Journal of Physics: Conference Series

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To cite this article: P Mendoza Zélis et al 2010 J. Phys.: Conf. Ser. **217** 012017

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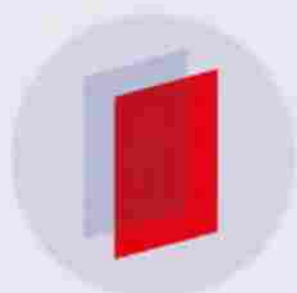
Mössbauer thermal scan study of a spin crossover system

P Mendoza Zélis[1,2], **G A Pasquevich**[1,2], **F H Sánchez**[1,2], **A Veiga**[1], **M Ceolin**[3], **A F Cabrera**[1,2], **E Coronado-Miralles**[4], **M Monrabal-Capilla**[4], **J R Galan-Mascaros**[4].

[1] Departamento de Física, FCE-UNLP, La Plata, Argentina
[2] Instituto de Física La Plata, CONICET,La Plata, Argentina
[3] Instituto de Investigaciones Físico-Químicas Teóricas y Aplicadas (UNLP-CONICET), La Plata, Argentina
[4] Instituto de Ciencias Moleculares, Universidad de Valencia, Valencia, España

E-mail: pmendoza@fisica.unlp.edu.ar

Abstract. Programmable Velocity equipment was used to perform a Mössbauer Thermal Scans to allow a quasi-continuous temperature study of the magnetic transition between the low-spin and a high-spin configurations in $[Fe(Htrz)_2(trz)](BF4)$ system. The material was studied both in bulk as in nanoparticles sample forms.

1. Introduction

Mössbauer Thermal Scans (MTS) were usually used to determine order temperatures [1,2]. Recently the technique was applied to obtain information on the temperature dependence of relative phase abundances, hyperfine and other spectrum parameters [3,4]. In these works different scans at one selected Doppler energy were done. The recent development of Programmable Velocity Scaler equipments [5], which allow to measure at arbitrary energies and for arbitrary times, highly improved the versatility of MTS techniques[6].

The experimental system developed in our laboratory allows the selection of Regions Of Interest (ROIs) in any spectral region, with a very high flexibility[7], while it undergoes changes due to the variation of an external parameter such as temperature, magnetic field, etc. The ROI can be composed of any number of points (up to 4096) with a freely selectable energy and live time for each point. We called the working mode of this equipment the Programmable Velocity Mode (PVM), to differentiate it from the conventional constant acceleration mode and constant velocity mode.

In this work we show that PVM can be used to perform Mössbauer Thermal Scans allowing a quasi-continuous temperature study of a thermally activated transition. In this case we study a spin crossover between a low-spin (LS) and a high-spin (HS) configuration.

Spin Crossover systems [8] are very interesting materials because of the ability to change their electronic state, between LS and HS configuration, under the influence of external stimuli (temperature, electromagnetic irradiation, pressure, etc.) being potential candidates e.g. for memory devices.

Among them, the $[Fe(Htrz)_n(trz)_{3-n}]X_m$ family (trz: triazole derivative) is a promising candidate for exhibiting bistability [9]. For the specific case of $[Fe(Htrz)_2(trz)](BF_4)$, the Fe(II) ions are coordinated by the ligands forming a 1-D polymeric structure exhibiting a cooperative spin transition from LS ($S=0$) to HS ($S=2$). Our study is performed with this material.

2. Experimental procedure

[Fe(Htrz)$_2$(trz)](BF$_4$) was prepared as bulk material and as 11 nm nanoparticles following the protocols described in reference [10] for compound 1a and using conventional reverse micelle techniques [11].

The experimental setup for a MTS 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 programmable constant-velocity scaler [5] 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 input/output interface used to record the temperature and to command a linear DC power source that is used to modify the temperature of the sample. Both NIM modules communicate serially with the PC that runs a high-level technical computing language that can interact directly with hardware. A previously developed interactive environment for data visualization and data analysis was used in the workstation. In this way the programmable scaler and the temperature control could be fully operated and re-programmed as required.

The MTS and the conventional Mössbauer spectroscopy were obtained with a 25 mCi ^{57}CoRh. Both calibrations were performed recording a complete α-Fe spectrum at RT.

3. Mössbauer spectroscopy

The LS and HS states of iron(II) can clearly be distinguished by Mössbauer spectroscopy by means of its hyperfine parameters (see figure 1). Both states are represented by a quadrupolar interaction but with a very different hyperfine parameters, while the LS state is characterized by an isomer shift of 0.42 mm/s and quadrupolar splitting of 0.27 mm/s at 298K, the HS state is characterized by an isomer shift of 0.97mm/s and quadrupolar splitting of 2.3 mm/s at 400K. Then these states can be clearly differentiated in the Mössbauer spectrum. It was noted that at temperatures beyond transition about 10% of the spectral area corresponds to LS phase.
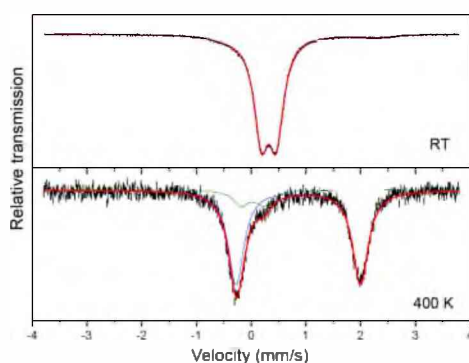

Figure 1. Mössbauer spectra of [Fe(Htrz)$_2$(trz)](BF$_4$) bulk sample. The LS and HS states of iron(II) are clearly distinguished. Each state is represented by a quadrupolar interaction.

4. Mössbauer Thermal Scans

We performed a Mössbauer thermal scan using a fixed ROI that was selected in order to include the patterns of the LS and HS phases, based on information previously obtained from Mössbauer Spectra taken at RT and 400 K. For the present case a ROI of 51 equally spaced points in the range from -1 to +3 mm/s, approximately centered at the isomer shift of the high temperature phase was chosen; and one additional point at an energy corresponding to background transmission (-8 mm/s) for control and normalization purposes was also incorporated. The ROI was periodically swept at 2 s/point while the sample was warmed up from RT to 411 K, and then cooled back to RT at rates of about ± 0.23 K/min. The whole experimental time was 16 h. Both scans of a [Fe(Htrz)$_2$(trz)](BF$_4$) bulk material absorber (6% effect at RT) are shown in figures 2-a and 2-b. This approach provided a detailed temperature and Doppler energy observation of the transition leading to a wealth of experimental information.
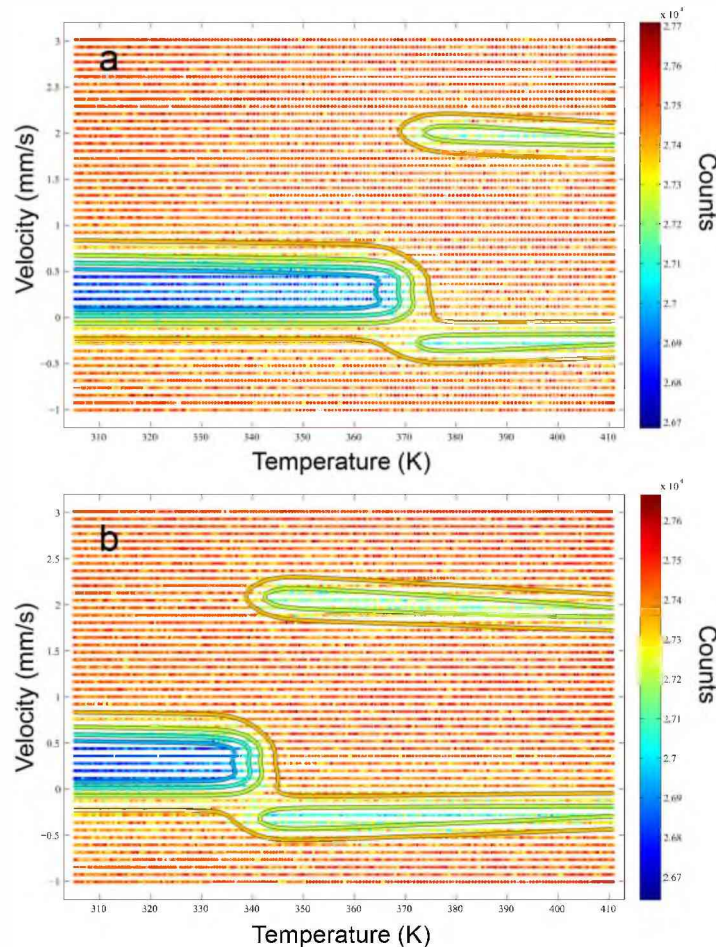
Figure 2. Mössbauer thermal scan (dots) for the $[Fe(Htrz)_2(trz)](BF_4)$ bulk material absorber using a fixed ROI (51 points) in the range from -1 to +3 mm/s and one additional point at an energy corresponding to background transmission (-8 mm/s) not shown in the figure. The ROI was periodically swept at 2 s/point while the sample was warmed up (a) to 411 K from RT, and then cooled back (b) to RT at rates of about ± 0.23 K/min. The continuous lines are the level curves of the fitted surface.

The whole set of MTS data was analyzed as an absorption surface $F(T,v)$ against velocity and temperature using an appropriate function. This consists of two quadrupolar interactions, each one with a fixed line width, but with temperature dependent isomer shift ($\delta(T) = \delta_0 + T \delta_I$), quadrupolar splitting ($\Delta Q(T) = \Delta Q_0 (1+T^{3/2})$)) and spectral areas. The spectra area temperature dependence was modeled considering the product of the Mössbauer–Lamb factor temperature dependence (assumed linear within the small scanned temperature interval) and the temperature evolution of the phases relative abundances $f(T)$.

The results obtained in figures 2-a and 2-b confirm the presence of thermal hysteresis in the transition. This hysteresis is due to the metastability of the high temperature configuration. For the time being we have decided to ignore metastability and treat the spin crossover transition within an equilibrium approach. A two level system with energy difference E and multiplicities 1 and Ω is proposed for the polymeric chain. The low spin configuration (S=0) has multiplicity 1, while the high spin one has multiplicity $\Omega = \omega^N$, where $\omega = 3 \times (2S+1) = 15$ (assuming that t_{2g} group is degenerate from where factor 3 arises[12]). N is the number of Fe atoms in the polymeric chain. Then

$$f_{HS}(T) = \frac{\Omega e^{(-E/T)}}{1 + \Omega e^{(-E/T)}} \qquad (1)$$

We define the transition temperature T_{05} through the condition $f(T_{05})=1/2$ and the temperature transition width ΔT by $f'(T_{05})\,\Delta T=1$. From these, it follows that

$$E = \frac{4(T_{05})^2}{\Delta T} \qquad \log(\Omega) = \frac{4T_{05}}{\Delta T} \qquad (2)$$

Since the transition presents hysteresis, at least two different T_{05} values will be required to reproduce the experimental data. However, the E and Ω values on the heating up process are not very different from those of the cooling down one. Owing this, we may take them as representative of the physics of the problem. The fitting parameters corresponding to the temperature evolution of the two phases relative abundances are E_{up} (heating up), E_{down} (cooling down) and Ω. The obtained values are: E_{up} = 4.1 eV, E_{down} = 4.5 eV, and Ω = 7×10^{60} corresponding to 371K (ΔT_{up}=10K) and 341K (ΔT_{down}=7K) for T_{05} in the heating up and cooling down respectively, and $N \sim 50$.

The experimental result and the level curves of the fitted surface corresponding to the warming and cooling process are shown in figure 2-a and 2-b. The level curves demonstrate the goodness of the fit.

In addition, in figure 3 we present temperature intersects of the previous figure at different temperature to show the agreement between experimental data and the fitted surface. In each graph are shown: the values measured in an interval of ±2K around the specified temperature (open blue circles), the measure average in this temperature interval (filled red points) and the intersect of the fitted surface (black line). In these intersects the presence at high temperature of the previously mentioned remnant LS phase fraction was clearly observed (see for example the 382 K intersect). As this fraction was not observed to be temperature dependent it was not considered in the analysis of the absorption surface $F(T,v)$ evolution.
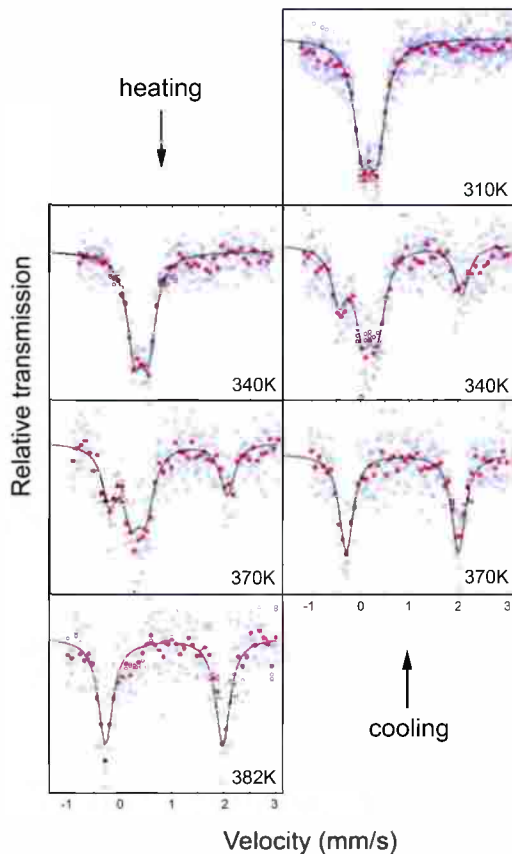

Figure 3. Temperature intersects of the MTS at different temperature. In each graph are shown the values measured in an interval of ±2K around the specified temperature (blue circles), the measure average in this temperature interval (red points) and the intersect of the fitted surface (black line).

The Mössbauer Spectra of the nanoparticles sample (not shown) indicate that the hyperfine parameters of both samples are similar (isomer shift: 0.44 mm/s, quadrupolar splitting: 0.35 mm/s at 298K for the LS phase and isomer shift: 1.0 mm/s, quadrupolar splitting: 2.6 mm/s at 411K for the HS phase). Mössbauer thermal scan of the nanoparticles warmed up to 415 K from RT is shown in figure 4 (the cooling back to RT is not shown). The whole experimental time was 80 hs. A 47 channels ROI plus background, and a time/channel ratio of 8 seconds were chosen. The data are analyzed as a absorption surface against velocity and temperature using the mentioned function. The level curves of the fitted surface corresponding to the warming process are shown in figure 4. The experimental result confirm the presence of magnetic bistability even in nanoparticles samples. The values of T_{05} determined in the fitting procedure are 372 K and 341 K corresponding to the heating up and cooling down respectively.
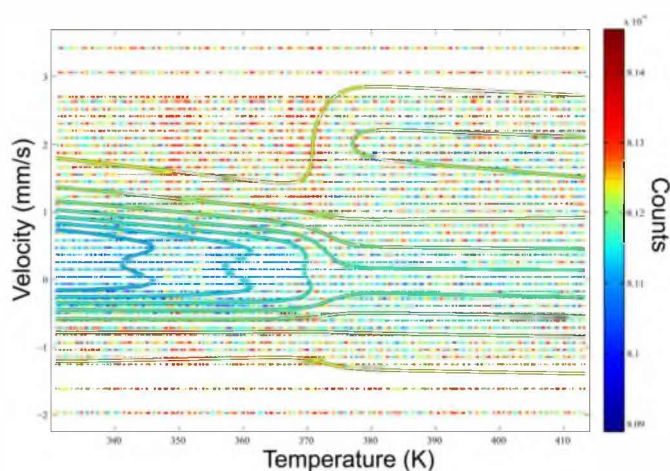

Figure 4. Mössbauer thermal scan of the nanoparticles warmed up from RT to 415K (dots). The continuous line are the level curves of the fitted surface.

5. Conclusions

Programmable Velocity Scaler equipment was used to perform Mössbauer Thermal Scans to follow up the magnetic transition through a quasi-continuous temperature study of the low-to-high spin transition of the [Fe(Htrz)2(trz)] (BF4) system. The study was made in bulk material and 11 nm nanoparticles. With information retrieved from conventional Mössbauer spectra, the ROI was chosen. Fitting the experimental data with an appropriate function, an absorption vs. energy⊗temperature surface was reconstructed. In this way a detailed quasi continuous observation of the spin thermal transition vs. temperature in terms of phases absorption spectral line intensities and positions was accomplished.

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