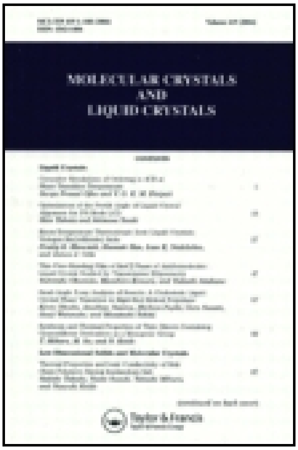

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Inhomogeneous Effects in the Light-Induced Bistability and Non-Linear Relaxation of Cooperative Spin-Crossover Solids

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Inhomogeneous Effects in the Light-Induced Bistability and Non-Linear Relaxation of Cooperative Spin-Crossover Solids

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We interpret experimental data associated with the light-induced bistability of the spin-crossover series $[Fe_xCo_{1-x}(btr)_2(NCS)_2].H_2O$ under permanent light irradiation, and with the underlying cooperative character of the relaxation of the metastable state after photoexcitation. Relaxation curves, light-induced thermal and optical hystereses (LITH, LIOH) and transient regimes are analyzed in the framework of a non-linear macroscopic master equation. Effects of compositional inhomogenities and bulk attenuation of light are accounted for in the model and provide an excellent agreement with the experimental data.

Keywords: spin-crossover; photoexcitation; cooperative relaxation; light-induced bistability; inhomogeneities

INTRODUCTION

Spin-crossover solids[1] are text-book examples of photo-excitable materials, which are studied for future applications as optical memories or numerical displays[2]. The optical switching is performed at low temperature, by the so-called direct or inverse LIESST effect (Light Induced Excited Spin State Trapping[3]), using different wavelengths for the direct and reverse processes. A light-induced bistability, i.e. a bistability of the steady state (dynamical equilibrium) under permanent irradiation, has been discovered recently[4,5,6] and explained in terms of a cooperative relaxation effect[6,7].

The LS ↔ HS switching is easily detected by magnetic measurements (for Fe^{II}, the spin states are 0, 2), or by reflectivity. Here we use both techniques simultaneously[8,9]. The best suited technique is reflectivity[9], which is free from bulk absorption effects, since it collects the « surface » signal, i.e. the signal coming from a surface layer, the thickness of which corresponds to the penetration depth of light. Correlatively, optical absorption leads to an inhomogeneous excitation of the sample, in layers parallel to the surface, i.e. in the « frontal mode ». This inhomogeneous character can be minimized by using thin samples and, following A. Hauser's advice, irradiating at the edge of the $^1A_1 \rightarrow {}^1T_1$ transition. Such conditions ensure a reasonable correlation between the magnetic and optical signals, as illustrated in Fig. 1 where the signals were recorded during the direct LIESST process. The small discrepancy between the curves illustrates the effect of a small attenuation of light in the bulk.

After photoexcitation, the photoinduced metastable state (high-spin HS) decays to the ground state (low-spin LS), with a relaxation rate which becomes fast (~ $minutes^{-1}$) in the range 60- 80K. The sigmoidal shape of the relaxation curve (time dependence of the HS fraction), shown in Fig. 2, is typical for a cooperative relaxation process[10] : the energy barrier of the metastable state progressively lowers while relaxation proceeds, leading to a « self-accelerated » process.

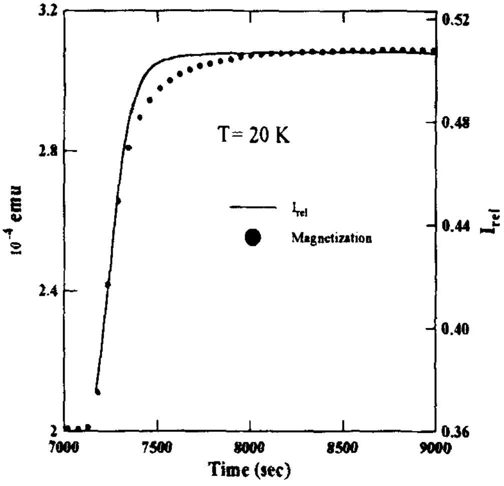

Figure 1 : Magnetic and reflectivity signals recorded at 20 K during the direct LIESST of $[Fe_xCo_{1-x}(btr)_2(NCS)_2].H_2O$, [x=0.5], 1 mg, 600nm, 40 mW/cm^2.

A macroscopic model[5,6,7] is used to describe the effects in terms of a thermally activated cooperative relaxation which can be expressed as :

$$k_{HL}(T,n_{HS}) = k_{\infty}\exp(-\frac{E_a(0)}{kT})\exp(-\alpha(T)n_{HS}) \qquad (1)$$

with n_{HS} the relative occupation of high spin (HS) state, $E_a(n_{HS})$ the barrier energy, $\alpha(T)$ the self-acceleration factor which is proportional to the inverse of temperature and to the effective interaction parameter. k_∞ represents the high-temperature value of the relaxation rate.

In the presence of a continuous irradiation of the sample, neglecting the reverse (LS→HS) spontaneous relaxation the master equation, which governs the evolution of the system, is written :

$$\frac{dn_{HS}}{dt} = I_0\sigma(1-n_{HS}) - n_{HS}k_{\infty}\exp(-\frac{E_a(0)}{kT})\exp(-\alpha(T,x)n_{HS}) \qquad (2)$$

where $I_0\sigma$ is the probability per time unit for a molecule to switch from LS to HS state; I_0 is the beam intensity (in photons/sec×cm^2), σ is the absorption cross section.

The steady state of the system (the state reached for time → infinity) corresponds to $dn_{HS}/dt = 0$, so that the state equation of the system defining the equilibrium states is written:

$$n_{HS} k_{\infty} \exp(-\frac{E_a(0)}{kT}) \exp(-\alpha(T,x) n_{HS}) = I_0 \sigma (1 - n_{HS}) \qquad (3)$$

Such a non-linear equation leads to bistability giving rise to hysteretic behaviour, when the self-acceleration factor α exceeds the threshold value of $\alpha_C=4$. This then gives rise to light-induced hysteresis loops, at constant intensity or temperature, respectively denoted LITH and LIOH (Light Induced Thermal and Optical Hysteresis).

In a previous paper[6], we presented experimental LITH and LIOH loops recorded with the spin crossover compounds $[Fe_xCo_{1-x}(btr)_2(NCS)_2].H_2O$, where x is the atomic concentration of the active spin-crossover element. We obtained a general agreement of all data with the macroscopic model, including the expected dependence of $\alpha(T,x)$. However, the detailed shape of the experimental curves was not perfectly reproduced by the original model proposed in ref. [6]. We introduce here some simple extensions, accounting for inhomogeneous effects : (i) compositional inhomogeneities which have been detected in the samples by microprobe analysis[11] and (ii) photoexcitation inhomogeneities associated with the progressive attenuation of light throughout the sample. Also, the transient regimes are quantitatively analyzed here for the first time.

Relaxation curves : the tail effect

Relaxation curves typically exhibit a monotically decaying tail, this is not reproduced by the original model (see Fig 2). We introduce a compositional inhomogeneity through a Gaussian distribution of x around the average value given by elemental analysis, as suggested in ref. [11]. We take into account the

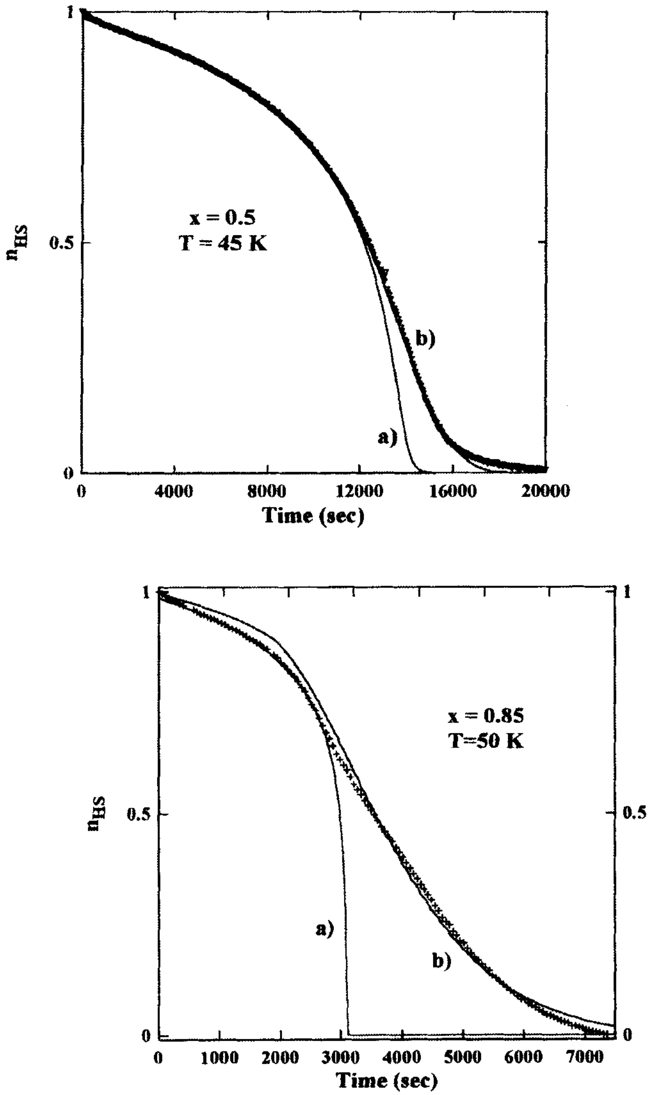

Figure 2 : Experimental relaxation for [x=0.5] and [x=0.85] with fitted curves with a) original model and b) x distribution

See Color Plate VIII at the back of this issue.

x-dependence of the self-acceleration factor $\alpha = Ax / T$, together with a linear dependence of x of $Ea(n_{HS})$, suggested by the experimental $\Delta H(x)$ data [11b]. The total curve is the sum of elementary contributions computed according to Eq. (2). Results show good agreement with experiment, as observed in Fig. 2, with narrow distributions (standard deviation $\sigma_x = 0.035$, 0.050 for x=0.5 and 0.85 respectively) which reasonably compare to the composition scatter revealed by the microprobe analysis. The amplitude of the tail effect is obviously correlated to the strength of cooperativity.

During relaxation, the n_{HS} inhomogeneities associated with the x distribution transiently increase and then decrease as shown in Fig.3. Such a dispersive effect is due to the self-accelerated relaxation and has been modeled in terms of spinodal instability[7]. The present explanation introduces inhomogeneities as a necessary parameter for the analysis of relaxation curves[12].

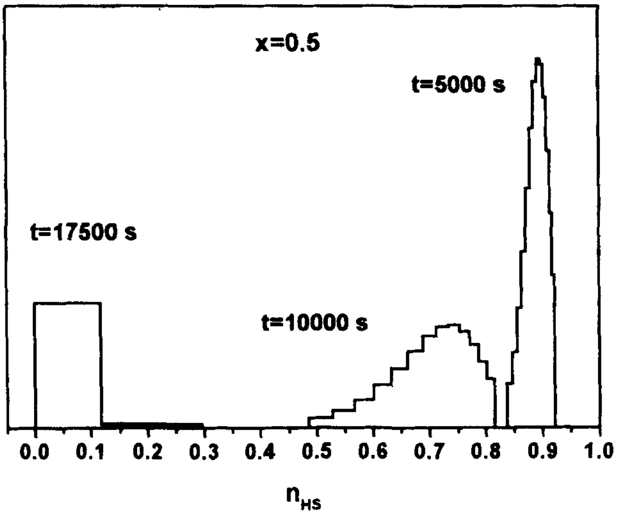

Figure 3 : Histograms showing the dispersion of n_{HS} values during relaxation using the fitted-parameters of Fig. 2b for [x=0.5].

Light-Induced Optical Hysteresis : the bulk attenuation of light

In Fig.5 we show a representative LIOH loop[6] which was observed at the constant temperature of 58 K using a stepwise variation of the light intensity. The optical data was not reliable due to the non-linear response of the photo-diodes at high intensities. The magnetic data, having a bulk character, are highly affected by the attenuation of the light through the sample. The LIOH loop exhibits a typical distortion, as seen in Fig. 5. The effect is modelled by introducing an intensity attenuation factor $\exp(\varepsilon^*z)$, where ε is the extinction coefficient of the material for the radiation used and z the depth of the layer. Then Eq. (3) is solved to provide the $n_{HS}(I_0,z)$ steady state value, and the total $n_{HS}(I_0)$ is obtained by simple integration over the thickness of the sample. In a first approach, we take ε as being independent of n_{HS}. A reasonably good fit of the bent-shape of the loop is obtained taking $\exp(\varepsilon^*z_{max}) \sim 0.37$.

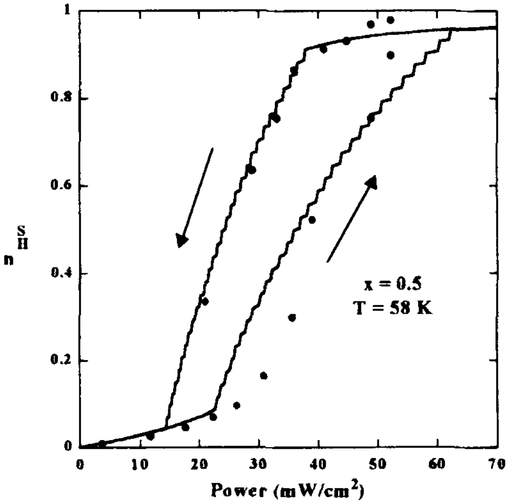

Figure 5 : LIOH loop and theoretical curve accounting for light inhomogeneities due to bulk absorption. [x=0.5], 58 K, 1 mg, 600nm.

The ε coefficient considered in this first approach takes into account the diffusion of light by the powder sample. As a further approximation, we should consider the bleaching effect, i.e. the n_{HS} dependence of the extinction coefficient. In the present case, the effect of compositional inhomogeneities is almost negligible with respect to excitation inhomogeneities.

A further effect of excitation inhomogeneities may be observed on the relaxation curves, the beginning of which takes the form of a stretched exponential, as previously observed by A. Hauser and H. Constant-Machado[11]. Such a distortion is hardly visible on the curves of Fig. 2. The stretched exponential results from a broad distribution of relaxation times, due to the initial n_{HS}-distribution. A detailed study of this effect is in progress.

Transient regimes

In Fig.6 we show the different time dependance of $n_{HS}(T)$ for [x=0.5] at T=59K after various thermo-optical histories of the sample. The bistability of the system for the experimental conditions (T,I_0) is evidenced by the top and bottom curves (a) and (b), respectively leading to the high and low steady-states. These curves could be nicely reproduced using the master equation (2), with the previous value of αT=265K. The other curves are explained by a demixtion process, i.e. a decomposition of the sample into domains of the low and high steady-states, which is analysed[7] as being due to the unstable situations encountered during the thermo-optical history of the sample

It is worth noting that the experimental results given in Fig. 6 provide very direct measurement of the self-acceleration parameter, which perfectly follows the original macroscopic master equation, irrespective of the inhomogeneous effects. This lack of sensitivity to compositional or excitation inhomogeneities probably originates from the fact that curves (a) and (b) were recorded far from the spinodal interval (i.e. the interval where n-fluctuations are unstable [7]). Also, the smooth shape of the curves is quite insensitive to to small variations in x or I_0, in contrast with hysteresis loops.

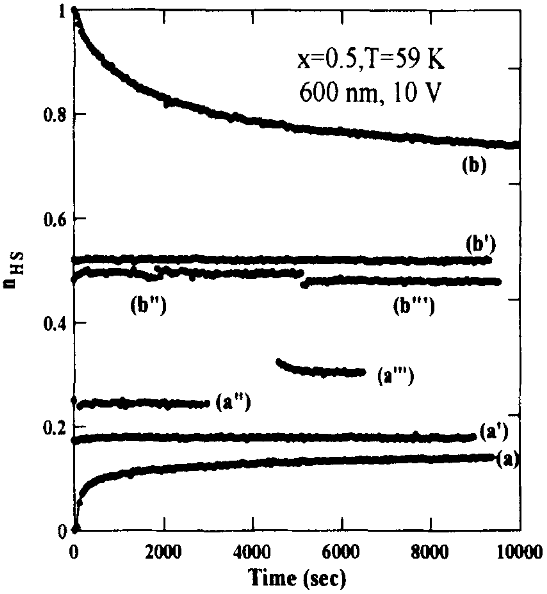

Figure 6 : Transient regimes leading to (a) pure low steady-state, (b) pure high steady-state and (a'→b''') demixed states. Computed curves perfectly match the experimental curves (a), (b).

Conclusion

The macroscopic model accounting for a non-linear term of the self-accelerated relaxation adequately reproduces all major experimental data concerning the light-induced bistability. The transient regime curves appear to be rather insensitive to the inhomogeneities of the system. Once the inhomogeneous effects can be accounted for, experimental investigation should be extended to other photoswitchable systems (for example photomagnetic Prussian Blue derivatives[8,9,13]), to higher intensities and temperatures, and to more sophisticated experimental procedures (such as flash illuminations, periodic variations of light and/or temperature, and minor hysteresis loops). It would also be very interesting to investigate non-linear effects in the photoexcitation process itself (the « domino effect »)[14].

We stress that the inhomogeneous character has to be accounted for as an additional parameter in relaxation models.

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