Habilitation Thesis

Hysteresis processes in spin crossover compounds: experimental and theoretical studies

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Summary

This thesis is dedicated to the study of the complex processes which takes place in spin crossover materials with an emphasis on the bistability character exhibit by these molecular solids that belongs to the bigger family of molecular magnets. The work is motivated by the unimaginably advances made in computers and information technology by the today society which pushed the magnetic storage paradigm to its physical limits and consequently to ask for novel approaches regarding the storage density (molecular level), information readiness (optical addressability) and processing power (quantum computing).

Spin crossover molecular magnets are inorganic compounds commutable between two states in thermodynamic competition described by different optical, geometrical (volume), magnetic and vibrational properties. In the case of strong elastic interactions between spin-crossover units, the transition is accompanied by a hysteresis loop. This bistability makes these materials suitable for applications, from memory devices and nanoelectronic switching to solid state temperature, pressure or thermo-chromic sensors and molecular actuators.

We guide ourself in understanding the hysteresis in spin crossover materials by looking at their properties at nano-, micro- and macroscopic scales and combining the experimental investigations with modeling and simulations.

In the first chapter, we briefly introduce the spin crossover research field, highlighting the measurement techniques that we probed the spin state modification (magnetic, change of color and calorimetry) and the external parameters used to trigger the spin transition (temperature, pressure and light). We extensively employed the first order reversal curves (FORC) diagram method to explore the hysteresis properties and so, it was described in a dedicated section. Next, the specific five compounds studied here and obtained from various collaborator were shortly described. The final part is dedicated to the models used to validate the new hypothesis we have introduced to explain the experimental data and to reproduce qualitatively but also quantitatively the measurements. Thus, beside the mean field macroscopic master equation-based model, a microscopic description was obtained with a static Ising-like model (solved in mean field approximation or explicitly accounting for short- and long-range interactions) or dynamic Monte Carlo approach (Ising and mechano-elastic models).

The second chapter is devoted to the investigation of spin-crossover nanoparticles as somewhat unexpected differences compared to the bulk compounds was observed, like the decrease of both the transition temperature and the fraction of spin-crossover species, or the spreading of transition and

the vanishing of hysteresis. Using Monte Carlo simulations based on Arrhenius dynamics applied to three dimensional Ising like model, we show that introducing specific boundary conditions, i.e. edge molecules interact stronger with the surrounding polymer than with the rest of the molecules forming the nanoparticle, it is possible to reproduce all the features experimentally observed. Moreover, we have documented the relaxation characteristics of nanoparticles and the amplitude of the kinetic component as function of the particle size, with the FORC method, respectively.

The role played by the environment on the physical properties of the micrometric spin crossover crystals seen as a composite system was systematical explored in the third chapter. By embedding the spin crossover particles in several dispersants, we measured an unexpected enlarged hysteresis loop compared to the bulk, but even more spectacular was the huge reversable component obtained while measuring first order reversal curves. We understand this effect as a variable internal pressure between the frozen matrix and the particles that decrease their volume together with the spin transition and validate this new mechanism, we called switch off/switch-on, with a mean field model. We also noticed that the thermal treatment of the composite influences the shape of the hysteresis so, we have performed differential scanning calorimetry experiments that allowed to probe the change of state of both particles and matrix separately and therefore to better disentangle the behavior inherent to the embedding matrices and that of the spin-crossover microparticles. Further, comparing the FORC diagrams obtained for different dispersants and measured by different techniques (magnetic and calorimetric; the calorimetric FORCs were recorded and interpreted for the first time by us) we have concluded that microparticles size distribution tunes the matrix-particle interactions and is also responsible for the negative regions in the diagrams. To complete the picture on this topic, we have measured the response of these hybrid systems at low temperature under light irradiation, as in real life applications, the photoactive object always interacts with the environment; it is not isolated. We show, in the framework of mechano-elastic model, that a faster start of the relaxation is due to an initial internal positive pressure, that diminishes and eventually become negative during relaxation. We provide evidences that the dispersing matrix used for elaborating photo-switchable materials plays a role both in the efficiency of photoexcitation and the kinetic of the subsequent relaxation. Moreover, it is responsible for inducing an unexpected quasistatic light induced thermal hysteresis loop despite the low cooperative parameter of the isolated microparticle. The switch-off/switch-on mechanism introduced to explain the thermal hysteresis is valid also for light induced thermal hysteresis and we adapt it within the macroscopic master equation and Ising models to reproduce the experiments. In the end, we selected a different matrix that adapts to the volume changes of the embedded microparticles, and the FORC analysis showed a behavior closer to the bulk, thus proving that, for the composite systems, the mechanical properties of the environment are as important as the spin crossover material characteristics.

Due to the similarities between the nano-particles and spin crossover materials in which the iron is chemically replaced during the synthesis by a neutral metal like Zn, Ni, Co, etc., we investigated in chapter four the way the impurities limit the propagation of elastic interactions and determine the size and distribution of like-spin domains in macroscopic, i.e. bulk, spin crossover crystals. Therefore, we have looked at the thermal behavior of pure and impure spin crossover materials and extended further the study to low temperature response where kinetic effects become evident and light induced thermal hysteresis occurs and surprisingly, overlap to the thermal loop. Moreover, to account for the effect of internal pressure induced by the matrix on embedded nano- or micro-particles, we have branched out our investigation towards the changes produced by the pressure (this time external) on diluted systems either in isobaric conditions or as dynamical pulses. Thus, the FORC analysis indicates that the hydrostatic and homogeneous character of the pressure is supported by the absence of a distribution of pressures and that the correlation between physical parameters in diluted compound is assigned to a composition distribution. Additionally, this distribution combined with an original model that favors cluster grow similarly to the one obtained in an Ising model driven by Kawasaki dynamics, but much faster, provides the relative increase of the like-spin domains size due to pressure.

Chapter five is dedicated to my professional evolution and the most important achievements in the research and teaching activities, as well as the objectives of my career development plan that divides between teaching, research activities and strengthening international collaborations.