ESRF	**Experiment title:** Möβbauer spectroscopy of Single Molecule Magnets on plasmonic nanostructures	**Experiment number:** HC4032
Beamline: ID18	**Date of experiment:** from: 21/11/2018 to: 27/11/2018	**Date of report:**
Shifts: 18	**Local contact(s):** Aleksandr Chumakov, Rudolf Rüffer	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Sessoli Roberta, Mannini Matteo, Poggini Lorenzo*

University of Florence Laboratory of Molecular Magnetism Department of Chemistry & INSTM RU Via della Lastruccia 3 Sesto Fiorentino IT -50019 FIRENZE

Pedrueza Villalmanzo Esteban*, Dmitriev Alexander

Gothenburg University Institutionen för fysik, Kemivägen 9 SE - 412 96 GOETEBORG

Vavassori Paolo

CIC nanoGUNE nanomagnetism Tolosa Hiribidea, 76 ES - E-20018 SAN SEBASTIAN

Cini Alberto*, Fittipaldi Maria

Universita di Firenze Dipartimento di Fisica e Astronomia Via Sansone, 1 IT - 50019 SESTO FIORENTINO

Cornia Andrea

University of Modena and Reggio Emilia Department of Chemical and Geological Science Via G. Campi 103 IT - 41125 MODENA

Pineider Francesco*

University of Pisa Chemistry and Industrial Chemistry Via Giuseppe Moruzzi 13 Pisa IT - 56124 PISA.

Report:

AIM OF THE EXPERIMENT

We propose to investigate the spin dynamics of iron-based bistable magnetic molecules, also known as Single Molecule Magnets (SMMs),[1] when a thin film of these molecules is deposited on an array of metallic plasmonic nanostructures that are expected to act as optical antennas and to enhance the electromagnetic field generated by irradiation in the visible-NIR range. The purpose is to employ the SMMs as model magnetic units to investigate the possibility to achieve plasmon-assisted optical switching with circularly polarized light. To detect this effect energy resolved Möβbauer spectroscopy as implemented at ID18, was than used. We have recently shown that this technique is able to study a monolayer of ^{57}Fe enriched SMMs.[2] Moreover, the spin dynamics is detectable over a time window (10^{-6}-10^{-9}s), which is better suited for the expected fast switching than XMCD.[2] We plan to highlight the induced modifications in the transition rates between spin levels using the protocol recently employed to reproduce the Möβbauer spectra of Fe_4 SMMs on gold. The study will allow to shed light on the phenomenon of optical switching of the magnetization at the nanoscale, whose rationalization is still to be achieved.

EXPERIMENTAL SETUP

The Mössbauer measurements were realized at the Synchrotron Mössbauer Source (SMS) set up at the ID 18 beamline of ESRF. The radiation coming from the SMS has an energy of 14.4 keV, suitable for the absorption by ^{57}Fe nuclei, it is narrow (its FWHM is less than three natural linewidths) and can be focused to mm^2 or μm^2 spot sizes. The sample was measured in grazing incidence geometry. Energy-domain Mössbauer spectra were realized by collecting the radiation scattered by the sample. The sample was inserted in a cryostat with minimum achievable temperature of about 3 K. The sample was mounted in the vertical plane. The radiation coming from the SMS is linearly polarized with the electric field lying in the vertical plane of the laboratory. The irradiation of the sample was realized by positioning a laser (wavelength = 405 nm, maximum power ~ 30 mW) on a lateral window of the cryostat. Consequently, the direction of laser light was perpendicular to the surface of the sample. In this setup a magnetic field (intensity ~ 5 T) was applied, that was directed parallel to the surface of the sample.

SAMPLE

We studied a sublimated sample of the Fe_4 SMM. Fe_4 was enriched in ^{57}Fe and sublimated on a SiO_2 substrate (thickness ~ 400 nm) having plasmonic structures on top. In particular, Al rings (external diameter = 331 nm, internal diameter = 63 nm, height = 20 – 25 nm) with absorption band at 390 nm were considered. A thickness of Fe_4 of the order of 10 nm was sublimated on this substrate. Other samples, such as 10 nm of Fe_4 sublimated on a SiO_2 substrate having plasmonic disks on top and a dropcast of Fe_4 on Au substrate, were studied, however their spectra show features that cannot be associated with Fe_4 alone and they are not reported here.

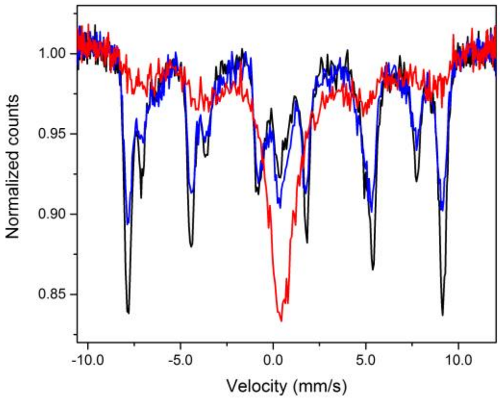

Figure 1: Mössbauer spectra as a function of temperature (black line = 3 K, blue line = 5 K, red line = 20 K).

MEASUREMENTS

As a first step a thermal characterization of the sample was realized. In Fig. 1, the spectra taken at three different temperatures are reported. The spectrum realized at 3 K shows the characteristic features of Fe_4, i.e. the presence of splitting of the external lines of the iron sextet due to the presence of inequivalent iron sites in the molecule. Moreover, as expected, a reduced intensity of the external lines and an increased intensity of the central one is encountered with increasing the temperature.

The irradiation measurements were realized by keeping the sample at 3 K and irradiating it with the maximum laser power in three different polarizations of light (linear polarization, right circular polarization and left circular polarization). In Fig. 2, the measured spectra are reported. The spectra do not differ much from the laser off spectrum, whatever is the polarization of light. Little differences in the height of the peaks with respect to the laser off spectrum can be associated with small fluctuations in the temperature.

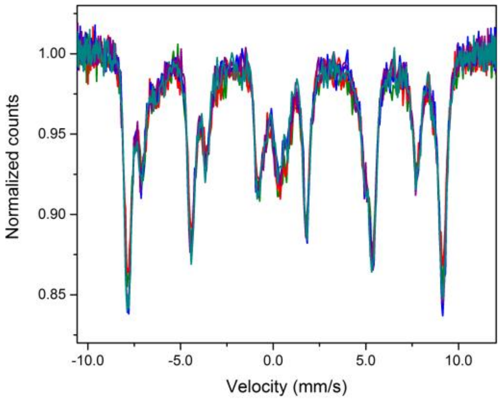

Figure 2: Mössbauer spectra realized at 3 K with laser off and laser on with different polarizations of light. The measurements were realized in this order: linear pol. (green line), left circular pol. (red line), laser off (blue line), right circular pol. (purple line) and left circular pol. (dark cyan line).

In Fig. 3, the measurements realized at different temperatures with an external magnetic field of 5 T are reported. The addition of this magnetic field leads to a simplification of the spectra, due to the presence of preferred transitions with respect to others. No differences can be encountered between the 3 K and 5 K spectra. The spectrum taken at 20 K is instead different, because the thermal energy exceeds the characteristic energy of the system. Finally, in Fig. 4, the spectrum measured at 3 K with 5 T and laser irradiation with left circular polarization light is reported. Little differences with the laser off spectrum can be encountered, that can be associated with thermal fluctuations.

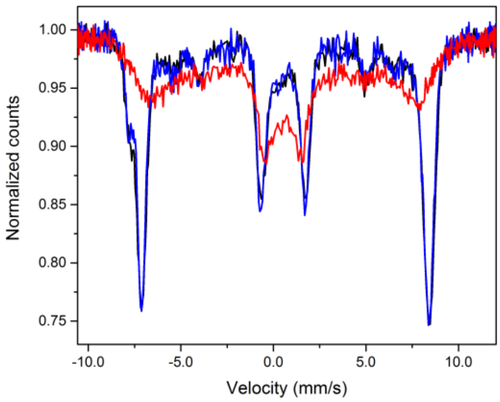

Figure 3: Mössbauer spectra realized with a magnetic field directed parallel to the surface of the sample as a function of temperature (black line = 3 K, blue line = 5 K, red line = 20 K).

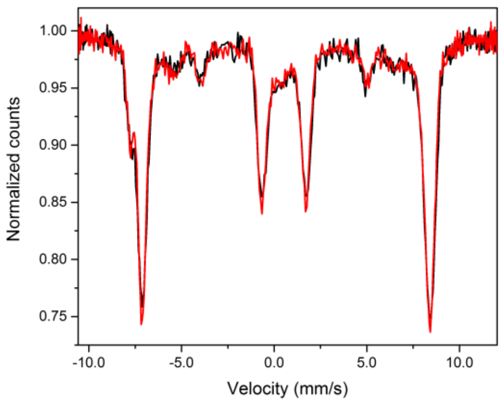

Figure 4: Mössbauer spectra realized with a magnetic field directed parallel to the surface of the sample with laser off (black line) and laser on with left circular polarization (red line).

CONCLUSIONS

A qualitative analysis of the spectra reveals that intact Fe_4 molecules are present in the sample and their thermal evolution is the expected one. Moreover, also the principal differences introduced in the spectra by the application of an external magnetic field are in line with the theoretical ones. The laser irradiation seems to have produced no detectable effect on the spectra, whatever was the polarization of light. However, a verification of this conclusions needs a proper fitting of the measured spectra.

Refrences

1. Gatteschi, D., et al., Molecular nanomagnets. Oxford University Press: Oxford, UK, 2006.
2. Cini, A., et al., Nat. Commun. 9,480 (2018).