Advances in the research of spin crossover compounds

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Abstract: The spin – crossover (SCO) or spin transition (ST) compounds have become of great interest recently due to their potential applications in memories, sensors, switches, and display devices. This article aims at presenting the main advances in the research of materials that undergo a ST, various ways in which SCO phenomena are manifested and some rationalisations of them, as well as the main requirements that must be fulfilled in order for the SCO compounds to be used for industrial applications.

Keywords: spin crossover, molecular, temperature, pressure, light effects, hysteresis.

1. Introduction

Molecular materials coming from the chemical synthesis offer a good alternative for the replacement of the microelectronic and optoelectronic conventional components. Among these materials, the spin crossover (SCO) compounds constitute an important class of this family.

The phenomena of spin transition (ST) (or spin crossover) was first observed in 1931 by Cambi et Szego [1] by varying the temperature and studying the magnetic susceptibility of a series of compounds based on Fe(III) 3d^5. It is not until thirty years later that the first spin transition compound based on Fe(II) was found, followed in 1956 by the notion of spin equilibrium [2]. Nowadays, there is a large database comprising complex compounds based on metal transition ions with a 3d^4 to 3d^7 electronic configuration that continues to grow with each day. Most studies are focused mainly on the ions of iron (II), iron(III), cobalt(II) and sometimes on cobalt(III), manganese(II), chrom(II), and nickel(II), but definitely the first one is the base for most of the complexes that present a ST.

Upon application of an external perturbation such as heat, light, pressure or other stimulus, the SCO compounds undergo a phase transition from a diamagnetic low spin (LS, S = 0) state to a paramagnetic high spin (HS, S = 2) state, often accompanied by an important change in color, volume or magnetic response.

2. Physical characterization of spin crossover compounds

Molecular compounds are studied by a wide spectrum of scientists, ranging from physicists, chemists and materials scientists to electrical and chemical engineers and even to biologists, so it has became a multidisciplinary re-search field. Currently these studies benefit from a very wide range of characterization techniques such as: structural characterization [3], magnetic susceptibility measurements, Raman spectroscopy [4], infrared and UV-visible spectroscopy, calorimetric [5], reflectance [6] and ellipsometry [7] measurements and optic microscopy. As a result, the transitions from a spin state to the other spin state in SCO compounds are analyzed by using the techniques mentioned above and an external or a combination of external perturbations such as temperature, pressure, light or magnetic field.

2.1 Spin transition induced by temperature

The temperature is the first and the most used perturbation for inducing a spin transition, being very often used in combination with other external factors. According to the type and the intensity of the interactions, the SCO compounds present different magnetic behaviours with the temperature variation: discontinue transition (with hysteresis), gradual or two-step transition.

A gradual transition corresponds to systems that possess a very weak intermolecular
interaction or to very diluted systems, where each metallic centre undergoes a spin transition independently of its neighbours. The transitions with hysteresis present a considerable industrial interest, due to their applicability, for example, in information storage. The presence of hysteresis may be associated with the presence of very strong long-range interactions within the solid or with a change of crystallographic phase [8] (in which case the system is called strongly cooperative).

![Fig. 1. Graphical representation of different spin transition in function of temperature: a) with hysteresis; b) gradual; c) in two steps, [9].](image)

The third category corresponds to a two step transition. The presence of the flat region is generally connected to the existence of two different crystallographic sites in the system [10]. These cooperative effects appear even if the spin transition is induced by pressure, magnetic field or in the relaxation process.

2.2 Spin transition induced by pressure

The first study concerning the effect of the pressure on a SCO compound was taken on a complex based on Co (II) in solution by Ewald [10]. When the compounds are in the HS state they are compressed and the ligand field around the central metal is altered to the point where the gap energy becomes higher than the pairing energy leading to a HS – LS transition. This process is very well described using the configuration diagram: adiabatic energy in function of the metal – ligand distance (Figure 2).

![Fig. 2. Pression effect on the configuration diagram.](image)

The application of an external pressure diminishes the metal – ligand distances. It is already well known that the ligand field is proportional with the inverse of the metal – ligand distance to the sixth power, so the application of an external pressure has the same effect as the ligands substitution on the central metal. When the pressure is applied on such a system, in solid or liquid state, these potential wells can be displaced vertically or horizontally modifying the fundamental state [11].

It has to be noted that this stabilisation of the LS state is not general. It was shown that the pressure can also induce a transition from the LS state to the HS due to the variation of the \( \pi \) connection intensity under pressure [12]. Therefore the application of pressure on a SCO compound can lead to: electronic structure modification [13], crystallographic structure modification or both on the same time.

2.1 Spin transition induced by light (the LIESST effect)

The LIESST effect was first observed in 1984 on the \([\text{Fe}(\text{ptz})_6](\text{BF}_4)_2\) compound (ptz = propyltetrazole), by Decurtins et al. They have shown that the compound, found initially on the LS state, can be changed into the HS state with light irradiation of a wavelength of 514 nm. The life of this metastable state was determined to be superior to \(10^6\) s. Two years later Hauser showed that the process is irreversible and that irradiating the molecule in HS state, with a different wavelength, could lead to its stabilization in the LS state [14].
Figure 3 offers an explication of this phenomenon by showing the LS and HS states and the intermediary states necessary for the LS $\rightarrow$ HS and HS $\rightarrow$ LS transitions. For the compound mentioned above, the first transition is achieved with a $\lambda = 514$ nm, while for the second one $\lambda = 820$ nm.

An explication of the phenomenon is given with the help of two successive intersystem sequences. The irradiation in the absorption band to the LS state (term $^1A_1$) populates one of the excited levels $^1T_1$. The system is going to relax in a non radiative way to a triplet intermediary state $^3T_1$, then to the metastable HS state $^5T_2$ (or returns in the fundamental state $^1A_1$). This is the LIESST effect.

**2.2 Spin transition induced by magnetic field**

The spin transition can also be triggered by applying a magnetic field, which stabilizes the "most magnetic" state (HS) of the molecule by Zeeman effect. This effect was reported for the first time in 1983 by Y. Qi et al. that observed a displacement of the hysteresis cycle towards lower temperatures with 0.12K for the [Fe(phen)$_2$(NCS)$_2$] under a magnetic field of 5.5T.

Bousseksou et al. have also studied the effect of a pulse magnetic field of approximately 30T on compounds based on Co(II) and Fe(II) [18]. The application of a field on a system found on the ascending branch of the thermal hysteresis loop induces a quasi-complete and irreversible transition from the LS to the HS state.

3. Potential applications of the spin crossover phenomenon

SCO compounds present several characteristics that make them possible candidates for use in a large type of applications such as information storage, data display, switches and sensors.

The presence of thermal hysteresis (especially at room temperature) and the possibility of switching the material by using light irradiation are two of the most important aspects that are approaching the SCO compounds towards applicability in industry. If a complex meets the first criterion then a memory feature can be obtained in the material and in order to exploit it, the bistability must have associated a response that can be read. This response is the change in magnetic field or color, the latter being suited to the development of display devices.

Another important aspect to the technical applications is that the hysteresis loop should be centered around room temperature. Some of these types of compounds are already known and further investigation is still underway. Other criteria that must be met in order for the SCO compound to be suited for applications is the chemical stability and the ability to reproduce the data for new compounds as well as after multiple cycling through the hysteresis loop.

Pressure sensors can also be built by using the changes of the ST behavior under applied pressure and observing the color change of the material. The LIESST effect is a promising effect for applications in data storage and optical data processing.
4. Conclusion

Important progress has been made in the recent years in the field of SCO compounds, such as the development of molecular devices has become feasible. The ST compounds have a tremendous potential for a large amount of industrial applications, therefore it will continue to stimulate research in this field in order to find new systems and new aspects of this phenomena. The fundamental objective of this research remains the understanding of the characteristics that lead to cooperativity in SCO systems.

Several other areas in this field are interesting to researchers to gain new insights into ST phenomenon, by which the most important are the coupling of magnetic exchange between metal centres and ST at the individual metal atom and structural characterisation of metastable states.

References


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