Book Section:

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Preface

The spin-crossover process involves the rearrangement of electrons in a metal ion, from a high-spin to a low-spin state. These correspond to the distributions of electrons within the metal orbital energy levels, that yield the maximum and minimum number of unpaired electrons respectively. The phenomenon is particularly prevalent in iron chemistry and can occur in any phase of matter, although it is most often studied in the solid state. Spin-crossover has a large impact on the physical properties of a solid material, including its magnetic moment, colour, dielectric constant and electrical resistance. Moreover some spin-crossover materials show pronounced hysteresis, which often reflects a structural phase change during the transition. Within the hysteresis loop, the materials are genuinely bistable switches that can be either high- or low-spin depending on their history.

Several practical applications of spin-crossover materials have been demonstrated, that make use of their switching properties. They include: display and memory devices, with pixels of a spin-transition material whose colour or dielectric constant is switched by spot-heating and cooling; electrical and electroluminescent devices, where changes in the electrical resistance of a spin-crossover thin-film can be detected, or used to quench light emission; and, using the switchable paramagnetism of a spin-crossover compound in a temperature-sensitive MRI contrast agent**.** Switchable liquid crystals, nanoparticles and thin films of spin-crossover materials have also been achieved, that function almost as well as the same materials in the bulk phase. Notably, most of these application studies have been carried out using just two materials, whose spin-transitions show thermal hysteresis of an appropriate width (30-50 K) that spans room temperature. The production of new switchable spin-crossover materials with technologically useful properties by design, rather than by trial and error, remains a problem of crystal engineering that is only now beginning to be addressed. This combination of technical challenge and practical application explains why an effect that was first observed in the early 1930s continues to be heavily studied by groups around the world.

For the past eight years, the "bible" in the field has been the three-book set from the *Topics in Current Chemistry* monograph series, edited by Philipp Gütlich and Harold Goodwin and published in 2004.[1] This book is intended to complement that earlier work, and concentrates on aspects of spin-crossover research that have developed since then, or are otherwise covered in less detail in the *Topics in Current Chemistry* volumes. Articles from the *Topics in Current Chemistry* series are cited in this book where appropriate, and should be referred to by the reader.

The first four chapters present an overview of the development of spin-crossover research (Murray), and more detailed surveys of the mononuclear (Weber), polynuclear (Olguín and Brooker) and polymeric (Muñoz and Real) spin-crossover complexes that have been discovered since 2004. The structures of these solid compounds are then examined, to describe the state of play in the crystal engineering of spin-transition molecular materials (Halcrow). As before, these first chapters are intended to supplement those in the *Topics in Current Chemistry* volumes,[1] which give a more comprehensive survey of the types of compounds that are known to exhibit spin-crossover.

The next chapters cover alternative types of spin-state transition found in molecule-based materials, whose chemistry has developed particularly rapidly since 2004. These include two different types of charge-transfer-induced spin-transition, based on electron transfer between different metal ions (Dunbar *et al.*), and between a metal and coordinated ligand (Boskovic). Other chapters cover spin-transitions based on reversible spin-pairing between organic radical centres (Rawson and Hayward), and magnetic transitions associated with Jahn-Teller switching in copper/radical coordination polymers (Ovcharenko and Bagryanskaya). The physical characteristics of these different types of transition show many similarities to metal ion spin-crossover, including examples of thermal hysteresis and excited spin-state trapping at low temperatures.

The following chapter by Shores *et al.*, updates the chemistry of spin-crossover in solution. The measurement of the thermodynamics and kinetics of spin transitions in solution is well-established. However, there has been a recent recognition that spin-crossover is also subject to supramolecular influences in solution, and can be responsive to host:guest binding interactions.

The next topic to be discussed is the application of spin-crossover compounds, in multifunctional switchable materials and in nanotechnology. This is covered in chapters describing materials combining spin-crossover with conductivity and magnetic ordering (Sato *et al.*), with liquid crystallinity and amphiphilic behaviour (Hayami), and with fluorescence (Bousseksou *et al.*). Several of these properties have been exploited to make functional or multifunctional nanoparticles, thin-films and surface patterns, or even in switchable single-molecule junctions. These aspects are brought together by Ruben *et al.*

The next set of chapters describes advances in the physical and theoretical methods for studying spin-crossover materials. Coverage is limited to methods that have grown in importance since 2004, and the reader is referred back to the *Topics in Current Chemistry* series for a more comprehensive treatment of the topic.[1] The chapter by Chergui covers ultra-fast measurements of high→low-spin switching, that have deconvoluted the electron redistribution and molecular structure changes that take place during a spin-transition. Next, Varret *et al.* describe the use of optical microscopy to monitor spin-crossover in single crystals at the macroscopic level. This is followed by two chapters describing advances in the theoretical description of spin-crossover, in single molecules (Deeth *et al.*) and in bulk lattices (Enachescu *et al.*). Lastly are discussions of advances in the study of light- or pressure-induced spin-state trapping phenomena, in bulk materials (Létard *et al.*) and in single crystals (Guionneau and Collet).

In the final chapter, Rueff describes the importance of pressure-induced spin-crossover to geology. A large proportion of the Earth's mantle contains iron-containing oxide materials, which undergo spin-crossover at high pressures in the laboratory. This has been intensely researched during the last eight years, to determine whether these spin-state changes also occur in the mantle, and whether they can explain certain anomalies in its physical properties.

Guionneau and Collet have dedicated their Chapter to Andrès Goeta. Andrès was one of the leaders of a team at the University of Durham, who pioneered the study of excited spin-states in spin-transition materials by photocrystallography. Andrès had been due to contribute to this book but passed away suddenly in July 2011. I would like to express my appreciation to Drs. Guionneau and Collet, for stepping into the breach and providing a chapter on this important topic at short notice. But, more importantly, I also dedicate this book as a whole to Andrès' memory.

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(1) Gütlich, P., Goodwin H. A. (Eds.) (2004) Spin crossover in transition metal compounds I-III. Top. Curr. Chem., vols. 233 – 235. Springer Verlag, Berlin / Heidelberg, Germany.