

Relaxation and Light Induced Thermal Hysteresis (LITH) behaviours in the atom-phonon coupling model for spin crossover compounds

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It is studied the atom-phonon coupling model introduced recently for spin-conversion phenomenon High-spin (HS) $\leftrightarrow$ Low-spin (LS). The originality of this model, performed on a linear chain of atoms, is that the interaction between two molecules is harmonic and the value of the elastic force constant values of the spring linking two atoms depends on their electronic states. In this model a Zeeman-like and an exchange-like interactions appear naturally. In this contribution we reproduce the sigmoidal behaviour in the HS $\rightarrow$ LS relaxation at low temperatures as obtained experimentally as well as the Light Induced Thermal Hysteresis (LITH).

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1. Introduction

It is well known that the spin crossover phenomenon [1,2] is related to the cooperative competitions between molecules. It has been established from the diluted system studies, that the width of the hysteresis loop must be related to the intermolecular interaction [3, 4].

Recently it has been shown that the behavior spin crossover compounds, either diluted or undiluted, can be quantitatively obtained by using a microscopic model based on an atom-phonon coupling mechanism [5, 6, 7]. In this model the spin crossover compounds molecules are modeled as atoms with two electronic states: a ground state (LS) and one excited state (HS); and are interconnected by springs.

The basic idea of this model is to assume that the elastic constant of the spring depends on the electronic state of the two near-neighbor coupled molecules. The interactions intensities being evaluated from phonon contribution. Then the thermal variation of the high spin fraction is obtained from the competition between the electronic parameter Δ , which is favoring the (LS) state and the phonons which are favoring the (HS) state. As far this model has been applied only for studying the thermal phase transitions. It is interesting to see if by using this model is possible to describe the behavior of the spin crossover compounds at low temperatures too. More precisely to see if it can be described the HS $\rightarrow$ LS relaxation curve and the Light Induced Thermal Hysteresis (LITH).

In this work we use the atom-phonon coupling model for studying the relaxation process as well as the LITH, taking into account the kinetic effect related to the velocity of the temperature variation.

2. Atom-phonon coupling model

It is considered the one-dimensional case where the molecules are coupled to each others by a spring. The molecules have two electronic level (LS) and (HS) and the difference in energy is Δ . To each molecule we associate a fictitious-spin $\hat{\sigma}$ with eigenvalues -1 (corresponding to the fundamental level LS) and +1 (corresponding to the HS level). The degeneracy of LS level is 1 and that of the HS level is r . The basic idea in this model [5, 6, 7] is that the elastic constant values of the "spring" linking two atoms, depends on their electronic states (see Fig. 1): λ when both molecules are in the (LS) state, ν when both are in the (HS) state and μ when one atom is in the (LS) level and the other in the (HS) level. This leads to the naturally introduction of long and short-range interaction.



Fig. 1. The three elastic constants as a function of the spin state of the nearest neighbor pair of atoms.

The total hamiltonian of the chain is the sum:

$$H = H_{\text{spin}} + H_{\text{phon}},$$

where

$$H_{\text{spin}} = \sum_i \frac{\Delta}{2} \hat{\sigma}_i \quad (1)$$

is the spin hamiltonian and

$$H_{\text{phon}} = E_c + E_p, \quad (2)$$

is the phonon hamiltonian.

The chain potential energy:

$$E_p = \sum_{i=1}^N \frac{1}{2} e_{i,j+1} q_i^2, \quad (3)$$

where: q_i is the displacement of the i -th atom from its equilibrium position which we assume to be independent of the electronic states of the atoms. Due to the periodic condition, $q_i = u_{i+1} - u_i = q_{p+N} = q_p$ for $p = 1, 2, \dots, N$; and r is elastic force constant which is given by: $e_{i,i+1}$

$$e_{i,i+1} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4} (\hat{\sigma}_i + \hat{\sigma}_{i+1}) + \frac{\lambda - 2\mu + \nu}{4} \hat{\sigma}_i \hat{\sigma}_{i+1}. \quad (4)$$

The potential energy can be decomposed as:

$$V_o = \sum_{i=1}^N \frac{\lambda + 2\mu + \nu}{8} q_i^2 \quad (5)$$

$$V_1 = \sum_{i=1}^N \frac{\nu - \lambda}{8} (q_i^2 + q_{i+1}^2) \hat{\sigma}_i, \quad (6)$$

$$V_2 = \sum_{i=1}^N \frac{\lambda - 2\mu + \nu}{8} q_i^2 \hat{\sigma}_i \hat{\sigma}_{i+1} \quad (7)$$

V_1 has a Zeeman-like energy form; each spin $\hat{\sigma}_i$ is subjected to an effective field h_i given by:

$$h_i = \frac{\nu - \lambda}{8} (q_i^2 + q_{i+1}^2) = h_0 (q_i^2 + q_{i+1}^2) \quad (8)$$

and has a exchange-like energy form. In the expression, $V_2 V_2$

$$J_{i,i+1} = \frac{\lambda - 2\mu + \nu}{8} q_{i+1}^2 = J_0 q_{i+1}^2, \quad (9)$$

can be seen like a exchange parameter.

In the mean-field approximation is replaced by an effective constant which does not depend on the site i . In this case, the field created by phonons is uniform in all atomic chain and moreover the exchange parameter $e_{i,i+1}$ $K_{i,i+1}^{h_i}$ is the same for each nearest neighbor pair. Therefore a hamiltonian which can be studied by using the transfer matrix method will be obtained [6].

The mean value of the phonon hamiltonian is given by:

$$\langle H_{phon}(K) \rangle = \frac{\hbar \omega_M(\lambda)}{2} \sqrt{\frac{K}{\lambda}} \cdot \left\langle \sin \frac{i\pi}{N} \right\rangle \coth \left(\frac{\beta \hbar \omega_M(\lambda)}{2} \sqrt{\frac{K}{\lambda}} \left\langle \sin \frac{i\pi}{N} \right\rangle \right) \quad (10)$$

where $i = 0, \pm 1, \dots, \pm \left(\frac{N}{2} - 1 \right), \frac{N}{2}$; and $\beta = 1/k_B T$.

By applying the variational method the following expression for the elastic constant is obtained:

$$K = \frac{2\mu + \lambda + \nu}{4} + 4h_0 m + 2J_0 s \quad (11)$$

By applying the transfer matrix method the system [12] is obtained:

$$\begin{cases} m = \langle \hat{\sigma}_i \rangle = \frac{\exp(\beta J) \sinh(\beta h_i)}{\sqrt{B}} = f_1(s, m) \\ s = \langle \hat{\sigma}_i \hat{\sigma}_{i+1} \rangle = 1 - \frac{2 \exp(-2\beta J)}{A \sqrt{B}} = f_2(s, m) \end{cases} \quad (12)$$

where $i = 1, \dots, N$

A, B and are given by the following equations: h_i

$$A = e^{\beta J} \cosh(\beta h) + \sqrt{B}, \quad (13)$$

$$B = e^{2\beta J} \sinh^2(\beta h) + e^{-2\beta J} \quad (14)$$

$$h_r = -\frac{\Delta}{2} - \frac{2h_0}{K} \frac{\langle H_{phon}(K) \rangle}{N} + k_B T \frac{\ln r}{2}$$

In the following we take $\hbar \omega_M(\lambda)$ as the unit energy, where $\omega_M(\lambda)$ is the maximum phonon frequency when the chain is periodic with an elastic force λ , given by

$$\omega_M(\lambda) = 2\sqrt{\frac{\lambda}{m}}, \text{ where } m \text{ is the atom mass.}$$

The “dilution” case (when active molecules are replaced by non-spin-crossover molecules) has been studied in [7]. In this case the system is:

$$\begin{cases} m = \langle \hat{\sigma}_i \rangle = \frac{\exp(\beta J') \sinh(\beta h'_i)}{\sqrt{B'}} \\ s = \langle \hat{\sigma}_i \hat{\sigma}_{i+1} \rangle = 1 - \frac{2 \exp(-2\beta J')}{A' \sqrt{B'}} \end{cases} \quad (15)$$

Where:

$$A' = e^{\beta J'} \cosh(\beta h'_i) + \sqrt{B'} \quad (16)$$

$$B' = e^{2\beta J'} \sinh^2(\beta h'_i) + e^{-2\beta J'} \quad (17)$$

$$h'_i = -(1 - c_1) \frac{\Delta}{2} + \frac{2 \langle H_{0ph}(K, m_a) \rangle}{4NK} \cdot ((1 - 2c_1 + c_2)(\lambda - \nu)m + 2(c_1 - c_2)(k_1 - k_2)), \quad (18)$$

and

$$J' = -(1 - 2c_1 + c_2)(\lambda - 2\mu + \nu) \frac{3 \langle H_{0ph}(K, m_s) \rangle}{8NK} \quad (19)$$

where: 1 is the concentration of impurities c_1 is the concentration of the pairs of the impurities atoms c_2 , k_1 is the elastic force constant between an active atom that is in the (LS) state and an inactive atom (impurity). k_2 is the elastic force constant between an active atom that is in the (HS) state and an inactive atom.

In this contribution we introduce the same reduced parameters as in [6]:

- Reduced temperature: $t_r = \frac{k_B T}{\hbar \omega_M(\lambda)}$;

- The dimensionless electronic excitation energy:

$$\delta = \frac{\Delta}{\hbar \omega_M(\lambda)};$$

- The elastic force constant ratio: $x = \frac{\nu}{\lambda}$;

- The dimensionless parameter defined by:

$$\mu = \frac{\lambda + \nu}{2} + \frac{\lambda - \nu}{2} y$$

3. The relaxation process

Most of the spin crossover systems can be switched from one state LS to the other HS state, at low temperature, under irradiation with suitable wavelength, according to the so-called LIESST (light induced excited spin state trapping) effect [8]. The relaxation HS $\rightarrow$ LS appears when after photo-excitation we switch off the light.

The HS $\rightarrow$ LS relaxation process was first studied by Hauser and the Mainz group [9, 10, 11]. The analysis was based on the fact that the energy gap $E_{HS} - E_{LS}$ is decreasing as function of high-spin fraction n_{HS} and then E_a , the height of the energy barrier, is expected to be an increasing function of n_{HS} (see Fig. 2).

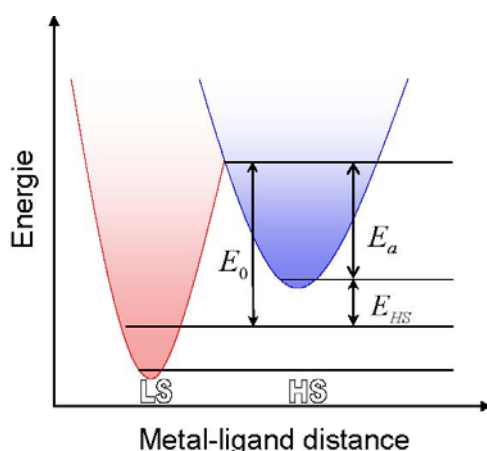


Fig. 2. The configuration diagram of a spin crossover molecule, i.e. the adiabatic energies of the lowest vibronic state, in each spin state, as a function of the metal-ligand distance.

A self-accelerated relaxation is then obtained: at the beginning of the relaxation (large energy barrier), the process is slow and it becomes faster and faster due to the lowering energy barrier.

A useful expression for the relaxation rate K_{HL} was given by Hauser [9,10,11] based on the experimental and theoretical data. They consider a linear dependence of the barrier energy with n_{HS} .

In the thermal activated regime, the relaxation rate is expressed by the relation:

$$K_{HL}(T, n_{HS}) = k_{\infty} \exp\left(-\frac{E_a(n_{HS})}{k_B T}\right) \quad (20)$$

where k_{∞} is the high temperature rate (associated with some vibrational frequencies), k_B is the Boltzmann constant and E_a is the activation energy given by the expression:

$$E_a(n_{HS}) = E_0 - E_{HS} \quad (21)$$

Enachescu et al. [12] have developed this idea in the framework of the Ising-like model. They have noticed that this mean field approach fails to reproduce the tail of the relaxation curves (see Fig. 3): a sizeable departure from

the mean-field curve is observed at long times.

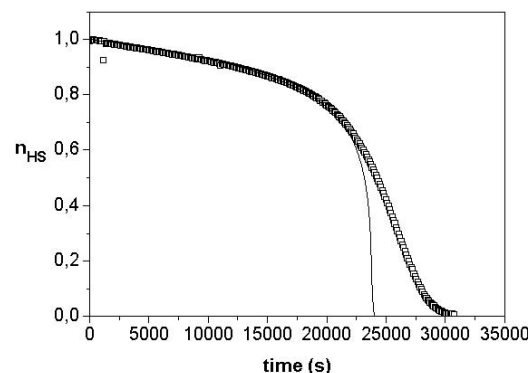


Fig. 3. The experimental relaxation curve (squares) in the dark. The continuous line is the theoretical curve obtained in the mean field approximation.

The purpose of this paper is to apply the atom-phonon coupling model to determine and to reproduce all the relaxation curve even the typical slowing down of relaxation “tail effect” E_{HS} .

In a chain of N molecules and taking into account the electronic and the phonon energy, E_{HS} we consider is expressed as:

$$E_{HS}(n_{HS}) = \frac{\Delta}{2} + \frac{E_{phonons}}{N} \quad (22)$$

Further, assuming a quasi-static relaxation process the equation (20) may be written in the form:

$$K_{HL}(T, n_{HS}) = k_{\infty} \exp\left(-\frac{A \cdot \frac{\delta}{2} - \frac{\langle H_{phon}(K) \rangle_T}{N}}{t_r}\right), \quad (23)$$

where: $A = \frac{E_0}{\hbar \omega_m(\lambda)}$,

and t_r is the reduced temperature previously defined, t_r .

The variation in time of the high spin fraction is given by a master equation:

$$\frac{dn_{HS}}{dt} = -n_{HS} k_{\infty} \exp\left(-\frac{A \cdot \frac{\delta}{2} - \frac{\langle H_{phon}(K) \rangle_T}{N}}{t_r}\right). \quad (24)$$

4. Light Induced Thermal Hysteresis (LITH)

If the irradiation of a spin crossover compound with a beam light at a properly wave length is maintained is possible to populate the metastable states at lower temperatures due to the LIESST effect. This kind of transition can be conserved if the irradiation is maintained. The obtained states by this way are not the so-called stable equilibrium states. Those are stationary states under light, what is the result of the competition between the photoexcitation effect and the relaxation one. The inhomogenous effect in this light-induced bistability has been analysed by O. Roubeau et al. [13].

The thermal hysteresis induced by light (LITH) was observed simultaneously by the group of François Varret from Versailles [14] and that lead by J. F. Letard from Bordeaux [15] and was explained for the first time by the group from Versailles. The explanation of this phenomenon is based on the cooperation between the photoexcitation process and cooperative relaxation.

More concretely, it is a LIESST effect on a spin crossover compound at low temperature, leading in this way to a stationary state of the system, which in some cases is the saturated macroscopic state (HS), when the photoexcitation is complete.

After, if the temperature is increased and the photoexcitation is maintained, a competition between non-cooperative photoexcitation which is favouring the transition $LS \Rightarrow HS$ and the temperature which is inducing a cooperative relaxation (therefore, nonlinear) between $HS \Rightarrow LS$ states is obtained. In this way is possible to obtain a bistable state between spin states, which leads to a spin transition out of the equilibrium.

Assuming a linear photoexcitation, the macroscopic master equation [14] is written as follow:

$$\frac{dn_{HS}}{dt} = -n_{HS}(t)K_{HL}(T, n_{HS}) + I\sigma(1 - n_{HS}(t)) \quad (25)$$

where I is the light intensity; σ is the absorption cross-section and t is the time in which the process is observed.

In the light induced hysteresis two cases, which are taking into account the speed of the temperature variation can be distinguished:

- static LITH, in which the speed of the temperature variation is so slow that can be neglected. In this case the solving of the resulting equation has to be done for

$$\frac{dn_{HS}}{dt} = 0 \quad (26)$$

- Dynamic LITH -this is the situation found in the reality, where it must be taken into account also the temperature velocity variation.

5. Results and discussion

In the following will be presented the relaxation curves obtained with the help of the relation (24), taking into consideration the factors which can act in the real situations, like the dilution effect or kinetic effects which are depending on the speed of the temperature variation.

In Fig. 4 we show a sigmoidal calculated curve for the relaxation $HS \Rightarrow LS$ on the framework of the atom-phonon coupling model. The “tail effect” is well reproduced. The difference with the simulated curve on the mean-field approach (see Fig. 3) is essentially at the end of the relaxation.

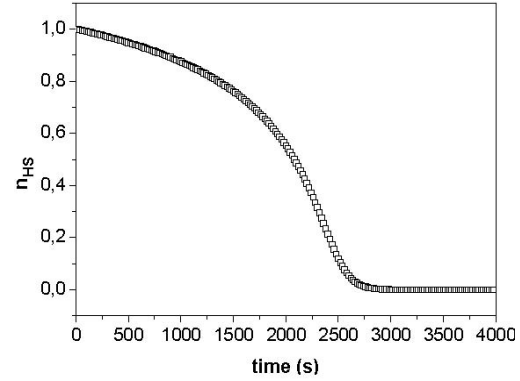


Fig. 4. The calculated relaxation curves in the dark obtained by using following parameters: $x = 0.3, y = 0.0, \delta = 0.6, t_r = 0.03, N = 2000, r = 5, A = 0.8, k_\infty = 100$.

In Figs. 5 and 6 we see the effect of the temperature and the rate of dilution, respectively, on the relaxations curves. From these last two representations, it can be observed a decreasing of the relaxation time as well as for relaxation tail when the temperature increases. In the case of dilution an elongation of the relaxation tail is obtained when the rate of dilution is increased. All this facts have been obtained experimentally [12,14,16].

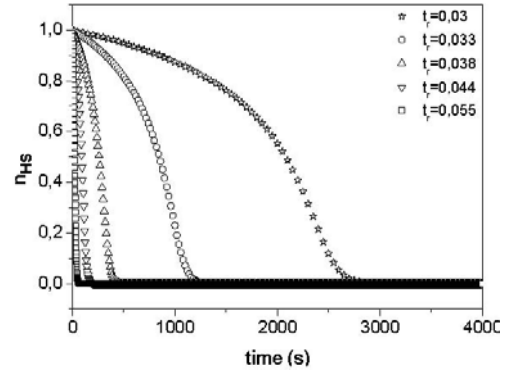


Fig. 5. The calculated relaxation curves in the dark obtained by using following parameters: $x = 0.3, y = 0.0, \delta = 0.6, N = 2000, r = 5, A = 0.8, k = 100$.

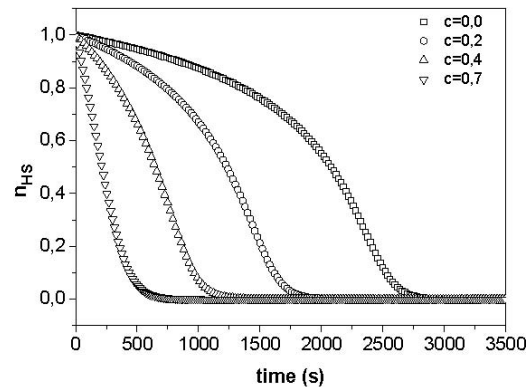


Fig. 6. The calculated relaxation curve in the dark at different concentrations of impurities obtained by using the parameters $x = 0.3, y = 0.0, \delta = 0.6, t_r = 0.03, N = 2000, r = 5, A = 0.8, k_\infty = 100$.

The relaxation experimental curve on $[\text{Fe}_{0.5}\text{Zn}_{0.5}(\text{btr})_2(\text{NCS})_2]\text{H}_2\text{O}$: as well as our simulated curve obtained using equation (24) are shown in Fig. 7. Remarkably the values obtained using the atom-phonon coupling model follow with an excellent accuracy the experimental data.

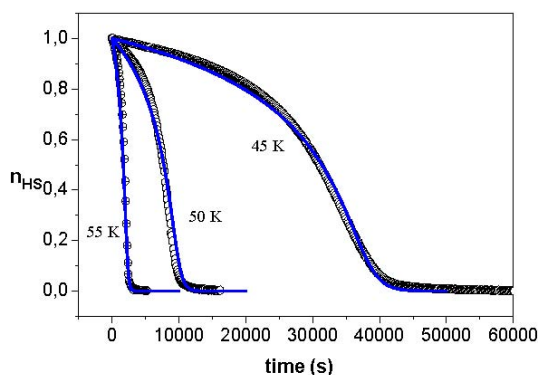


Fig. 7. The experimental curves at different temperatures after the photoexcitation at 55. The continuous lines are theoretical curves 0 nm.

In the Fig. 7 we have used the parameters: $E_0 = 0.8$, $k_\infty = 100$, $x = 0.48$, $y = 0.0$, $t_{45\text{K}} = 0.0208$, $t_{50\text{K}} = 0.0270$.

In the dilution case (see Fig. 6 and 8 for two different x values) we reproduce the experimental results concerning the modification of relaxation curve: the system relaxes faster as dilution increases. From these results we can conclude that the concentration of impurities effects is more clear when the x parameter increases as it is observed by magnetic measurements [12].

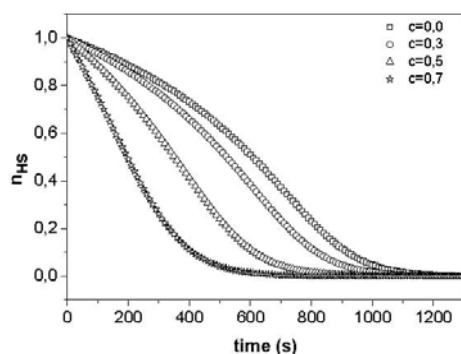


Fig. 8. The relaxation curve in the dark at different concentrations of impurities obtained by using the parameters: $x = 0.5$, $y = 0.0$, $\delta = 0.6$, $t_r = 0.03$, $N = 2000$, $r = 5$, $A = 0.8$, $k_\infty = 100$.

To reproduce the LITH curve we have used equations (25). Fig. 9 and Fig. 10 show simulated results for different values of $x = \lambda/\nu$. So a typical hysteresis curve is obtained in the framework of the atom-phonon coupling model. From the comparison of these figures we can conclude that the x parameter controls the width of the hysteresis at low temperature. We can observe that for the small values of the x parameter, the cycle width is bigger.

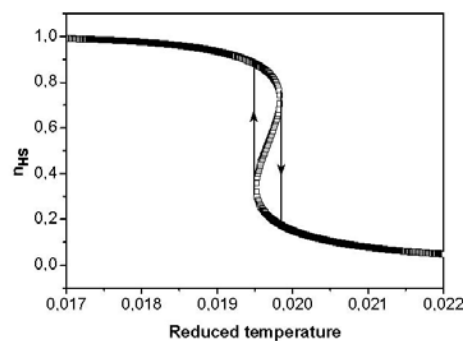


Fig. 9 The calculated static LITH. The values of the computational parameters are: $I_\sigma = 0.0005 \text{ s}^{-1}$, $A = 0.8$, $\delta = 0.6$, $x = 0.5$, $y = 0.0$, $N = 2000$, $r = 5$, $k_\infty = 100$.

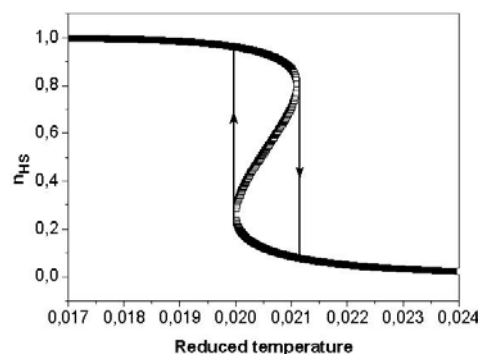


Fig. 10. The calculated static LITH. The values of the computational parameters are: $I_\sigma = 0.0005 \text{ s}^{-1}$, $A = 0.8$, $\delta = 0.6$, $x = 0.4$, $y = 0.0$, $N = 2000$, $r = 5$, $k_\infty = 100$.

In this work it is presented also the study of the dilution effect on light induced hysteresis in order to study the interaction between molecules.

In the dilution case, for the used parameters in simulation, it can be observed (see Fig. 11) that for the values of the hysteresis is disappearing, it means that the cooperativity between molecules vanishes $c > 0.5$.

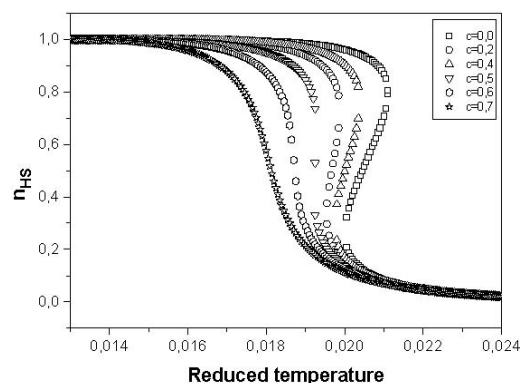


Fig. 11. The calculated static LITH at different concentration of impurities. The values of the computational parameters are: $I_\sigma = 0.0005 \text{ s}^{-1}$, $A = 0.8$, $\delta = 0.6$, $x = 0.5$, $y = 0.0$, $N = 2000$, $r = 5$, $k_\infty = 100$, $\nu = 0.000005 \text{ min}^{-1}$.

As was expected, the speed of the temperature variation has as effect the modification of the hysteresis loop width, namely with increasing the speed of the temperature variation the system does not have the necessary time to react for the external excitation. In other words this means an increasing in width for the hysteresis loop (see Fig. 12). In Figs. 13 and 14 we show the effect on the x parameter for a given speed of the temperature variation.

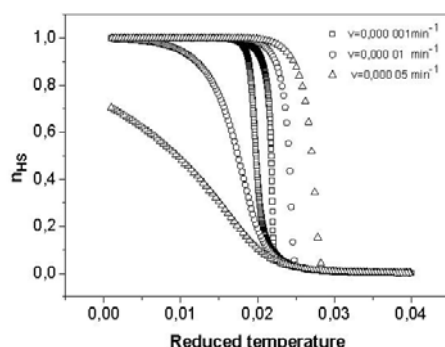


Fig. 12. The calculated dynamic LITH for different variation velocity of temperature. The computational parameters values are: $I_\sigma = 0.0005 \text{ s}^{-1}$, $A = 0.8$, $\delta = 0.6$, $x = 0.5$, $y = 0.0$, $N = 2000$, $r = 5$, $k_\infty = 100$.

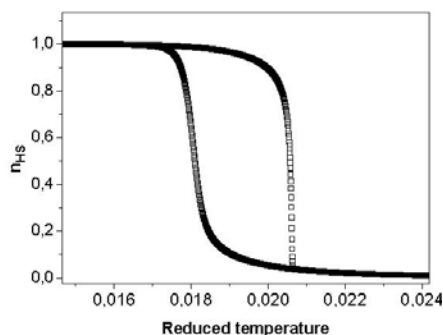


Fig. 13. The calculated dynamic LITH. The values of the computational parameters are: $I_\sigma = 0.0005 \text{ s}^{-1}$, $A = 0.8$, $\delta = 0.6$, $x = 0.4$, $y = 0.0$, $N = 2000$, $r = 5$, $k_\infty = 100$, $v = 0.000005 \text{ min}^{-1}$.

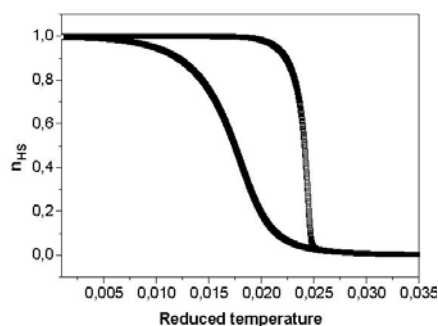


Fig. 14. The calculated dynamic LITH. The values of the computational parameters are: $I_\sigma = 0.0005 \text{ s}^{-1}$, $A = 0.8$, $\delta = 0.6$, $x = 0.5$, $y = 0.0$, $N = 2000$, $r = 5$, $k_\infty = 100$, $v = 0.000005 \text{ min}^{-1}$.

Finally in Fig. 15 it is shown the effect of the dilution in the dynamical LITH. The dilution effect acts in the way to reduce the hysteresis width until it is vanished.

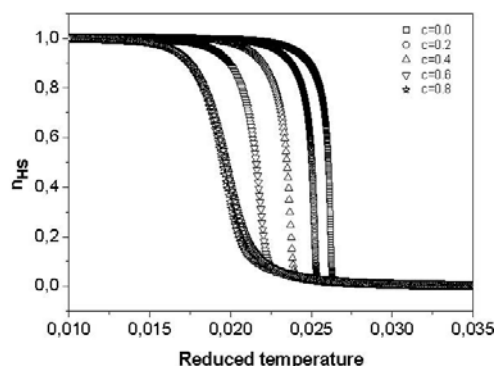


Fig. 15. The calculated dynamic LITH at different concentration of impurities. The values of the computational parameter are: $I_\sigma = 0.0005 \text{ s}^{-1}$, $A = 0.8$, $\delta = 0.6$, $x = 0.5$, $y = 0.0$, $N = 2000$, $r = 5$, $k_\infty = 100$, $v = 0.000005 \text{ min}^{-1}$.

6. Conclusions

On the base of good agreement between the simulated results and the experimental one we can conclude that the atom-phonon coupling model for spin crossover compounds can be applied to describe the relaxation process and LITH into a system with spin conversion.

Regarding the relaxation process, by introduction of the Andreas Hauser's idea, that the activation energy gap is function of the high spin fraction, we succeed to reproduce the sigmoidal like shape of the relaxation curves which agrees well with those obtained experimentally [12, 16, 17].

By introduction of light action on molecules which are in low spin state at low temperature we have reproduced the LITH which is resulting from the competition of the relaxation which is favouring low spin state and the light which is favouring the high spin state. In the present paper it has been studied also the kinematics effects depending on the speed variation of light, the obtained results agree with experimental observations [12].

Using the result from [7] leads us to the conclusion that atom-phonon coupling model may describe also the behaviour of diluted systems, in other words the change of active atoms with inactive atoms (which are not changing the spin state). It has been studied the dilution effect for relaxation process as well as for the LITH and have been obtained the same behaviour with that experimentally observed [12].

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