	Experiment title: Pressure-induced changes of the vibrational entropy of spin-crossover complexes studied by nuclear resonant scattering of synchrotron radiation	Experiment number: CH-1049
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Report:

Nuclear inelastic scattering (NIS) and nuclear forward scattering (NFS) spectra have been recorded for polycrystalline samples of the two iron(II) complexes STP and ETP (STP = $[\text{Fe}(1,1,1\text{-tris}\{[\text{N}-(2\text{-pyridylmethyl})\text{-N-methylamino}]\text{methyl}\}\text{ethane})](\text{ClO}_4)_2$ and ETP = $[\text{Fe}(1,1,1\text{-tris}\{[\text{N}-(2\text{-pyridylmethyl})\text{-N-methylamino}]\text{methyl}\}\text{butane})](\text{ClO}_4)_2$). The spectra were recorded at room temperature applying pressures up to 2.6 GPa in a diamond-anvil cell (DAC). The ETP sample was in addition studied at ambient pressure. The NIS spectra were recorded with an energy resolution of 3.5 meV.

STP and ETP are both spin-crossover complexes and exhibit, with decreasing temperature, at about 180 K a gradual transition from a high-spin (HS) to a low-spin (LS) state. The driving force for this spin transition is the difference of the vibrational entropy between both spin states, which arises from a softening of some vibrational modes when going from the LS to the HS state. Former angular resolved NIS measurements on an STP monocrystal demonstrated that mainly the iron-ligand bond stretching modes are affected by this mode softening [1,2] (see also experimental report CH-738).

It is known that several spin-crossover complexes, which are in the HS phase at room temperature, can be forced into the LS phase by application of pressure, since with increasing pressure the LS state is energetically favored due to its smaller volume. For a more quantitative understanding, however, it is also necessary to obtain detailed information about the changes of the vibrational entropy from NIS spectra under pressure.

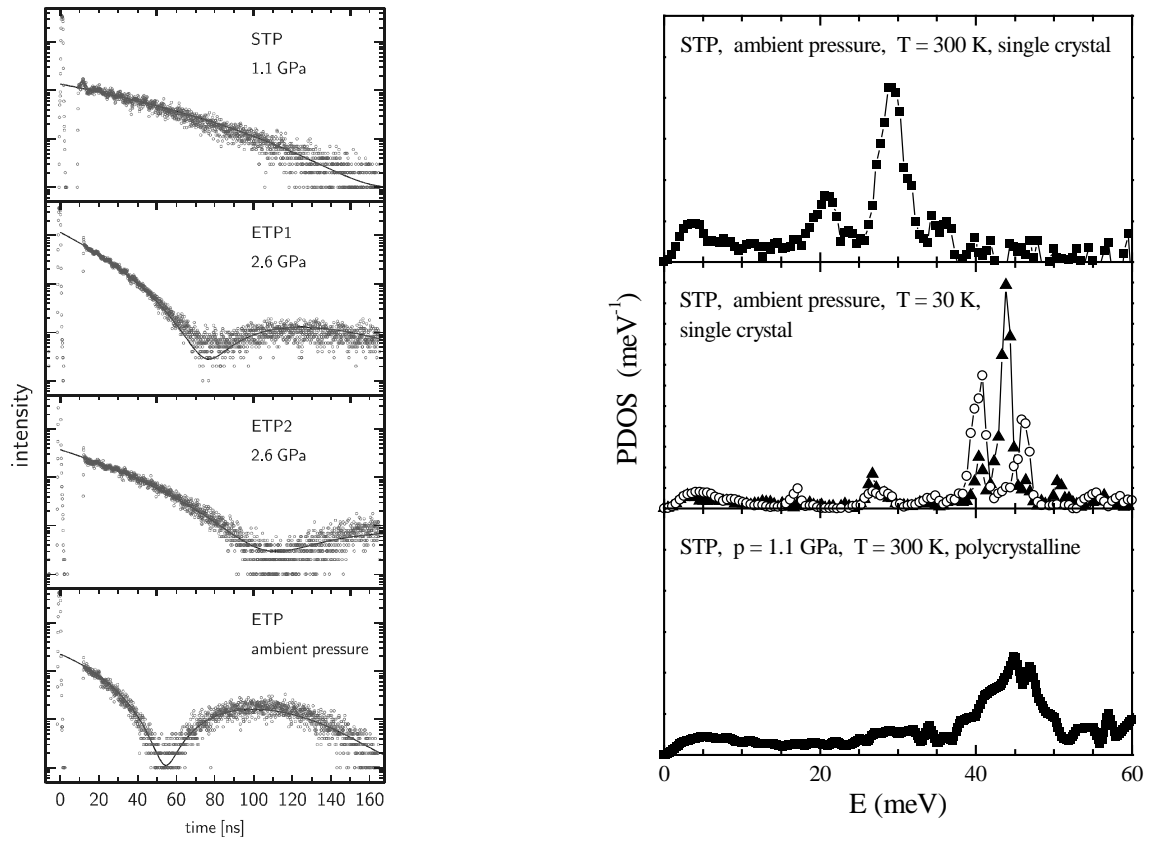


Figure 1. NFS (left panel) and NIS (right panel) spectra of STP and ETP for temperatures and pressures as indicated. The high-pressure NFS spectra of ETP were recorded for two different sample thicknesses (denoted by ETP1 and ETP2) by tilting the DAC with respect to the SR beam.

The NFS spectra of ETP (Fig. 1) and STP (not shown) at ambient pressure exhibit a first quantum beat minimum at about 55 ns (corresponding to $\Delta E_Q = 0.8$ mm/s) indicative of the HS phase. When applying a pressure above 0.9 GPa, both ETP and STP samples undergo the HS-LS transition, monitored optically in the DAC by a characteristic change of the sample colour from green to red. The NFS spectra look quite different in the LS phase, the modulation of the NFS spectra of the ETP sample is now due to thickness effects. The quadrupole splitting of the LS phase of 0.2 mm/s is not observable in the time window of 160 ns. The partial density of phonon states (PDOS) of Fe in STP, extracted from the NIS spectrum measured at 1.1 GPa, is shown in Fig. 1 together with PDOS spectra obtained previously from a STP single crystal [1]. The comparison with the PDOS of STP at ambient pressure and 300 K (HS state) and 30 K (LS state) strikingly demonstrate that STP at 1.1 GPa and 300 K has transformed into the LS phase with comparable frequencies of the high-energy stretching modes (note that the PDOS of STP at 30 K in Fig. 1 is shown for two different directions (\blacktriangle, \circ) [1], while for the present (polycrystalline) sample all directions are averaged). Currently density functional calculations are performed to support a more detailed analysis of the NIS spectra.

References

- [1] H. Paulsen, R. Benda, C. Herta, V. Schünemann, A. Chumakov, L. Duelund, H. Winkler, H. Toftlund, and A.X. Trautwein, *Phys.Rev.Lett.* **86** (2001) 1351.
- [2] H. Paulsen, H. Grünsteudel, W. Meyer-Klaucke, M. Gerdan, H.F. Grünsteudel, A.I. Chumakov, R. Rüffer, H. Winkler, H. Toftlund, *Eur. Phys. J. B* **23** (2001) 463.