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Diluted spin conversion compounds behaviours in the atom-phonon coupling model: case of not too large dilution

Role of the Lennard-Jones potential?

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Abstract. We use an atom-phonon coupling model, introduced recently for spin-conversion phenomenon, in order to describe the behaviours of diluted spin conversion compounds. We keep the basic assumption of the model which is that the interaction between two molecules is harmonic and that the value of the elastic force constant of this interaction is reduced when one molecule becomes High-Spin. The main features of the experimental behaviours of diluted spin conversion compounds are qualitatively reproduced. This model can be founded on the Lennard-Jones potential between molecules.

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1 Introduction

Spin conversion (SC) compounds are molecular complexes in which the central ion, a transition metal ion, exhibits a low-spin state (LS) $\longleftrightarrow$ high-spin state (HS) crossover when the temperature increases. Due to the metallic ion ligand field and to the pairing energy, the central ion energy diagram displays a fundamental level with a spin value which is less than that of the first excited level [1–4]. For example, for iron(II) complexes, the low spin value is $S = 0$ and the high spin one is $S = 2$. For these complexes, Δ, the distance in energy between both levels, is typically 1000 K.

Mössbauer spectroscopy, magnetic susceptibility measurements, X-ray diffraction, FIR spectroscopie, differential scanning calorimetry (DSC) and heat capacity measurements allow to obtain data on (SC) phenomenon [1,5–11]. From such studies, one can deduce, for example, the thermal variation of n_{HS}, the (HS) fraction, that is the fraction of transition metal in the high spin level.

The high spin fraction function, $n_{\mathrm{HS}}(T)$, deviates from a Boltzmann population law and can display two different behaviours [4,12–14]: (i) either n_{HS} increases continuously with increasing temperature and does not show a thermal hysteresis; (ii) or n_{HS} shows with increasing temperature a discontinuity and a thermal hysteresis, which is characteristic of a first order phase transition (called spin transition).

Other external factors than temperature, such as pressure, magnetic field and light irradiation, can induce (LS)$\longleftrightarrow$ (HS) crossover [15–19].

In some compounds, a "two-step" spin-conversion can be observed with or without first order phase transition. In such compounds, the high spin fraction increases smoothly in a range of temperature of few kelvin [7,12,20,21].

It is worth noticing an increasing interest in (SC) compounds for these material have many potential applications in nanotechnology, for example, in information storage, processing devices or pressure sensors [20,21,30–32].

In order to know more about the interactions between molecules, studies have been done on (SC) crystalline compounds in which the central ion is replaced by a transition metal ion, M, which keeps the same spin state over the scanned temperature range [22–29]. Such studies have been performed when the central ion is iron (II) or iron (III).

The principal effects of the dilution of the iron ion are the following:

- when the pure (SC) compound displays a first order transition, this transition disappears for a large enough concentration of the metal M;
- when it displays a continuous spin crossover, the conversion curve, that is the curve which represent the $n_{\mathrm{HS}}(T)$ function, is generally shift towards low temperature values and its slope is reduced.

Recently it has been shown that the main features of the experimental behaviours of non diluted spin conversion crystalline compounds can be qualitatively reproduced by

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using a microscopic model based on an atom-phonon coupling mechanism [33,34]. In this model, the (SC) compounds molecules are modeled as atoms, each with two electronic states, a (LS) ground state, and a (HS) excited state. It is assumed that the interaction between two first neighbours atoms is harmonic and that the elastic force constant of this interaction has values which depend on the electronic states of both atoms. Those values are chosen such as to favour the (HS) level. Thus, it is assumed that the elastic force constant value is reduced when one atom becomes (HS). Then, the thermal variation of the high spin fraction results from the competition between the electronic parameter Δ which favours the (LS) level and the lattice acoustic phonons which favour the (HS) level. The model is performed on a linear chain of atoms. The aim of this article is to use this model in order to interpret the dilution effects. So, we use the previous assumption which is that the elastic force constant value between two atoms is reduced when one atom becomes (HS).

In Section 2 we present the model and the chain Hamiltonian, in Section 3 we describe the study method used, in Section 4 we give the obtained results and the last section is devoted to discussion and conclusion.

2 The model and the chain Hamiltonian

Let us consider a linear chain of N atoms, consisting of two kinds of atoms: atoms which we call M and atoms which we call Fe. We suppose that M atom has only one electronic energy level and that Fe atom has two electronic energy levels (LS) and (HS) (others levels can't be occupied). The degeneracy of the fundamental level, (LS), is $g_{(\mathrm{LS})} = 1$ and that of the excited level, (HS), is $g_{(\mathrm{HS})} = r$. We call Δ the difference in energy between the two levels. To each Fe atom we associate a fictitious-spin $\hat{\sigma}$ which has two eigen-values $\sigma = \pm 1$. Eigenvalue -1 (resp.$+1$) corresponds to electronic level (LS) (resp. (HS)).

Neighbouring atoms i and $i{+}1$ ($i = 1$ to N) are assumed to interact with an elastic force constant $k_{i,i+1}$. We assume the periodic conditions, so the atom N is elastically linked to the atom 1.

The total Hamiltonian of the chain is then the sum:

$$H = H_{spin} + H_{phonon} \tag{1}$$

where the spin Hamiltonian, H_{spin}, is

$$H_{spin} = {\sum_i}' \frac{\Delta}{2} \hat{\sigma}_i \tag{2}$$

where $\sum'$ corresponds to the summation on the Fe atoms. The phonon Hamiltonian H_{phonon} is

$$H_{phonon} = E_c + E_p \tag{3}$$

E_c is the total kinetic energy of the chain and E_p its elastic potential energy. The kinetic energy can be written

$$E_c = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} \tag{4}$$

where p_i is momentum of atom i, and m_i its mass. The mass of atom i is equal to m_{Fe}, when this atom is a Fe atom, and to m_{M} when it is a M atom.

The potential energy can be written

$$E_p = \sum_{i=1}^{N} \frac{1}{2} k_{i,i+1} (u_{i+1} - u_i)^2. \tag{5}$$

In this expression, u_i is the displacement of the ith atom from its equilibrium position which we assume to be independent of the electronic states of the atoms. Due to the periodic condition, $u_{p+N} = u_p$ for $p = 1, 2, \ldots, N$.

We assume that the elastic force constant $k_{i,i+1}$ is equal to $e_{i,i+1}$ when atoms i and $i{+}1$ are both Fe atom, to $\eta_{i,i+1}$ when one of both atoms is Fe atom and the other M atom and to k_3 when both atoms are M atoms.

For $e_{i,i+1}$ we use the assumptions done for non diluted compounds [33,34]. Thus, $e_{i,i+1}$ is equal to λ when both Fe atoms are in (LS) state (or in the fundamental level), to ν when both are in (HS) state (or in the excited level) and to μ when one atom is in the (LS) level and the other in the (HS) level. Moreover we assume that

$$\lambda > \mu > \nu. \tag{6}$$

For $\eta_{i,i+1}$, the elastic force constant between a Fe atom and a M atom first neighbour, we assume that it is equal to k_1 when the Fe atom is (LS) and to k_2 when it is (HS).

The expression of $e_{i,i+1}$ in terms of the fictitious spins of the atoms i and $i{+}1$ is [33]

$$e_{i,i+1} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4} (\hat{\sigma}_i + \hat{\sigma}_{i+1}) + \frac{\lambda - 2\mu + \nu}{4} \hat{\sigma}_i \hat{\sigma}_{i+1}. \tag{7}$$

Using this expression of $e_{i,i+1}$ in the relation (5), $E_{p(\mathrm{Fe-Fe})}$, the elastic potential energy between two Fe atoms first neighbours, i and $i{+}1$, can be decomposed as

$$E_{p(\mathrm{Fe-Fe})} = V_0 + V_1 + V_2 \tag{8}$$

with

$$V_0 = \frac{\lambda + 2\mu + \nu}{8} (u_{i+1} - u_i)^2 \tag{9}$$

$$V_1 = \frac{\nu - \lambda}{8} (u_{i+1} - u_i)^2 (\hat{\sigma}_i + \hat{\sigma}_{i+1}) \tag{10}$$

and

$$V_2 = \frac{\lambda - 2\mu + \nu}{8} (u_{i+1} - u_i)^2 \hat{\sigma}_{i+1} \hat{\sigma} i.$$

In the energy term V_1, each spin appears as submitted to a field-like term which depends on the atoms displacements. In V_2 two spins first neighbours appear as coupled by an exchange-like term which also depends on the atoms displacements.

The expression of $\eta_{i,i+1}$ in terms of the fictitious-spin of the Fe atom is

$$\eta_{i,i+1} = \frac{k_1 + k_2}{2} + \frac{k_2 - k_1}{2} \hat{\sigma}_i. \tag{11}$$

In this expression it is assumed that the atom i is the Fe atom.

Using the relation (11) in the relation (5), $E_{p(\mathrm{Fe-M})}$, the elastic potential energy between a Fe atom, i, and a M atom first neighbour, $i{+}1$, can be decomposed as

$$V_3 = \frac{k_1 + k_2}{4}(u_{i+1} - u_i)^2 \tag{12}$$

and

$$V_4 = \frac{k_2 - k_1}{4}(u_{i+1} - u_i)^2 \hat{\sigma}_i. \tag{13}$$

In the energy term V_4, the Fe atom fictitious spin, $\hat{\sigma}_i$, appears as submitted to a field-like term which depends on the atoms displacements.

In the next section, we study the chain Hamiltonian.

3 Effective elastic force constant K

3.1 Self-consistent equations

We have studied the chain Hamiltonian H, (Eq. (1)), by using a variational method [35,36]. We introduce a variational Hamiltonian H_0 which is easy to study and which depends on a few number of parameters. We write

$$H = H_0 + H - H_0. \tag{14}$$

By considering $(H - H_0)$ as a perturbation as compared to H_0, it is possible to calculate $\tilde{F}$, the free energy associated to H. At the first order

$$\tilde{F} = F_0 + \langle H - H_0 \rangle_0 \tag{15}$$

where F_0 is the free energy associated to H_0 and $\langle H - H_0 \rangle_0$ is the thermal mean value of $H - H_0$ calculated by using the density matrix associated with H_0 at temperature T.

For H_0 we take a periodic Hamiltonian:

$$H_0 = H_{0s}(h, J) + H_{0ph}(K, m_a) \tag{16}$$

with

$$H_{0s}(h, J) = \sum_{i=1}^{N} -h\hat{\sigma}_i + \sum_{i=1}^{N} -J\hat{\sigma}_i\hat{\sigma}_{i+1} \tag{17}$$

and

$$H_{0ph}(K, m_a) = \sum_{i=1}^{N} \frac{p_i^2}{2m_a} + \sum_{i=1}^{N} \frac{K}{2}(u_{i+1} - u_i)^2. \tag{18}$$

The Hamiltonian $H_{0s}(h, J)$ is that of a linear chain of N fictitious spins in presence of an uniform field, h, and interacting with an exchange constant, J, which is the same between any first neaghbours pair.

As for the Hamiltonian $H_{0ph}(K, m_a)$, it is that of a linear chain of N atoms, with equal masses, m_a, attracting one another with an elastic force constant K.

The Hamiltonian $H_{0s}(h, J)$ can be studied by using the transfer matrix method [37]. Using this method, F_{0s}, the free energy related to $H_{0s}(h, J)$, is

$$F_{0s} = -NkT\frac{\ln r}{2} - NkT \ln A \tag{19}$$

with

$$A = \exp(\beta J) \cosh \beta h_r + \sqrt{B} \tag{20}$$

and

$$B = \exp(2\beta J) \sinh^2 \beta h_r + \exp(-2\beta J). \tag{21}$$

In the above relations, kT is the thermal energy, $\beta = \frac{1}{kT}$ and

$$h_r = h + kT\frac{\ln r}{2}. \tag{22}$$

The relation (22) takes into account the degeneracy of the excited level ((HS) level).

Since the field h and the exchange constant J are independent of the site i, the mean values $\langle \hat{\sigma}_i \rangle$ and $\langle \hat{\sigma}_i \hat{\sigma}_{i+1} \rangle$ are independent of the site i. So, we introduce the parameters m and s defined by

$$m = \langle \hat{\sigma}_i \rangle \text{ for } i = 1, N \tag{23}$$

and

$$s = \langle \hat{\sigma}_i \hat{\sigma}_{i+1} \rangle \text{ for } i = 1, N. \tag{24}$$

In the transfer matrix method the parameters m and s verify [37]

$$m = \frac{\exp(\beta J) \sinh \beta h_r}{\sqrt{B}} \tag{25}$$

and

$$s = 1 - \frac{2\exp(-2\beta J)}{A\sqrt{B}}. \tag{26}$$

The expression of F_{0ph}, the free energy related to the phonon Hamiltonian, $H_{0ph}(K, m_a)$, is well known. It is given by

$$F_{0ph} = kT \sum_{\alpha} \ln\left(2 \sin h\beta\frac{\hbar\omega_\alpha}{2}\right) \tag{27}$$

where $\sum_\alpha$ is the sum over phonon normal modes. The frequencies of the normal modes are given by

$$\omega_\alpha = \omega_{\mathrm{M}}(K, m_a)) \left|\sin \frac{\alpha\pi}{N}\right| \tag{28}$$

where $\alpha = 0, \pm 1, \pm 2, ..., \pm(\frac{N}{2} - 1), \frac{N}{2}$. The maximum frequency is given by

$$\omega_{\mathrm{M}}(K, m_a) = 2\sqrt{\frac{K}{m_a}}. \tag{29}$$

The free energy associated to H_0 is then

$$F_0 = F_{0s} + F_{0ph}. \tag{30}$$

As mentioned previously, the free energy associated to H is

$$\tilde{F} = F_0 + \langle H - H_0 \rangle_0. \tag{31}$$

It is clear that $\tilde{F}$ depends on the temperature, on the parameters introduced in H_0, that is h, J, K and m_a, and on the parameters contained in H. To improve our approximation, we must choose the parameters introduced in H_0 such as to minimize the function $\tilde{F}(h, J, K, m_a)$, the temperature and the parameters introduced in H being constant.

The minimization of $\tilde{F}$ versus the variational parameters h, J, m_a and K, leads to the equations:

$$\frac{1}{m_a} = (1 - c_1)\frac{1}{m_{\mathrm{Fe}}} + c_1\frac{1}{m_{\mathrm{M}}} \tag{32}$$

where c_1 is the concentration of M atoms in the chain. Calling N_1 the number of M atoms in the chain,

$$c_1 = \frac{N_1}{N} \tag{33}$$

$$K = (1 - 2c_1 + c_2)\langle e_{i,i+1}\rangle + 2(c_1 - c_2)\langle \eta_{i,i+1}\rangle + c_2k_3 \tag{34}$$

where c_2 is the concentration of sets (M-M), that is the concentration of pairs of atoms M which are first neighbours. If we call N_2 the number of sets (M-M) in the chain, c_2 is given by

$$c_2 = \frac{N_2}{N}. \tag{35}$$

The thermal mean values contained in the relation (34) are given by

$$\langle \eta_{i,i+1}\rangle = \frac{k_1 + k_2}{2} + \frac{k_2 - k_1}{2}m \tag{36}$$

and

$$\langle e_{i,i+1}\rangle = \frac{2\mu + \lambda + \nu}{4} + \frac{\nu - \lambda}{2}m + \frac{\lambda - 2\mu + \nu}{4}s. \tag{37}$$

The parameters h and J are given by

$$\begin{aligned} h = -(1 - c_1)\frac{\Delta}{2} &+ \frac{3\langle H_{0ph}(K, m_a)\rangle}{4NK} \\ &\times ((1 - 2c_1 + c_2)(\lambda - \nu) + 2(c_1 - c_2)(k_1 - k_2)) \end{aligned} \tag{38}$$

and

$$J = -(1 - 2c_1 + c_2)(\lambda - 2\mu + \nu)\frac{3\langle H_{0ph}(K, m_a)\rangle}{8NK}. \tag{39}$$

In the above relations we have taken into account the three phonon polarizations. For simplicity, we have assumed that the phonon energy is independent of the polarization [33].

Inserting in $\tilde{F}$ the expressions of h, J, m_a and K given by the equations (32, 34, 38 and 39), we obtain F, the chain free-energy corresponding to the approximation made in this study. The expression of F is given in Appendix A.

When the elastic force constants values, the masses and the degeneracy r are fixed, the free-energy is only a function of Δ and T. The expression of the free-energy differential and that of the chain entropy are given in Appendix A.

3.2 Chain isotherms study

To solve numerically the self-consistent equations (Eqs. (25) and (26)), we take $\hbar\omega_{\mathrm{M}}(\lambda)$ as the unit of energy and λ as the unit of elastic force constant value. We introduce the following reduced parameters:

- the reduced temperature t

$$t = \frac{kT}{\hbar\omega_{\mathrm{M}}(\lambda)} \tag{40}$$

- the reduced electronic excitation energy δ

$$\delta = \frac{\Delta}{\hbar\omega_{\mathrm{M}}(\lambda)}. \tag{41}$$

We also introduce the dimensionless parameters:

- the elastic force constants ratio x

$$x = \frac{\nu}{\lambda} \tag{42}$$

- the parameter y defined by

$$\mu = \frac{\lambda + \nu}{2} + \frac{\lambda - \nu}{2}y. \tag{43}$$

Due to the assumptions made on the elastic force constant values for the non diluted chain [33,34], the parameters x and y must verify the conditions

$$0 < x < 1 \tag{44}$$

and

$$-1 < y < 1. \tag{45}$$

By solving numerically the self-consistent equations, we have studied the chain isotherms in the δ-m plane. This study allows us to obtain the coordinates δ_C and t_C of the chain critical points, and to obtain, for $t < t_C$, the values of δ at the first order phase transition. Consequently, we can deduce the chain phase diagram in the δ-t plane. From this phase diagram we can predict the thermal behaviour of the parameter m. Indeed, the thermal variation of m displays a discontinuity when the value of the chain parameter δ is lower than the critical value δ_C, and this thermal variation is continuous when the δ value is higher than the δ_C value (see liquid gas transition in the pressure-temperature phase diagram).

4 Results

The role of the phonon parameters λ, μ and ν has been already studied in the case of the non diluted chain [33,34]. So, in this article we are essentially concerned by the role of the parameters k_1, k_2 and k_3. Following the basic assumption of the model, we take

$$k_2 \neq k_1 \tag{46}$$

and we introduce the elastic force constants ratio z

$$z = \frac{k_2}{k_1} = \frac{k_{(\mathrm{HS-M})}}{k_{(\mathrm{LS-M})}} \tag{47}$$

with

$$z < 1. \tag{48}$$

For lack of information and for simplicity, in this study we take

$$k_1 = k_3 = \lambda. \tag{49}$$

As for the masses, we admit that

$$m_{\mathrm{Fe}} = m_{\mathrm{M}}. \tag{50}$$

Indeed, when, in a (SC) molecule, we replace iron by cobalt or by another transition metal, the relative variation of the molecule mass is small, near of 0.005.

4.1 Chain phase diagram in the δ-t plane

For $x = 0.2$ and $y = 0.00$ the non diluted chain displays a first order phase transition between the (LS) and the (HS) states and the transition line does not display in the δ-t plane a critical point [33]. In this article, we have studied how that transition line is modified when the parameters c_1, c_2 and z vary. In the Figures 1 to 7, $x = 0.20$ and $y = 0.00$. In the numerical study the size of the chain is $N = 2000$.

When Fe atoms are progressively replaced by M atoms the transition line is shift and a critical point appears. The numerical study allows to separate the role of the parameter z from that of the parameter c_2.

The position of the chain transition line and that of the critical point for different values of the parameters c_1 and z are shown in Figure 1. In this figure, c_2 is kept equal to zero; that means that there is no set (M-M), or no pair of M atoms first neighbours.

As shown in the Figure 2, the position of the transition line and that of the critical point in the δ-t plane depends also on the value of c_2. For the following, we use for c_2 the value

$$c_2 = \frac{N_1}{N}\frac{N_1 - 1}{N - 1}. \tag{51}$$

As N and N_1 are large compared to the unit, we can take

$$c_2 = c_1^2. \tag{52}$$

That value of c_2 corresponds to the mean value of the number of set (M-M) in the chain, the mean value being taken on all the chain configurations.

The chain transition lines for different values of c_1, the M atom concentration, are shown in the Figure 3 for $z = 0.48$ and in the Figure 4 for $z = 0.46$.

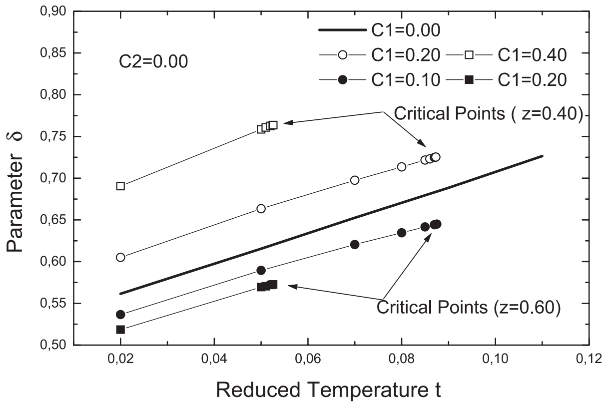

Fig. 1. Dilution effect on the chain phase diagram in the δ-t plane for different values of c_1 and of the ratio $z = \frac{k_{(\mathrm{HS-M})}}{k_{(\mathrm{LS-M})}}$. In Figures 1 to 4, the black full line is the first order phase transition line for the non diluted chain; this transition line is not ended by a critical point;the chain is (HS) (resp. (LS)) below (resp. above) this line. Dilution shifts the transition line toward high (low) values of δ for low (high) values of z. Moreover critical point appears with the dilution.

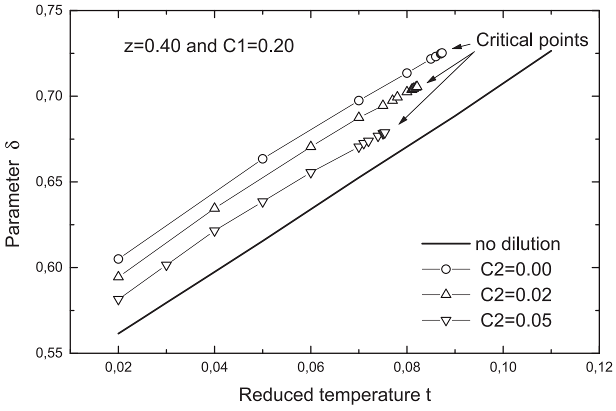

Fig. 2. Influence of the parameter c_2 on the chain phase diagram. When c_2 increases the transition line is shift toward small values of δ and the coordinates, δ_C and t_C of the critical point, decrease. For now on we set $c_2 = c_1^2$.

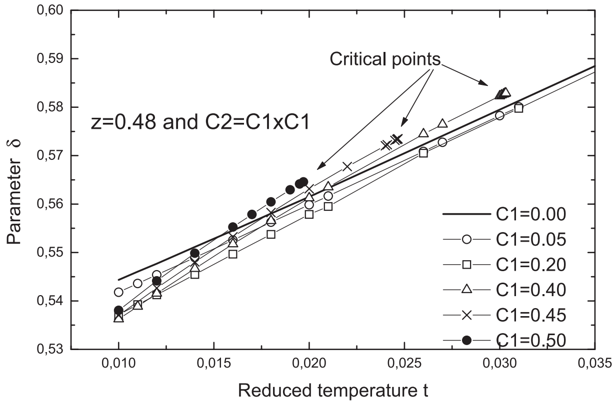

Fig. 3. Phase diagrams of the diluted chain for $z = 0.48$ and for different values of c_1. The coordinates of the critical point decreases when the dilution increases. As shown in the figure, the abscissa of the intersection points between these transition lines with the horizontal line $\delta = 0.573$ are close each other.

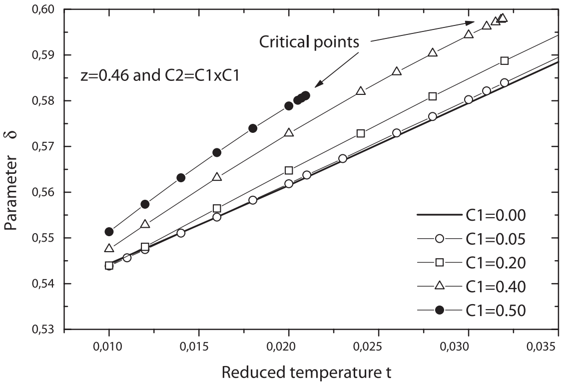

Fig. 4. Phase diagrams of diluted chain for $z = 0.46$ and for different values of c_1. The coordinates of the critical point decreases when the dilution increases. As shown in the figure, the abscissa mentioned in Figure 3 are more separated.

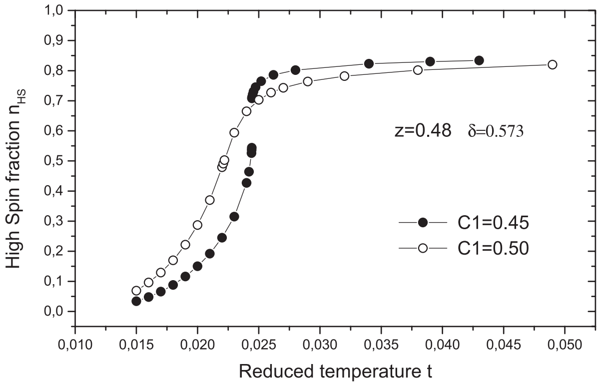

Fig. 5. Thermal variations of n_{HS} for $z = 0.48$. For $c_1 = 0.45$ (solid circle) the chain displays a first order phase transition at the transition temperature value $t_{\mathrm{HS}} = 0.02443$. For $c_1 = 0.50$ (open circle) the conversion is continuous and $t_{\frac{1}{2}} = 0.02217$. So the threshold value c_{1s} (see text) is comprised between 0.45 and 0.50 for $z = 0.48$.

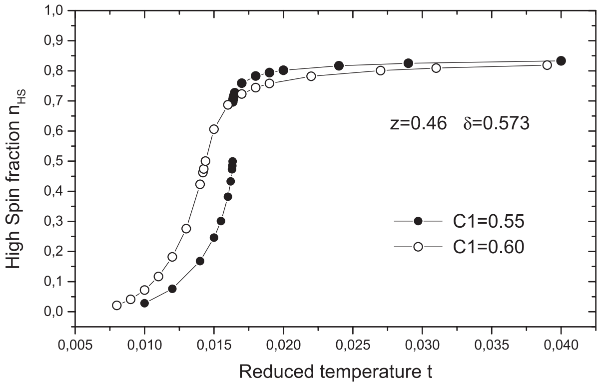

Fig. 6. Thermal variations of n_{HS} for $z = 0.46$. For $c_1 = 0.55$ (solid circle) the chain displays a first order phase transition at $t_{\mathrm{HS}} = 0.01634$. For $c_1 = 0.60$ (open circle) the conversion is continuous and $t_{\frac{1}{2}} = 0.01439$. So the threshold value c_{1s} is comprised between 0.55 and 0.60 for $z = 0.46$.

4.2 Thermal variation of the high-spin fraction

Let us call N_+ and N_- the numbers of Fe atom in the (HS) and (LS) states respectively. It is clear that

$$n_{\mathrm{HS}} = \frac{N_+}{N - N_1} \tag{53}$$

where $N - N_1$ is the number of Fe atoms in the chain. Moreover we have

$$N_+ + N_- = N - N_1 \tag{54}$$

and

$$(N - N_1)m = N_+ - N_-. \tag{55}$$

From the above equations we deduce

$$n_{\mathrm{HS}} = \frac{1+m}{2}. \tag{56}$$

So the expression of n_{HS} as a function of m is the same for the diluted chain as for the non diluted one.

In order to calculate the thermal variation of the high-spin fraction, we fix the values of the phonon parameters (x, y, z), that of the electronic parameters $(\delta,\ r)$ and that of the dilution parameters $(c_1, c_2 = c_1^2)$, and we solve the self-consistent equations for different temperature values.

When the spin conversion takes place through a first order phase transition our numerical study shows the existence of thermal hysteresis. However, the calculated thermal hysteresis can't be compared to the observed one. So, in this study, we only display the stable thermodynamic states. So, in the case of first order phase transition, the (HS) fraction displays a discontinuity at t_{HS}, the transition temperature value.

When the spin conversion is continuous, the thermal variation of (HS) fraction is characterized by the temperature value $t_{\frac{1}{2}}$ which is the temperature at which $n_{\mathrm{HS}} = 0.5$.

We have studied the thermal variations of n_{HS} for the phase diagrams displayed in Figures 3 and 4 (we recall that $x = 0.20$, $y = 0.00$ and $r = 5$). For the value of the chain parameter δ, we have taken a value independent on the values of z and of c_1. Let 0.573 be this value, so $\delta = 0.573$.

In Figures 3 and 4, it is clear that the coordinates δ_C and t_C of the critical points are depending on the values of the parameters z and c_1. Moreover, when z is fixed, δ_C is a decreasing function on c_1.

Consider first, the case $z = 0.48$ (Fig. 3). The δ_C values are 0.57348 and 0.56458 for the transition lines corresponding to $c_1 = 0.45$ and $c_1 = 0.50$ respectively. As the critical value 0.57348 is higher than the chain δ value, 0.573, the thermal variation of n_{HS} is discontinuous for $c_1 = 0.45$. But, as the value 0.56458 is lower than the chain δ value, the thermal variation of n_{HS} is continuous for $c_1 = 0.50$. Those results are shown in Figure 5.

Moreover, in Figure 3 ($z = 0.48$), as the value of δ_C decreases when c_1 increases, it is clear that there is a threshold concentration value, c_{1s}, such as for $c_1 < c_{1s}$ the thermal variation of n_{HS} is discontinuous and for $c_1 > c_{1s}$ this thermal variation is continuous. Following the results obtained for $c_1 = 0.45$ and $c_1 = 0.50$, it is clear that that threshold value, c_{1s}, is comprised between 0.45 and 0.50.

The values of $t_{\rm HS}$ for $z = 0.48$ and c_1 varying from zero to 0.45 are shown in Figure 7. We have also reported in this figure the value of $t_{\frac{1}{2}}$ for $c_1 = 0.50$.

All that said for Figure 3, can be repeated for Figure 4 ($z = 0.46$). Only the value of the threshold concentration is different. As shown in the Figure 6, the thermal variations of $n_{\rm HS}$ is discontinuous for $c_1 = 0.55$ while it is continuous for $c_1 = 0.60$. So, for $z = 0.46$, the value of the threshold concentration is comprises between 0.55 and 0.60.

The values of $t_{\rm HS}$ for $z = 0.46$ and c_1 varying from zero to 0.55 are shown in Figure 7. We have also reported in this figure the value of $t_{\frac{1}{2}}$ for $c_1 = 0.60$.

The "two-step" spin conversion observed in non diluted (SC) compound [7] has been reproduced in the atom phonon coupling model by taking for the parameters x, y, δ and r the respective values 0.20, −0.20, 0.606 and 5 [34].

For the diluted chain, keeping the above parameters values and taking for z the value 0.40, we have calculated the thermal variation of $n_{\rm HS}$ for c_1 equal to 0.11 and 0.22. The results are shown in Figure 8. Our results look like those observed by Köhler et al. [12].

5 Discussion and conclusion

Martin et al. have studied iron(II) dilution by nickel(II) and cobalt(II) in the (SC) compound $[\mathrm{Fe}(btr)_2(\mathrm{NCS})_2]\cdot\mathrm{H_2O}$ with $(btr = 4,4'-bis-1,2,4-triazole)$ [27] to [29]. In their studies, for the non diluted compound, the thermal variation of $n_{\rm HS}$ displays a thermal hysteresis which indicates a first order transition. Due to this hysteresis, the authors can't determine the compound transition temperature. They determine $T_C\uparrow$ and $T_C\downarrow$ which are the temperatures at which the (HS) fraction, $n_{\rm HS}$, is equal to 0.5 in the heating mode and the cooling mode respectively. And they assume that the transition temperature value is the mean value of $T_C\uparrow$ and $T_C\downarrow$.

When iron(II) is progressively replaced by Ni(II) the hysteresis width progressively diminishes and vanishes for a Ni concentration near of 0.55, and the mean value of $T_C\uparrow$ and $T_C\downarrow$ is constant whatever the concentration in Ni(II) between 0.00 and 0.55. For a Ni concentration larger than 0.55, the (SC) is continuous. For a Ni concentration equal to 0.60 they have found for $t_{\frac{1}{2}}$ a value equal to the previous mean value.

When iron(II) is progressively replaced by Co(II) they found that the first order transition disappears for a Co concentration near of 0.63 and that the mean value of $T_C\uparrow$ and $T_C\downarrow$ decreases. When the Co concentration increases from 0.00 to 0.45 the relative decrease of this mean value is near of 20 per cent.

In Figure 7 we see that the chain first order phase transition disappears for a M atom concentration comprises between 0.45 and 0.50 for $z = 0.48$ and between 0.55 and 0.60 for $z = 0.46$. Moreover, when the M atom concentration increases from 0.00 to 0.45, the relative decrease of the transition temperature is equal to 7.5 per cent for $z = 0.48$ and to 28.5 per cent for $z = 0.46$. So our results look like those of Martin et al. if we consider that the case $z = 0.48$ corresponds to the dilution with Ni, and the case $z = 0.46$ to the dilution with Co. So, in framework of the atom-phonon coupling model, dilution with Ni and with Co leads to two different behaviours because

$$k_{(\rm HS-Ni)} > k_{(\rm HS-Co)} \tag{57}$$

where $k_{(\rm HS-Ni)}$ is the value of the elastic force constant between a molecule having for central ion an Fe ion in its HS state and a molecule having for central ion a Ni ion, and $k_{(\rm HS-Co)}$ is defined in the same way.

It is worth noticing that in Figure 7, in the case $z = 0.48$, the transition temperature increases for low concentrations of M atom. Or, in some (SC) compounds, iron dilution shifts toward high temperature values the curve representing the function $n_{\rm HS}(T)$. Moreover, in our study,

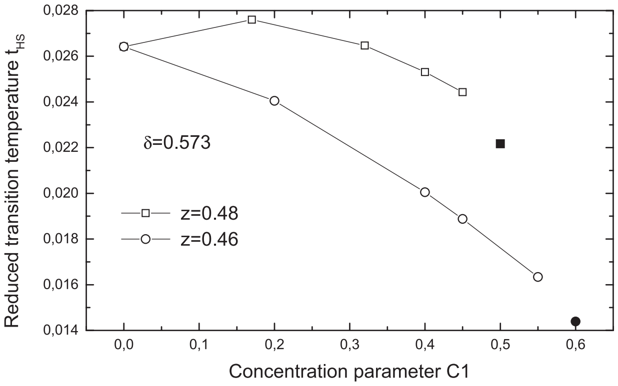

Fig. 7. Variation of $t_{\rm HS}$, the chain transition temperature value with c_1 for $z = 0.48$ (open squares) and for $z = 0.46$ (open circles). It is worth noticing that the relative variation of $t_{\rm HS}$ is much larger for $z = 0.46$ than for $z = 0.48$. For $c_1 > c_{1s}$, the conversion is continuous and the abscissa of the solid square (resp. circle) is the value of $t_{\frac{1}{2}}$ for z equal to 0.48 (resp. 0.46).

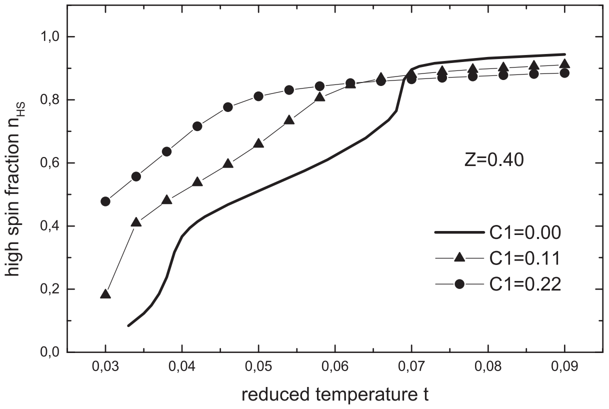

Fig. 8. Effect of dilution on the high spin fraction in the case of the "two-steps" spin conversion. The full line corresponds to the non diluted chain. It is obtained for $x = 0.2$, $r = 5$, $y = -0.20$, $\delta = 0.606$ and $N = 2000$ (see [35]). Taking $z = 0.40$ we can qualitatively reproduce the behaviour observed by Köhler et al. [12].

this small effect can be suppressed by taking for z a value lightly smaller than 0.48.

In the case of dilution with Co, Martin et al. have observed at very low temperature an amount of residual high-spin form which gets larger for a concentration value in Co higher than 0.60. Such result which have not been obtained in the present study could be obtained by modifying the value of the parameter k_3 of the model. However, as shown in the equation (34), this parameter is multiplied by the weight c_2 which is large only for large dilution. Or, the method used in this article is based on the assumption that the Fe atom dilution is not too large. So, the presence or not of residual high-spin form at low temperature can't be done in this study. We underline that the parameter k_3 of the model, corresponds to the elastic force constant $k_{(\mathrm{Co-Co})}$ or $k_{(\mathrm{Ni-Ni})}$ in the studies of Martin et al.

From our study, we can conclude that the atom-phonon coupling model allows us to reproduce qualitatively the high spin fraction thermal behaviours observed in diluted spin conversion compounds.

We recall that the basic assumption of this model is that the elastic force constant value between two atoms is reduced when one atom becomes (HS). Now, we can ask why this elastic force constant value varies?

Let us consider the Lennard-Jones potential between two molecules of a (SC) compound. The pair potential energy is

$$U = \frac{A}{r^{12}} - \frac{B}{r^6}. \tag{58}$$

This energy form has a repulsive potential energy (or Fermi term) and a van der Waals attractive term. The values of the A and B positive constants depend on both molecules and r is the distance between both molecules.

The equilibrium value of the intermolecular distance, d, is found by setting the derivative of U with respect to r equal to zero. Thus

$$\frac{dU}{dr} = 0 = \frac{-12A}{r^{13}} + \frac{6B}{r^7} \tag{59}$$

from which

$$d = \left(\frac{2A}{B}\right)^{\frac{1}{6}}. \tag{60}$$

The value of the elastic force constant for vibrations around the equilibrium distance is equal to the value, for $r = d$, of the second derivative of U with respect to r. Thus calling k this elastic constant value

$$k = \frac{156A}{d^{14}} - \frac{42B}{d^8}. \tag{61}$$

From the equation (60) we can express A as

$$A = \frac{Bd^6}{2}. \tag{62}$$

Reporting this value of A in the equation (61) we obtain

$$k = 36\frac{B}{d^8}. \tag{63}$$

It is well known that in (SC) compound the size of a molecule increases when it becomes (HS). So the equilibrium distance between two molecules increases when one or both become (HS). So we have

$$d_{(\mathrm{HS-HS})} > d_{(\mathrm{HS-LS})} > d_{(\mathrm{LS-LS})}. \tag{64}$$

So, if we assume that the van der Waals constant B does not vary or does not vary too much when one or both molecules become (HS), one can conclude from the relations (63) and (64) that in a non diluted compound

$$k_{(\mathrm{HS-HS})} < k_{(\mathrm{HS-LS})} < k_{(\mathrm{LS-LS})} \tag{65}$$

which is the assumption made in the atom phonon coupling model for non diluted (SC) compound.

In the present study, analyzing the results obtained by Martin et al. we have concluded that $k_{(\mathrm{HS-Co})} < k_{(\mathrm{HS-Ni})}$. Following the previous discussion, this relation can be due to the fact that in the compound studied by Martin et al.

$$d_{(\mathrm{HS-Co})} > d_{(\mathrm{HS-Ni})}. \tag{66}$$

It will be interesting to determine for the (SC) compound studied by Martin et al. the sizes of the molecules containing Co and Ni ion. Such study can be done by ab initio calculations.

As pointed by Sorai [38], there are in molecular compounds different types of first order phase transitions which are accompanied with a change in the electronic state of the molecules, and (SC) compounds are only one of those types. In the case of (SC) compounds the change of the electronic state leads to vary the Fermi parameter, i.e. parameter A, in the Lennard-Johns potential. We can imagine that, in others types, it is the van der Waals parameter, i.e. parameter B, which varies in such a way that we can describe the experimental results by using the atom phonon coupling model.

In this article as in the two previous one [33,34], we have only taken into account the inter-molecular vibrations. Or, it is known that some frequencies of intra-molecular vibrations decrease when the molecule become (HS). So the atom-phonon coupling model can be extended so as to include the intra-molecular vibrations. However, it is worth noticing that the lowest frequencies values of the inter-molecular vibrations are near of zero, while the values of the intra-molecular vibrations frequencies are typically 400 K. So, the intra-molecular vibrations frequencies are less excited at low temperature than those of the inter-molecular vibrations.

We are indebted to L. Chassagne and D. Haddad for their help.

Appendix A

A.1: Chain thermodynamic function

In the used approximation, F, the chain free-energy is

$$F = -NkT\left(\frac{Lnr}{2} + \ln A\right) + 3kT\sum_{\alpha}\ln\left(2\sinh\beta\frac{\hbar\omega_{\alpha}}{2}\right) + (N - N_1)\frac{\Delta}{2}m + NJs + Nhm. \quad (67)$$

The meaning of the different parameters are contained in Section 3.1.

A.2: Chain free-energy differential and entropy

Taking the infinitesimal variation of F, we find

$$dF = -SdT + (N - N_1)md\frac{\Delta}{2} \quad (68)$$

where S, the chain entropy, is given by

$$S = S_{spin} + S_{ph} \quad (69)$$

with

$$S_{spin} = -N\frac{h\,m + Js}{T} + Nk\ln A + Nk\frac{\ln r}{2} \quad (70)$$

and

$$S_{ph} = \frac{3\langle H_{0ph}(K, m_a)\rangle}{T} - 3k\sum_{\alpha}\ln\left(2\sinh\beta\frac{\hbar\omega_{\alpha}}{2}\right). \quad (71)$$

The spin entropy is that of N spin (± 1) interacting with first neighbour exchange interaction and submitted to the applied field h. The phonon entropy is that of a periodic chain with elastic force of constant K.

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