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A quasi-continuous observation of the α-transition of $Fe_{1+x}S$ by Mössbauer line tracking

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Abstract Mössbauer absorption line tracking methodology, under a constant velocity strategy, is used for a quasi-continuous observation of the α-transition on slightly non stoichiometric $Fe_{1+x}S$ alloy. To this end, two strategies were applied: an intelligent absorption line tracking with a control algorithm that uses the data measured in the previous region to establish the position of the next partial spectral range; and a predetermined line tracking in which temperature evolution of a partial spectral region of interest (ROI) is programmed. The latter uses results from the former, in order to achieve a quasi-continuous partial spectral observation. These experiments clearly demonstrate that line tracking allows a more efficient use of the radioactive source, as the effort is concentrated in a partial region of the spectra from which the desired information can be obtained.

Keywords Mössbauer Line Tracking · FeS alpha-transition · Programmable constant-velocity scaler

1 Introduction

Mössbauer Line Tracking (MLT) [1] is a methodology designed to record the evolution of a spectral region of interest (ROI) while it undergoes changes due to the variation of an external parameter such as temperature, magnetic field, etc. The main advantage of this approach is the possibility of tracking and recording the Mössbauer absorption only of the ROI (which may or not include the center of the spectrum). This features allows to achieved a higher speed at which the external

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physical parameter can be swept. Also, it allows the recording of quasicontinuous experimental response functions and the study of processes which occur too fast to be followed by Mössbauer spectroscopy. In this work we choose the reversible α-transition in $Fe_{1+x}S$ to demonstrate the capabilities of the MLT technique to follow a structural phase transition.

The goal of the configuration described in [1] is to enable the recording of a reduced ROI which can be continuously displaced along the whole velocity range in response to an intentional change in the temperature of the sample. In this way the automatic tracking of a Mössbauer absorption line as its energy position varies can be implemented.

Slightly non stoichiometric $Fe_{1+x}S$ presents a structural transition (α-transition). On heating, the Low Temperature Phase (LTP), the superstructure (*P*62*c*) derived from the NiAs-type structure, transforms at around 400 K into the High Temperature Phase (HTP), a transitional phase which can be described by the MnP (*Pnma*) orthorhombic structure [2–4]. The transition is reversible and of the first order, then both phases coexist within a temperature interval which, depending on stoichiometry, goes from a few degrees to around 200 K. Both phases are antiferromagnetic with iron atoms located at unique crystallographic sites. The probe environments are different enough to allow hyperfine fields from both phases to be distinguished within their coexistence temperature region.

MLT methodology is used to perform a quasi-continuous temperature study of the α-transition. The tracking was performed within a ROI which allows the observation of two absorption lines (one from each phase) and the background simultaneously, while temperature is varied within the coexistence region, both heating and cooling.

2 Experimental procedures

Commercially available FeS powder was treated during 12 h at 870 K and during 72 h at 1,270 K to improve sample homogeneity. Phase identification was achieved through Mössbauer Effect (see Fig. 1a). At RT 92% of the iron atoms are in the LTP, 4% in α-Fe and 4% in a paramagnetic impurity phase barely distinguishable in the spectrum central zone. The presence of the α-Fe signal suggests that FeS stoichiometric is slightly Fe rich, what is confirmed by the fact that the LTP phase spectrum coincides with that of troilite, a phase that is not observed in the case of iron deficiency.

The Mössbauer spectra reflect the α-structural transition. At 430 K it corresponds to the HTP structure plus the already mentioned minor contributions (Fig. 1a). The spectrum recorded at 400 K shows the superposition of LTP and HTP subspectra (Fig. 1a, middle).

The experimental setup for a MLT consists of a conventional pulse height selection branch, a commercial driving system and two recently developed NIM modules serially interfaced with a computer. The first one is a previously introduced [5] programmable constant-velocity scaler that replaces the usual multiscaler. This module allows the independent acquisition of every spectrum channel based on a constant-velocity strategy and consequently the acquisition of partial Mössbauer spectra in selected energy regions. The second module is an analog microprocessor-based input/output interface that records the temperature and commands a linear

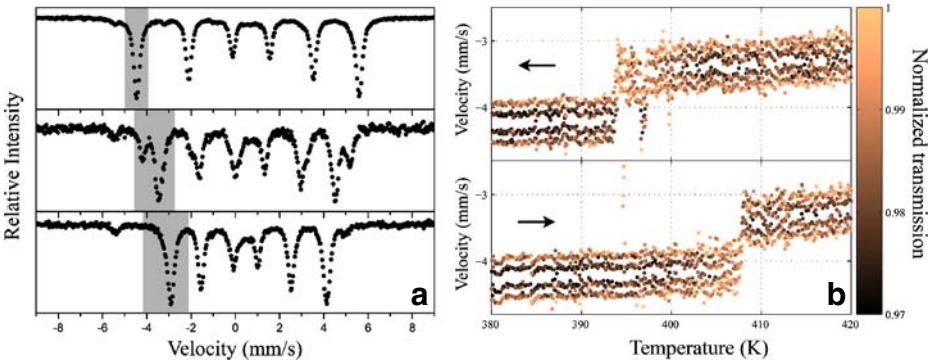

Fig. 1 **a** Mössbauer spectra of $Fe_{1+x}S$ ($x << 1$) at 300, 400 and 430 K from *top* to *bottom*. At high and low temperature a single phase is present, while at 400 K both phases can be observed. The *grey bars* stand to indicate ROI position and extension. **b** Line tracking results over the first line of the magnetically split spectrum, heating (below) and cooling (above)

DC power source that heats the sample. The line tracking and temperature control algorithms are hosted in the computer. These algorithms are written in a high-level technical computing language that interacts directly with hardware, where an environment for algorithm development, data visualization and data analysis was also developed. This configuration enables the programmable scaler and the input/output module to be fully operated using a re-programmable strategy that is closely related with the experiment.

A 25 mCi ^{57}Co*Rh* source was used for all the experiments.

3 Line tracking experiments

As a first approach, we applied an intelligent line tracking methodology where a control algorithm determines the position of the ROI using the measured data. The following result was obtained from a FeS absorber (4% effect at lines 1, 6) while it was warmed up to 435 K from 300 K, and then cooled back down to 300 K. The wall time of the experiment was 13.5 h. A four channel ROI plus background, and a time/channel ratio of 5 s were chosen. The initial ROI was selected in order to match Line 1 of the LTP based on information previously obtained from Mössbauer Spectra. While the temperature was swept the ROI was successfully repositioned by the tracking algorithm, holding the transmission minimum approximately in the center of the ROI (see Fig. 1b). In the temperature transition region, where both phases coexist, the algorithm succeeded in tracking the HTP when the LTP faded. When the temperature was lowered this process occurred in the opposite way.

In a final experiment, a predetermined tracking using a temperature dependent ROI(T) of Lines 1 of both phases was produced, based on the information retrieved from the line tracking experiment discussed above. A 25 point ROI(T) and a time/channel ratio of 5 s were chosen. The background was simultaneously measured at a fixed channel. The sample was cooled to 300 K from 435 K and then warmed back to 435 K. The wall time of the experiment was 70 h. The experimental

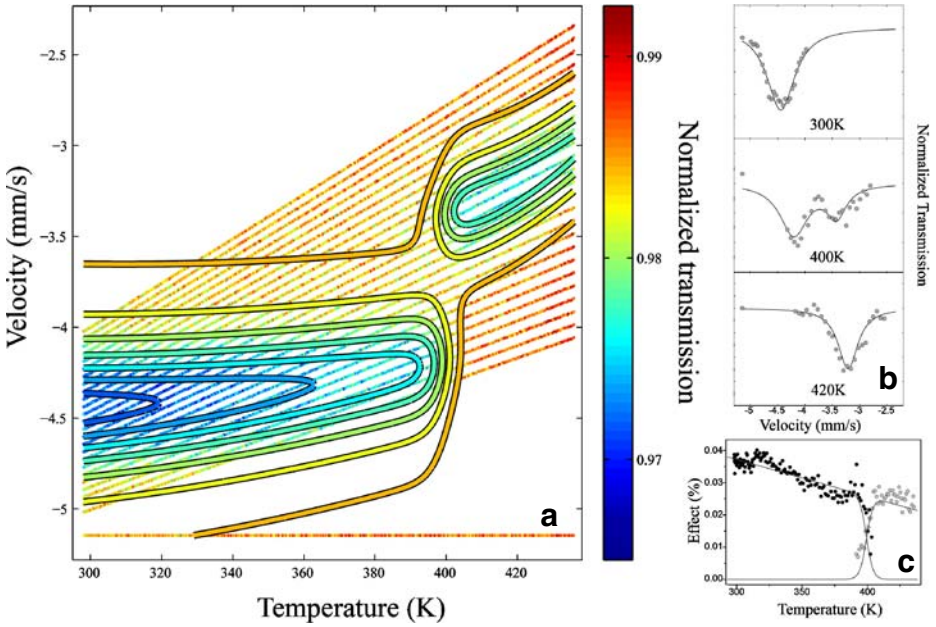

Fig. 2 **a** 3D plot of the Mössbauer transmission as a function of source velocity and sample temperature determined using a temperature dependent ROI chosen to have a good observation of the phase transition. This data correspond to the warming process. In *black* the contour lines of the fitted surface absorption function. **b** Comparison of the function and experimental data at specific temperatures. **c** First absorption line effect obtained from the fit procedure (*solid-line*) compared with those obtained from individual fits at each temperature for both phases (LTP *black points*, HTP *gray point*)

result corresponding to the warming process are shown in the Fig. 2a. The result corresponding to the cooling process shows a similar behavior but a lower transition temperature.

The whole set of data was analyzed as a velocity-temperature absorption surface using an appropriate function f(v, T). This function consists of two Lorentzian lines, each with a fixed width, but with temperature dependent center and intensity. The centers were allowed to vary quadratically with temperature while the intensities were modeled as a product of a linear and a hyperbolic tangent temperature functions. The linear factor accounts for the Mössbauer–Lamb temperature dependence and the hyperbolic tangent for the transformation temperature evolution. To compare the fitted function and the experimental data, level curves of the first one are plotted over the experimental results (Fig. 2a). Comparison of the function and experimental data at 300, 400 and 420 K are shown in Fig. 2b.

Independent fits of each individual ROI with one or two Lorentzian lines (two at phase coexistence temperatures) were also made. In Fig. 2c we show the normalized effects for each phase as a function of the temperature obtained from the individual fits (points) and from the whole surface fit (lines) in the warming process. When warming (cooling) the sample the transition starts at around 390 K (400 K) and the coexistence region size is, in both cases, about 22 K.

4 Conclusions

Mössbauer Line Tracking was applied to record the $Fe_{1-x}S$ α-transition in a quasi-continuous way. Tracking was performed on the lowest energy lines of the low and high temperature magnetically split spectra of the $Fe_{1-x}S$ phases, using a feedback procedure assisted by on-line analysis. The algorithm succeeded in tracking the HTP when the LTP faded and vice versa. With the information retrieved from the line tracking experiment a predetermined temperature dependent ROI(T) experiment was designed from which an absorption vs energy–temperature surface was reconstructed through the fitting of the experimental data with an appropriate function. In this way a detailed quasi continuous observation of the α-transition vs. temperature in terms of absorption spectral line intensities and positions of both phases was accomplished.

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