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NON-LINEAR BEHAVIOUR OF THE SPIN TRANSITION COMPOUNDS DURING PHOTO-EXCITATION AND RELAXATION

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Spin-crossover solids are photo-excitable materials, which are studied for future applications as optical memories or numerical display. The spin transition is a first order phase transition produced by variations of temperature, pressure or light. Cooperative effects constitute the basic mechanism for the spin crossover transition. They induce instability in the thermodynamic competition between the two states of the spin-crossover molecules: high-spin (HS) and low spin (LS).We investigate here the photo-excitation process and the relaxation of the photo-excited state in photo-switchable solids, such as spin transitions systems $[(Fe_xM_{1-x})(btr)_2(NCS)_2]\ H_2O$, with M=Co, Ni, Zn. We follow the competition between the relaxation and the photo-excitation processes (up and eventually down). The experimental kinetics gives evidence for a non-linear character of the relaxation at all temperatures, including the tunnelling regime, and for non-linear behaviours of the photo-excitation rates.

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1. Introduction

Spin transition compounds are photo-magnetic molecular compounds which have two states in thermodynamic competition; for Fe^{II}: diamagnetic low spin state S = 0 (LS), and paramagnetic high spin state S = 2 (HS). The absorption optical bands in these states are different, and give the two states different colours, so that these compounds are thermo- and photo- chromic [1], [2].

At low temperature, the compounds are in the LS state (deep purple) but are switched to the HS state (colourless) by irradiation at ~550 nm, in a LS absorption band, by the so called LIESST effect [3]. The transformation is reversible, an appealing property for optical information storage.

A better insight to the relaxation properties could be achieved by inducing a competition between relaxation and photo-excitation. The occurrence of a light-induced instability was discovered [4-6], in the permanent regime driven by light, and it was explained [4-5] in the frame of a simple macroscopic master equation including a linear photo-excitation term and the previously known cooperative relaxation.

We have performed further experiments, initially designed to follow more closely the competition between the photo-excitation and relaxation terms. We aimed to systematically record the response of the system, as a function of time, starting from various initial states, with various intensities of light, and using various wavelengths in the IR range, so as to induce both LS→HS and HS→LS transitions.

The analysis of the data shows that the assumption of a linear photo-excitation effect is highly questionable, so that a phenomenological approach based on novel grounds is needed.

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2. Experimental methods

The spin transition solids with formula $[(FeII,MII)(btr)_2(NCS)_2]H_2O$ were prepared as polycrystalline powders and submitted to successive thermal shocks which reduce the grain size, and are known to stabilize the position and shape of the hysteresis loop of the spin transition

The magnetisation curves were recorded using a SQUID magnetometer (Quantum Device MPMS5) operating in the alternative mode, equipped with an optical fibre, made of multiwire silica.

Reflectivity measurements were performed in the visible – near IR range also using (Y shaped) optical fibres. Reflectivity is considered as a surface probe reasonably free from bulk absorption problems. Light was provided by tungsten halogen lamp (100 W), through interferential filters (100 nm bandwidth). For experiments requiring larger intensities, up to ~100mW/cm^2, we merely used a cut-off "IR" filter $\lambda > 665$ nm. It was controlled that reflectivity and magnetic measurements led to identical results, if the bulk absorption effects were negligible.

3. Results

3. 1 The relaxation process

A major result concerning the relaxation of the photoexcited spin state (back to the ground spin state) has been the observation and modelling of cooperative effects, i.e. of the effect of steric interactions between the spin crossover units. The cooperative relaxation is characterized by the sigmoidal shape of the time dependence of the population of the excited spin state: high spin fraction, denoted here as n_{HS} [7].

Strongly non-linear processes are illustrated by several typical shapes of the relaxation curve (in the figure for M=Co, x=0.5 at two different temperatures), combining in various proportions a sigmoidal shape associated with the mean-field effect of cooperativity, and a tail due to the onset of correlations which slow down the relaxation at long times [8]

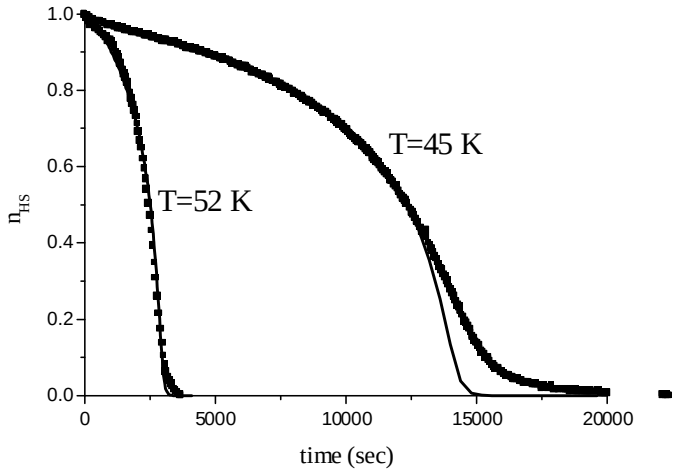


Fig. 1. Relaxation curves for $[Fe_{0.50}Co_{0.50}(btr)_2(NCS)_2]$, H_2O: experiments and mean field treatment.

The relaxation data of after complete photo-excitation by a 550 nm radiation are shown in Fig. 1 (after [9]). In agreement with literature work [7, 10] and previous analyses of compounds in the [Fe, Co] series [4, 5, 9], the sigmoidal shape of the relaxation curve $n_{HS}(t)$ can be precisely reproduced by the phenomenological form:

$$\frac{dn_{HS}}{dt} = -k_{HL} n_{HS} \exp(-\alpha n_{HS}), \quad (1)$$

where k_{HL} is the relaxation rate, i.e. the probability per time unit for a molecule to switch spontaneously from high spin to low spin state and α is the self-acceleration factor (cooperativity parameter [7, 10]).

An interesting result is the relaxation obtained after partial excitation. In this situation the shape of the relaxation curves depends of the manner in which the sample was prepared. In Fig. 2 we present two different cases. In Fig. 2a we excited the sample with a green light and then we switched off the light when a high spin fraction ~ 0.07 was reached. The subsequent relaxation curve in dark has approximately the same shape as when of starting from the saturated state. Indeed, in this case the photo-excitation state is quite inhomogeneous, due to bulk absorption of light : the high spin molecules are concentrated in the front region, while the rear region mostly remains in the LS state (Fig. 2c) : the signal compares to that of a complete photo-excitation, with smaller amplitude. In Fig. 2b the relaxation is observed starting from a photo-stationary state, obtained by long-time irradiation in the IR which simultaneously induces the opposite transitions (see section 3.3). In this case the density of high spin molecules is almost identical throughout the sample (a little larger in the front part of the sample - Fig. 2d). The subsequent relaxation rate compares to the rate obtained *for the same HS fraction*, when starting after complete excitation. Of course the latter experimental procedure has to be preferred for minimizing the effects of bulk absorption, which remains a major problem in these experiments of relaxation after partial excitation (for which the reflectivity technique is obviously not suited)

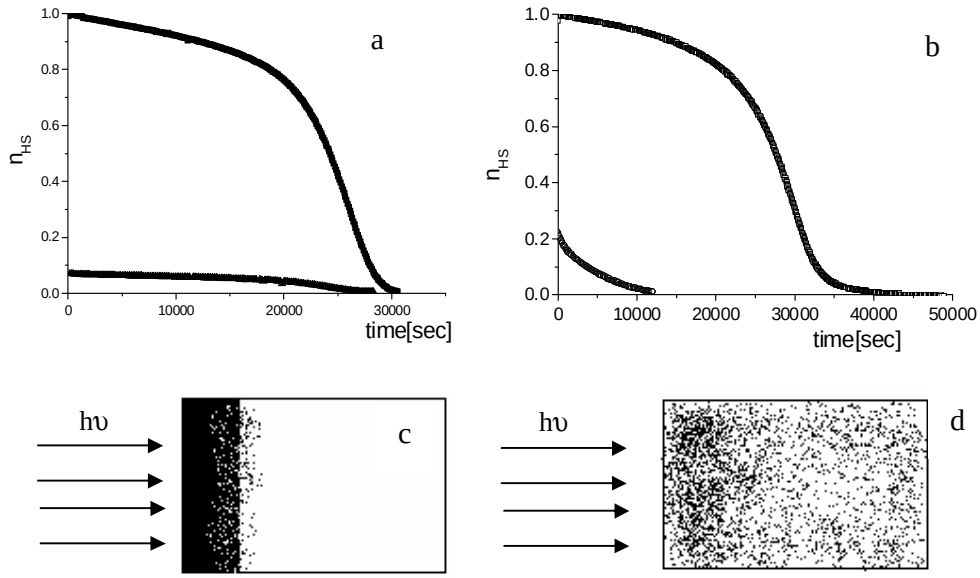


Fig. 2. Relaxation starting after partial excitation for M=Zn. (a)after an interrupted photoexcitation (b) starting from a photo – stationary state. (c), (d) Schematic view of the excitation state of the sample : dark = HS state.

3.2 The photo-excitation process

We recorded photo-excitation curves under permanent irradiation, starting from the non-excited state, for different intensity values, see Fig. 3a. The data were derived from reflectivity measurements, a technique which is reported to be less sensitive to bulk absorption of light than the magnetization measurements [11].

The derivative of the data, $dn_{HS}(t)/dt$, is plotted in Fig. 3b, for the four experiments, as a function of n_{HS}. As a remarkable qualitative feature, all curves exhibit an initial increase which is clearly associated with the S-shape of the photo-excitation curves at short times.

In [12] we used such curves to separate the photo excitation and relaxations contributions to a mean field macroscopic master equation and we succeeded in measuring the very slow relaxation rate, in the tunnelling regime.

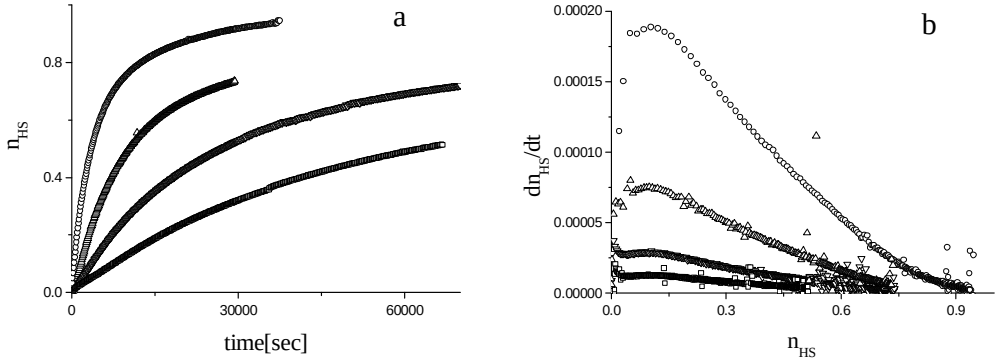


Fig. 3. [Fe $_{0.50}$Zn $_{0.50}$(btr) $_2$(NCS)$_2$], H_2O: photoexcitation curves at 10 K, under permanent irradiation at 400 nm (a) and the derivatives of the photoexcitation curves plotted as a function of n_{HS}.(b).

3.3 Combined LS→HS and HS→LS photo-excitations

Irradiation in the IR simultaneously induces the upwards and downwards transitions. This method for obtaining a photo-stationary state was introduced in [12] where the non-linearity of the resulting process was reported.

We present here the case of $[(Fe_{0.8}Zn_{0.2})(btr)_2(NCS)_2]H_2O$ irradiated with different wavelengths. The cross sections associated with the two processes both depend upon the wavelength and lead to various photo-stationary states according to the wavelength.

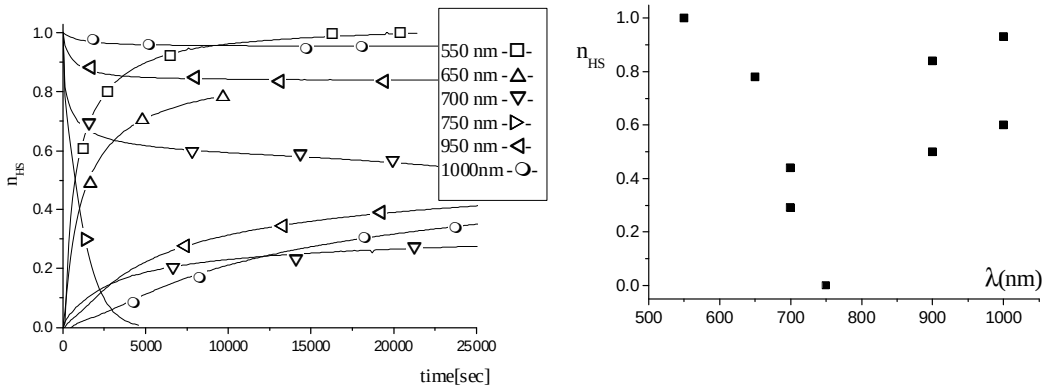


Fig. 4. The photoexcitation curves for [$Fe_{0.8}Zn_{0.2}$(btr) $_2$(NCS)$_2$], H_2O at different wavelengths: kinetic curves (a) and the photostationary states as a function of wavelength (b).

The suited phenomenological macroscopic master equation is written:

$$\frac{dn_{HS}}{dt} = I\sigma_1 \cdot (1 - n_{HS}) - I\sigma_2 \cdot n_{HS} - k_{HL} n_{HS} \exp(-\alpha n_{HS}), \qquad (2)$$

where $I\sigma_1$ ($I\sigma_2$) is the probability per time unit for a LS (HS) molecule to be switched by light to the HS (LS) state, and I the intensity of radiation.

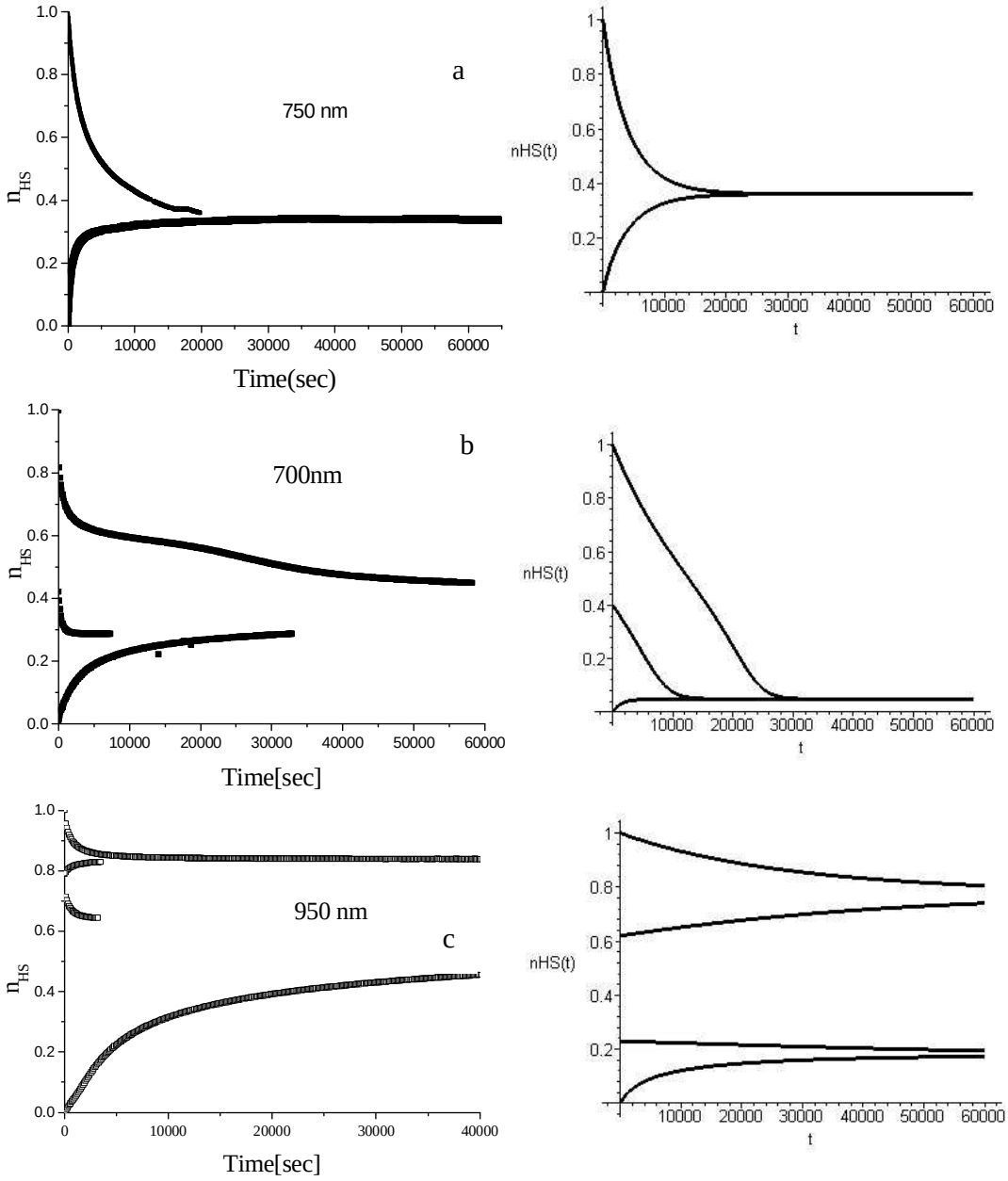


Fig. 5. Photoexcitation at different wavelengths for $[F_{0.5}Zn_{0.5}(btr)_2(NCS)_2]$, H_2O (a) and $[Fe_{0.8}Zn_{0.2}(btr)_2(NCS)_2]$, H_2O (b,c) , experiment and simulations.

In Fig. 4a we present the photo-excitation curves obtained for different wavelengths, from 550nm to 1000 nm. In Fig. 4b, are reported the high spin fractions of the photo-stationary states as a function of wavelength. A hysteresis of *novel type,* i.e. a s a function of the wavelength is evidenced. The minimum value of n_{HS} in the photo-stationary state is observed at ~ 750 nm, two photo-stationary states are obtained at $\lambda > 750$ nm and around 700 nm.

Three main situations, presented in Fig. 5, can be distinguished, as a function of the ratio of LS→HS and HS→LS transitions rates (i.e. of cross-sections). Simple simulations using the master equation (2) are presented in the right part of the figure. The relaxation process has been accounted for with, to start with, the parameter values derived from the relaxation curves in the dark. The photo-excitation terms have been taken linear, i.e. constant values were given to where $I\sigma_1$, $I\sigma_2$, to be best fitted to the photo-excitation curves.

The computed curves do not reproduce the unstable behaviour observed at 700, 950 nm, unless the relaxation rates are increased *by a large factor* with respect to the values measured in the dark. Then, the bistable character (bottom figure) and the quasi-bistable character (middle figure) could be reproduced. We believe this discrepancy in the analysis is due to the non-linearity of the photo-excitation, previously reported in [9], however in a situation which did reach the bistable character

Further work is needed to investigate specifically the non-linear character of the photo-excitation terms. Due to the importance of bulk absorption effects, the investigation of thin films, together with improvements of the reflectivity device (use of snapshots for relaxation in the dark) are possible ways.

4. Conclusions

We investigated the basic features of photo-excitation and relaxation in spin-crossover complexes by recording the time dependence of the excited state relative population under various circumstances.. The variety of experiments: low/high temperatures, in the dark/under permanent irradiation, as a function of light intensity, enabled us to follow the photo-excitation and relaxation terms. A major feature revealed by the study is the non-linear character of the photo-excitation response, the mechanism of which remains to be elucidated, and which obviously contributes to instability of the system under permanent irradiation. A challenging aspect of these experiments is the enhancement of the non-linear character when irradiation induces both the upwards and downwards transitions.

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References

[1] H. Toftlund, Coord. Chem. Rev. **94**, 67 (1989).
[2] E. Konig, Struct. Bonding (Berlin) **76**, 51 (1991).
[3] S. Decurtins, P. Gütlich, K. M. Hasselbach, A. Hauser, H. Spiering, Inorg. Chem. **24**, 2174 (1985).
[4] A. Desaix, O. Roubeau, J. Jeftic, J. G. Haasnoot, K. Boukheddaden, E. Codjovi, J. Linarès, M. Nogues, F. Varret. Eur. Phys. J. B **6**, 183 (1998).
[5] F. Varret, K. Boukheddaden, J. Jeftic, O. Roubeau, J. Mol. Cryst. Liq. Cryst. **335**, 273-284 (1999).
[6] J. F. Letard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau, O. Kahn, Inorg. Chem. **37**, 4432 (1998).
[7] A. Hauser, P. Gütlich, H. Spiering. Inorg. Chem. **25**, 4345 (1986).
[8] B. Hoo, K. Boukheddaden, F. Varret. Europ. Phys. J. B **17**, 317-326 (2000).
[9] C. Enachescu, J. Linares, F. Varret, J. Phys. Condens. Matter. **13**, 2481-2495 (2001).
[10] A. Hauser, J. Chem. Phys. **94**, 2741 (1991).
[11] E. Codjovi, W. Morscheidt, J. Jeftic, J. Linares, M. Nogues, A.Goujon, O. Roubeau, H. Constant-Machado, A. Desaix, A.Bousseksou, M. Verdaguer, F. Varret, J. Mol. Cryst. Liq. Cryst. **335**, 1295-1304 (1999).
[12] C. Enachescu, H. Constant-Machado, K. Boukheddaden, E. Codjovi, J. Linares, F. Varret, J. Phys. Chem. Solids **62**, 1409 (2001).