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Numerical simulation of a device with two spin crossover complexes: application for temperature and pressure sensors

Jorge Linares,^{1,2} Salah Eddine Allal,³ Pierre Richard Dahoo,³ Yann Garcia⁴

¹GEMAC, Université de Versailles Saint-Quentin-en-Yvelines, 45 Av. des Etats-Unis, CNRS-UMR 8635, 78035 Versailles Cedex, France

²Departemento de Ciencias, Sección Física, Pontificia Universidad Católica del Perú, Apartado 1761, Lima, Perú

³LATMOS, Université de Versailles-Saint-Quentin-en-Yvelines, CNRS-UPMC-UVSQ (UMR 8190), 11 boulevard d'Alembert, 78280 Guyancourt, France

⁴Institute of Condensed Matter and Nanosciences, Molecules, Solids and Reactivity (IMCN/MOST), Université catholique de Louvain, 1348, Louvain-la-Neuve, Belgium.

Abstract: The spin-crossover (SCO) phenomenon is related to the ability of a transition metal to change its spin state *vs.* a given perturbation. For an iron(II) SCO complexes the reversible changes involve the diamagnetic low-spin ($S = 0$) and the paramagnetic high-spin (HS $S = 2$) states [1,2,3]. In this contribution we simulate the HS Fraction (n_{HS}) for different set values of temperature and pressure for a device using two SCO complexes with weak elastic interactions. We improve the calculation given by Linares *et al.* [4], taking also into account different volume (V_{HS} , V_{LS}) changes of the SCO. We perform all the calculation in the frame work of an Ising-like model solved in the mean-field approximation. The two SCO show in the case of "weak elastic interactions", gradual spin transitions such that both temperature and pressure values can be obtained from the optical observation in the light of calculations discussed in this article.

1. Introduction

The increasing demand regarding safety and security rules require applications that involve advanced sensors with higher sensitivity, better technical specifications, lower dimensions and low energy consumption. A special class of sensors is represented by temperature and pressure solid state sensors that allow direct or remote detection. This kind of sensing devices can be realized by developing new multifunctional materials exhibiting appropriate properties that can be controlled at the atomic or molecular level. Interesting properties that could be used in these applications are exhibited by spin crossover (SCO) molecular materials [1,2,3]. The SCO phenomenon is a molecular process which combines an electronic transformation and atomic displacements in the coordination sphere of a central metal ion $3d^4-3d^7$. Thus, the SCO usually occurs between a diamagnetic low-spin (LS) state and a paramagnetic high-spin (HS) state, which can be triggered by various external perturbations such as temperature, pressure, light or magnetic field. In the course of the SCO phenomenon, the physical properties (magnetic, optical, electrical, vibrational, etc.) of the material change dramatically and the process can be followed by various detection techniques (magnetic, optical, electrical, etc.) [4-12]. In this work we show that SCO compounds can be used as a visual detector of strong mechanical contact pressure and temperature. This result is based on the thermal dependence of the optical



reflectivity measurements, a correlation of the optical SCO properties with the pressure contact and temperature highlighted thanks to an Ising-like model. These results provide the basis for the construction of a thermal and pressure sensor.

2. Model and principle of calculation

For the complete understanding of our phenomena, we use both experimental and theoretical results in order to determine the way SCO materials are influenced by external factors. We proceed from the knowledge of the temperature and pressure influence on the SCO behavior, as studied in the frame of the Ising-Like model. The mean field approximation is applied to solve the Hamiltonian of the interacting spins. The Ising-Like model proposed by Wajnsflasz and Pick^[13,14] uses a fictitious spin operator σ which can take the value +1 or -1 to specify respectively the HS and LS state with degeneracies g_{HS} for the HS and g_{LS} for the LS state. Linares *et al.*^[15,16] proposed an explicit extension of this model by introducing short- and long-range interactions, termed J and G respectively in the model. As a result, the Hamiltonian is written in the following form:

$$H = \frac{\Delta + \alpha p - T \ln(g)}{2} \sum_i \sigma_i - J \sum_{ij} \sigma_i \sigma_j - G \langle \sigma \rangle \sum_i \sigma_i$$

Where Δ represents the difference between the energy of the HS and that of the LS states, $\sum_{(I,j)}$ is the sum over nearest neighbors, $g = g_{HS}/g_{LS}$ is the degeneracy ratio and αp is the pressure operator. The term $\langle \sigma \rangle$ is the average value of σ which can also be expressed in terms of the fraction of HS species by:

$$n_{HS} = \frac{\langle \sigma \rangle + 1}{2}$$

Then we can develop our Hamiltonian by considering for each particle, the σ_j having the same value $\langle \sigma \rangle$, such that $\sum_j \sigma_j = q \langle \sigma \rangle$, where q is the number of nearest neighbors.

$$H = \frac{\Delta + \alpha p - T \ln(g) - 2G \langle \sigma \rangle}{2} \sum_i \sigma_i - Jq \langle \sigma \rangle \sum_i \sigma_i$$

After collecting together the terms factorized by $\sum_i \sigma_i$ in order to simplify the equation, then the Hamiltonian is expressed as:

$$H = \frac{\Delta + \alpha p - T \ln(g) - 2G \langle \sigma \rangle - 2Jq \langle \sigma \rangle}{2} \sum_i \sigma_i$$

$$H = \frac{\Delta + \alpha p - T \ln(g) - 2\Gamma \langle \sigma \rangle}{2} \sum_i \sigma_i$$

Where finally $\Gamma = G + Jq$ is introduced for simplification and represents both the short- and long-range interactions.

As usual, if we have an Hamiltonian of the form $H = -h\sigma_i$, then after some transformations we can obtain $\langle \sigma \rangle$, by solving the following equation $\langle \sigma \rangle = \tanh(\beta h)$

So in our case if we consider that:

$$h = -\frac{\Delta + \alpha p - T \ln(g) - 2\Gamma \langle \sigma \rangle}{2}$$

$$\beta = \frac{1}{k_B T}$$

Then our equation to solve can be written as:

$$\langle \sigma \rangle = \tanh\left(-\frac{\Delta + \alpha p - T \ln(g) - 2\Gamma \langle \sigma \rangle}{2k_B T}\right)$$

$$\langle \sigma \rangle = \tanh\left(-\frac{\Delta/k_B + pc\delta V - T \ln(g) - 2\Gamma \langle \sigma \rangle/k_B}{2T}\right)$$

Where c is a constant, $c = 0.0724$, when the external applied pressure, p , is expressed in MPa and the volume variation of the molecule, δV , is expressed in \AA^3 .

In order to determine the two variables (T,p) from one equation, our device must include two SCO compounds characterized by the corresponding parameters $\Delta_1, \delta V_1, g_1, \Gamma_1, \langle \sigma_1 \rangle$, and $\Delta_2, \delta V_2, g_2, \Gamma_2, \langle \sigma_2 \rangle$, respectively (we make the difference δV_1 , and δV_2 , in this contribution)

Then we have the following system:

$$\begin{cases} \langle \sigma_1 \rangle = \tanh \left(-\frac{\Delta_1 + pc\delta V_1 - T \ln g_1 - 2\Gamma_1 \langle \sigma_1 \rangle}{2T} \right) \\ \langle \sigma_2 \rangle = \tanh \left(-\frac{\Delta_2 + pc\delta V_2 - T \ln g_2 - 2\Gamma_2 \langle \sigma_2 \rangle}{2T} \right) \end{cases}$$

From these equations we can derive the expression of p and T:

$$\begin{cases} T = \frac{\beta_2 - \beta_1 \frac{\delta V_2}{\delta V_1}}{\lambda_2 - \lambda_1 \frac{\delta V_2}{\delta V_1}} \\ p = \frac{\lambda_1 \cdot \left[\beta_2 - \beta_1 \frac{\delta V_2}{\delta V_1} \right] - \beta_1 \cdot \left[\lambda_2 - \lambda_1 \frac{\delta V_2}{\delta V_1} \right]}{c\delta V_1 \cdot \left[\lambda_2 - \lambda_1 \frac{\delta V_2}{\delta V_1} \right]} \end{cases}$$

In order to simplify the lecture of the equations we introduce the following terms:

$$\begin{cases} \lambda_1 = \ln g_1 - 2 \tanh^{-1} \langle \sigma_1 \rangle \\ \lambda_2 = \ln g_2 - 2 \tanh^{-1} \langle \sigma_2 \rangle \end{cases} \quad \begin{cases} \beta_1 = \Delta_1 - 2\Gamma_1 \langle \sigma_1 \rangle \\ \beta_2 = \Delta_2 - 2\Gamma_2 \langle \sigma_2 \rangle \end{cases}$$

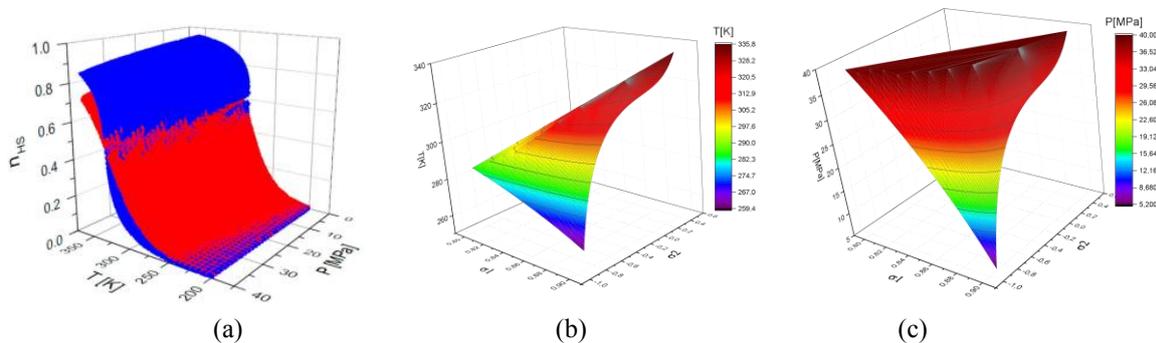


Figure 1. (a) Simulated HS fraction as a function of temperature and pressure variation for two values of the interaction parameter (red- $\Gamma/k_B = 160$ K and blue- $\Gamma/k_B = 300$ K). The calculation parameters are: $\Delta/k_B = 1978.6$ K, $\ln(g) = 6.906$, $\delta V = 100 \text{ \AA}^3$ [4]. (b) Simulated temperature as function of two mean spin values $\langle \sigma_1 \rangle$ and $\langle \sigma_2 \rangle$, using two SCO compounds with the same interaction parameter $\Gamma/k_B = 300$ K and different parameters' values $\Delta_1/k_B = 1300$ k, $\delta V_1 = 93.8 \text{ \AA}^3$, $\ln(g_1) = 6.01$, and $\Delta_2/k_B = 1978.6$ k, $\delta V_2 = 100 \text{ \AA}^3$, $\ln(g_2) = 6.906$, respectively. (c) Simulated pressure as function of two mean spin values $\langle \sigma_1 \rangle$ and $\langle \sigma_2 \rangle$, using two SCO compounds with the same interaction parameter $\Gamma/k_B = 300$ K and different parameters' values $\Delta_1/k_B = 1300$ k, $\delta V_1 = 93.8 \text{ \AA}^3$, $\ln(g_1) = 6.01$, and $\Delta_2/k_B = 1978.6$ k, $\delta V_2 = 100 \text{ \AA}^3$, $\ln(g_2) = 6.906$, respectively.

Figure 1a gives the HS fraction vs. the variation of temperature and pressure for each complex, and shows clearly the overlapping between the two HS fraction 2D surfaces, the overlap range representing the solutions of the combined system from which the simultaneous graphical values of temperature and pressure can be obtained. Fig. 1b and Fig. 1c show respectively the temperature and pressure variation vs. $\langle \sigma_1 \rangle$ and $\langle \sigma_2 \rangle$. As we can see, we can have several pairs of values of $\langle \sigma_1 \rangle$ and $\langle \sigma_2 \rangle$ for one value of temperature or pressure. But the number of pairs decreases for high temperatures in the thermal case, and for low pressure in the pressure case.

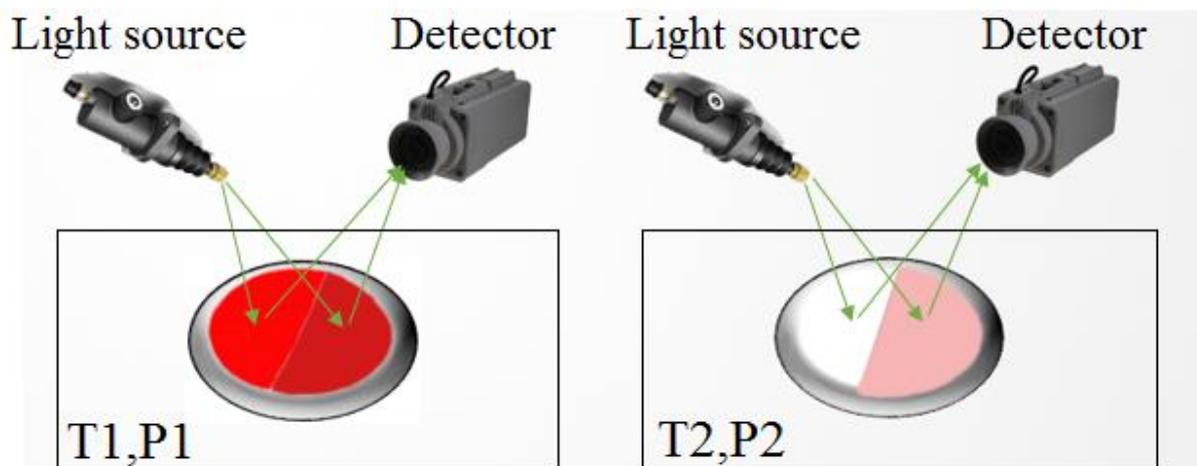


Figure 2. Principle to measure simultaneously temperature and pressure using two SCO compounds.

3. Conclusion

In this work we have presented a novel concept for spin crossover-based sensors that allows the concomitant detection of both temperature and pressure. This new approach is based on the use of two complexes exhibiting gradual spin transitions that leads to the identification of a single set of (P-T) values for a single set of optical densities of each complex. Thus, a simple colour identifier is sufficient to detect and measure the variation of both temperature and pressure, opening new perspectives in the multifunctional sensors field. As far as the necessary apparatus needed to monitor temperature and pressure changes is concerned, the one proposed here is comparatively much simpler to implement than the existing ones using sophisticated X-Ray diffractometers and apparatuses needed for Brillouin spectroscopy. It consists of a standard laser source, a detector and an associated computer for data analysis. Signal to noise ratio is much better with the detection of a reflected laser beam than that of laser induced fluorescence or luminescence.

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