



Experiment title:

Experiment number:
CH-1667

Beamline:
ID18

Date of experiment:
from: 15/05/2004 to: 25/05/2004

Date of report:
22/05/2005

Shifts:
9

Local contact(s):
A. I. Chumakov

Received at ESRF:

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Report:

Octamethylferrocene (OMF), like some other highly substituted ferrocenes, exhibits a sharp decrease of the Lamb-Mössbauer factor (also called recoilless or elastic fraction) far below its melting point $T_m = 431$ K [1]. For a related compound, octamethyl-ethinyl-ferrocene (OMFA), we have been able to show that this phenomenon is due to a first-order solid-solid phase transition to a nearly cubic rotator phase having a wide thermal hysteresis [2]. When trying to correlate structural and dynamical properties, however, we observed that in OMFA the hysteresis of structural (as evidenced by powder diffraction and SC) and dynamical properties (rotational relaxation rate as evidenced by SRPAC) does not coincide [3]. In addition to high-resolution powder diffraction (NSLS, Brookhaven), we have therefore carried out a study of rotational relaxation rates of OMF across its phase transition using the new technique of SRPAC [4].

The experiment was carried out at the ID18 beamline, using a nested high-resolution monochromator (HRM) yielding an overall energy resolution of 6 meV. The sample, a pressurized pellet of about 0.3 mm thickness, was mounted between thin Be sheets into a copper holder sealed with Kapton windows in a high-temperature oven. In order to protect the sample from oxidation at elevated temperatures but also to prevent its sublimation into the gas phase owing to an isolation vacuum, the oven was slowly flushed with a nitrogen gas stream throughout the experiment.

Using SRPAC, time spectra were obtained as shown in Fig. 1 a–c. The sudden onset of rotation leads to a strong damping of the quantum beats that arise from the quadrupole splitting of the excited nuclear state above T_{pc} .

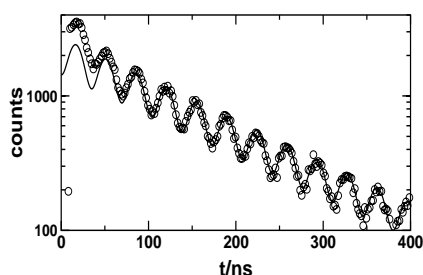


Fig. 1a: 296 K

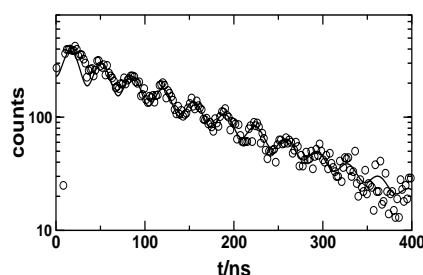


Fig. 1b: 348.1 K

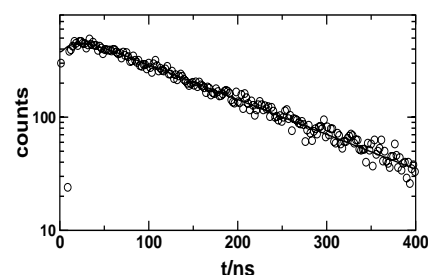


Fig. 1c: 348.8 K

SRPAC yields information on the ns–ps timescale about the rotation of the electric field gradient associated with the $\text{Cp}^*\text{-Fe-Cp}^*$ axis of the molecule, where Cp^* is a cyclopentadienyl ring carrying four methyl groups. A sketch of the molecule is shown in Fig. 2.

We obtained the rotational relaxation rate λ of OMF versus temperature through a full hysteresis cycle, as shown in Fig. 3. For data fitting, the strong-collision model, which assumes arbitrarily large random angular jumps [5,6], gave a satisfactory description of the time spectra for almost all temperatures, with the only exception at $T = 348.5\text{ K}$, where probably restricted librational motion dominates and the assumption of large angular jumps does not hold.

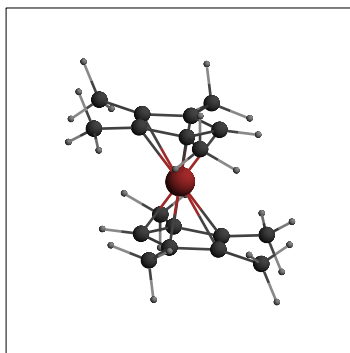


Fig. 2: OMF molecule

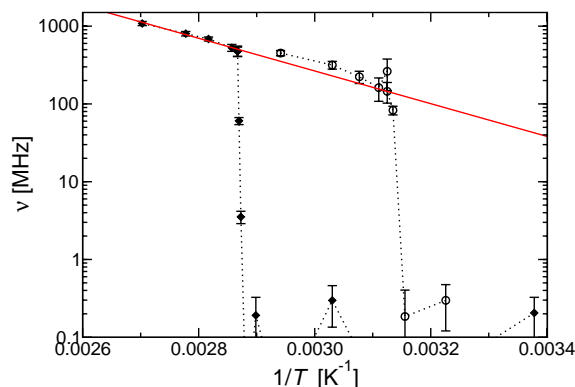


Fig. 3: Rotational frequency of OMF

We can conclude that SRPAC has provided us with the first direct evidence of quasi-free rotation in the rotator phase of OMF. SRPAC is not directly sensitive to mutual "gear-wheel"-type rotations of the two substituted cyclopentadienyl rings located at the same molecule, which were postulated in [7]. Instead, SRPAC provides us with a proof of reorientations of the EFG and hence to reorientations of the entire molecule. SRPAC is therefore complementary e.g. to quasielastic neutron scattering, which "sees" a superposition of both types of motion. As for the temperature dependence of ν , it is interesting to note that the hysteresis follows precisely the structural hysteresis. This is in contrast to OMFA, where we observe precursor effects on heating and a deviation from Arrhenius behaviour on cooling.

Using the powder XRD data and plotting only the Fe atom positions, we obtain an arrangement of the molecular centre of mass (COM) for low- and high-temperature phase as shown in Fig. 4 a+b. Obviously, the transition between both phases only implies a minor shift of the COMs of neighbouring molecules. As OMF is a rather symmetric molecule, different relative conformations of the Cp^* rings do not influence strongly the overall molecular shape; hence, rotational dynamics appears to occur in a single activated step.

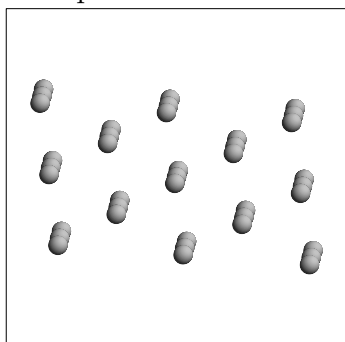


Fig. 4a: Monoclinic LT phase

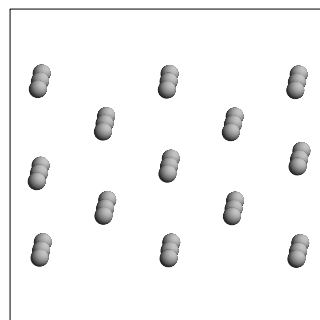


Fig. 4b: Hexagonal HT phase

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