

A typical example of a photomagnetic study carried out on a spin-crossover material

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Abstract. The light-induced excited spin state trapping (LIESST) is a well known phenomenon in an iron(II) spin-crossover (SCO) material which offers some interesting prospects in data storage. In this work, we present a typical investigation of the photomagnetic properties of a SCO material. At the surface of the sample, the light-induced phenomenon is investigated by using a home-built reflectivity set up and in bulk material by using a quantum design SQUID magnetometer coupled to a light source.

Keywords. Spin crossover; coordination chemistry; magnetism; photomagnetism.

1. Introduction

In the domain of transition metal complexes, there are several possibilities to induce light sensitive electronic changes accompanied by a drastic modification of magnetic and/or optical properties, like metal-centred thermal spin transition (observed in iron(II) spin-crossover materials), valence tautomerism (catecholate complexes of Co(II)), metal-to-metal charge transfer (Prussian blue analogues), metal-to-ligand charge transfer (nitroprusside complexes), and finally, all ligand modifications which induce change of the spin state, such as isomerization (stilbenoid complexes) and open/close (diarylethene type ligands) processes (Gütlich *et al* 2001).

The first evidence of the light-induced excited spin state trapping (LIESST) in an iron(II) spin-crossover (SCO) material was reported by McGarvey and Lawthers (1982) in solution and then by Decurtins *et al* (1984) in solid state. These authors demonstrated the possibility of converting a low-spin (LS) state into a metastable high spin (HS) state at low temperatures (≤ 50 K) by using a green light irradiation. This phenomenon was completed later on by Hauser (1986) who showed that red light switches the system back to the LS state (reverse-LIESST). Today, the LIESST effect has been observed in many different iron(II) complexes (Gütlich and Goodwin 2004) and one of the challenge is to design a suitable material with a long lived photoinduced lifetime at room temperature compatible with technical applications in data displays and/or in information storage (Létard *et al* 2004). The lifetime of the photoinduced HS state is usually long at very low temperature, e.g. weeks at 20 K for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (Hauser *et al*

1986), but above 50 K the relaxation process becomes thermally activated and in a few seconds the stored light-induced information vanished. Fortunately, it exists in the literature some examples with atypical long-lived lifetimes up to 100 K (Buchen *et al* 1994, 1996; Wu *et al* 1997; Renz *et al* 2000; Hayami *et al* 2001) which demonstrate that some unidentified factors are able to stabilize the photoinduced HS state.

Since several years, we have decided to systematically investigate the LIESST phenomenon and we have recently proposed a guideline for elaborating some SCO material with long-lived lifetimes (Létard *et al* 2005; Létard 2006). In this communication, we would like to report a typical photomagnetic study performed on a molecular spin crossover (SCO) complex. The selected material is the $[\text{Fe}(\text{bpp})_2](\text{NCSe})_2$ ($\text{bpp} = 2,6\text{-bis}(\text{pyrazol-3-yl})\text{pyridine}$) compound well-known to exhibit an abrupt thermal spin transition at around 230 K (Sugiyarto *et al* 2000; Marcen *et al* 2002).

2. Magnetic and photomagnetic properties

Figure 1 reports the magnetic properties recorded for the $[\text{Fe}(\text{bpp})_2](\text{NCSe})_2$ complex. At 290 K, the magnetic signal expressed in $\chi_M T$ product (χ_M stands for the molecular magnetic susceptibility and T the temperature) is $\sim 2.9 \text{ cm}^3 \text{ K mol}^{-1}$, as expected for a fully occupied quintet paramagnetic HS state ($S = 2, t_{2g}^4 e_g^2$). When the temperature is lowered the complex exhibits a complete and abrupt spin-transition, with a small but reproducible hysteresis loops of 2 K occurring at $T_{1/2\downarrow} = 230$ K and $T_{1/2\uparrow} = 232$ K. At 10 K, the diamagnetic response is consistent with the signal expected for a fully populated LS ground state ($S = 0, t_{2g}^6 e_g^0$).

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Such a thermal spin-crossover can also be monitored by following the visible spectrum of the sample as a function of temperature, measured by diffuse reflectance. Figure 2 shows the spectral changes along the thermal spin transition. The band at 800–850 nm corresponds to the $d-d$ transition of the high-spin iron(II) centre, while the absorptions around 500–650 nm region can be assigned to both $d-d$ and MLCT transitions of the low-spin material. Consequently, any change of the signal can be used to directly monitor the thermal SCO transition at the surface of the sample. Hence, increase of the reflectivity signal recorded at 647 nm upon cooling (figure 2, inset) corre-

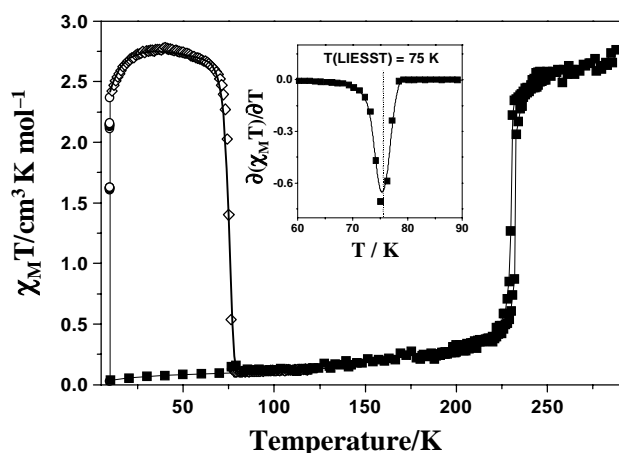


Figure 1. Temperature dependence of $\chi_M T$; ■, data recorded in cooling and warming modes without irradiation; ○, data recorded with irradiation at 10 K; ◆, $T(\text{LIESST})$ measurement data recorded in warming mode with the laser turned off after irradiation for 1 h. The solid line through the $T(\text{LIESST})$ measurement shows the fit generated from the deduced experimental thermodynamic parameters. The insets show the derivative of the $d\chi_M T/dT$ curves, whose minimum corresponds to $T(\text{LIESST})$.

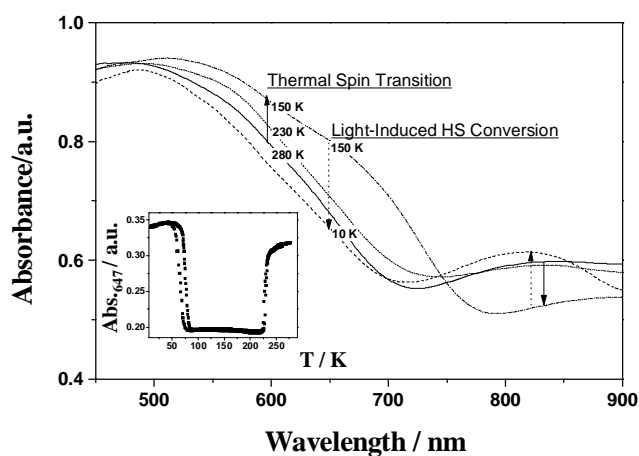


Figure 2. Changes in the absorption spectra of the $[\text{Fe}(\text{bpp})_2](\text{NCSe})_2$ complex upon cooling, and upon laser irradiation. The inset graphs show the intensity of the absorption at 647 nm (Abs_{647}) under the same conditions.

ponds to the increasing population of the low-spin state following thermal SCO. The same reflectivity experiment can also monitor any light-induced phenomena occurring at the surface of the sample. When the temperature is sufficiently low, relaxation of the photoinduced high-spin state is slow; the light intensity at the surface of the sample can be used to tune the spin-state of the complex. In this sense, the reflectivity signal, which decreases along the thermal spin transition, reversely increases at lowest temperature (figure 2), proving that the LIESST phenomenon occurs at the surface of the sample.

The low \rightarrow high spin photoconversion can also be investigated by using a MPMS-55 Quantum Design SQUID magnetometer coupled to a Spectrum Physics Series 2025 Kr^+ laser ($\lambda = 647$ nm, optical power adjusted to 5 mW cm^{-2}) (Létard *et al* 2005; Létard 2006). One of the advantages of using the SQUID technique is the sensitivity: a signal can be detected down to 10^{-6} emu. The quantity of the studied SCO material is typically around 0.1 mg. The use of such small quantity is not negligible, particularly when the sample is strongly coloured, like the one investigated in this study, to avoid light penetration problem in a bulk material. Another interest of studying a complex through photomagnetism is that the sample, in powder or crystal form, is easily deposited on a commercial transparent adhesive tape placed close to the edge of an optical fibre installed in the rod sample holder, and slowly slid down in the cavity of SQUID. The weight of the sample was obtained by comparison of the thermal spin crossover curve with that of a more accurately weighed sample of the same material.

Figure 1 shows the determination of $T(\text{LIESST})$, which somewhat represents a limiting value above which the light-induced magnetic high-spin information is erased in a SQUID cavity (Létard *et al* 1998, 2005; Létard 2006). For recording this value, a standard procedure is applied, i.e. an optical irradiation until saturation of the signal, then the light is switched off and the temperature slightly increased to 0.3 K min^{-1} . The $T(\text{LIESST})$ temperature is finally estimated at the minimum of $d\chi_M T/dT$ vs T curve. Today, this method is applied on more than sixty SCO compounds (Létard *et al* 2005; Létard 2006) and a direct relation between $T(\text{LIESST})$ and thermal spin transition ($T_{1/2}$) temperatures is seen, i.e. $T(\text{LIESST}) = T_0 - 0.3 T_{1/2}$ with T_0 , the value extrapolated at $T \rightarrow 0$. Moreover, it appears that changes outside the sphere (cooperativity factor, nature of the salt, hydration degree) are relatively negligible for stabilizing the photoinduced HS state, while the influence of the coordination degree of the ligand involved into the inner coordination sphere seems to be preponderant (Létard *et al* 2005; Létard 2006).

On a $T(\text{LIESST})$ curve, typically the magnetic response of the light-induced HS state remains almost constant up to 40–50 K. Only a slight increase of $\chi_M T$ is observed between 10 to ~ 20 K which can be attributed to the zero-field splitting of the HS state in a non-perfect octahedral

surrounding. Up to 40–50 K, the relaxation process is, in fact, governed by the non-adiabatic tunnelling regime through the barrier (Buhks *et al* 1980; Hauser 1991, 1995) and the experimental time scale is negligible in regard to the lifetime of the photoinduced HS state. This behaviour contrasts with the region above 50 K where the system reaches the thermally activated regime, i.e. more strictly speaking, the tunnelling from thermally populated vibrational levels of the HS state (Buhks *et al* 1980; Hauser 1991, 1995). In this temperature range, the $\chi_M T$ product drastically decreases and rapidly recovers its initial value.

The measurement of the $T(\text{LIESST})$ curve also gives some additional information. Firstly, the maximum of $T(\text{LIESST})$ curve can be used for estimating the level of photoconversion. For instance, in the case of the $[\text{Fe}(\text{bpp})_2](\text{NCSe})_2$ complex, the fact that the maximum of $T(\text{LIESST})$ curve is close to the $\chi_M T$ product recorded at room temperature (fully HS state) is an indication that the LIESST phenomenon in the bulk material is almost quantitative. Secondly, an indication given by the $T(\text{LIESST})$ curve concerns the sharpness of the $d\chi_M T/dT$ vs T minima (figure 1 inset), which provides some information on the existence of cooperative interactions into the material (Létard *et al* 2003). When the relaxation process follows simple stretched exponential (or exponential) behaviour, as encountered in non-cooperative SCO systems, the minimum of the $d\chi_M T/dT$ vs T curve is not well-defined, while in cooperative SCO system displaying sigmoidal behaviour, the derivate is finely defined. This latter situation seems to occur for the $[\text{Fe}(\text{bpp})_2](\text{NCSe})_2$ complex, as illustrated by the inset in figure 1. The existence of cooperative interactions governing the LIESST phenomenon is, in fact, in agreement with the observation of an abrupt thermal spin transition with more or less a thermal hysteresis loop of few Kelvins and with the existence of a light-induced thermal hysteresis (LITH) loop at loop temperature under constant light irradiation, as recorded by reflectivity technique (figure 2) (Létard *et al* 1998).

3. LIESST relaxation properties

The LIESST relaxation kinetics have been investigated on the $[\text{Fe}(\text{bpp})_2](\text{NCSe})_2$ at different temperatures between 10 K and the highest temperatures accessible with our SQUID set up, which are close to the $T(\text{LIESST})$ values (figure 3). The strong deviation of these relaxation curves from a single exponential is striking, and they can be modelled using a sigmoidal law, consistent with the self-accelerated behaviour predicted for strong cooperative SCO systems. This cooperativity arises from the large difference in metal–ligand bond lengths between high-spin and low-spin states, resulting in elastic interactions caused by the change in internal pressure inside the solids

as the spin transition proceeds (Hauser 1991, 1995). Thus, the height of activation barrier to LIESST relaxation changes as a function of γ_{HS} (the fraction of spin centres in the sample that are high-spin at a given temperature), and the relaxation rate, $k_{\text{HL}}^*(T, \gamma_{\text{HS}})$ depends exponentially on both γ_{HS} and T ((1) and (2)), where $\alpha(T) (= E_a^*/k_B T)$ is the acceleration factor at a given temperature.

$$\frac{d\gamma_{\text{HS}}}{dt} = -k_{\text{HL}}(T, \gamma_{\text{HS}})\gamma_{\text{HS}}, \quad (1)$$

$$k_{\text{HL}}(T, \gamma_{\text{HS}}) = k_{\text{HL}}(T) \exp[\alpha(T)(1 - \gamma_{\text{HS}})], \quad (2)$$

$$k_{\text{HL}}(T) = k_{\infty} \exp\left(-\frac{E_a}{k_B T}\right). \quad (3)$$

The solid lines in figure 3 reports the calculated curves by using the sigmoidal treatment with $k_{\text{HL}}(T)$ and $\alpha(T)$ as free parameters. The apparent activation energy, $E_a (= 1160 \text{ cm}^{-1})$, and the apparent pre-exponential factor, $k (= 3.6 \times 10^6 \text{ s}^{-1})$, of the activated region are calculated from the straight line given by plotting $\ln k_{\text{HL}}(T)$ vs $1/T$ (figure 4). Now with the additional activation energy linked to the cooperativity, E_a^* is 125 cm^{-1} .

An elegant way to test the validity of the deduced kinetic parameters is to use the fitted parameters to reproduce the experimental $T(\text{LIESST})$ curve (Létard *et al* 2003; Létard 2006). For that we have to reproduce the time and temperature dependencies. As previously mentioned, along a $T(\text{LIESST})$ experiment, the sample was first irradiated at 10 K, then without further irradiation the temperature was slowly warmed at the rate of $\sim 0.3 \text{ K min}^{-1}$. Rigorously, the temperature during a $T(\text{LIESST})$ mea-

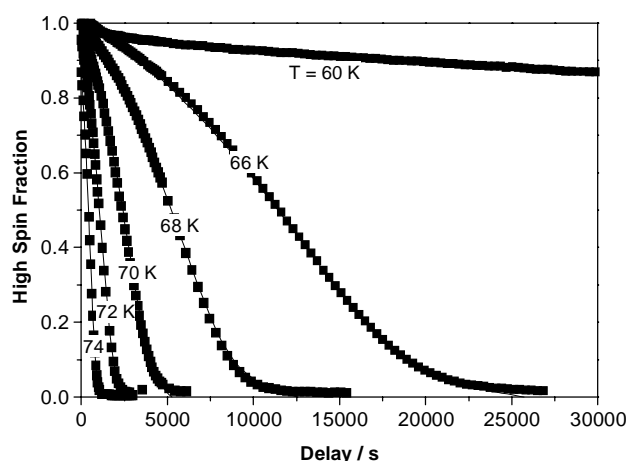


Figure 3. Time dependence at various temperatures of the high spin molar fraction generated by light irradiation at 10 K. Each point represents the high spin fraction deduced from the magnetic response measured within the SQUID magnetometer during around 30 s. The relaxation curves are fitted according to sigmoidal behaviour.

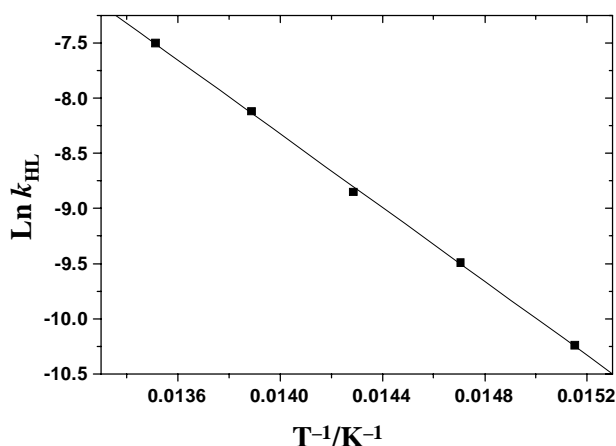


Figure 4. Evolution of the $\ln k_{HL}$ vs $1/T$.

surement, in a SQUID cavity, is changed in 1 K steps. At each temperature, T_i , the time for the signal acquisition is 60 s and the time to reach the next temperature is 120 s. In reality, it is difficult to reproduce the relaxation connected to the stabilization of the temperature. In a first approximation, we have decided to neglect this subtle effect and the relaxation is calculated at each temperature, T_i , during the global time of 180 s. The γ_{HS} fraction obtained after 180 s of relaxation at T_i is used as starting value for the next temperature, T_{i+1} ; i.e. $(\gamma_{HS})_{t=180}^{T=T_i} = (\gamma_{HS})_{t=0}^{T=T_{i+1}}$.

Another important point in the simulation of the $T(\text{LIESST})$ curve is that such an experiment combines the relaxation of both tunnelling and thermally activated regions. Rigorously, this imposes to use the theory of the non-adiabatic multi-phonon process in the strong vibronic coupling limit (Buhks *et al* 1980; Hauser 1991, 1995). In a first approximation, we have assumed that the evolution of HS fraction is just a summation of the two effects (Létard *et al* 2003; Linert and Verdagner 2003; Létard 2006). For a cooperative compound exhibiting sigmoidal relaxation curves, the time dependence of HS fraction at temperature, T_i , is given by

$$\left(\frac{\partial \gamma_{HS}}{\partial t}\right)_{T_i} = -\gamma_{HS} \{k_{HL}(T \rightarrow 0) + k_{\infty} \exp(E_a/k_B T_i)\} \exp[\alpha(T_i)(1-\gamma_{HS})]. \quad (4)$$

But then one of the difficulty is to satisfactorily estimate the rate constant, $k_{HL}(T \rightarrow 0)$, for relaxation by quantum mechanical tunnelling region. For this, we have decided that the last complete kinetic measurement recorded at low temperature can be regarded as an upper limit for the $k_{HL}(T \rightarrow 0)$ value. In the case of $[\text{Fe}(bpp)_2](\text{NCSe})_2$ complex, the last kinetic fully recorded on the investigated time window is 66 K for relaxation curve and the upper limit of $k_{HL}(T \rightarrow 0)$ value is estimated to be $3.6 \times 10^{-5} \text{ s}^{-1}$.

The last difficulty to simulate a $T(\text{LIESST})$ curve is to reproduce the effect of the anisotropy of HS iron(II) ion in an octahedral surrounding. This phenomenon, called zero-field splitting, is associated to the spin-orbit coupling between the ground state and the excited state in a zero applied magnetic field. For an iron(II) ion in HS configuration, the $S = 2$ ground state is split into three levels. The magnetic contribution of each state is determined by their energy separation, D , and their thermal population (Kahn 1993). For a powder sample, the $(\chi_M T)_{\text{ZFS}}$ product associated to the zero-field splitting and the $\chi_M T$ of the $T(\text{LIESST})$ curve are, respectively, given in (5) and (6).

$$(\chi_M T_i)_{\text{ZFS}} = \frac{\chi_M T_{i\parallel} + 2\chi_M T_{i\perp}}{3}, \quad (5)$$

$$\text{with } \chi_M T_{i\parallel} = \frac{3}{4} g^2 \frac{e^{-D/k_B T_i} + 4e^{-4D/k_B T_i}}{1 + 2e^{-D/k_B T_i} + 2e^{-4D/k_B T_i}},$$

$$\text{and } \chi_M T_{i\perp} = \frac{1}{4} g^2 \frac{k_B T_i}{D} \frac{9 - 7e^{-D/k_B T_i} - 2e^{-4D/k_B T_i}}{1 + 2e^{-D/k_B T_i} + 2e^{-4D/k_B T_i}},$$

$$\chi_M T_i = (\chi_M T_i)_{\text{ZFS}} \gamma_{HS}(t, T_i). \quad (6)$$

Based on (6) and by using the deduced $k_{HL}(T)$, $\alpha(T)$ and $k_{HL}(T \rightarrow 0)$ parameters, the $T(\text{LIESST})$ curve can be satisfactorily fitted (figure 1). Both these validate the model as well as the deduced kinetics parameters.

4. Conclusions

We have reported a typical study of the thermal- and light-induced properties of an iron(II) complex, the $[\text{Fe}(bpp)_2](\text{NCSe})_2$ ($bpp = 2,6\text{-bis}(\text{pyrazol-3-yl})\text{pyridine}$) compound. We have recorded the $T(\text{LIESST})$ value, the reflectivity spectra as function of both temperature and light irradiation as well as the kinetics of the photoinduced $\text{HS} \rightarrow \text{LS}$ relaxation. Based on that we have reproduced the $T(\text{LIESST})$ experiment. The challenge is now to systematically investigate a large number of SCO materials and to identify the key parameter allowing to shift the $T(\text{LIESST})$ value up to the working room temperature.

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