Study of spin-conversion compound nanoparticles in the atom-phonon coupling model including a surface effect.

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Abstract. We discuss a two dimensional model that is capable of reproducing, at least qualitatively, some of the experimentally observed features of spin-conversion compounds. The molecules of these compounds have two electronic energy levels separated by $\Delta$. The values of the elastic constants of the springs contained in the molecules are lower in the upper level. Consequently, the crystal's phonon branches depend on the electronic states of the molecules. The fundamental level is a low spin (LS) state and the excited one is a high-spin (HS) state. We study the thermal variation of the high spin fraction, i.e., the fraction of molecules in the (HS) level by using a model of atom-phonon coupling with a boundary effect: $\Delta = \Delta_b$ for molecules within the bulk, and $\Delta = \Delta_s < \Delta_b$ for molecules on the boundary. These values are compound-dependent, but independent of the crystal's size. Our model reproduces qualitatively two seemingly contradictory experimental results as well as the disappearance and reappearance of the hysteresis loop that is observed when the number $N$ of crystal's molecules is very small. Our model explains why the width of the hysteresis loop decreases with decreasing $N$. We find that for any $N$ the crystal's entropy vanish at $0K$, in accordance with the third law of thermodynamics.

1. Introduction
Spin crossover (SCO) compounds are materials that exhibit several interesting features. The underlying phenomenon to which SCO refers to, is the transition from a low-spin (LS) state to a high-spin (HS) state. These states correspond to the fundamental and to the excited energy levels, respectively, of the molecules that constitute the compound. Different models have been proposed to explain the experimentally observed features of SCO compounds. At the present time, the basic building block of these models is a two-level system, i.e., a fictitious spin -1/2 particle, in terms of which the Hamiltonian of the system can be written down. This Hamiltonian takes into account the contribution of individual spins modeling the compound, as well as the interactions between them. DFT calculations combined with data from different vibrational spectroscopy techniques show that the elastic of "spring" constant of the majority of springs contained in the molecules has a values that is
lower in the HS state than in the LS one [1]. Consequently, in a crystal of such molecules, the branches of the phonon depend on the electronic states of the molecules. It is clear that some optical branches give only a contribution to the entropy of the crystal. However, the optical branches which display a dispersion and the acoustic branches can give a contribution to the intermolecular interactions. How are the variations of those last branches related to the thermal behaviour of the crystal? To our knowledge, the atom phonon coupling model is the simplest model for answering this question. In this model the SCO molecules are considered as two-level atoms and it is assumed that the elastic constant of the spring linking two first neighbors depends on the electronic states of both atoms [2-3]. When the crystal’s size passes from a thermodynamic size to a nano-size, some parameters are no longer extensive or intensive and surface effects start playing an important role in the thermal behavior of the nano-size crystal. In the atom phonon coupling model the free energy of lattice vibrations is no longer an extensive parameter when the number of the atoms in the crystal, N, is small. So, if we add to this model a surface effect, we have all the ingredients which allow us to study nanoparticles. Concerning boundary effects, we assume that the energy difference between the fundamental and the excited states of the two-level system, \( \Delta \), can acquire two different values: \( \Delta_b \) for the atoms in the bulk of the crystal and \( \Delta_{se} \) for those on the boundary.

In this study, we take \( \Delta_{se} \geq 0.9 \Delta_b \).

Concerning the difference between the values \( \Delta_b \) and \( \Delta_{se} \), we assume the following:

i) if the energy diagram of a molecule stems only from electronic interactions within this molecule[4], the difference between \( \Delta_b \) and \( \Delta_{se} \) is due to the interaction between the crystal and its environment. We have

\[
\Delta_{se} = \Delta_b - env \quad (1)
\]

and in this study we take

\[
\frac{\Delta_{se}}{\Delta_b} \leq 0.1 \quad (2)
\]

where "env" means the interaction energy between the crystal and its environment.

ii) if the energy diagram of the molecule stems mainly from electronic interactions contained in this molecule and a little bit from interactions with molecules nearest neighbors, then the difference is due to the number of nearest neighbors. Since \( \Delta_{se} \approx \Delta_b \), we do not have to take into account the interaction with next-nearest neighbors.

Finally, we notice that the present study addresses the case of a two-dimensional, square lattice.

2. The model Hamiltonian

The Hamiltonian of our model is taken to be given by

\[ H = H_e + H_{phonon} \]

\( H_e \) describes the electronic contribution

\[ H_e = \sum_{\ell} \frac{\Delta_{\ell}}{2} \hat{\sigma}_{\ell} \quad (3) \]

where \( \hat{\sigma}_{\ell} \) is the fictitious spin associated to the atom \( \ell \). It has two eigenvalues +1 and -1 which corresponds to the (HS) and (LS) level, respectively. The value of the energy difference \( \Delta \) is \( \Delta_{\ell} \) for the atom \( \ell \). The sum is done on the \( N \) atoms of the crystal.

The Hamiltonian of the lattice vibrations is

\[ H_{phonon} = E_c + E_{p1}(\lambda, \mu, \nu) + E_{p2}(\bar{E}) \quad (4) \]

where \( E_c \) is the kinetic energy, \( E_{p1}(\lambda, \mu, \nu) \) is the harmonic interaction between nearest neighbors and \( E_{p2}(\bar{E}) \) is the harmonic interaction between next nearest neighbors.

As already said, we address a 2D lattice in which position vector of the atoms are of the form \( \ell_{1} \bar{a}_{1} + \ell_{2} \bar{a}_{2} \). Here, \( \bar{a}_{1} \) and \( \bar{a}_{2} \) are orthogonal vectors having the same length \( a \), while \( \ell = 0, 1, \ldots N \), \( k = 1, 2 \).

For studying the movements of the atoms, we introduce the orthogonal axes \( \bar{O}_{x} \) and \( \bar{O}_{y} \), parallel to \( \bar{a}_{1} \) and \( \bar{a}_{2} \), respectively, and we call \( u_{\ell} \) and \( v_{\ell} \) the components of the displacement of the atom \( \ell \), along the axes \( \bar{O}_{x} \) and \( \bar{O}_{y} \) respectively.
We assume that $E_{p1}(\lambda, \mu, \nu)$ is given by

$$E_{p1}(\lambda, \mu, \nu) = \frac{1}{2} \sum_\ell E_{p1}(\ell)$$

where

$$E_{p1}(\ell) = \frac{1}{2} \left( e_{\ell,\ell(1)}(u_\ell - u_{\ell(1)})^2 + e_{\ell,\ell(2)}(u_\ell - u_{\ell(2)})^2 + e_{\ell,\ell(4)}(u_\ell - u_{\ell(4)})^2 \right)$$

Here, the first neighbor of atom $\ell = (\ell_1, \ell_2)$ sit at positions $\ell(1) = (\ell_1 + 1, \ell_2)$, $\ell(2) = (\ell_1, \ell_2 + 1)$, $\ell(3) = (\ell_1 - 1, \ell_2)$, $\ell(4) = (\ell_1, \ell_2 - 1)$. The parameter $e_{\ell,\ell(a)}$, with $\alpha = 1, 4$, is the elastic constant of the spring linking the atom $\ell$ and its nearest neighbor $\ell(a)$.

In the atom phonon coupling model it is assumed that $e_{\ell,\ell(a)}$ takes three different values, which are given by:

$$e_{\ell,\ell(a)} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\mu - \nu}{4} (\delta_\ell + \delta_{\ell(a)}) + \frac{\lambda - 2\mu + \nu}{4} \delta_\ell \delta_{\ell(a)}$$

we can verify that the above formula gives $e_{\ell,\ell(a)} = \lambda$ when $\delta_\ell = \delta_{\ell(a)} = -1$, $e_{\ell,\ell(a)} = \nu$ when $\delta_\ell = \delta_{\ell(a)} = +1$, and $e_{\ell,\ell(a)} = \mu$ when $\delta_\ell \neq \delta_{\ell(a)}$. Moreover, it is assumed that $\lambda > \mu > \nu$.

In this contribution, we consider the case in which we may neglect the spin-spin exchange interaction between $\delta_\ell$ and $\delta_{\ell(a)}$, so we have: $\lambda + 2\mu + \nu = 0$.

We assumed that $E_{p2}(\vec{E})$ is given by:

$$E_{p2}(\vec{E}) = \frac{1}{2} \sum_\ell E_{p2}(\ell)$$

where $E_{p2}(\ell)$ is the potential energy between atom $\ell$ and its four nearest neighbors. We assume that the spring constant $\vec{E}$ is independent of the electronic state of the atoms. The explicit form of $E_{p2}(\vec{E})$ can be found in [3].

### 2.1 Variational method : effective parameters

We apply now a variational method [5] and to this end we introduce two parameters, $h$ and $E$. The first one describes a uniform, effective field $h$ and the second one an effective spring constant $E$ that replaces the spring constants $e_{\ell,\ell(a)}$. This $E$ does not depend on the electronic states of the atom. We call our variational Hamiltonian $H_0$. With the partition function related to $H_0$, the thermal mean value of the fictitious spins $\delta_\ell$ is equal to $m$. It verifies the self-consistent equation

$$m = \frac{\exp(-\beta h) + r \exp(\beta h)}{\exp(-\beta h) + r \exp(\beta h)}$$

The thermal variation mean values $\langle (u_\ell - u_{\ell(a)})^2 \rangle$ ($\alpha = 1, 3$) and $\langle (v_\ell - v_{\ell(a)})^2 \rangle$ ($\alpha = 2, 4$) are all set equal to $\langle (u_\ell - u_{\ell(1)})^2 \rangle_0$. This last thermal mean value is calculated for a square lattice with spring constants $E$ and $\vec{E}$. In Eq. (11), $r$ is the denegeracy of the excited level. We consider the case $r=5$.

Minimisation of the variational free energy leads to

$$h = -\frac{\Delta_{eff}}{2} + h_{ph}$$

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

with

$$h_{ph} = \frac{\lambda - \nu}{2} \langle (u_\ell - u_{\ell(1)})^2 \rangle_0$$

$$\Delta_{eff} = P_b \Delta_b + P_{se} \Delta_{se}$$

$$P_b = \frac{N_b}{N}$$

and

$$P_{se} = \frac{N_{se}}{N}$$

as $N_b$ and $N_{se}$ are the numbers of atoms in the bulk and in the periphery, respectively, $\Delta_{eff}$ appears as a kind of mean values between $\Delta_b$ and $\Delta_{se}$. The solutions of the self consistent equation depend on $T$, $N$.
and $\Delta_{eff}$, while all the others parameters of the model remain fixed. The high spin fraction is given by:

$$ n_{HS} = \frac{1+m}{2} $$

(17)

The expression of the crystal free energy is known.

### 2.2 Surface effect

From Eqs. (14, 15, 16) we have

$$ \Delta_{eff} = coef \Delta_{p} $$

(18)

with

$$ coef = P_{h}(1 - rat) + rat $$

(19)

and

$$ rat = \frac{\Delta_{eff}}{\Delta_{p}} $$

(20)

Moreover, the values of $\Delta_{eff}$ for two crystal sizes $N$ and $N'$ are linked by

$$ \Delta_{eff}(N') = \frac{coef(N')}{coef(N)} \Delta_{eff}(N) $$

(21)

### 2.3 Mechanism and Results

We consider crystals with square or nearly square shape. Our model leads to a first order phase transition and so to an hysteresis loop. The phase diagrams of the crystal are shown in Fig.1: in the $(\Delta_{eff}, T)$ plane the (HS)- (LS) coexistence curve has a positive slope because the degeneracy of the LS level is the unit, while that of the HS level is $r = 5$.

![Fig 1. The critical value $\Delta_{eff,c}$ decreases with $N$ for nanoparticles; $\delta_{eff,c}$ is the reduced value of $\Delta_{eff,c}$.

Moreover, the coordinates $(\Delta_{eff,c}, T_{c})$ of the critical point decrease with $N$ for small values of $N$. This is so because the free energy of the lattice vibrations is no longer an extensive parameter. We consider that a crystal size is macroscopic when $N \geq 10^4$. For $rat < 1$, $coef(N)$ and $\Delta_{eff}(N)$ decrease with $N$ (Fig.2). The decrease of $\Delta_{eff}(N)$ leads to the decrease of the transition temperature, since the slope of the coexistence curve is positive.
The transition, and so the hysteresis loop, exists only if
\[ \Delta_{\text{eff}}(N) < \Delta_{\text{eff}}(N) \]
This condition explains the disappearance of the hysteresis loop.

Fig 2 The parameter \( \text{coef}(N) \) decreases with \( N \). It depends on the ratio \( \text{rat} = \frac{\Delta_{\text{se}}}{\Delta_{\text{b}}} \) and on the parameters \( N_{\text{b}} \) and \( N_{\text{se}} \).

Fig 3 Thermal variations of the high spin fraction for \( N=36 \), \( N=120 \) and \( N=10^4 \). The values \( \delta_{\text{eff}}(120), \delta_{\text{eff}}(10^4), \delta_{\text{eff}}(24) \) and \( \delta_{\text{eff}}(16) \) are calculated using Eq. (23) with \( \delta_{\text{eff}}(36) = 0.55 \).
and \( \text{rat}=0.9 \). The values \( \delta_{\text{eff}}(120) \) and \( \delta_{\text{eff}}(10^4) \) are lower than \( \delta_{\text{eff}} c(120) \) and \( \delta_{\text{eff}} c(10^4) \), respectively. While the values \( \delta_{\text{eff}}(24) \) and \( \delta_{\text{eff}}(16) \) are higher than \( \delta_{\text{eff}} c(24) \) and \( \delta_{\text{eff}} c(16) \), respectively. So, the first order phase transition, and so the hysteresis cycle, disappear for \( N \leq 36 \). The values \( \delta_{\text{eff}}(N) \) is the reduced value of \( \Delta_{\text{eff}}(N) \).

The crystal stiffness increasing is taken into account for \( N = 24 \) and \( N = 16 \). The hysteresis loop reappears for \( N = 16 \).

The results are in agreement qualitatively with the experimental results of Forestier \textit{et al} [6]. Those contained in Fig 3 and Fig 4 can be compared to the experimental results of Volatron \textit{et al} and Peng \textit{et al}, respectively [7-8].

3. Conclusion

In this study we have been able to reproduce, at least qualitatively, experimental results which are apparently contradictory, by simply varying the value of the ratio \( \Delta_{\text{se}} / \Delta_{\text{h}} \). Moreover, we have been able to reproduce the reappearance of the hysteresis loop, and to explain how this reappearance is related to the stiffness increase of the crystal.

In order to study the influence of the crystal shape, we start from a square shape, which displays an hysteresis loop and we progressively increases one side, \( N \) being constant. The results depend on the value of \( N \). For a small value of \( N \), the critical value \( \Delta_{\text{eff}} c(N) \) decreases faster than \( \Delta_{\text{eff}} (N) \) and this eliminates some hysteresis loops. So the hysteresis loop observed in a sample with small values of \( N \), is the result of summing up a few number of hysteresis loops which are alike.

For the case \( N = 10^4 \), the critical value \( \Delta_{\text{eff}} c(10^4) \) does not vary when the shape varies, while \( \Delta_{\text{eff}} (N) \) decreases. So, all the crystals with rectangular shape display an hysteresis loop. Consequently, the hysteresis loop observed in a sample with large values of \( N \), is the result of summing up many hysteresis loops, all of them having different transition temperature values.

Finally, it is worth to mention that, in this study, all the molecules in a crystal are in their fundamental level at 0K. As the degeneracy of this level is the unit, the entropy of the crystal is equal to zero at 0K, in agreement with the third law of thermodynamics. It is worth to recall that the role of edge atoms and
the size effects on SCO have also been studied by Linares et al. and by Chiruta et al. [9-12] in the framework of the Ising Model.

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