Hyperfine Interactions (2019) 240:116
https://doi.org/10.1007/s10751-019-1671-y

Preparation and characterization of spin crossover thin solid films

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Abstract

Iron(II) spin crossover complexes display a reversible transition from low-spin (LS) state to high-spin (HS) state by e.g. variation of temperature, pressure or by irradiation with light. Therefore, these systems are promising candidates for information storage materials. In view of practical device applications thin films of these materials are needed. The SCO-compound [Fe(Htrz)$_2$(trz)] (BF$_4$) (**1**) switches between the LS and the HS state with a 50 K wide thermal hysteresis loop above room temperature. We have prepared thin films of **1** on a SiO$_2$ substrate by spin coating. The spin states of the films have been characterized by Mössbauer spectroscopy in reflection mode using a MIMOS II spectrometer. A low quadrupole splitting (LS state) at 300 K and a high quadrupole splitting (HS state) at 400 K were found for the film, as well as for bulk powder of **1**. This confirms that a spin crossover occurs above room temperature. Furthermore, synchrotron based nuclear resonance scattering measurements from 80 K to 400 K indicate that the hyperfine parameters are similar to those of the bulk powder of **1.** DFT calculations reproduce the experimentally determined Fe-vibrational density of states of the bulk and of the thin film sample of **1**. These results indicate that a higher fraction of HS Fe atoms is present in the film of **1**. Therefore, we conclude different SCO properties of the thin film and the bulk material of **1**.

Keywords Spin crossover · Thin films · Mössbauer spectroscopy · Nuclear inelastic scattering

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This article is part of the Topical Collection on *Proceedings of the International Conference of the Application of the Mössbauer Effect (ICAME 2019) held in Dalian, China, 1-6 September 2019*
Edited by Tao Zhang, Junhu Wang and Xiaodong Wang

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10751-019-1671-y) contains supplementary material, which is available to authorized users.

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1 Introduction

Some transition metal compounds, particularly those carrying $3d^4$-$3d^7$ metal ions in an octahedral surrounding, display a transition between a low-spin state (LS) and a high-spin state (HS) upon external stimuli like temperature, pressure and illumination by light. This phenomenon is called spin crossover (SCO) and was first discovered in 1931 by L. Cambi [1]. SCO materials remain the subject of extensive studies due to (i) a dependence of the spin transition on small variations in ligand and crystal packing [2] and (ii) potential technological applications [3] like molecular switches, memory elements [4], temperature sensors [5], pressure sensors [5] and in photovoltaic elements [6].

Of particular interest are 1D polynuclear materials based on 1,2,4-triazole ligands [7, 8] which generally display an abrupt transition. This property can be attributed to an efficient propagation along the 1D-chains through direct covalent connections of the local modifications to the SCO [9].

Due to the complicated application of powder materials in modern technology a great effort has been made towards the growth of thin films and the fabrication of nanostructures of SCO compounds [10]. This article focuses on the SCO properties of a 650 nm thin film of the SCO complex **1** studied by means of the complementary techniques Mössbauer spectroscopy geometry and nuclear inelastic scattering (NIS).

2 Materials and methods

The SCO material **1** was synthesized according to ref. [7] using 98% enriched $^{57}Fe(BF_4)_2 \cdot (H_2O)_6$. Thin films of the compound were made out of a solution of 7.2 mg of SCO material **1** and 5 ml of purified water using a vacuum spin-coating setup with a rotational speed of 250 rpm.

By use of a surface profilometer (Bruker Dektak XT) and an atomic force microscope (Park XE-70), the thickness of the film was measured to be 650 ± 100 nm. The determined surface roughness is shown in Fig. 1.

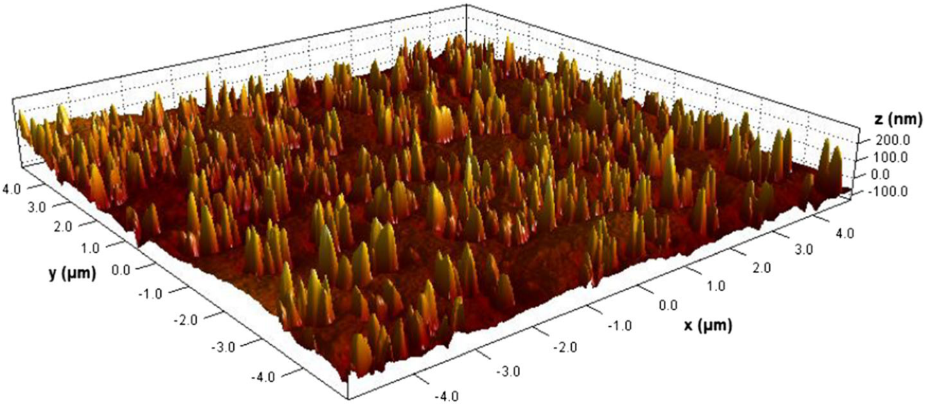

Fig. 1 Atomic force microscopy image of the thin film of **1**

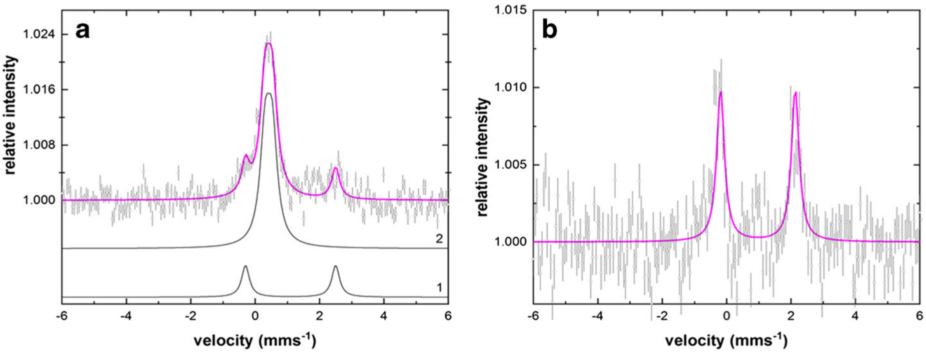

Fig. 2 Mössbauer spectrum in reflection mode of the thin film of **1** obtained at **a**) 298 K and **b**) 410 K

The Mössbauer spectra were recorded using a miniaturized Mössbauer spectrometer (MIMOSII, manufactured by SPESI, Space and Earth Science, Instrumentation. Ortenberg, Germany, [11]) mounted 3 (± 1) mm above the sample. The MIMOSII Al holder with Al window was mounted with a ^{57}Co Mössbauer source in a Rh matrix with an active diameter of 4.5 mm. The emitted γ-rays penetrated the sample and resonantly scattered 14,4 keV γ-rays were detected in backscattering geometry. Temperature dependent measurements were performed by the use of a cryostat (Heating/freezing stage THMS600, manufactured by Linkam Scientifics, Ettlingen, Germany).

NIS experiments were performed at the Dynamics Beamline P01, DESY in Hamburg, Germany. The monochromatisation of the initial beam was achieved using a two-step monochromatisation setup. At first the bandwidth of the incident beam was rendered down to approximately 2 eV through the use of a Si(111) double-crystal monochromator. A following high resolution monochromator (HRM) decreased the bandwidth of the beam down to 1 meV. This beam was used to excite the 14.4125 keV transition of the ^{57}Fe nuclei in the sample. The excited nuclear state with a lifetime of 141 ns decays in the ground state under emission of conversion electrons with a probability of 90%. The subsequent 6.4 keV K-fluorescence radiation which is delayed compared to electronic scattering was measured with avalanche photodiodes (APD) with a time resolution of ca. 1 ns. Temperature dependent measurements were accomplished with a liquid nitrogen cryostream (Oxford Cryosystems). The partial density of vibrational states (pDOS) were calculated by adding up six scans and binning the data with 1 meV in order to minimize statistical fluctuations due to a sensitivity of the pDOS calculation to spectral noise in the NIS data.

Table 1 Mössbauer Parameters as obtained from the simulations shown in Fig. 2

temperature (K)	298	350			360		410
component	1	2	1	2	1	2	1
δ (mms^{-1})	1.04 ± 0.02	0.44 ± 0.02	1.03 ± 0.02	0.40 ± 0.02	1.02 ± 0.02	0.39 ± 0.02	0.97 ± 0.02
ΔE_Q (mms^{-1})	2.64 ± 0.02	0.22 ± 0.03	2.45 ± 0.02	0.20 ± 0.02	2.42 ± 0.02	0.19 ± 0.02	2.32 ± 0.02
relative area (%)	25 ± 3	75 ± 2	71 ± 2	29 ± 2	81 ± 2	19 ± 2	100 ± 0

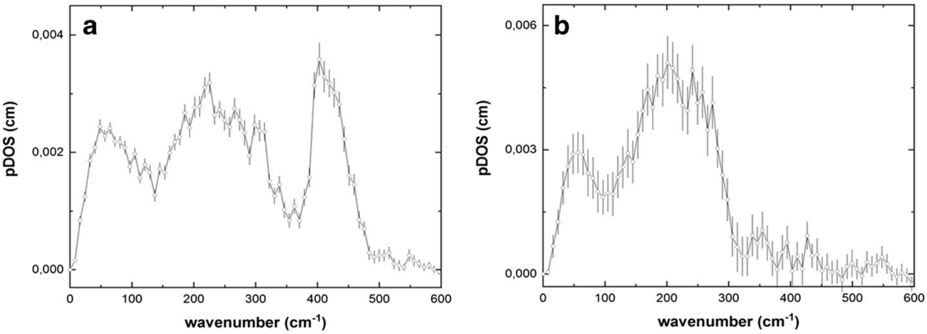

Fig. 3 Experimental partial density of vibrational states (pDOS) of a thin film of **1** at **a**) 80 K and **b**) 400 K

DFT calculations were conducted with the GAUSSIAN 16 programme [12] using the B3LYP* functional [13] and CEP-31G basis set [14]. Further details to the calculations are given in ref. [8].

3 Results and discussion

3.1 Mössbauer spectroscopy

The Mössbauer spectrum obtained at room temperature in backscattering geometry of a thin film of **1** is shown in Fig. 2a. It reveals two components (Parameter see Table 1). Component 1 exhibits Mössbauer parameters typical for the iron(II) HS state of compound **1** while component 2 shows parameters characteristic for the iron(II) LS state of compound **1** [7]. Therefore, both spin states coexist at room temperature and ca. 75% of the iron(II) sites occupy the LS state. After heating the thin film to 410 K, the Mössbauer spectrum (see Fig. 2b) consists of a single doublet characteristic for the iron(II) HS state. This indicates the spin crossover behaviour of the sample [7]. Further measurements at 350 K and 360 K (see Fig. S1) yield a rather abrupt spin crossover transition below

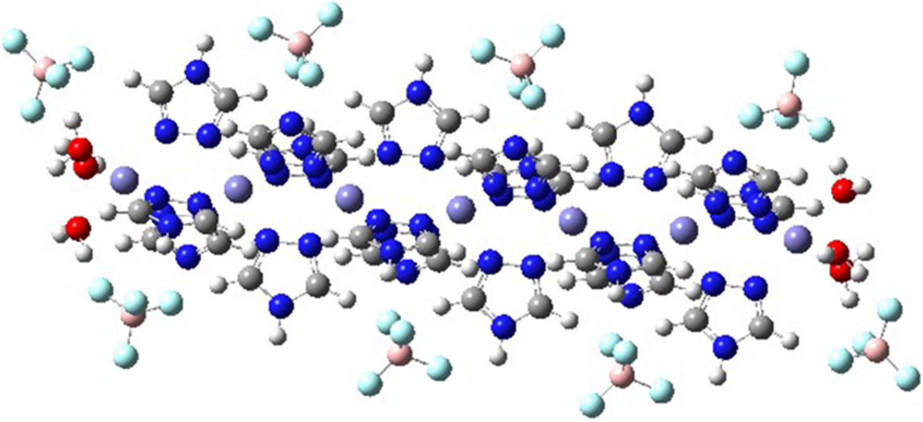

Fig. 4 Graphical representation of the heptameric model molecule used for DFT calculations

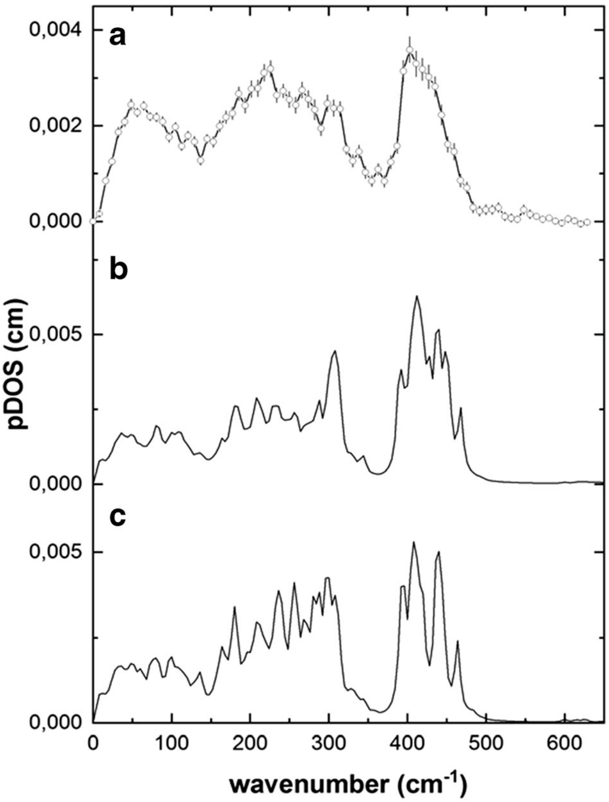

Fig. 5 Comparison of **a**) experimental (T = 80 K) and calculated (B3LYP*/CEP-31G) pDOS of (**b**) the HHLLLLH spin isomer and (**c**) the HHLLLHH spin isomer

350 K. However, a critical temperature of 380 K has been reported for bulk powder materials of **1** [7]. This difference may be attributed to the influence of the difference in polymer chain lengths of the bulk powder and thin film sample on the critical temperatures.

3.2 Partial density of vibrational states

The pDOS obtained from the NIS data at 80 K of the ^{57}Fe enriched SCO thin film of **1** is shown in Fig. 3a. The pDOS shows vibrations involving the displacement of iron atoms in the energy region of 150–350 cm^{-1} and 350–500 cm^{-1}. For a pure LS state of this compound vibrations in the energy region of 350–500 cm^{-1} have been reported [8] while vibrations in the energy region of 150–350 cm^{-1} have been related to the HS state in literature [8]. Therefore, we conclude the coexistence of the LS and HS state at 80 K. This coexistence is also evident in the results of our Mössbauer measurements as we deduce a LS and a HS component at room temperature. The pDOS obtained at 400 K shown in Fig. 3b exhibits vibrations in the energy region of 150–350 cm^{-1} which is characteristic for the iron(II) HS state of this region.

In order to investigate the ratio of the iron(II) LS fraction to iron(II) HS fraction in the thin film density functional theory (DFT) calculations were performed. The 1-D iron(II) chains were modelled with the heptameric linear chain model of $[Fe_7(trzH)_{12}(trz)_6(H_2O)_6](BF_4)_8$ shown in

Fig. 4. The two terminal iron atoms were always kept in the HS state due to their FeN_3O_3 coordination. Therefore, the pDOS were calculated with different distributions of HS and iron(II) LS centers among the inner five centers. The HS centers were modeled with Zn^{2+} centers due to their similar ionic radii in the starting geometry for optimization. The calculations were performed by consideration of the contributions of all seven iron atoms in the 1-D linear chain.

For further discussion, we will denote the following notation for the different spin isomers. HHLLLLH describes a heptamer with one inner iron(II) center next to the terminal iron(II) HS centers being in the HS state and the remaining four iron centres in the LS state. HHLLLHH stands for the heptamer with the inner three iron(II) centers being in the LS state and the remaining iron centers in the HS state while HHHHHHH means that the heptamer with all iron(II) centers being in the HS state.

A comparison of the experimental pDOS at 80 K, the calculated pDOS of the HHLLLLH model and the HHLLLHH is depicted in Fig. 5. Both calculated pDOS reproduce the experimental data in good agreement.

Both heptameric models show vibrations in the characteristic HS and LS energy regions as described above. While the HHLLLLH model reproduces the experimental pDOS in the energy region of 350–500 cm^{-1} showing more intensive bands at 180, 212, 236, 256 and 296 cm^{-1}, the HHLLLHH model is in better agreement in the energy region between 150 and 350 cm^{-1} due to the broader band structure in this region. Overall the HHLLLHH is in better

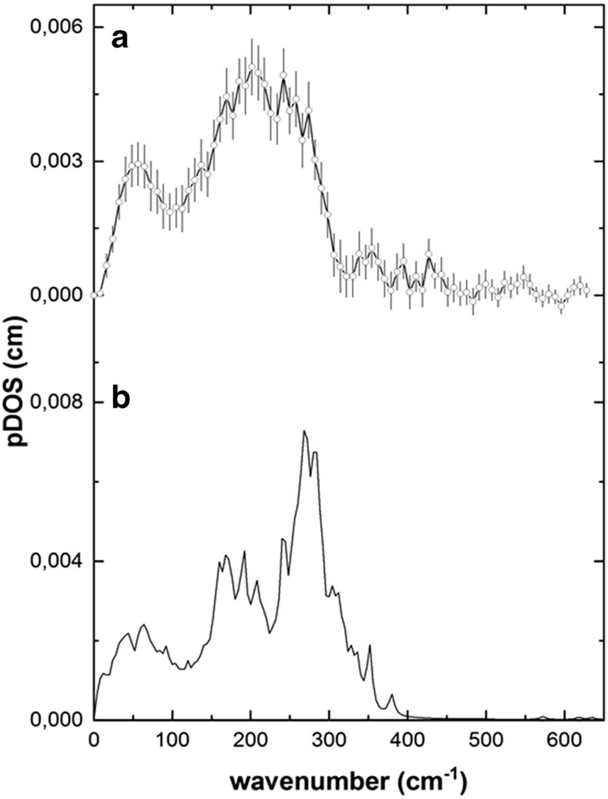

Fig. 6 Comparison of **a**) experimental (T = 400 K) and calculated (B3LYP*/CEP-31G) pDOS of (**b**) the HHHHHHH spin isomer

accordance to the experimental pDOS due to the match in the characteristic HS energy region and a good agreement in the LS energy region. In addition, a composition of both spin isomers may also exist in the thin film sample.

The experimental pDOS obtained at 400 K and the calculated pDOS of the HHHHHHH spin isomer are shown in Fig. 6. The two pDOS reveal similar bands in the energy region between 150 and 300 cm^{-1} although with different intensities. By and large the theoretical simulation reproduces the experimental data well.

4 Conclusions

In conclusion the SCO character of an iron(II) polymeric thin film has been studied and confirmed by Mössbauer spectroscopy and NIS experiments. The studies indicate similar SCO properties compared to a bulk powder sample of the same compound. Additional DFT calculations demonstrate a model for both the HS state and the LS state of the thin film sample.

Acknowledgements This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through SFB/TRR 173 SPIN+X.

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