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Foreword/*Avant-propos*

Preface and introduction



The spin-crossover (SCO) area is a wonderful research field for a fruitful collaboration between chemists and physicists and between experimentalists and theoreticians. The SCO phenomenon, which is the reversible change between two different spin states of some peculiar transition-metal ions (mainly 3d) in a number of specific compounds (mainly coordination complexes), was first observed in 1931, induced by temperature in a ferric compound. This transition and the further examples reported were found to proceed gradually as a function of temperature and could be accounted for by the simple variation of the electronic population of the metal ion high-spin and low-spin levels. It is only since 1964, when the first abrupt thermoinduced SCO of a polycrystalline compound was reported, that the specific research field in SCOs was really initiated, and then, it soared. Such a cooperative transition showed that, in the solid state, the mechanism was more complex than the one previously suggested: a challenge that remained to be taken up.

More than 50 years later, which general features can be deduced from a survey of the development of this research area? It clearly appears that, from the multiple facets of their fundamental nature, SCOs have stimulated the creativity of researchers in many domains.

Chemistry first played a driving role in inducing the investigations. By using molecular engineering processes to predict and fine-tune an SCO behavior, a large number of new coordination compounds were designed and then synthesized. Meanwhile, the SCO family was widely expanded by the discovery of various chemical mechanisms to induce spin transformation, for instance, an electron transfer between metal ions and ligands, a modification of the coordination structure, a change in the configuration of a photo-sensitive ligand, or the capture and loss of solvent molecules. This resulted in a period of intense activity for the design and the synthesis of new switchable systems. The reported SCOs were found to occur with a more or less abrupt or complete character, with possible hysteresis and/or multistep behaviors, and could be accompanied by crystalline phase transitions. This unprecedented flood of compounds and data provided both

the materials and the topics for experimental and theoretical investigations.

SCO compounds are highly appealing to experimentalists because of the concomitant variations of a large number of physical properties: optical, magnetic, vibrational, dielectric, acoustical, luminescent behaviors, as well as volume, hardness, porosity. This provided the possibility to investigate the phenomenon by means of a large variety of physical techniques, as well as a serious touchstone for the theoretical concepts that aim at understanding the process. Also, excitations of all kinds were used to trigger the transitions, such as temperature, pressure, light, stresses, magnetic field, and electric field (in a few cases). As a general trend, the refinement of the experimental methods, especially the diffractometric ones, may be noticed. Moreover, the possibility of locally inducing SCO by means of a laser pulse, and then monitoring the subsequent propagation of the transformations in the solid by time-resolved optical and structural experiments, provided theoreticians with a novel approach toward a sensible description of the transformations in the solid state. At last, huge efforts are presently directed toward the investigation of nanoparticles, nanostructures, and single-molecule devices.

The in-depth theoretical approach to the SCO phenomenon started in the 1990s with the recognition of a thermally assisted tunneling mechanism at the molecular state. Presently, a noticeable effort is being made to understand the origin of the peculiar electronic structure responsible for the SCO phenomenon, through quantum chemical approaches. Elsewhere, their solid-state properties were first modeled by introducing phenomenological interactions between fictitious spins (inspired from magnetism) before the elastic nature of the interactions was fully recognized so as to lead to a realistic view of the propagation properties of the transition. The fundamental role of the lattice for the transition mechanism is now accepted and offers a fascinating field to theoreticians and experimentalists, where numerical simulations with elastic lattices play a key role. However, key features of the SCO remain to be elucidated: the ability of the molecular structure to accommodate the large atomic displacements

and the resilience of the lattice to repeated molecular switching.

The manifold changes associated with the transition in SCO systems, as well as the bistability and hence the memory effect presented by part of these systems, pave way to a lot of possible practical applications. Research in this field has significantly increased in the last decade, owing to two main reasons: the progress in the fundamental knowledge of the SCO phenomenon and the widespread development of nanotechnologies, size reduction of materials being essential to a range of foreseen devices. One may hope to use SCO systems as nanometric multifunctional machines that are able to transform signals of a given type into different signals or actions. The recent achievements of sensors, actuators, switches, information storage devices are the first steps towards a future molecular electronics, incredibly versatile. Further links to “spintronics” may be anticipated. However, numerous challenges remain to be addressed in order to develop durable systems that meet the requirements for commercial applications. If the chemical fragility of the materials (due to oxidization and loss of solvent molecules) may be prevented by encapsulation of the samples, the physical brittleness resulting from the mechanical stresses induced by repeated SCO transitions remains the blocking point. This major drawback might disappear in the case of nanosystems, the high specific area of which is expected to better accommodate and relax the stresses.

The SCO research area has now reached a state of maturity and is striding ahead. We are extremely grateful to Dr. Azzedine Bousseksou, a member of the French Academy of Sciences, who promoted important achievements in the field and recently published reference review papers on SCOs, for directing the redaction of the present special work. This thematic issue aims to concretize the large and sustained effort of the European SCO community of scientists. This well-alive community was gathered in the recent past through the European Network for Molecular Magnetism (MAGMANet) and through two successive “groupements de recherche” of the French CNRS: Molecular Switching at the Solid State (CoMES) and Molecular Magnetism and Switching (MMS). There is no doubt that such an open and pluridisciplinary research field will remain active and attractive for a long time.

The number of publications on SCO has virtually exploded over the past decades, and the aim to review the subject in just one issue of the *Comptes rendus* is very ambitious. Thanks to the efforts of all the authors as well as of the editorial staff (Pierre Braunstein, Fatima Messadi, Marie-Christine Brissot, and Jean-Michel Blengino), the combination of topics covered in this one issue meets the set goal to perfection.

The appealing ON–OFF properties associated with the SCO phenomenon have always been the main motivation in the search for new switchable materials. The interplay between SCO and other relevant properties to afford multifunctional materials, their amenability to be processed at the micro- or macroscale, and the possibility to be integrated in devices have given additional strong impetus to the SCO field. Guided by these incentives, a rich variety of new SCO compounds and SCO properties have been

reported in recent years. This thematic issue of *C. R. Chimie* devoted to SCO reflects in two different contributions the bustling activity carried out in the search for new interesting SCO materials. On the one hand, the contribution by Boillot and Weber reviews the recent work devoted to mononuclear iron (II) and iron (III) SCO complexes using multifunctionality as one of the main vectors to select relevant new results. On the other hand, in a systematic work, Galán-Mascarós, Aromí, and Darawsheh review the progress made in the synthesis and characterization of polynuclear iron (II) SCO complexes including coordination polymers during the last five years. Both contributions are a very useful update for researchers interested in the SCO phenomenon. Of particular importance is the confection of SCO systems into nanoparticles and nanocomposites with, for instance, interesting mechanoelastic properties as described by Salmon and Catala. In the same vein, Mallah and Cavallini review the properties of thin films and the surface patterning of SCO molecules down to the single-molecule level. This is especially important with respect to the futuristic applications in molecular electronics as discussed by Bellec, Lagoute, and Repain, using single-molecule probes such as STM and AFM.

The fact that so many of the physical properties of SCO compounds change upon a spin-state change invites a large number of experimental methods to be applied for their investigation. Even though the traditional experimental methods, such as magnetic susceptibility and heat capacity measurements, Mössbauer spectroscopy, and steady-state optical and vibrational spectroscopies—which are introduced in the contributions by Costa and by Wolny, Schünnemann, Németh, and Vankó—are still important in order to establish the basic properties of a given compound, novel experimental methods have given detailed insights into the phenomena associated with SCO, which is not possible otherwise. Accordingly, Wolny et al. also give an overview of the application of NMR, nuclear inelastic scattering, and the different X-ray spectroscopies including time-resolved methods. First-principle calculations based on density functional theory were also introduced as a powerful tool for the investigation of SCO compounds. The access to the intramolecular vibrational spectra in the LS and HS states as well as to the hyperfine structure parameters (like quadrupolar splitting and isomer shift), which were found to be in very good agreement with Raman and Mössbauer spectroscopies, confirmed the accuracy of the method. In particular, the evaluation of the vibrational entropy change at the transition led us to infer that most of the entropy change comes from intramolecular vibrations, which constitute important information about the identification of one of the driving forces of the spin transition. However, it is worth mentioning that, with a larger view covering all DFT investigations of the SCO compounds, one can easily notice from the literature an important mismatch and divergence between the results. This raises the question about the choice of the suitable DFT functionals that has been noted by Wolny et al.

In view of the large difference in molecular volumes between the high-spin and the low-spin states, the high-pressure studies described by Gaspar, Molnár, Rotaru, and Shepherd provide an additional important puzzle stone for

the thermodynamic characterization of SCO systems. Then, with the advent of synchrotron radiation, 2D detectors, and powerful software, particular progress has been made in structural methods, as described in the article by Guionneau and Collet. Structural studies using powder and single-crystal X-ray diffraction allowed detailed insight into crystallographic phase transitions, superstructures, incommensurate phases, conformational changes in the ligands, and even slow relaxation phenomena such as nucleation and growth processes and other cooperative effects associated with the thermal spin transition and the high-spin to low-spin relaxation following the light-induced population of the high-spin state at low temperatures. Indeed, the contribution by Chastanet, Lorenc, Bertoni, and Desplanches is dedicated to the latter phenomenon, generally referred to as light-induced excited spin-state trapping (LIESST), and related phenomena. Up to a few years ago, only indirect evidence for the exact mechanism of this astonishing photophysical phenomenon with a double intersystem crossing step has been available, and novel ultrafast optical and X-ray absorption spectroscopic methods using laser pump probe techniques allowed for a detailed characterization of the electronic states involved and revealed that the transition from the low-spin to the high-spin vibronic manifold only takes time of the order of 100 fs! Furthermore, the time-resolved structural studies making use of the intense and very short pulses of an X-FEL laser included in the contribution by Guionneau and Collet demonstrate that a cascade of subsequent processes on very different timescales follow this initial ultrafast process, that is, from local vibrational cooling to the response of the crystal lattice to the local deformation and the final equilibration of the system covering timescales from the abovementioned femtoseconds all the way to milliseconds.

These experimental advances have been key to the elaboration of the theoretical concepts. Despite their shortcomings, thermodynamic and microscopic Ising-like models are still very popular because of their diversity and efficiency in describing the tremendous number of experimental situations emerging from the “jungle” of experimental data. Although nonquantitative, they present the advantage of catching the essential physics of the SCO phenomenon and are still able to achieve impressive results.

The microscopic models, which are based on the description of the SCO phenomenon by coupled two-state fictitious spins, are among the most popular models because of the simplicity of their implementation, both from the analytical and numerical viewpoints. These two-state models based on Ising-like descriptions, which are discussed by Pavlik and Linares, provide a simple formalism, allowing one to treat almost all experimental data encountered in magnetic experiments, leading to first-order, gradual, multistep, and incomplete spin transitions. Their simple form allows not only their resolution using variational techniques of statistical mechanics, like mean-field methods and even going beyond (Bethe–Peierls and cluster variational approaches) as well as Monte Carlo simulations to include short-range correlations. Their versatility also allowed several extensions, which included

short- and long-range competing interactions, vibrations, as well as the study of the time evolution of the high-spin fraction using the stochastic master equation formalism. These time-dependent equations of states of the high-spin (HS) fraction had the merit to allow one to investigate the relaxation of the photoinduced metastable HS states as well as new instabilities under light, like the light-induced thermal hysteresis (LITH) and the light-induced optical hysteresis (LIOH), which have been widely studied on the experimental side. Recent works, based on these microscopic models, also demonstrated their relevant spatio-temporal extensions, using reaction–diffusion equations, allowing the understanding of the spatiotemporal properties of SCO transitions that emerged from imaging of SCO transitions by optical microscopy, a field that is spectacularly expanding. One of the most severe criticisms that one may formulate on these useful models relates to the fact that they totally discard the volume change at the transition and consequently the effects of mechanical stresses on the transition mechanism. In all two-level models, the first-order thermal transition is then obtained through a phenomenological interaction parameter.

At variance from the previous electronic models, the continuous medium model developed in 1982 showed that an elastic interaction could as well give rise to the observed first-order transitions in SCO solids. Here, the interactions relate to the molecular volume change between the low-spin and the high-spin states of the molecule. The latter change deploys to the surrounding molecules thanks to the lattice network, hence delocalizing the induced strain field far from the epicenter of the excitation. While the problem of the insertion of a defect having a specific volume in a lattice is tractable in continuous mechanics, thanks to Eshelby's work, the extension to several defects poses formidable mathematical challenges because of the interferences induced between their strain fields, which lead to a highly anisotropic spatial distribution of the resulting stress (regions under tensile and others under compressive stresses exist depending on the direction of observation), which precludes any possible analytical resolution of this problem. Mean-field approximations have been successfully developed, and they reproduced qualitatively the experimentally observed first-order transitions, with the merit to give a physical meaning and origin to the interactions between the SCO species, compared to the microscopic Ising models (see Nicolazzi and Bousseksou).

More recently, discrete atomistic models based on deformable lattices have been developed by several groups with the aim to mimic the spatiotemporal features of the nucleation, growth, and propagation process of spin phases at the thermal transition, which were revealed by optical microscopy investigations since 2009 on high-quality SCO single crystals. These models combine electronic and elastic degrees of freedom, which opens the possibility to discriminate the contribution of these two important aspects of the spin transition, which had often been treated separately in the past. The main idea here was to consider the fact that the equilibrium distance between two neighboring atoms depends on their spin states. This dependence may be written using harmonic, van der Waals, or quartic potentials. Other extensions using more adequate

potentials to molecular crystals are both warranted and welcomed. Hence, the advantage of these electro- or mechanoelastic models, as discussed by Enachescu and Nicolazzi, lies in the fact that they reconcile the Ising-like and continuous medium models, so as to reproduce both the lattice and spin transformations of the system, thus also giving access to spatiotemporal properties of the SCO solids. These new treatments have undoubtedly marked a turning point in the better understanding of the leading role of the mechanical stresses in the mechanism of emergence of the SCO transition and its propagation dynamics in single crystals. They have also clarified the macroscopic nucleation nature of the SCO phenomenon and hence the important role of the global shape of the material on that of the high-spin/low-spin interface shape and its propagation velocity. This emerging field is very fertile, and many other studies remain to be done, particularly in the description of ultrafast dynamics, which requires to go beyond the two-state description of the SCO object.

As mentioned above, future developments in the field of SCO materials will be driven by the need for practical applications, which themselves should be based on a better knowledge of the material from the nano- to meso- and then to macroscale. This multiscale (time, space, and energy) physics can be addressed by using the power of ab initio calculations, combined with molecular dynamics and/or kinetic Monte Carlo simulations. Here, the idea is to outline numerical results and theoretical models. Hence, the data derived from ab initio calculations (equilibrium morphologies at the atomic scale, electronic structures, vibrational properties, etc.) are complemented and generalized using simple models, capable of identifying relevant parameters and predictable trends for other systems.

It is fair to say that the collaborative efforts of experimentalists and theoreticians and chemists and physicists, of which this thematic issue of *C. R. Chimie* is the best proof, have propelled the knowledge and understanding of the phenomena associated with SCO in transition-metal complexes and compounds to unequalled heights. We are sure that we may expect a lot of more interesting results and developments in the years to come.

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