Complete temperature study of the relaxation from HS to LS state in the mixed \([\text{Fe}_x\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]\) systems (with \(x = 1, 0.73, 0.5, 0.32, 0.19\) and 0.04)

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Abstract. The thermal and light-induced spin transitions in \([\text{Fe}_x\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]\) (Phen = 1,10-phenantholine) have been investigated by magnetic susceptibility, photomagnetism and diffuse reflectivity measurements. These complexes display a thermal spin transition and undergo the light-induced excited spin state trapping (LIESST) effect at low temperatures. For each compound, the thermal spin transition temperature, \(T_{1/2}\), and the relaxation temperature of the photo-induced high-spin state, \(T_{\text{(LIESST)}}\), have been systematically determined. It appears that \(T_{1/2}\) decreases with the metal dilution while \(T_{\text{(LIESST)}}\) remains unchanged. This behaviour is discussed on the basis of the kinetic study performed by combining the use of SQUID magnetometer, up to the \(T_{\text{(LIESST)}}\) value, and the dynamic diffuse reflectivity setup, from the \(T_{\text{(LIESST)}}\) temperature up to the thermal spin transition.

1. Introduction

The design of molecular materials able to store information represents a fascinating challenge for the future development of magnetic and optical data storage. In this context, spin crossover compounds (SCO), encountered in 3d metal ions with electronic configuration \(d^4-d^7\) in octahedral environment, are particularly interesting. SCO Materials exhibit high-spin (HS) low-spin (LS) crossover under an external perturbation like a change of temperature, application of pressure, light or application of a high magnetic field [1-3]. Some information can be written and erased by light irradiation, according to the so-called LIESST (Light-Induced Excited Spin State Trapping) and reverse LIESST phenomena [2,3]. Since the discovery of this effect, many studies have been dedicated to identify the parameters which impact the lifetime of the photo-induced metastable HS state.

In 1998, Létard et al. have proposed to systematically record the \(T_{\text{(LIESST)}}\) value. It represents the limiting temperature above which the photo-induced information, namely the photo-induced HS fraction, is erased under specific conditions [4]. Using this procedure, we have up to now compared...
the photomagnetic properties of more than sixty SCO compounds and reported an empirical linear relation between the thermal spin transition \((T_{1/2})\) and the T(LIESST) temperature: \(T(\text{LIESST}) = T_0 - 0.3 \times T_{1/2}\) \([5,6]\). This phenomenological relationship appears to reflect rearrangement processes in the coordination sphere accompanying the SCO at the metal center. In a recent investigation, the applicability of this relationship has been extended to metal-diluted SCO systems, viz. \([\text{Fe}_x\text{Zn}_{1-x}\text{(Phen)}_2(NCS)_2]\) \([7]\), \([\text{Fe}_x\text{Mn}_{1-x}\text{(bpp)}_2](\text{NCSe})_2\) \([8]\), \([\text{Fe}_x\text{Zn}_{1-x}\text{(btzp)}_3](\text{BF}_4)_2\) \([9]\) and \([\text{Fe}_x\text{Zn}_{1-x}\text{(endi)}_3](\text{BF}_4)_2\) \([9]\) (Phen = 1,10-phenanthroline, bpp = 2,6-bis(pyrazol-3-yl)pyridine, btzp = 1,2-bis(tetrazol-1-yl)propane and endi = 1,2-bis(tetrazol-1-yl)ethane). It has been found in all these mixed-crystal series that the thermal spin transition \(T_{1/2}\) decreases with metal dilution (decrease of \(x\)) whereas the relaxation temperature \(T(\text{LIESST})\) remains constant \([7-9]\). Our interpretation of this phenomenon is that the thermal spin crossover regime is mainly governed by the thermodynamics and the cooperative interactions while the photomagnetic properties appear to be mainly controlled at the molecular scale, accounting for the use of two potential wells in interpreting the relaxation process \([10]\).

In the present work, we will focus on the mixed \([\text{Fe}_x\text{Zn}_{1-x}\text{(Phen)}_2(NCS)_2]\) systems (with \(x = 1, 0.73, 0.5, 0.32, 0.19\) and 0.04), and our primary objective is to carefully determine the kinetic parameters governing the photo-induced HS / LS relaxation and to attempt to understand why the T(LIESST) value remains constant. The second motivation of this work is based on the recent observation done on the cooperative phase I of \([\text{Fe}(\text{PM-BiA})_2(NCS)_2]\) compound (PM-BiA = 2’-pyridylmethylene-4-aminobiphenyl), which exhibits an abrupt thermal spin transition at 178 K with a hysteresis loop of few Kelvins \([11]\). Using two complementary techniques, the magnetic susceptibility and diffuse reflectivity, the relaxation of a photo-induced spin state transition has been measured from 10 K to 160 K; i.e. in a temperature range where the lifetime of the photo-induced HS state is almost infinite to the one where the decay occurs in few milliseconds \([11]\). As expected up to 150 K, the relaxation rate has been founded to increase with temperature. But at the approach of the thermal spin transition, obviously a stabilization of the high-spin state has been observed. We would like to confirm such a behavior with a similar cooperative complex and measure the impact of the metal dilution. Along that we will investigate in details the relaxation process of the \([\text{Fe}_x\text{Zn}_{1-x}\text{(Phen)}_2(NCS)_2]\) series by combining both the SQUID magnetometer coupled to a CW optical source and the diffusive reflective setup coupled to pulsed Nd-Yag laser.

2. Experimental Section

The \([\text{Fe}_x\text{Zn}_{1-x}\text{(Phen)}_2(NCS)_2]\) (with \(x = 1, 0.73, 0.5, 0.32, 0.19\) and 0.04) complexes have been prepared along the procedure described by Gutlich et al. \([12]\) with a slight modification \([7]\). The iron fraction values \(x\) were calculated from the iron and zinc atomic percentage determined by quantitative analysis \([7]\). Powder diffractograms techniques have been used to insure that the Fe and Zn compounds are isomorphs, justifying the character of solid solution of \([\text{Fe}_x\text{Zn}_{1-x}\text{(Phen)}_2(NCS)_2]\) series \([7]\).

The photomagnetic measurements were performed using a Spectrum Physics Series 2025 Kr+ laser \((\lambda = 531\,\text{nm})\) coupled via an optical fibre to the cavity of a MPMS-55 Quantum Design SQUID magnetometer. The optical power at the sample surface was adjusted to 5 mW cm\(^{-2}\), and it was verified that this resulted in no change in magnetic response due to heating of the sample. Photomagnetic samples consisted of a thin layer of compound whose weight was obtained by comparison of the thermal spin crossover curve with that of a more accurately weighed sample of the same material. Our previously published standardized method for obtaining T(LIESST) value was followed \([5,6]\). After slowly cooling to 10 K, the sample in the low spin state was irradiated and the change in magnetism followed. When the saturation point was reached the laser was switched off and the temperature increased at a rate of 0.3 K min\(^{-1}\). The magnetization was measured every 1 K. T(LIESST) was determined from the minimum of a \(d\chi_M/dT\) vs. \(T\) plot for the relaxation process.

The kinetics measurements were performed with the SQUID magnetometer up to the T(LIESST) temperature. For higher temperatures, the LIESST cannot be induced using CW excitation and the
very short relaxation time cannot be measured. The appropriated setup for investigating the relaxation process up to the thermal spin transition is based on the diffuse reflectivity technique, as previously published for investigating the cooperative phase I of \([\text{Fe(PM-BiA)}_2(\text{NCS})_2]\) compound (PM-BiA = 2’-pyridylmethylene-4-aminobiphenyl) [11,13]. In short, the sample sandwiched between two optical windows was placed into a cryostat. The white light produced by a halogen lamp was focused on the sample. The diffuse light reflected by the powder was collected and sent into a monochromator followed by photomultiplier tube (PMT). The compound was excited by laser pulses produced by a Q-switched-nanosecond-frequency-doubled Nd\(^{3+}:\text{YAG}\) laser emitting at \(\lambda = 532\) nm (pulse width 8 ns) [8]. The LIESST effect results in a change of the reflectivity of the sample. Above 80 K, the photo-excited HS state relaxes and the sample rapidly recovers its initial reflectivity. All the experiment where performed with a Nd:YAG laser pulse energy of \(\sim 1\) mJ focused on the sample on a surface of \(\sim 1\) cm\(^2\). This level of energy density makes it possible to fully populate the sample in the HS state.

3. Results

In this study, we have selected one of the most studied iron(II) spin crossover complexes, the \([\text{Fe(Phen)}_2(\text{NCS})_2]\) (Phen = 1,10-phenanthroline), which undergoes an extremely abrupt thermal spin transition at 176 K [14] with a narrow thermal hysteresis of < 1 Kelvin [15]. The thermal spin crossover properties of the iron(II) mixed complexes \([\text{Fe}_{1-x}\text{M}_{x}\text{(Phen)}_2(\text{NCS})_2]\) with \(M = \text{Co(II)}, \text{Ni(II)}, \text{Mn(II)}\) and \(\text{Zn(II)}\) ions have been originally described by Gütlich et al. [12] and it was also reported that the \([\text{Fe(Phen)}_2(\text{NCS})_2]\) shows the LIESST phenomenon [16]. In a recent paper, we have re-investigate the mixed \([\text{Fe}_{x}\text{Zn}_{1-x}\text{(Phen)}_2(\text{NCS})_2]\) system (with \(x = 1, 0.73, 0.5, 0.32, 0.19\) and 0.04) with the objective to study the influence of the metal dilution on the \(T(\text{LIESST})\) properties [6].

The figure 1 recall the temperature dependence of the high spin fraction, \(\gamma_{\text{HS}}\), deduced from the magnetic susceptibility measurements on the mixed crystal system \([\text{Fe}_{x}\text{Zn}_{1-x}\text{(Phen)}_2(\text{NCS})_2]\) (with \(x = 1, 0.73, 0.5, 0.32, 0.19\) and 0.04) [6]. As originally mentioned by Gütlich et al. [12] when \(x\) decreases (i) the spin crossover regime becomes more gradual, (ii) the thermal spin transition is lowered, and (iii) the residual HS fraction at low temperature increases. All that was so far explained in the following way:

(i) The increase of the gradual character with the metal dilution reflects the progressive loss of cooperativity, as expected from the increasing distance between active iron(II) metal centers in the diluted \([\text{Zn}]\) lattice [1b].

(ii) The shift of the thermal spin transition towards lower temperature can be understood through change of internal pressure. The radius of zinc(II) ion \((r = 74\, \text{pm})\) is close to the ionic radius of iron(II) HS ion \((r = 78\, \text{pm})\) and higher than the ionic radius of iron(II) LS ion \((61\, \text{pm})\) [16]. Thus, if iron(II) LS ions are highly diluted in a \([\text{Zn}]\) lattice, the zinc lattice induces a ‘negative’ pressure on the Fe(II) site leading to an increase of the Fe-N bond lengths (decrease of the crystal field potential) which favours the HS state [1b,18]. On the contrary, the effect of zinc lattice is negligible when the iron(II) HS ions are highly diluted. Consequently, the \(T_{1/2}\) is shifted towards lower temperature with increasing metal dilution.

(iii) The increase of the residual HS fraction at low temperature is also a consequence of the negative pressure occurring on the iron(II) LS ions in the highly diluted \([\text{Zn}]\) lattice. The HS state is in fact stabilized by the \([\text{Zn}]\) lattice.
The low → high spin photoconversion have been investigated in bulk condition using the static diffuse reflectivity setup [11,13] as well as the SQUID magnetometer connected to a CW optical source. For all the complexes, a drastic increase of the magnetic signal under light irradiation was observed at 10 K. The Figure 2 shows the T(LIESST) curves recorded for all the [FeₓZn₁₋ₓ(Phen)₂(NCS)₂] series (with x = 1, 0.73, 0.5, 0.32 and 0.19). The shapes of all the T(LIESST) curves are almost identical. The χₘT product firstly increases upon warming from 10 K due to the zero-field splitting of the high spin iron(II) ion and reaches a plateau near 30 K. The comparison of the χₘT value at the maximum of the T(LIESST) curve and the magnetic response recorded at room temperature confirms that even in bulk condition for all the [FeₓZn₁₋ₓ(Phen)₂(NCS)₂] complexes a quantitative photoconversion occurs. The different T(LIESST) values are collected in Table 1. Interestingly, while the T 1/2 temperature has been found to decrease with the metal dilution, the T(LIESST) temperature remains almost constant. In other words, we have found an exception to the empirical T(LIESST) = T₀ – 0.3T 1/2 relation [5,6].

Figure 2: Magnetic and photomagnetic properties of [FeₓZn₁₋ₓ(Phen)₂(NCS)₂] systems. ○ = data recorded in the cooling and warming mode without irradiation; ∆ = data recorded with irradiation at 10 K; ◇ = T(LIESST) measurement, data recorded in the warming mode at a rate of 0.3 K/min with the laser turned off after irradiation for one hour.

The relaxation curves of all these materials were firstly recorded between 10 K and the highest temperatures accessible with a SQUID set up, which are close to the T(LIESST) values. In that temperature range the relaxation time is typically on the range of hours/minutes. Then, for the temperature between the T(LIESST) and T 1/2, the dynamic diffuse reflectivity setup was used. The decays in that region are extremely fast in comparison to the low temperature regime. For the diffuse reflectivity technique, the HS state fraction, γ_HS(t), was deduced from reflectivity measurements by calculating the ratio ΔR(t)/ΔR_{TS}, where ΔR(t) is the change of reflectivity induced by the laser at time t (the pulse being fired at t = 0) and ΔR_{TS} corresponds to the variation of reflectivity measured for the thermally induced spin transition. Note that such computation was easily performed, thanks to the large change of sample reflectivity induced by the spin transition. The Figure 3 reports a typical example of study performed on the pure [Fe(Phen)₂(NCS)₂] system.
Figure 3: Time dependence of the pure [Fe(Phen)$_2$(NCS)$_2$] at various temperatures for the high spin molar fraction generated by light irradiation. The Solid lines on the relaxation curves represent the sigmoidal least-squares fits. The linear regression of the plot ln[k$_{HL}$] versus 1/T is used to determined the activation energy $E_a$ and the pre-exponential factor $k_\infty$ (Table 2).

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 cooperative 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 as the spin transition proceeds. Thus, the height of the activation barrier to LIESST relaxation changes as a function of $\gamma_{HS}$ (the molar fraction of HS molecules at a given temperature), and the relaxation rate $k_{HL}(T, \gamma_{HS})$ depends exponentially on both $\gamma_{HS}$ and $T$ (Eqs. 1 and 2), where $\alpha(T) (=E_a*/k_BT)$ is the acceleration factor at a given temperature.

$$\frac{\partial \gamma_{HS}}{\partial T} = -k_{HL}^\gamma$$  \hspace{1cm} (1)  

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

$$k_{HL}(T) = k_0 + k_\infty \exp[-E_a/k_BT]$$ \hspace{1cm} (3)

Equation (3) supposes that the evolution of the HS fraction is induced by two processes [19]: a tunnelling process [10] which is independent of temperature and a thermally activated process. Least squares fits of all the kinetics measured for the [Fe$_x$Zn$_{1-x}$(Phen)$_2$(NCS)$_2$] systems were performed using a sigmoidal model where $k_{HL}(T)$ and $\alpha(T)$ were refined as free parameters. The calculated curves are shown as solid lines in Figures 3 and 4 and the kinetic parameters $k_0$, $k_\infty$, $E_a$ and $E_a^*$ are reported in table 2.

| Dilution factor | T(LIESST) /K | T$_{1/2}$ /K |
|-----------------|--------------|-------------|
| 1               | 62           | 176         |
| 0.73            | 62           | 168         |
| 0.5             | 63           | 161         |
| 0.32            | 62           | 137         |
| 0.19            | 62           | 125         |
| 0.04            | 63           | 106         |

Table 1: T(LIESST) and T$_{1/2}$ values of [Fe$_x$Zn$_{1-x}$(Phen)$_2$(NCS)$_2$] systems.
Figure 4: Time dependence of the \([\text{Fe}_{x}\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]\) systems at various temperatures for the high spin molar fraction generated by light irradiation. Solid lines are sigmoidal least-squares fits (Table 2).
From all these kinetics recorded it can be concluded that basically the relaxation rate steadily increases as the temperature of the sample increases. However for the pure [Fe(Phen)2(NCS)2] (Figure 3) and the [Fe0.73Zn0.27(Phen)2(NCS)2] (Figure 4) complexes, as we further approach the temperature of the hysteresis loop, instead of increasing, the relaxation rate decreases. In contrast, for the less cooperative mixed systems [Fe0.5Zn0.5(Phen)2(NCS)2] and [Fe0.19Zn0.81(Phen)2(NCS)2] such an atypical behavior is not present (Figure 4). This phenomenon can be easily understood by taking into account a competition between LS/HS equilibrium associated to the thermal spin transition process and the temperature dependence of the LIESST lifetime. Concerning the thermal regime for the pure compound presented in Figure 2, the abrupt thermal transition is associated to a second order LS-HS phase transition. This accounts for the critical divergence of the magnetic susceptibility in the vicinity of T1/2. Furthermore, this second order phase transition is also associated to a divergent increase of the HS lifetime close to T1/2. Now, as we got away from T1/2 by decreasing the temperature, the HS lifetime should decrease. On the other hand, concerning the LIESST phenomenon, when the temperature increases the relaxation process is more and more thermally activated, and the photo-induced HS lifetimes has to decrease. Let us now consider the competition between the two mechanisms. First of all, close to T1/2 the divergence of the HS lifetime should overpass the thermally activated relaxation, but far away from T1/2, the contribution of the second order phase transition is negligible and only the natural temperature dependence of the thermally activated relaxation of LIESST effect is expected. This is indeed what we observed for the pure sample, that is stabilization and an increase of the photo-induced HS lifetime in the vicinity of T1/2.

A direct confirmation of such proposed idea is the observation that when the cooperativity of the sample decreases by metal dilution, or introducing defect in the sample in phase transition thermology, the competition between the two phenomena is less and less evidenced. It is in fact clear that with the metal dilution the thermal spin crossover properties become more and more gradual due to the increase of the distance between active iron(II) metal centers in the diluted [Zn] lattice. The second order character of the phase transition is consequently more and more altered with the increase of the metal dilution, and a smooth stabilization of the HS lifetime is anticipated. Experimentally what we observe is that for the metal diluted sample x = 0.73, the photo-induced lifetime at the approach of T1/2 is no more decreasing but just saturated. For more diluted metal complexes (x=0.5 and x=0.19), the second order character of the thermal spin transition is no more present, and a classical decreases of the photo-induced lifetime is recorded.

| SCO systems                        | \(E_a\) / cm\(^{-1}\) | \(k_f\) / s\(^{-1}\) | \(k_0\) / s\(^{-1}\) | \(E_{a^*}\) / cm\(^{-1}\) |
|------------------------------------|------------------------|-------------------|-------------------|-----------------|
| [Fe(Phen)\(_2\)(NCS)\(_2\)]      | 990                    | 1.5.10\(^7\)     | 9.6.10\(^6\)     | 95              |
| [Fe\(_{0.73}\)Zn\(_{0.27}\)(Phen)\(_2\)(NCS)\(_2\)] | 1005                   | 2.1.10\(^7\)     | 9.6.10\(^6\)     | 80              |
| [Fe\(_{0.5}\)Zn\(_{0.5}\)(Phen)\(_2\)(NCS)\(_2\)] | 985                    | 1.1.10\(^7\)     | 1.2.10\(^6\)     | 45              |
| [Fe\(_{0.19}\)Zn\(_{0.81}\)(Phen)\(_2\)(NCS)\(_2\)] | 980                    | 1.1.10\(^7\)     | 2.4.10\(^6\)     | 0               |

An elegant way to test the validity of the kinetic parameters is to reproduce the experimental \(T(LIESST)\) curve [6,19]. For that it is necessary to carefully take into account the time and the temperature dependencies. The main difficulty of this simulation is to estimate satisfactorily the rate constant \(k_0\) for relaxation in the quantum mechanical tunnelling region. For this, we consider that the complete kinetic measurement recorded at the lowest temperature can be regarded as an upper limit for the \(k_0\) value (Table 2). Figure 5 shows the calculated \(T(LIESST)\) curve deduced from the kinetics parameters listed in Table 2. The perfect agreement between the experimental and the simulated \(T(LIESST)\) curves provides some confidence about the kinetics parameters determined in this study.
which are slightly different from those previously reported by Lee et al. [20] using the L-edge absorption technique.

Figure 5: T(LIESST) curves of $[\text{Fe}_x\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]$ systems ($\diamond$). The solid line represents the fit obtain using the kinetic parameters listed in Table 2.

4. Concluding remarks

We have reported the thermal and photo-induced spin-crossover properties of $[\text{Fe}_x\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]$ systems. Although the thermal spin transition temperatures are lowered with increasing metal dilution, the T(LIESST) temperatures remains almost constant. In other words, the thermal spin transition appears to be sensitive to the change of internal pressure in the lattice while the T(LIESST) limit temperature remains unaffected, at least in the range of internal pressures generated by metal dilution in this study.

Previous studies on the thermal spin crossover phenomenon have shown that any change of pressure in the lattice by chemical metal dilution or by external stimulus affects the Gibbs free energy through a change of the molecular volume of reaction giving rise to the additional term $p\Delta V_{\text{HIL}}$ [3]. The shift of $T_{1/2}$ towards lower temperature with increasing zinc metal dilution is a direct consequence of the fact that we are pushed away from the critical point in the phase diagram. This clearly indicates that the link so far made between T(LIESST) and $T_{1/2}$ is more complex than so far considered. From all the works done on the metal dilution we have found that the T(LIESST) limit temperature remains constant with increasing metal dilution [7-9]. That contradicts the role along which ‘the lower the thermal spin transition temperature ($T_{1/2}$) is, the slower is the HS $\rightarrow$ LS relaxation after LIESST’. It can be therefore concluded that the two interconversion processes are controlled by different processes. This is particularly important if one considers the believed existence of a relationship between these two quantities. If we adopt the picture so far proposed by Hauser, our experiment confirms that the photomagnetic properties are governed at the molecular scale while the thermal spin crossover regime is more complex in nature. In fact, the T(LIESST) temperature is defined by a balance between the interaction between the molecule and thermal fluctuation. The study of the kinetics parameters on $[\text{Fe}_x\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]$ systems has shown that when $x$ varies from 1 to 0.19, the cooperativity factor $E_a^*$ accounting for the LIESST effect decreases from 90 cm$^{-1}$ to 0 cm$^{-1}$. As cooperativity arises from elastic interactions between iron centres, it is not surprising that the strength of cooperativity decreases with increasing dilution and thus increasing distance between the interacting iron centres. The changes in $k_c$ and $E_a$ are in contrast negligible, explaining why in the $[\text{Fe}_x\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]$ series the T(LIESST) values remain constant with the metal dilution. Similar kinetics studies on other metal-dilution complexes (Cd, Co, Zn, Ni) are currently in progress, where we expect to learn more about the parameters governing the relaxation of the photo-induced HS state in metal-diluted SCO systems.

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