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1. Objectives

The goal of this experiment is to measure angular dependent transition metal (Tm: Fe, Mn and Co) 1s2p resonant inelastic X-ray scattering linear dichroism (RIXS-MLD) in TmPc thin films to elucidate the ground state. In addition, RIXS LD signal is expected shed light on the stacking geometry to the molecular magnets observed LD signal taking advantage of the spectral details revealed in the plane. This knowledge of the exact Tm 3d electronic configuration and the geometrical stacking of the molecules in thin films is essential in context of spintronics applications by opening the possibility to control the orientation and strength of the magnetic interaction of the molecule.

2. Experiment details

2.1 Samples

Two samples were studied during the beamtime:

- i- FePc thin film (150ML) grown on silicon substrate. The FePc molecules lie nearly perpendicular to the substrate. Fig. 1a shows a sketch of the sample
- ii- CoPc (200ML) thin film grown on Au on Mica (Fig 1b). The CoPc molecules lie nearly parallel to the substrate.



Figure 1: Samples measured at the beamtime. (a) sketch of FePc thin film, (b) of CoPc and (c) TmPc molecule.

2.2 Description of the measurement

The measurement were carried out at room temperature in air. Fe and Co 1s2p RIXS angular dependence was studied for the two samples. Fig. 2 shows a sketch of the scattering geometry used.



Figure 2: Normal incidence scattering geometry of the RIXS measurement for (a) FePc and (b) CoPc.

3. Preliminary results

3.1 FePc thin film

Radiation sensitivity test were done to check for the stability of the thin film (Fig. 3). We determined that we can stay up to 10minutes per spot. The angular dependence of the high energy fluorescence detected X-ray absorption near edge structure (HERFD-XANES) was measured taking into account the damage rate of the molecules. Fig. 4 shows the HERFD-XANES results that show strong dichroism between normal and grazing incidence measurement. Resonant X-ray emission slices (RXES) were measured at several incident energies (7.1118, 7.1127, 7.114, 7.116, 7.118 KeV) and are shown in Fig. 5. No dichroism was observed in the RXES measurement as can be seen from Fig. 5(a) and (b).



Figure 3:Radiation damage assessment for the FePc thin films. (a) HERFD measured at normal incidence, (b) and (c) at grazing incidence of angles 15° and 0.6° as shown at the right side.



Figure 4: HERFD-XANES of FePc thin film as a function of angles.(a) shows the geometries used for the measurement from normal to grazing incidence. (b) is a zoom of the pre-edge region and (c) shows the full range.



Figure 5: Fe 1s2p RXES slices measured at different incidence energies. (a) grazing and (b) normal incidence configuration.

3.2 CoPc thin film

Radiation sensitivity test were done to check for the stability of the thin film (Fig. 6). We determined that we can stay up to 2 minutes per spot given the statistics of the measurement. Given the quick damage of the CoPc film the measurement, we needed to measure on many spots of the sample. We have noticed many inhomogeneities in the sample combined with the radiation sensitivity made the measurement of the CoPc thin films very difficult. Fig. 7 shows the HERFD-XANES at different positions of the sample in normal and grazing incidence configurations. We have concluded from the measurement that it is essential to carry-out the experiment in a cryostat and under vacuum to minimise beam damage.



Figure 6: Radiation damage assessment for the CoPc thin films. (a) raw data and (b) smoothed.



Figure 7: (a) Normal incidence measurement: Left graph shows the different sample spots that were measured probed, the colour of the spot correlated to the type of pre-edge observed. Right graph shows the different pre-edge features observed at different positions of the sample and (b) for grazing incidence.

4. Conclusions

- Fe 1s2p HERFD-XANES of FePc (150ML) shows strong angular dependence. Comparison of the angular dependent HERFD with DFT and multiplet calculation will be performed to elucidate the ground state.
- Fe RXES slices of FePc (150ML) didn't show angular dependence
- CoPc thin film are very sensitive to the beam and it is necessary to measure them at low temperature under vacuum.