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Experimental design and methodology for a new Mössbauer scan experiment: absorption line tracking

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Abstract A new experimental setup and methodology that allows the automatic tracking of a Mössbauer absorption line as its energy position varies during the experiment is introduced. As a test the sixth spectral line of $FeSn_2$ was tracked while temperature was varied between room temperature and a value slightly above its Néel temperature.

Keywords Mössbauer · Instrumentation · Spectrometer · Constant-velocity · Line tracking

1 Introduction

Mössbauer effect is a versatile tool which provides valuable information on a variety of phenomena involving both static and dynamic situations. Different experimental approaches have been proposed depending on the investigated subject [1–3]. In particular, scans at constant source-absorber velocity have been introduced as an efficient way to study the hyperfine interactions temperature dependence [4–6], the thermal evolution of metastable materials [7, 8], the degree of advance of a solid state reaction [9] and the magnetic response to dc and ac fields [6, 10].

Here, we present an experimental setup and a novel methodology which allows the selection of a velocity (energy) in regions of interest (ROI) which can be con-

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tinuously moved along the complete velocity range. Some important features are its low cost, and the fact that it can be easily incorporated to a standard Mössbauer lab (switching between spectrum and scan mode setups is simple and timeless). As an example we tracked selected spectral lines of $FeSn_2$ when the temperature is intentionally varied.

2 Experimental layout and simulation environment

The experimental setup, shown in Fig. 1, consists of a conventional pulse height selection branch, a conventional Mössbauer driving system, and a previously introduced [11, 12] programmable scaler replacing the usual multiscaler. This layout allows the independent acquisition of every spectrum channel based on a constant velocity strategy.

Calibration was performed recording a complete α-Fe spectrum, which was compared with a conventional constant acceleration one taken with the same instruments, replacing the programmable scaler by a Nucleus MCS-II multiscaler board. The two spectra, taken one immediately after the other, resulted coincident, with a line width of 0.21 mm/s, considering the sample thickness.

Automation was achieved through a basic but complete set of high-level language communication routines. In this way, the programmable scaler can be fully operated using a re-programmable algorithm hosted in a PC. Additionally, a simulation environment was developed, consisting of a set of procedures that can be used to test the experimental strategies and control algorithms without spending expensive laboratory time. The simulation, communication and line tracking routines were developed using the Matlab environment.

3 General design considerations and closed loop operation

In order to exploit the described functionality, we propose the selection of an energy region of interest (ROI) for a certain experiment, determined by the following parameters: number of channels to be recorded N, ROI center C and channel spacing (mm/s), and finally net time t of event counting in each channel in seconds. The time required to record a ROI is determined by $T = Nt/e$, being e the efficiency of the constant-velocity scaler.

The experiment design is completed with the ROI displacement strategy. At this point, different methodologies can be considered, like *static* (where the center of the ROI is always at the same velocity), *programmed* (the center of the ROI describes a pre-decided open-loop trajectory), or *tracking* (the center of the ROI follows a measurable singularity of the spectrum in closed-loop operation mode).

The latter is the most interesting case to evaluate, more specifically in the case of an absorption line tracking. When time is a critical parameter, as is the case of rapidly changing physical situations, it is advisable to spend time collecting events in a relevant region of energy, taking advantage of the programmable velocity scaler. But, when a transformation is under study, the location of the significant region changes in time and cannot be known in advance. A tracking strategy that allows the recording of a dynamic region of interest is proposed, in which a closed-loop algorithm is in charge of determining the position of the next ROI based on the recorded data.

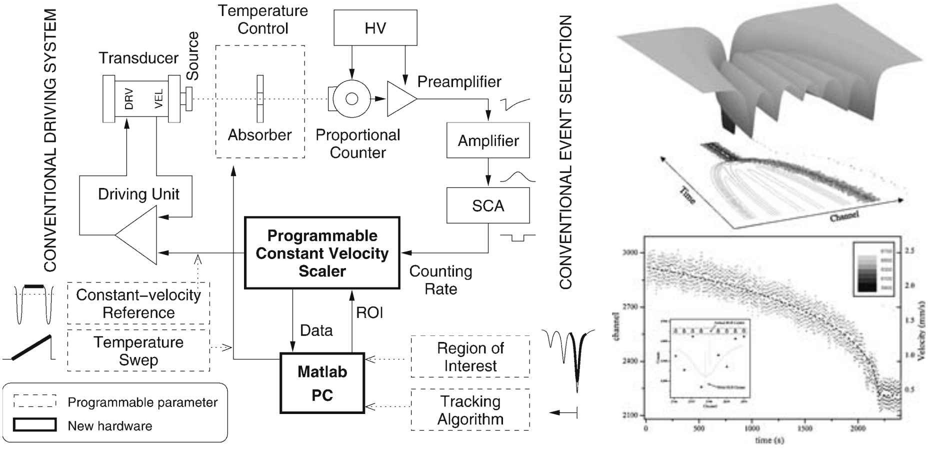

Fig. 1 *Left*: Involved instruments with available programmable parameters. *Right and top*: $FeSn_2$ sixth line tracking simulation (3% effect) with a non-uniform eight channel ROI, when a rate of 6,500 c/s is available, below absorption as a function of time and energy (*channels*) is shown; contour levels are shown at the *bottom*, together with the simulated measured channels. *Right and bottom*: simulated ROI evolution in time, compared with the sixth line center position (*dashed*); in the *inset* a single ROI is fitted in order to determine the minimum

The initial parameters of the ROI must be selected according to the previous knowledge about the material under study and the experimental requirements. Based on these initial parameters, the control algorithm establishes a set of source-absorber relative velocities and enables the scaler for recording gamma ray transmission within this ROI. Using the retrieved data and its history, the algorithm relocates the ROI center on its new expected position. All recorded velocities and their corresponding data are stored to allow a further post-experiment analysis and spectral reconstruction.

It is important to note that the algorithm is only implemented for tracking purposes. The reconstruction is performed off-line by a different procedure. The quality of the reconstruction will depend on both the spectrometer tracking efficiency and the previous ROI selection.

The time spent in recording each ROI determines the allowed dynamics for the experiment. Depending on the algorithm ability to determine the tracked parameter beyond the ROI boundaries, a closed loop tracking can fail if the region of interest takes too long to be recorded. On the other hand, the time per channel must be selected long enough to reduce the dispersion due to the process statistical nature and guarantee the tracked singularity discrimination. This time depends on the event rate m and the relative Mössbauer effect f. Then a compromise arises between the amount of data recorded and how fast the line can move and still be tracked. In order to achieve the mentioned discrimination, the criteria could be to make the relative statistical error at least k times smaller than f, resulting that the time per channel t must be longer than $(k/f)^2/m$. In practice, a k factor over 3 is recommended for a good overall behavior, while smaller values may result in noisy tracking or even fail. The quadratic dependence on f restricts the application of this method when the Mössbauer effect is small, by limiting the tracking capabilities. Optimum thickness and rate optimization are advisable to maximize tracking speed. The limit in the velocity at which the absorption line can move is imposed by the time T necessary to record data for the selected ROI. If high precision is required the line should not move faster than a few channels per T. In that case, being q (mm/s) the allowed line displacement while a ROI is being measured, results that the line velocity over the energy axis L (mm/s/s) must be smaller than q/T.

A number of further remarks should be made about the ROI geometry. Regarding the number of channels N, although there is no hardware limit, it is important to note that a compromise exists with t when T is imposed by the experiment dynamics. Raising the number of recorded channels necessarily implies a reduction in the time per channel, increasing the statistical uncertainty. About the channels spacing, it must be noted that the programmable scaler can record any of its 4096 channels independently. This means that no restriction applies to the ROI channel spacing. At this point several arrangements where tested, including *uniform*, *logarithmic* and *lorentzian* spacing. Uniform spacing is advisable for a large value of q (the line moves significantly inside the ROI while it is being recorded). With non-uniform spacing the channels can be concentrated in the ROI center or in the most sensitive region of it (for example the points where the derivative of the lorentzian absorption line has a maximum), being a small value of q imperative for this strategy to succeed.

From the wide spectrum of possibilities, two different line-tracking strategies were considered. The first consists of a multipoint ROI covering twice the line width, plus an additional point to record the background; the tracking algorithm is based on setting the ROI next center at the minimum absorption energy of the actual ROI, which is determined by fitting the recorded data with a lorentzian. The second strategy is an interesting case that arises from the minimum amount of channels that a ROI can contain in order to maximize the available time per channel and minimize the statistical uncertainty; if background and line width are known in advance and are supposed to remain constant, only two channels are enough in order to estimate the absorption and line position by finding the lorentzian that contains these points; the next ROI two channels are placed approximately at one third of the line width at each minimum side, where the lorentzian slope has a maximum. In both cases it is straightforward to add prediction by means of the position first derivative. If required, a more complex algorithm can be implemented with variable ROI parameters (N, S and t) and more sophisticated prediction (for example, dual line tracking with merging ROIs).

4 Experimental results

In order to quantitatively exemplify the previous expressions a $FeSn_2$ absorber is considered. $FeSn_2$ is an antiferromagnet with a unique structural site for the iron probe, with no nuclear quadrupolar interaction. Its Mössbauer spectrum consists of a unique sextet that collapses into a singlet about 70 K above room temperature (RT), where the Néel transformation (T_N) occurs. Mössbauer spectra showing this transformation can be found in literature [4]. The low value of T_N makes it suitable for fast scans testing. In this case, considering a sample with 3% effect in its sixth line (the more energetic and intense) with a counting rate of 6,500 counts per s, in order to reach $k = 3$, a time of 1.5 s per channel is required. Assuming an efficiency of 0.75, an eight channel ROI takes approximately 16 s to be recorded (note that for a natural iron foil with an effect of 18%, the same ROI requires less than 1 s). Finally,

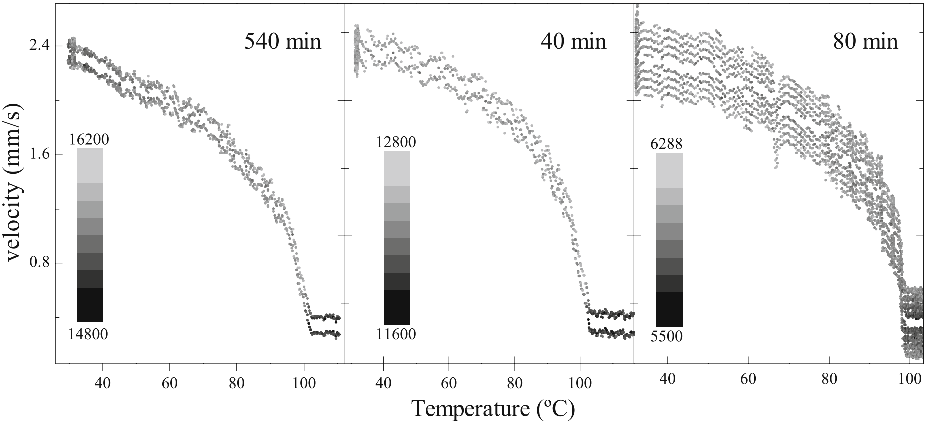

Fig. 2 $FeSn_2$ sixth line (2.5% effect) tracking experiments. *Left figure* shows results for a low activity source (2 mCi, 850 c/s) scan using a two channel ROI with 20 s per channel. *Center and right figures* show results for a high activity source faster scans (50 mCi, 6,500 c/s, 100°C per h) using a two channel ROI with 2 s per channel (*center*), and an eight channel ROI with 1 s per channel (*right*)

if a value of $q < 0.02$ mm/s is imposed (less than 10% of the line width), results that the line can move as fast as 0.001 mm/s per s. This means that the whole range of 2 mm/s can be swept in less than half an hour.

Previous to the experiments, simulations were run in order to anticipate the expected experimental outcome, avoiding laboratory time misuse. Figure 1 shows the output for a multipoint region of interest with temperature shifting from RT to 380 K. The optimal parameters obtained from the simulation were applied to the sixth line experimental tracking while the temperature was increased. In order to test the technique under different working conditions, two different sources (Rh-Co^{57}) with activities of 2 mCi and 50 mCi were used. In the first case a slow temperature sweep (0.1°C/min) and a two channel ROI were necessary in order to meet the criteria previously discussed. In the high activity source case a faster sweep could be applied (in order of 1°C/min) and a two channel and an eight channel strategies were tested.

Figure 2 shows three different runs for the mentioned conditions. The sixth line was successfully tracked in all the cases up to the magnetic collapse, where the tracking algorithm catches the more intense paramagnetic line. In the last experiment a large discontinuity in the ROI position is observed at 65°C. This kind of variations in the ROI trajectory is due to the process statistical nature. Its frequency depends on the k factor defined in the previous section, while its magnitude also depends on the tracking algorithm complexity. These fluctuations are unavoidable, but its impact can be attenuated with the selection of a proper control algorithm. All counting rates and temperature measurements are stored, even if the tracking is not optimal, since they will also contribute to the post-analysis process.

A closer result examination indicates that tracking is less reliable near and below the critical point, owing to the line fast movement. But it has been shown that ROI data post-analysis by suitable physical models retrieves the hyperfine field temperature dependence correctly within a reasonable uncertainty, as it will be reported in a forthcoming paper.

5 Conclusions and perspectives

We have shown that experimental tracing of a rapidly moving absorption line (2.7 mm/s/h on the average) can be successfully performed using the introduced experimental setup along with an especially designed automated remote controlled procedure. The measuring strategy presents interesting perspectives for a number of different applications where the detailed observation of a particular spectral region is important. Applications where spectral modifications are expected as a consequence of a physical phase transformation are among the most interesting, for example transitions which involve the coexistence of two phases within a temperature interval and whose hysteresis may depend on the rate at which temperature is swept [13]. Extinction of a particular phase can also be estimated on the basis of tracking failure of a characteristic phase absorption line assisted by the post evaluation of line intensity diminution as the extinction point is approached.

References

1. Paulsen, H., Schünemann, V., Trautwein, A.X., Winkle, H.: Mössbauer studies of coordination compounds using synchrotron radiation. Coord. Chem. Rev. **249**, 255–272 (2005)
2. Mørup, S.: Mössbauer studies of relaxation effects by use of a polarized source. Hyperfine Interact. **1**, 533–543 (1975)
3. Hesse, J., Graf, T., Kopcewicz, M., Afanas'ev, A., Chuev, M.: Mössbauer experiments in radio frequency magnetic fields: a method for investigations of nanostructured soft magnetic materials. Hyperfine Interact. **113**, 499–506 (1998)
4. Mendoza Zélis, P., Pasquevich, G.A., Sánchez, F.H., Veiga, A., Martínez, N.: A new application of Mössbauer effect thermal scans: determination of the magnetic hyperfine field temperature dependence. Phys. Lett. A **298**, 55–59 (2002)
5. Pasquevich, G.A., Mendoza Zélis, P., Fernández van Raap, M.B., Sánchez, F.H.: Hyperfine field temperature dependence of Fe_3Si from Mössbauer thermal scans. Physica B **354**, 369–372 (2004)
6. Pasquevich, G.A., Mendoza Zélis, P., Sánchez, F.H., Fernández van Raap, M.B., Veiga, A., Martínez, N.: Magnetic and thermal Mössbauer effect scans: a new approach. Hyperfine Interact. **167**, 839–844 (2006)
7. Mendoza Zélis, P., Rodriguez Torres, C., Cabrera, A.F., Fernández van Raap, M., Pasquevich, G.A., Sánchez, F.H., González, A., Sunyol, J.J.: Thermal evolution of $Fe_{65}Ni_{20}Nb_6B_9$ nanocrystalline metastable alloy. J. Metastable Nanocryst. Mater. **20**, 571–575 (2004)
8. Sánchez, F.H., Pasquevich, G.A., Mendoza Zélis, P., Cabrera, A.F., Ying-feng, L., Vázquez, M.: Study of magnetic materials by Mössbauer thermal scans. Application to nanocrystalline systems. J. Metastable Nanocryst. Mater. **22**, 39–44 (2004)
9. Saccone, F.D., Rodríguez Torres, C.E., Pasquevich, G.A., Fernández van Raap, M.B., Sánchez, F.H.: Crystallisation kinetics of B-rich mischmetal-Fe-B nanocomposite ribbons. Physica B **354**, 237–240 (2004)
10. Pasquevich, G.A., Mendoza Zélis, P., Sánchez, F.H., Fernández van Raap, M.B., Veiga, A., Martínez, N.: Determination of the iron atomic magnetic moments dynamics in the nanocrystalline ribbons $Fe_{90}Zr_7B_3$ by Mössbauer magnetic scans. Physica B **384**, 348–350 (2006)
11. Veiga, A., Martínez, N., Mayosky, M., Spinelli, E., Mendoza Zélis, P., Pasquevich, G.A., Sánchez, F.H.: A constant-velocity Mössbauer spectrometer with controlled temperature sweep. Rev. Sci. Instrum. **73**, 3579–3583 (2002)
12. Veiga, A., Martínez, N., Mendoza Zélis, P., Pasquevich, G.A., Sánchez, F.H.: Advances in constant-velocity Mössbauer instrumentation. Hyperfine Interact. **167**, 905–909 (2006)
13. Nam, H.D., Kim, E.C., Han, J.S.: Mössbauer study of iron sulfides doped with 3d-transition metals. Solid State Commun. **135**, 327–329 (2005)