**Monte Carlo simulations for 1D- and 2D spin
crossover compounds using the atom phonon
coupling model**

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$\text{Fe}(\text{btr})_2(\text{NCS})_2 \cdot \text{H}_2\text{O}$

$$\text{Fe}-\text{N}_{\text{NCS}} = 2.125(3) \text{ \AA}$$

$$\text{Fe}-\text{N}_{\text{btr}} = 2.188(2) \text{ \AA} \\ 2.180(3) \text{ \AA}$$

S. Pillet *et al.*, *Eur. Phys. J. B*, 2004, 38, 541.

Spin crossover compounds

Fe(II)
 d^6

Fe(II)
 d^6

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Spin crossover compounds

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g : degeneracy

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Light Induced Excited Spin State Trapping (LIESST)

S. Decurtins, P. Güthlich, K. Hasselbach, A. Hauser, H. Spiering, *Chem. Phys. Lett.*, 105 (1984) 1.

A. Hauser, *Chem. Phys. Lett.*, 124 (1986) 543.

$\lambda \sim 514 \text{ nm}$ direct

$\lambda = 820 \text{ nm}$ invers

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Fe(btr)₂(NCS)₂·H₂O: Cell parameters during the thermal transition

S. PILLET et al Eur. phys J. B. 2004, 38, 541

- Isostructural transition : no space group change
- Abrupt changes *a*, *b*, *c* : $\Delta a/a = +2.2\%$, $\Delta b/b = -4.1\%$, $\Delta c/c = -2.8\%$, $\Delta V = -91(9) \text{ \AA}^3$

Fe(ptz₆)(BF₄)₂

High Spin State

Low Spin state

Ising-like model:

phenomenological model

$$H = \frac{\Delta}{2} \sigma$$

$$H = \frac{\Delta - kT \ln g}{2} \sigma$$

$$H = \frac{\Delta'}{2} \sum_{(i)} \sigma_i - J \sum_{\langle i,j \rangle} \sigma_i \sigma_j$$

J **????**

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MONTECARLO - METROPOLIS

$$H = \frac{\Delta'}{2} \sum_{(i)} \sigma_i - J \sum_{\langle i,j \rangle} \sigma_i \sigma_j$$

Square Lattice

tab[size][size]

tab[i][j] in -tab[i][j]

Probability = deg[-tab[i][j]] / deg[tab[i][j]] * exp (-beta*(Enew-Eold))

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Atom-phonon coupling model

J. Nasser, K. Boukheddaden, J. Linares, *Eur. Phys. J. B.* 39 (2004) 219-227

Elastic constant values of the « spring » linking two atoms depends on their electronic states

$$C_{LL} > C_{LH} > C_{HH}$$

$$H = H_{spin} + H_{phonon}$$

$$H_{spin} = \sum \frac{\Delta}{2} \hat{\sigma}_i$$

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Atom-phonon coupling model

$$H_{phonon} = E_c + E_p$$

$$E_p = \sum_{i=1}^N \frac{1}{2} e_{i,i+1} q_i^2 \quad q_i = u_{i+1} - u_i$$

$$e_{i,i+1} = \frac{C_{LL} + 2C_{LH} + C_{HH}}{4} + \frac{C_{LH} - C_{LL}}{4} (\hat{\sigma}_i + \hat{\sigma}_{i+1}) + \frac{C_{LL} - 2C_{LH} + C_{HH}}{4} \hat{\sigma}_i \hat{\sigma}_{i+1}$$

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Atom-phonon coupling model

$$E_p = V_o + V_1 + V_2$$

$$V_o = \sum_{i=1}^N \frac{C_{LL} + C_{LH} + 2C_{HH}}{8} q_i^2$$

$$V_1 = \sum_{i=1}^N \hbar \omega [q_{i-1}^2 + q_i^2] \hat{\sigma}_i$$

$$V_2 = \sum_{i=1}^N J_o q_i^2 \hat{\sigma}_i \hat{\sigma}_{i+1}$$

$$J_o = \frac{C_{LL} - 2C_{LH} + C_{HH}}{8}$$

Exchange energy

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Thermal hysteresis

$$m = \langle \hat{\sigma}_i \rangle$$

$$s = \langle \hat{\sigma}_i \hat{\sigma}_{i+1} \rangle$$

$$m = \frac{\exp(\beta J) \sinh(\beta h_r)}{\sqrt{B}} = f_1(s, m)$$

$$s = 1 - \frac{2 \exp(-2\beta J)}{A\sqrt{B}} = f_2(s, m)$$

$$t_r = \frac{T}{\hbar \omega_{\max}}$$

$$x = \frac{C_{HH}}{C_{LL}}$$

$$\mu = \frac{C_{LL} + C_{HH}}{2} + \frac{C_{LL} - C_{HH}}{2} y$$

$$y = \frac{J_0}{\hbar \omega_0}$$

$$\delta = \frac{\Delta}{\hbar \omega_m}$$

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Thermal hysteresis

$$m = \langle \hat{\sigma}_i \rangle$$

$$s = \langle \hat{\sigma}_i \hat{\sigma}_{i+1} \rangle$$

$$m = \frac{\exp(\beta J) \sinh(\beta h_r)}{\sqrt{B}} = f_1(s, m)$$

$$s = 1 - \frac{2 \exp(-2\beta J)}{A\sqrt{B}} = f_2(s, m)$$

$$t_r = \frac{T}{\hbar \omega_{\max}}$$

$$x = \frac{C_{HH}}{C_{LL}}$$

$$C_{LH} = \frac{C_{LL} + C_{HH}}{2} + \frac{C_{LL} - C_{HH}}{2} y$$

$$y = \frac{J_0}{h_0}$$

$$\delta = \frac{\Delta}{\hbar \omega_m}$$

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thermal relaxation

$$\frac{dn}{dt} = -n K_{HL}(T, n)$$

$$K_{HL}(T, n) = k \exp\left(-\frac{E_a}{k_B T}\right)$$

$$E_a = E_0 - E_{HS}$$

$$\frac{dn}{dt} = -n * k * \exp\left(-\frac{E_0 - \frac{\Delta}{2} - \frac{\langle H_{\text{phonons}} \rangle_T}{N}}{k_B T}\right)$$

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relaxation

Simulation

Experimental results

A. Rotaru, J. Linares

J. Optoelectronics and Advanced Materials, 9, 2724-2730 (2007)

Size effect

Size effect

Metastables states at low temperature à 1D:
 $X=(HS-HS \text{ elastic constant})/(LS-LS \text{ elastic constant})$

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$$H = H_{spin} + H_{phonon}$$

$$H_{spin} = \sum \frac{\Delta}{2} \hat{\sigma}_i$$

$$\begin{cases} m\ddot{u}_{i-1} = C_{i-1,i}(u_i - u_{i-1}) + C_{i-1,i-2}(u_{i-2} - u_{i-1}) \\ m\ddot{u}_i = C_{i,i+1}(u_{i+1} - u_i) + C_{i,i-1}(u_{i-1} - u_i) \\ m\ddot{u}_{i+1} = C_{i+1,i+2}(u_{i+2} - u_{i+1}) + C_{i+1,i}(u_i - u_{i+1}) \end{cases}.$$

$$u_j = A_j e^{-i\omega t}, \quad \ddot{u}_j = -\omega^2 A_j e^{-i\omega t}.$$

$$\begin{vmatrix} \frac{C_{1,N}}{m} + \frac{C_{1,2}}{m} - \omega^2 & \frac{-C_{1,2}}{m} & 0 & \cdots & 0 & \frac{-C_{1,N}}{m} \\ & \ddots & \ddots & & & \\ \vdots & \frac{-C_{i-1,i-2}}{m} & \frac{C_{i-1,i}}{m} + \frac{C_{i-1,i-2}}{m} - \omega^2 & \frac{-C_{i-1,i}}{m} & & \vdots \\ \vdots & & \frac{-C_{i,j-1}}{m} & \frac{C_{i,j-1}}{m} + \frac{C_{i,j+1}}{m} - \omega^2 & \frac{-C_{i,j+1}}{m} & \vdots \\ & & \frac{-C_{i+1,i}}{m} & \frac{C_{i+1,i}}{m} + \frac{C_{i+1,i+2}}{m} - \omega^2 & \frac{-C_{i+1,i+2}}{m} & \\ & & & \ddots & \ddots & \\ \frac{-C_{N,1}}{m} & 0 & \cdots & 0 & \frac{-C_{N,N-1}}{m} & \frac{C_{N,N-1}}{m} + \frac{C_{N,1}}{m} - \omega^2 \end{vmatrix} = 0.$$

some results: (no hysteresis)

$\delta=0.606$, $y=0$, $N=200$

$$r = \frac{\text{deg energy HS}}{\text{deg energy LS}} = 15$$

With additional long-range interaction

$$H = \sum \frac{\Delta}{2} \sigma_i - G \langle \sigma \rangle \sum \sigma_i + H_{\text{phonon}}$$

$\delta=0.606$, $y=0$, $N=200$

$$r = \frac{\text{deg energy HS}}{\text{deg energy LS}} = 15$$

$$g = \frac{G}{\hbar w_{\text{max}}} = 0.21$$

Monte Carlo – Metropolis simulations for 2D spin crossover systems

2D square lattice of spin crossover compounds:

nearest as well as next-nearest interactions have been taken into account

The dynamical equation for each displacement's atom and for a perpendicular wave is given by:

$$m\ddot{u}_{i,j} = I_1 + I_2$$

$$I_1 = e_{i-1,j/i,j}(u_{i-1,j} - u_{i,j}) + e_{i,j+1/i,j}(u_{i,j+1} - u_{i,j}) + e_{i+1,j/i,j}(u_{i+1,j} - u_{i,j}) + e_{i,j-1/i,j}(u_{i,j-1} - u_{i,j})$$

$$I_2 = K(u_{i-1,j-1} + u_{i-1,j+1} + u_{i+1,j-1} + u_{i+1,j+1} - 4u_{i,j})$$

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Then we construct the dynamical matrix of the system.

The eigenvalues of this matrix are the phonon frequencies.

$$\sum_{n=0}^{\infty} e^{-\beta \hbar \omega_i (n + 1/2)} = \frac{1}{2 \sinh\left(\frac{\beta \hbar \omega_i^\alpha}{2}\right)}$$

$$P(\alpha) = \frac{1}{Z} e^{-\beta \left(\frac{\Delta - k_B T \ln r}{2} m_\alpha \right)} \prod_{i=1}^N \left(\frac{1}{2 \sinh \frac{\beta \hbar \omega_i^\alpha}{2}} \right)$$

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The high spin fraction evolution in function of the reduced temperature, obtained for 2D system using: $x=0.1$, $r=15$, $K=0.01$ for a) $y=0.02$, b) $y=0.10$

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Summary

-atom-coupling model can help to understand the physical origin of the interaction

-Atom-coupling model :

- thermal hysteresis 1D + long range int.
- thermal relaxation
- Size effet
- thermal hysteresis for 2D systems

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