The spin-crossover (SCO) phenomenon corresponds to the switching of the electronic configuration of a transition metal compound between high spin and low spin states as a result of a perturbation. The latter can be of many kinds including modifications of temperature, pressure, light irradiation, magnetic field or pH. The SCO inevitably induces a change of magnetic, optical and structural properties of the material. Whereas in solution the SCO takes place without cooperativity between metal centres resulting in a conversion that is always very gradual, in the solid state the conversion presents a large diversity of behaviours ranging from very abrupt with hysteresis to multi-step or incomplete reversible SCO for instance. It is therefore in the solid state that the SCO offers the best circumstances to investigate its fundamental aspects and to offer rational molecular engineering through the establishment of structure-properties relationships with applications in view [1].

In molecular solids, the SCO is always associated to structural modifications that start at the atomic level and then propagate from the coordination sphere to the crystal-packing and to the sample scales. As a consequence of these structural modifications, the phase-transition diagrams of SCO molecular solids can appear rather intricate in some cases, as illustrated in the figure below showing the interplay between the crystal symmetry, the spin state and external perturbations in the case of an iron(II) molecular complex (adapted from [1]).

We will discuss the structural modifications in molecular SCO solids considering various physical scales. A focus will be made on the amplitude of the multiscale volume variations as well as on the transition mechanisms and the resulting phase diagrams, including unexpected behaviours. Structural movies determined thanks to X-ray diffraction [2] will be used to illustrate the results. Last but not least, discrepancies between observation made on molecular SCO solids in the form of powders and single-crystals will be highlighted and opened to discussions.


**Keywords:** Spin-Crossover, X-Ray Diffraction, phase-transition