [2]. The Lamb–Mössbauer factor for α-Fe *f* = 0.80 was used. The selfabsorption of the already decayed ^{57}Co in the source was accounted for [3]. **The line width of the α-Fe absorber is no free parameter; all fits were compatible with Γ(α-Fe) = $\Gamma_{natural}$ = 0.0971 mm/s.**

^{57}Co(Rh) vs. α-Fe, triangular mode

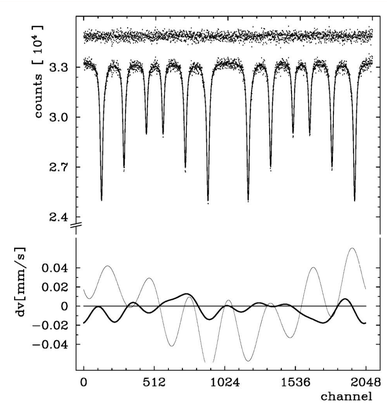

Fig. 2: The α-Fe spectrum measured with a single-line source in constant acceleration (triangular) mode at a drive frequency of 17 Hz. The fitted non-linearity *dv* of the velocity-to-channel scale is the thick function line varying close to *dv* = 0 was obtained with the full asymmetric correction function allowing for phase shift. Large corrections (thin function line) were needed for the spectrum measured at 4.25 Hz (not shown, by eyes looks indistinguishable from the 17 Hz spectrum). The relative χ^2-values of both spectra are very close to unity (1.038 and 1.015, for 17 Hz and 4.25 Hz, respectively).

^{57}Co(Rh) vs. α-Fe, sinusoidal mode

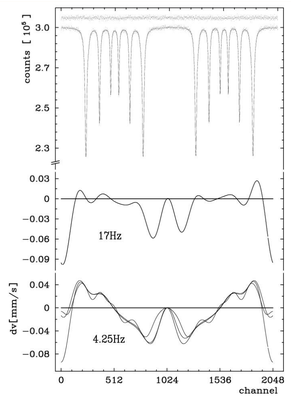

Fig. 3: The α-Fe spectrum measured with a single-line source in sinusoidal velocity mode at a drive frequency of 17 Hz. The spectrum measured at 4.25 Hz is not shown, by eyes it looks indistinguishable from the 17 Hz one. Both spectra were fitted with the full asymmetric correction function *dv* allowing for phase shift and resulting in the smallest variation between the absorption lines (lower part of the figure). The 4.25 Hz spectrum was fitted also with two further, symmetric correction functions resulting in almost the same relative χ^2-values of 1.041, 1.060, and 1.040.

^{57}Co(α-Fe) vs. α-Fe, triangular mode

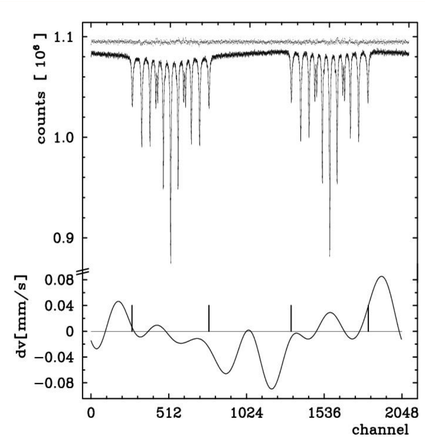

Fig. 4: The α-Fe spectrum measured with a hyperfine-split ^{57}Co(α-Fe) source gives 15 (13 visible) absorption lines, the outermost ones being at ±10.7 mm/s. The spectrum measured in triangular velocity mode at a drive frequency of 17 Hz was fitted with the full asymmetric correction function in the range of ±15 mm/s. In the range of the absorption lines ±10.7 mm/s indicated by vertical markers the deviation *dv* is a smooth function compared to the spacing of line positions and varies between ±0.03 mm/s.

^{57}Co(α-Fe) vs. α-Fe, triangular mode

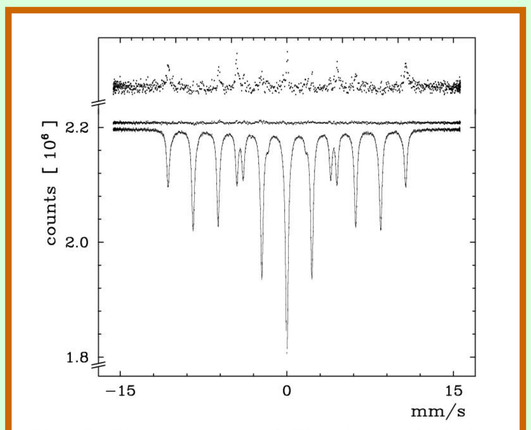

Fig. 5: The spectrum of Fig. 4 was folded by adding interpolated counts from the right half to the velocity channels of the left half of the spectrum. An additional residue is shown on an enlarged scale in the upper part of the figure which belongs to the same parameters except that the texture parameters were put to zero. The relative χ^2-value increased from 1.37 to 3.22 neglecting the texture of the iron foils. This shows, on one hand, that in a proper theory the magnetic texture of source and absorber should be accounted for and, on the other hand, that the original theory was already slightly incomplete.

Conclusions

There is no way to get a true velocity-to-channel scale from a calibration spectrum which has only a finite number of positions. The standard methods compare theoretical line positions with measured one and calculate by some interpolation methods (spline function) a velocity-to-channel function or only by averaging a velocity range per channel. The proposed multi-parameter correction function enables a fit to the calibration spectrum down to a relative χ^2 of 1. This fit means that not only the positions but also the shapes of the absorption lines are reproduced which is equivalent or at least comes close to the requirement of an infinite number of positions. The velocity-to-channel function has the property even to fit with one correction function the velocity-to-channel scale of a double spectrum as obtained with the triangular or sinusoidal driving mode. This way all problems connected with the folding constant are avoided. In order to visualize the experimental spectrum together with the theoretical one the "folding" procedure is shifted to the plot program which is allowed to manipulate the experimental data neglecting the strict rules to preserve Poisson statistics. The proposed velocity-to-channel function visualizes the non-linearity of the drive unit and can serve as a tool of controlling the stability of the drive. The criteria for the best drive frequency are not any more shifts of folding points and line positions but the smoothness of the velocity-to-channel function inside the velocity range of the spectra to be measured.

Relative χ^2 and the number of counts

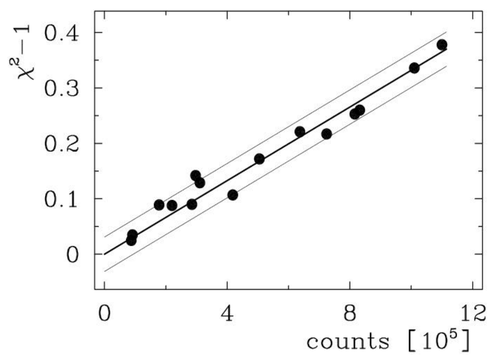

Fig. 6: The linearly increasing value of the relative χ^2-value minus 1 with the number of counts indicates a systematic misfit of the theory. The data correspond to various stages of the experiment shown in Fig. 5 when fitted with magnetic texture. The two lines on both sides are at a distance of $1\sigma = \sqrt{2/N}$ with *N* being the number of channels.

References

[1] C.E. Violet, D.N. Pipkorn, J. Appl. Phys. 42 (1971) 4339.
[2] K.M. Hasselbach, H. Spiering, Nucl. Instr. Methods 176 (1980) 537.
[3] H. Spiering, V. Ksenofontov, O. Leupold, J. Kusz, L. Deák, Z. Németh, C. Bogdán, L. Bottyán, D. L. Nagy, Hyp. Int. 58 (2016) 237.