Mössbauer spectroscopy, Raman- and IR- microscopy studies of hysteretic behaviour in spincrossover systems.

A Ahrens-Botzong1, K Muffler1, S M Stuppy1, S Rackwitz1, R Rüffer2, V Schünemann1 and J A Wolny1

1Department of Physics, University of Kaiserslautern, D-67663 Kaiserslautern, Germany

2 ESRF, F-38043 Grenoble Cedex, France

E-mail: wolny@physik.uni-kl.de, schuene@physik.uni-kl.de

Abstract. The polymeric spin-crossover systems [Fe(atz)(X)2]n (X =Cl−, CH3SO3−) have been investigated by complementary Mössbauer, and Raman and IR-microscopy as well as nuclear inelastic scattering (NIS). The systems reveal SCO transition temperatures around room temperature including hysteresis. Within the hysteresis loop the areas of LS and HS phases could be detected.

1. Introduction
Iron (II) spin crossover (SCO) complexes can be switched reversibly from the low-spin state (LS, S=0) to a high-spin state (HS, S=2) [1-5] by variation of temperature, pressure or by irradiation with light [6-8]. A feature important for the practical applications of SCO materials [9-11] is their hysteretic behaviour and the resulting bistability of the systems. One of the central questions is whether a domain structure is present during the spin transition [5,12]. The recently introduced techniques of Raman and IR-microimaging may shed more light on the above problem. To the best of our knowledge there is only one published study describing the use of Raman microscopy to study the SCO systems. Molnar et. al.[12] showed the absence of domains smaller than 1µ in the studied Fe(pz)[Ni(CN)4] system.

The polymeric material investigated in this study is based on 4-aminotriazole ligand [Fe(atz)3(X)2]n (X=Cl−, CH3SO3−) [13]. The complexes have SCO transition temperature at ca. 300 and 323 K, respectively and reveal a hysteresis. In order to elucidate whether spin domain structures are present in these systems the complementary techniques like Mössbauer spectroscopy, nuclear inelastic scattering (NIS) as well as Raman- and IR-microscopy have been employed.

2. Experimental and methods
The polymer [Fe(atz)3(CH3SO3)2]n (1) has been prepared by means of reaction of water solution of Fe(CH3SO3)2⋅7H2O with ethanol solution of the ligand in a 1:3 ratio. [Fe(atz)(Cl)]2n⋅(H2O)2 (2) has been prepared according to the method of Lavrenova et al.[14]. The Mößbauer spectra have been measured in a closed cycle-cryostat manufactured by Cryo Industries of America, Inc. coupled to a Mößbauer spectrometer from WissEL GmbH. Raman mapping has been performed with a Senterra Raman microscope (Bruker AG) equipped with a cryostat (Linkam Ltd) at an excitation wavelength of 785 nm. The IR spectra were collected using a Hyperion IR microscope (Bruker AG) also equipped
with a cryostat (Linkam Ltd). The spectra were detected in reflection with the sample mounted on a copper plate. For the nuclear inelastic scattering (NIS) experiments the Senterra Raman microscope was coupled to the synchrotron beam at ID18 of the ESRF during exp. CH 3829. The assignment of the vibrational modes presented here is based on DFT calculations for a model trimeric system \([\text{Fe}_3(\text{atz})_6(H_2O)_6]\) [15] which were performed with Gaussian 2003 package, using the B3LYP functional and the CEP-31G basis set as described previously [16].

3. Results and Discussion
Mössbauer spectroscopy of (1) reveals a spin transition temperature of \(\sim 300\) K as well as a strong hysteresis effect (figure 1). As a representative example a Mössbauer spectrum at the spin crossover temperature \(T_c\) is shown in figure 1a. The LS component exhibits \(\delta = (0.48 \pm 0.02)\) mm/s and \(\Delta E_Q = (0.38 \pm 0.01)\) mm/s while the HS component shows \(\delta = (1.03 \pm 0.02)\) mm/s and \(\Delta E_Q = (2.90 \pm 0.01)\) mm/s. Figure 1b shows a strong the hysteresis effect which obviously depends on the history of the sample: During heating from \(T = 260\) K, a temperature where \(\sim 10\%\) of the HS isomer is still present, the HS component stays relatively constant but increases very fast at \(295\) K to almost \(100\%\). Subsequent cooling to \(240\) K leads to a slow decrease of the HS component starting at \(290\) K.

![Figure 1](image1.png)

**Figure 1.** Mössbauer spectrum of the polymeric SCO system (1) taken at 299 K with parameters given in the text (a) and temperature dependence of the HS component which shows a strong hysteretic behaviour of the SCO system (b).

Raman spectroscopy shows the presence of two distinct LS marker bands (see figure 2). Preliminary DFT calculations identify the marker bands for LS (ca. 250 cm\(^{-1}\)) and HS (ca. 135 cm\(^{-1}\)) as vibrations with mainly Fe-N bending character.

![Figure 2](image2.png)

**Figure 2.** Raman spectra of (1) obtained at 273 K (LS, bottom) and 293 K (HS, top).

The temperature dependence of the Raman spectra shows a hysteretic behaviour of the spin transition (see figure 3). In addition and the SCO temperature \(T_c\) increases from \(\sim 15\) °C at 10 mW laser power to \(\sim 24\) °C at 1 mW laser power. Therefore Raman mapping experiments have been performed with a laser power of 1 mW. Figure 3b shows the presence of LS as well as HS domains with domain sizes of ca. 20*30 µm. Surprisingly, thermal cycling back to 10 °C after each mapping experiment
leads to a consecutive build up of HS domains instead of an expected statistical arrangement of the spin domains with fixed proportions of HS and LS.

![Figure 3](image1.png)

**Figure 3.** (a) Temperature dependence of relative intensity of LS marker band (254 cm\(^{-1}\)) on temperature for laser power of 1 mw (●) and 10 mw (■) for (1). (b) Raman mapping for (1) at 25 °C, (laser power 1 mW). After each measurement the sample was cooled back to 10 °C. The areas of the LS state are denoted with white squares, while those of the HS state have red crosses.

The question arises whether the observed spin distribution is due to a real spin domain structure at the SCO temperature or whether this effect is caused by local heating of the sample by means of the Raman excitation laser. In order to answer this question we have performed infrared microimaging of the IR-active HS and LS marker bands at 880/920 cm\(^{-1}\) and 865/910 cm\(^{-1}\) with a spatial resolution of 10 \(\mu\)m at the SCO temperature of 25 °C. These experiments (not shown here) show indeed a different space distribution of HS and LS phases in two adjacent areas (20 \(\mu\)m * 10 \(\mu\)m).

Since the spatial resolution of infrared microimaging has a diffraction limit of ~10 \(\mu\)m nuclear inelastic scattering (NIS) on 57Fe samples is an attractive alternative to Raman and IR microspectrometry. Therefore we have performed first experiments in order to measure simultaneous NIS and Raman microspectrometry on the same sample spot. The chosen sample grain of compound (2) had a diameter in the order of 100 \(\mu\)m and is shown in figure 5. With the focus of the Senterra Raman microscope (less than 1 \(\mu\)m diameter spot size) in the middle of the sample we oriented the whole microscope with respect to the focussed synchrotron beam (area 15 * 8 \(\mu\)m) in such a way that the beam was passing the short axis of the sample grain (figure 4). The corresponding Raman spectrum reveals a signature typical for the LS form as shown in figure 5 together with the corresponding NIS spectrum. These preliminary experiments show that NIS measurement with a beam size of less than 1 \(\mu\) can answer the question whether spin domains are really present in SCO systems during spin crossover.

![Figure 4](image2.png)

**Figure 4.** Micrograph of the sample grain of (2) which has been investigated by NIS and Raman spectroscopy in parallel. The arrow depicts the synchrotron beam and the black dot the focus point of the Raman excitation.
4. Conclusion
The hysteretic behaviour of an iron (II) polymeric SCO system has been studied by combining the Mössbauer spectroscopy and Raman and IR microimaging. The Raman mapping at the spin crossover temperature revealed a complicated behaviour: Obviously there is a spatial distribution of HS and LS phases, but the distribution is strongly dependent on laser power, time and thermal cycling.

Acknowledgments
Financial support of BMBF (05-KS7UK2) and the DFG (Schu1251/9-1) and the ESRF (exp. CH 2839) is gratefully acknowledged.

References
[1] Gülich P 1981 Struct. and Bond. 44 83
[2] Toftlund H 2001 Monatshefte für Chemie 132 1269
[3] König E 1991 Struct. and Bond. 76 51
[4] Toftlund H 1989 Coord. Chem. Rev. 94 67
[5] Gülich P, H.A. Goodwin 2004 In P. Gülich, H. Goodwin (eds.), Spin Crossover in Transition Metal Complexes. Top. Curr. Chem. 233 1
[6] McGarvey J.J, Lawthers I 1982 J. Chem. Soc. Chem. Commun. 906
[7] Gülich P, Hauser A, Spiering H 1994 Angew. Chem. 106 2109
[8] Decurtins S, Gülich P, Köhler CP, Spiering H, Hauser A, 1984 Chem. Phys. Lett. 105 1
[9] Kahn O, Martínez CJ 1998 Science 279 44
[10] Gülich P, Hauser A, Spiering H 1994 Angew. Chem. Int. Edition in English 33 2024
[11] Létard JF, Guionneau P, Goux-Capes L 2004 In P. Gülich, H. Goodwin (eds.), Spin Crossover in Transition Metal Complexes. Top. Curr. Chem. 235 221
[12] Molnar G, Bousseksou A, Zwick A, McGarvey JJ 2003 Chem. Phys. Lett 367 593
[13] van Koningsbruggen PJ 2004 In P. Gülich, H. Goodwin (eds.), Spin Crossover in Transition Metal Complexes. Top. Curr. Chem. 233 123
[14] Lavrenova LG, Shakirova OG, Ikorskii VN, Varnek VA, Sheludyakova LA, and Larionov SV 2003 Russ. J. Coord. Chem. 29(1) 24
[15] Garcia Y, Ksenofontov V, Levchenko G, Gülich P 2000, J. Mater. Chem. 10 2274
[16] Wolf M M N, Groß R, Schumann C, Wolny JA, Schünemann V, Dössing A, Paulsen H, McGarvey JJ, Diller R 2008 Phys. Chem. Chem. Phys. 10 4264