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First order high-spin/low-spin phase transition induced by acoustic-phonons

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Abstract. A model for high spin/ low spin transitions in solid is presented. It is assumed that interaction between molecules is only due to the dependence of the crystal elastic constants on the electronic states of the molecules. This work is performed for a linear chain of molecules modeled as atoms each with two electronic states. Only adjacent atoms are linked by springs. We suppose that the elastic force constant of the springs can have three values, corresponding to the electronic states of the particular atoms. In this article, we obtain the exact expression for the Hamiltonian of the atom-phonon coupling assumed. We then deduce that this coupling creates an effective field on each atom and an exchange-like interaction between the two first neighbouring atoms. Here we only study the effect of the field. The phase diagram for the chain is established. We show that the chain does or does not exhibit a first order transition, depending on the elastic force constant values. The results obtained in this study could be used for chain-like spin conversion compounds, or for any spin conversion compound if we assume that only one type of spring (*e.g.* those linking nn, or nnn, etc.) have an elastic force constant which varys with the electronic states of atoms linked by such springs.

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1 Introduction

In some molecular crystals containing transition metal ions (d^4 to d^7) in an octahedral environment, the spin value of the fundamental level of the metal ion may be lower than that of the first excited level. The magnetic susceptibility then has an unusual temperature dependence related to a thermally induced change of the populations of the levels [1]. In the literature the phenomenon is named spin crossover (or spin conversion). For example, in iron (II) complexes the low spin value is $S = 0$ and the high spin value is $S = 2$, and the electronic degeneracy is one for the ground level and 15 for the excited level (product of an orbital triplet and a spin quintet). The distance in energy between the levels is typically in the range 500–1000 K.

Mössbauer-effect results and magnetic susceptibility measurements are of great value in studying the thermal variation of n_{HS}, the high-spin fraction. On the basis of such experiments two kinds of spin crossover have been identified [1–3]:
- the parameter n_{HS} increases gradually with increasing temperature and does not show a thermal hysteresis;
- the parameter n_{HS} displays a discontinuity with increasing temperature and shows a thermal hysteresis. Such behaviour is characteristic of a first order phase transition (designated as spin transition).

In both cases of spin crossover, at low temperature (LS phase) n_{HS} is very near to zero and at high temperature (HS phase) very near to one. Moreover, when going from (LS) to (HS) states, *Mössbauer* spectrometry data show that the crystal Debye temperature is reduced by about 10 per cent (this parameter is typically near 150 K).

It is well known that the characteristic of spin crossovers is cooperative behaviour of the intermolecular interactions, and different models have been proposed to describe this [3–9]. In the model of Wajnflasz and Pick [8,9], the molecules are considered as Ising-like spins interacting with a ferro-like interaction. Ten years ago, Bousseksou *et al.* [10] showed that the unusual behaviour of “two-step” spin conversion systems can be described by introducing an antiferro-like interaction into the Wajnflasz and Pick model [9].

The Ising-like model is easy to use, and gives a correct description of the main features of spin conversion phenomena. However in the model of Wajnflasz and Pick as in that of Bousseksou *et al.* the physical origin of the intermolecular interactions is not specified, and the exchange-like constants included in both models are considered as phenomenological parameters.

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From heat capacity studies of some spin conversion compounds, Sorai and Seki [11] have concluded that there is a significant coupling between the molecular electronic states and the phonon system and that excitation of phonons is much easier in the (HS) state. This result is certainly related to the dependence of the molecule size on its electronic state.

In the Zimmermann and König model, the origin of the cooperation is the dependence of the ligand field acting on metal ions in the molecular electronic states. However, to take into account the experimental results of Sorai and Seki, they introduced, in addition to the previous interaction, the assumption that the crystal Debye temperature depends on the high spin fraction [7]. In the conclusion of their study, they underline the importance of the phonon contribution in (LS)/(HS) transition. We think that their study involves a description of the atom-phonon coupling which is too macroscopic. Moreover they have not tried to see if the atom-phonon coupling by itself could lead to a first order phase transition. It is thus interesting to test if the assumption that the crystal elastic force constants depend on the electronic states of the molecules, can introduce intermolecular interactions leading to first order phase transition in spin crossover crystal.

It is known that in molecular crystals the values of the intra-molecular elastic force constants are higher than the inter-molecular values. Moreover, the spin conversion phenomenon takes place at low temperature, around 100 K. So, for both reasons it is sufficient to study the coupling between the molecules and the crystal acoustic phonons.

We model the molecules as identical atoms each with two electronic states and we assume that the elastic force constant of the spring linking two atoms depends on the electronic states of the particular atoms concerned. In this paper we apply our assumption to a linear chain of atoms with effective springs connecting only adjacent atoms. We can then obtain and study the exact expression of the atom-phonon coupling Hamiltonian.

Many experimental studies have been carried out on spin-conversion compounds with structures comprising chains (see [12] and references in it). The results obtained here could be applied to such 1D systems. In the conclusion we discuss the condition under which this study can be used in any lattice.

The aim of this study is to see whether the form of the the atom-phonon coupling we use is sufficient to give rise to a first order phase transition in the chain and to investigate the mechanism that drives this transition.

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 results obtained and the last section is devoted to the conclusion.

2 The model and the chain Hamiltonian

Let us consider a linear chain of identical atoms, each with a fundamental electronic level (a) with degeneracy $g_\mathrm{a} = 1$ and with an excited level (b) with degeneracy $g_\mathrm{b} = r$ (r is the product of orbital and spin degeneracies). We call Δ the difference in energy between the two levels. Neighbouring atoms i and j $(= i \pm 1)$ are assumed to interact with an elastic force constant e_{ij}, which is equal to λ when both atoms are in level (a), ν when they are both in (b) and μ when one is in level (a) and the other in level (b). We suppose that ν is smaller than λ.

To each atom $i, (i = 1 \text{ to } N)$, we associate a fictitious-spin $\hat{\sigma_i}$ which has two eigen-values $\sigma_i = \pm 1$. Eigenvalue -1 (resp.$+1$) corresponds to electronic level (a) (resp. (b)).

The total Hamiltonian of the chain is the sum:

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

where H_spin, the spin Hamiltonian, is

$$H_\mathrm{spin} = \sum_{i=1}^{N} \frac{\Delta}{2}\hat{\sigma}_i \tag{2}$$

and H_phonon, the phonon Hamiltonian, is

$$H_\mathrm{phonon} = E_\mathrm{c} + E_\mathrm{p} \tag{3}$$

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

$$E_\mathrm{p} = \sum_{i=1}^{N} \frac{1}{2} e_{i,i+1}(u_{i+1} - u_i)^2 \tag{4}$$

with

$$e_{i,i+1} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4}(\hat{\sigma}_i + \hat{\sigma}_{i+1}) + \frac{\lambda - 2\mu + \nu}{4}\hat{\sigma}_i\hat{\sigma}_{i+1}. \tag{5}$$

In these expressions, u_i is the displacement of the ith atom from its equilibrium position which we assume to be independent of the electronic states of (i) and its neighbours. Moreover we assume the periodic condition, $u_{p+N} = u_p$ for $p = 1, 2, \ldots, N$.

The chain potential energy, E_p, can be decomposed into three terms

$$E_\mathrm{p} = V_0 + V_1 + V_2 \tag{6}$$

with

$$V_0 = \sum_{i=1}^{N} \frac{\lambda + \nu + 2\mu}{8}(u_{i+1} - u_i)^2, \tag{7}$$

$$V_1 = \sum_{i=1}^{N} \frac{\nu - \lambda}{8}\left[(u_i - u_{i-1})^2 + (u_{i+1} - u_i)^2\right]\hat{\sigma}_i \tag{8}$$

and

$$V_2 = \sum_{i=1}^{N} \frac{\lambda - 2\mu + \nu}{8}\left(u_{i+1} - u_i\right)^2 \hat{\sigma}_i.\hat{\sigma}_{i+1}. \tag{9}$$

The energy V_1 is the sum of one-spin interactions, and has a Zeeman-like form. Each spin $\hat{\sigma}_i$ is submitted to an effective field h_i given by

$$h_i = \frac{\nu-\lambda}{8}\left[(u_i-u_{i-1})^2+(u_{i+1}-u_i)^2\right]. \tag{10}$$

From the hypothesis $\nu < \lambda$, this field favours the eigen value +1 ((b) level).

The energy V_2 is the sum of two-spin interactions, and has an exchange-like form. The exchange parameter J_{ii+1} between spin σ_i and σ_{i+1} is

$$J_{ii+1} = \frac{\lambda-2\mu+\nu}{8}\left(u_{i+1}-u_i\right)^2. \tag{11}$$

The sign of this parameter is the same as that of the expression $(\lambda-2\mu+\nu)$. For example, when J_{ii+1} is negative, V_2 is a ferromagnetic-like interaction. In this article we are concerned by the case $V_2 = 0$. So, we adopt the condition

$$\lambda+\nu-2\mu = 0. \tag{12}$$

3 Effective elastic force constant K: Variational method

3.1 Self-consistent equation

If we replace the elastic force constant $e_{i,i+1}$ by an effective elastic force constant K which does not depend on the chain sites, then the thermal mean value of the parameter $(u_{i+1}-u_i)$ does not depend on the site i, and the field created by the phonon on the spins is uniform along the chain. We then obtain an spin Hamiltonian which is easy to study.

We obtain the expression of the effective elastic constant K and that of the uniform field h by a variational method [13]. The variational Hamiltonian H_0 is given by:

$$H_0 = H_{0\mathrm{s}}(h) + H_{\mathrm{ph}}(K) \tag{13}$$

with

$$H_{0\mathrm{s}} = \sum_{i=1}^{N} -h\hat{\sigma}_i \tag{14}$$

and

$$H_{\mathrm{ph}}(K) = \sum_{i=1}^{N}\frac{p_i^2}{2m} + \sum_{i=1}^{N}\frac{K}{2}(u_{i+1}-u_i)^2. \tag{15}$$

It is clear that $H_{0\mathrm{s}}(h)$ is the Hamiltonian of N independent spins in the presence of the uniform field h, and $H_{\mathrm{ph}}(K)$ is the Hamiltonian of a linear chain of atoms attracting one another with an elastic force of constant K.
One can write

$$H = H_0 + H - H_0 \tag{16}$$

In the approximation method that we use, $H - H_0$ is considered as a perturbation compared to H_0. Hence, the statistical physics calculations can be done by using the density matrix associated with H_0. This density matrix gives

$$\langle\hat{\sigma}_i\rangle = m \text{ for } i = 1, N \tag{17}$$

and

$$m = \frac{g_{\mathrm{b}}\mathrm{e}^{\beta h} - g_{\mathrm{a}}\mathrm{e}^{-\beta h}}{g_{\mathrm{b}}\mathrm{e}^{\beta h} + g_{\mathrm{a}}\mathrm{e}^{-\beta h}} \tag{18}$$

where $\beta = \frac{1}{kT}$. It is clear that the range of variations of m is from -1 to 1. The equation (18) is called the self-consistent equation.
At the first order perturbation calculation, $\tilde{F}$, the free energy of H is given by

$$\tilde{F} = F_0 + \langle H - H_0\rangle_0 \tag{19}$$

where $F_0(T,h,K)$ is the free-energy associated with H_0 and $\langle H-H_0\rangle_0$ is the thermal mean value calculated by using the density matrix associated with H_0 at temperature T.
If we call F_{th} the thermodynamical free-energy associated with H, it can be shown [13] that

$$F_{\mathrm{th}} \leq \tilde{F}. \tag{20}$$

So, to improve our approximation, we must lower the variational free energy, $\tilde{F}$, by choosing the parameters h and K such as to minimize the function $\tilde{F}(T,h,K)$ at a given temperature (all the model parameters r, $\Delta, \lambda, \mu, \nu$ being constant, and m being related to h through the Eq. (18)).

The minimization of $\tilde{F}$ *versus* h and K, leads to the equations:

$$K = \frac{2\mu+\lambda+\nu}{4} + \frac{\nu-\lambda}{2}m \tag{21}$$

$$h = -\frac{\Delta}{2} - \frac{1}{K}\frac{\nu-\lambda}{4}\frac{1}{N}\langle H_{\mathrm{ph}}(K)\rangle_T. \tag{22}$$

Up to now, we have only taken into account one phonon polarisation. For simplicity, we assume that the phonon energy is independent of the polarisation. Then, taking into account the three polarisations, equation (22) becomes:

$$h = -\frac{\Delta}{2} - \frac{3}{K}\frac{\nu-\lambda}{4}\frac{1}{N}\left\langle H_{\mathrm{ph}}(K)\right\rangle_T. \tag{23}$$

The parameter K is the effective elastic force constant. We can show that when condition (12) is satisfied it is positive for $-1 \leq m \leq 1$.

3.2 Chain isotherms study

When we use the equations (21, 23) in $\tilde{F}$, we obtain F, the chain free-energy corresponding to the approximation made in this study. The expression of F is given in the Appendix.

We have studied the chain isotherms in the $\Delta - m$ plane. For this purpose, we fix the value of the temperature and that of the model parameters λ, μ, ν and r, and we solve the self-consistent equation for different values of Δ. It is worth noticing that the solutions of the self consistent equation (Eq. (18)), are the extrema of the function $F(m)$ obtained by fixing in the right hand of equation (41), the temperature, the phonon parameters λ, μ, ν and the electronic parameters r and Δ and by using the relations (21) and (23).

We verify by numerical study the following results:

- when the self-consistent equation has only one solution, this solution is a minimum of $F(m)$ (stable thermodynamic state);
- when the self-consistent equation has several solutions (in our case three), the intermediate solution corresponds to a maximum of $F(m)$ (unstable thermodynamic state), and the two others are minima of $F(m)$ (the lower minimum is the stable thermodynamic state and the other is a metastable state). When the two minima of $F(m)$ have the same value, both solutions are equally stable which identifies a first order phase transition. For the two stable solutions, one is near 1, corresponding to a (b)-rich phase, and the other is near -1 corresponding to an (a)-rich phase.

When the parameters λ, μ, ν and r are fixed, F appears in equation (41) as a function of Δ, T and m. However, as m verifies the self consistent equation (Eq. (18)), m is a function of Δ and T. Hence the free energy F is only function of Δ and T. The differential of F is given in the Appendix.

From the isotherm study we deduce the chain phase diagram in the $\Delta - T$ plane.

Our study of chain isotherms in the $\Delta - m$ plane is similar to the study of real gas isotherms in the $P - V$ plane and our phase diagram is similar to that of real gas in the $P - T$ plane.

4 Results

In order to numerically solve equation (18), we take $\hbar\omega_{\mathrm{M}}(\lambda)$ as the unit of energy, where $\omega_{\mathrm{M}}(\lambda)$ is the maximum phonon frequency when the chain is periodic with an elastic force of constant λ ($\omega_{\mathrm{M}}(\lambda) = 2\sqrt{\frac{\lambda}{m}}$ where m is atom mass). We introduce the following reduced parameters:

- reduced temperature:

$$t = \frac{kT}{\hbar\omega_{\mathrm{M}}(\lambda)} \tag{24}$$

- the dimensionless electronic excitation energy

$$\delta = \frac{\Delta}{\hbar\omega_{\mathrm{M}}(\lambda)} \tag{25}$$

- the elastic force constant ratio

$$x = \frac{\nu}{\lambda} \tag{26}$$

(we have assumed that $0 < x < 1$),

- the dimensionless parameter y defined by:

$$\mu = \frac{\lambda + \nu}{2} + \frac{\lambda - \nu}{2} y \tag{27}$$

with $y = 0$ from condition (12).

4.1 Phase transition at zero temperature

At 0 K the solutions of the self-consistent equation are $m = \pm 1$. For the solution $m = 1$, $K = \nu$ and the chain energy, E_+, is given by

$$E_+ = 3\langle H_{\mathrm{ph}}(\nu)\rangle_{0\ \mathrm{K}} + N\frac{\Delta}{2}\cdot \tag{28}$$

For the solution $m = -1$, $K = \lambda$ and the chain energy, E_-, is given by

$$E_- = 3\langle H_{\mathrm{ph}}(\lambda)\rangle_{0\ \mathrm{K}} - N\frac{\Delta}{2}\cdot \tag{29}$$

In these expressions, $\langle H_{\mathrm{ph}}(\nu)\rangle_{0\ \mathrm{K}}$ and $\langle H_{\mathrm{ph}}(\lambda)\rangle_{0\ \mathrm{K}}$ are the zero-point energies of the chain with elastic force constants ν and λ respectively.

When Δ is zero, E_+ is lower than E_- for $\nu < \lambda$. So, the chain is in the (b) phase. When Δ increases, E_+ increases and E_- decreases. So, E_- is lower than E_+ when

$$\Delta > \Delta_{\mathrm{s}} \tag{30}$$

with

$$\Delta_{\mathrm{s}} = 3\frac{\langle H_{\mathrm{ph}}(\lambda)\rangle_{0\ \mathrm{K}} - \langle H_{\mathrm{ph}}(\nu)\rangle_{0\ \mathrm{K}}}{N}\cdot \tag{31}$$

So, the phase transition between the (b) and (a) phases happens for $\Delta = \Delta_{\mathrm{s}}$. This transition is first order for both phases have different values of m and the same energy value when $\Delta = \Delta_{\mathrm{s}}$.

It is easy to show that the zero-point energy of a periodic chain with an elastic force of constant e is

$$\langle H_{\mathrm{ph}}(e)\rangle_{0\ \mathrm{K}} = N\frac{2}{\pi}\frac{\hbar\omega_{\mathrm{M}}(e)}{2} \tag{32}$$

where $\omega_{\mathrm{M}}(e)$ is the maximum phonon frequency of the chain. So, using this equation and the parameter x we can write

$$\Delta_{\mathrm{s}} = 3\frac{2}{\pi}(1 - \sqrt{x})\frac{\hbar\omega_{\mathrm{M}}(\lambda)}{2}; \tag{33}$$

or, using the parameter δ,

$$\delta_{\mathrm{s}} = \frac{3(1 - \sqrt{x})}{\pi}\cdot \tag{34}$$

It is worth noticing that the threshold value δ_{s} depends only on the value of the parameter x.

The chain phase diagram at 0 K is shown in Figure 1.

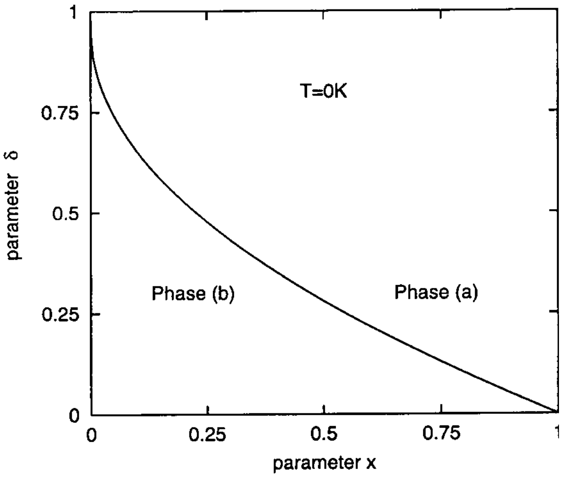

Fig. 1. The chain phase diagram at 0 K. The phase transition is first order, and the coexistence curve (full line) is given by the relation (34).

4.2 General results for isotherm at T $\neq$ 0 K

The self-consistent equation of our model can be discussed graphically in the same way as the well known Curie-Weiss self-consistent equation for ferromagnetic transition: when we fix the values the parameters λ, μ, ν, the solutions of the self-consistent equation for the set of values ($T = T_1, \Delta = \Delta_1$ and $r = r_1$) are the same as for the set ($T = T_1, \Delta = \Delta_2$ and $r = r_2$) when both sets are related by the relation

$$\frac{kT_1 \ln r_1}{2} - \frac{\Delta_1}{2} = \frac{kT_1 \ln r_2}{2} - \frac{\Delta_2}{2}\,. \tag{35}$$

The parameter r is the degeneracy of the excited level. So, studying the chain isotherms for $r = 1$, we can obtain the isotherms for any value of r by using the transformation (35). In the following, we have studied the chain only for $r = 1$.

4.3 Isotherms and phase diagram

4.3.1 Isotherms for x = 0.3 and r = 1

We have found that for $t < t_c$ the isotherms display a discontinuity in m as shown in Figure 2. This discontinuity becomes progressively smaller as t approaches t_c. For temperature values higher than t_c this discontinuity disappears as shown in Figure 3. For $x = 0.3$ and $r = 1$, t_c is equal to 0.075. The discontinuity in m corresponds to a first-order phase transition and t_c is the critical temperature.

From the isotherms study, we can deduce the chain phase diagram. For $x = 0.3$ and $r = 1$, this phase diagram is shown in Figure 4.

For a first order phase transitions, the slope of the coexistence curve is given by the Clapeyron relation. In our model, the intensive parameter associated with the extensive parameter Nm is $\frac{\Delta}{2}$, as shown in the expression of the spin Hamiltonian, H_{spin} (Eq. (2)). So, in our model, the Clapeyron equation reads

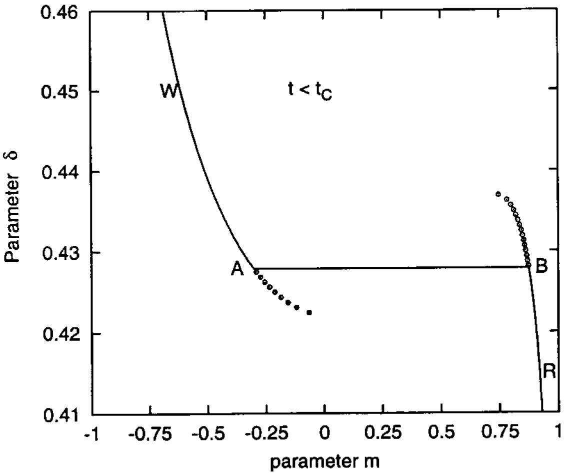

Fig. 2. The chain isotherm for $y = 0$, $x = 0.3$, $r = 1$ and $t = 0.06$. The region RB is in phase (b). The region WA is in phase (a). The plateau BA corresponds to a mixture of the two phases. The free-energy values of the points B and A are equal. The ordinate of the horizontal plateau is $\delta = 0.4279$. Open circles correspond to metastable solutions of the self-consistent equation.

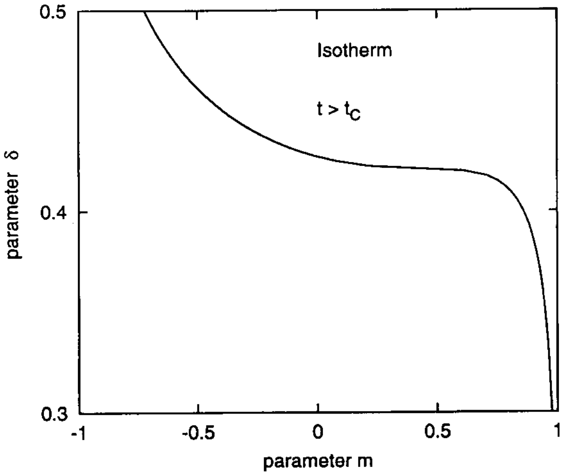

Fig. 3. The chain isotherm for $y = 0$, $x = 0.3$, $r = 1$ and $t = 0.077$. The parameter m varies continuously from 1, phase (b), to -1, phase (a). The temperature of this isotherm is just higher than the critical temperature $t_c = 0.075$.

$$\frac{\mathrm{d}\frac{\delta}{2}}{\mathrm{d}t} = \frac{s_{\text{b}} - s_{\text{a}}}{m_{\text{b}} - m_{\text{a}}} \tag{36}$$

where m_{b} and m_{a} are the values of m in each both phases at the transition, that is at the B and A ends of the isotherm plateau (see Fig. 2). Similarly, s_{b} and s_{a} are the entropies per atom at the ends of the plateau.

As m decreases when the chain passes from phase (b)($m \simeq 1$) to phase (a)($m \simeq -1$), the quantity $m_{\text{b}} - m_{\text{a}}$ in relation (36) is always positive. So, from the Clapeyron relation, the sign of the slope of the coexistence curve is the same as that of the entropy discontinuity, $s_{\text{b}} - s_{\text{a}}$.

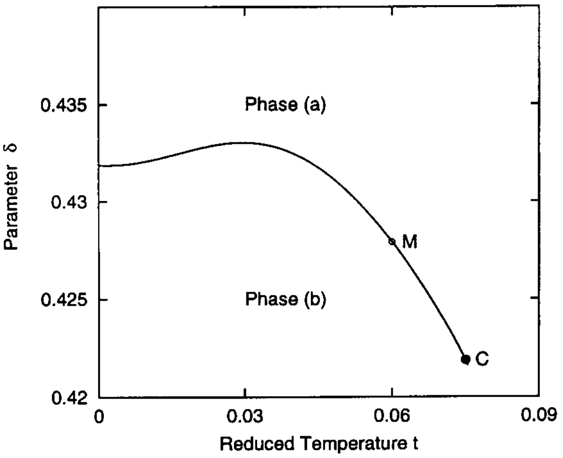

Fig. 4. The chain phase diagram for $y = 0$, $x = 0.3$ and $r = 1$ ($N = 2000$), built up from the chain isotherms study. The full line is the coexistence curve which ends at the critical point C. The coordinates of C are $t_c = 0.075$ and $\delta_c = 0.4219$. Below the coexistence curve, the chain is in phase (b) and above in phase (a). For the slope of the coexistence curve at the point M ($t = 0.06$ and $\delta = 0.42791$) we find -0.33 by using the Clapeyron equation and to -0.29 by using the variation of the δ values between $t = 0.06$ and $t = 0.07$ along the coexistence curve. The small discrepancy is due to the large variation of t between $t = 0.06$ and $t = 0.07$.

The chain entropy can be analysed as the sum of the phonon and spin entropies. That is,

$$s_b - s_a = (s_b - s_a)_{ph} + (s_b - s_a)_{sp}. \tag{37}$$

The expressions for the two entropies are given in the Appendix.

When the chain state passes from the (b) to the (a) phase, the effective elastic force constant, K, increases from a value near ν to a value near λ. For $\nu < \lambda$, the chain vibrational frequency values are smaller in phase (b) than in phase (a). So, at a given non zero temperature, the number of occupied vibrational levels in phase (b) is higher than that in phase (a). Hence, at the transition, the phonon entropy discontinuity, $(s_b - s_a)_{ph}$, is always positive. It is worth noticing that this discontinuity value increases as x decreases. At 0 K, the entropy of the phonon system is zero whatever the value of the elastic force constant while the phonon entropy discontinuity is zero at 0 K.

As for $(s_b - s_a)_{sp}$, the spin entropy discontinuity, it is clear that, at 0 K, this quantity is equal to zero for $r = 1$ (and to $\ln r$ for $r > 1$). However, for $T \neq 0$ K, the sign of this quantity is not easy to predict. We have verified by numerical computation that $(s_b - s_a)_{sp}$ is negative at low temperature($t = 0.01$) and at high temperature ($t = 0.06$) in the case of the Figure 4. So, the sign of the slope of the transition line in Figure 4, results from the competition between a term that is positive or zero, $(s_b - s_a)_{ph}$, and a term which is negative or zero, $(s_b - s_a)_{sp}$. This is the reason why the sign of the coexistence curve slope changes in Figure 4.

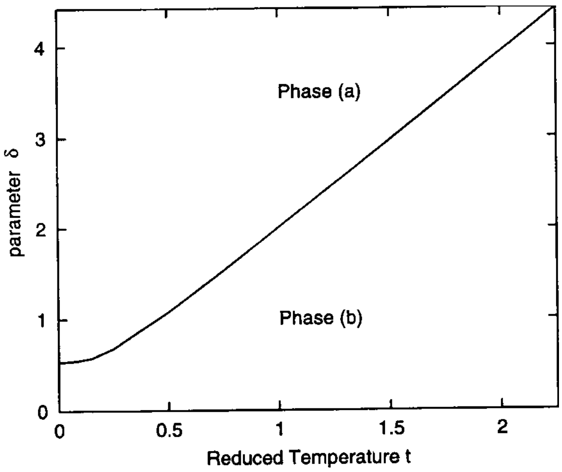

Fig. 5. The chain phase diagram for $y = 0$, $x = 0.2$ and $r = 1$. The coexistence curve does not display a critical point (or t_c is infinite).

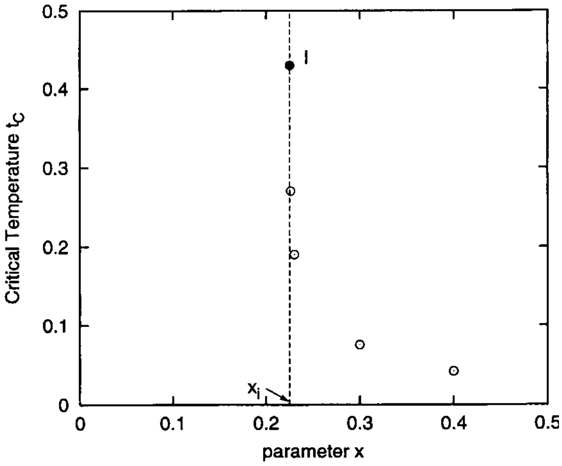

Fig. 6. Values of t_c, the critical temperature in reduced unit, *vs.* x. The open and dark circles are t_c values obtained by solving the self consistent equation for $y = 0$ and for different values of x (the t_c values do not depend on r). The coordinates of the point I are $x_i = 0.225$ and $t_c = 0.43$. The abscisse x_i is a threshold value: for $x < x_i$ the first order transition line in δ-T diagram does not display a critical point (or t_c is ∞); for $x \geq x_i$, t_c has a finite value. Moreover, t_c tends towards zero when x is increased. The vertical dotted line is the boundary between the two chain behaviours (with or without critical point).

4.3.2 Varying x

We have studied chain isotherms for $x = 0.2$ and $r = 1$. From this study we deduce the phase diagram shown in Figure 5. The coexistence curve does not display a critical point.

The values of the chain critical temperature for different values of the parameter x are shown in Figure 6. These values are obtained by studying chain isotherms for different values of x, keeping $r = 1$ and $y = 0$ (in fact, the t_c values do not depend on the r values). There is a threshold value x_i such that the coexistence curve does not display a critical point for x smaller than x_i.

The graphical study of the self consistent equation leads to study the intersection of two curves: the familiar hyperbolic tangent curve, $m = \tanh(u)$, and a curve (C), $u = f(m)$, the abscissa u being a parameter depending on the temperature, on the phonon parameters and on the electronic parameters r and Δ. The curve (C) is not a straight line as in the graphical study of the Curie-Weiss equation for a ferromagnetic transition. When Δ varies, all the others parameters being constant, the curve (C) is translated along the u-axis (this is different compared to the Curie-Weiss situation). Depending on the shape of the curve (C) and on its position along the u-axis, the number of intersection point is one or three. The curve (C) is a monotonous increasing function, and we can characterize its shape by a slope mean value. We verify by numerical calculation that the hyperbolic tangent and the (C) curves have only one intersection point when the slope mean value of (C) is higher than unity and that they have three intersections points when this slope mean value is lower than unity. So we deduce this rule: an isotherm displays a plateau (or a phase transition) when the following inequality is satisfied

$$\frac{h_{\mathrm{ph}}(m=1) - h_{\mathrm{ph}}(m=-1)}{2} > kT \tag{38}$$

where kT is the Boltzmann factor, the factor of 2 comes from the variation of m between the two phases and h_{ph} is the phonon part of the mean field h, that is

$$h_{\mathrm{ph}} = \frac{3\lambda}{K}\frac{1-x}{4}\frac{1}{N}\left\langle H_{\mathrm{ph}}(K)\right\rangle_T . \tag{39}$$

It is clear that increasing the temperature, the inequality (38) will be violated and the first order transition disappears. So, T_{c}, the chain critical temperature value, is the solution of the equation

$$\frac{h_{\mathrm{ph}}(m=1) - h_{\mathrm{ph}}(m=-1)}{2} = kT. \tag{40}$$

When equation (40) has no solution, the chain phase diagram does not have a critical point.

We have verified that the values of the chain critical temperature obtained by solving equation (40) are in agreement with those obtained by studying the self consistent equation, (Eq. (18)), *i.e.* by doing the chain isotherms study.

5 Conclusion

In this article, we first obtain the exact expression for the Hamiltonian of the atom-phonon coupling assumed. From this expression we show that the used atom-phonon coupling creates: (i) an effective field on each atom, which favours the (HS) state and (ii) an exchange-like interaction between two nearest neighbours, which can be a ferro- or an antiferromagnetic-like interaction, or which can be equal to zero, depending on the the values of elastic force constant. Both interactions are temperature dependent *via* the atoms displacements. It is worth noticing that both interactions have not been studied by Zimmermann and König.

In this study we have only considered the case where the exchange like interaction is zero.

At a given temperature, the value of the elastic force constant varies along the chain. In this article, we replace the exact elastic force constant by an approximate one, K, which has the same value at all sites on the chain. With this approximation, the field acting on the atoms is uniform. The expressions of K and h, the uniform field, are obtained by the variational method. We then can show that the effective elastic force constant K depends on the high spin fraction (or on m). This result is an assumption in the Zimmermann and König model.

We have shown that the chain exhibits a first order phase transition with or without a critical temperature, depending on the ratio of strengths of the elastic force constant in the excited and the fundamental electronic states. We have shown that the value of the critical temperature does not depend on the electronic parameters Δ and r.

As the phases (a) and (b) belong to the same symmetry group, the presence of a first order transition line is not surprising. It is however surprising that there is no critical point. We note, that the absence of a critical point in the coexistence curve of two phases is generally attributed to the difference in symmetry of the two phases (for example the solid-liquid coexistence curve). In our study the critical temperature value may go to infinity because the Zeeman interaction related to the field created by phonons can be made to vary, at high temperature, as fast as the thermal energy, kT.

The field created by phonons on the atom i is proportional to the parameter $(u_{i+1} - ui)^2$, where u_i is the displacement of the atom i. The value of this parameter depends on the dynamic matrix of the chain, that is on the electronic state of all the chain atoms. So the Zeeman interaction related to the phonon field is not short-ranged. Therefore, there is no exact result in the statistical-physics which prevents the existence of a phase transition in this model.

To have a first order transition in Ising-like models [8–10], it is necessary to assume the existence of an exchange-like interaction and that r, the degeneracy of the excited atomic level is bigger than unity. Indeed, this degeneracy creates an effective field which favours the excited level, HS level, and which have the value $kT\mathrm{Ln}(r)$. So, in Ising-like models, the values of the exchange-like parameter and that of r are chosen to provide the best agreement with experimental observations. When the value of r is very large ($r = 400$), intra molecular degeneracies are invoked. This study shows that, in our model, the condition $r > 1$ is not necessary to have a first order phase transition. Moreover the assumed atom-phonon coupling creates an exchange-like interaction and an effective field which favours the (HS) level.

Following the study of Sorai and Seki [11], we may take for the unit of energy, $\hbar\omega_{\mathrm{M}}(\lambda)$, the value 50 cm^{-1}, and for the transition temperature the value 170 K. This temperature corresponds, in reduced temperature units, to the value 2.4. From Figure 5, we deduce for the reduced parameter δ, the value 4.5 and for the parameter $\varDelta$, 324 K. This calculated value has the same order of magnitude as the experimental data which range from 500 to 1000 K. The above value of $\varDelta$ has been calculated for $r = 1$. If we take for the parameter r the value 15, using equation (25), we obtain for $\varDelta$ the value 784 K which is well in the experimental data range.

The previous discussion allows us to conclude that the atom-phonon coupling used in this model could play an important role in spin conversion phenomenon. However, it is necessary to introduce lattice deformation into the model.

The study of the exchange-like interactions can be carried out by using the expression given by the transfer matrix method for the variational free energy.

The method used in this article to study atom-phonon coupling can be applied to any lattice if we assume that only one type of spring, *e.g.* those linking nearest neighbour atoms, have an elastic force constant which depends on the electronic states of these atoms. In the case where several types of springs have elastic force constants varying, the discussion of the phase diagram can be very complicated due to the great number of parameters. In that case a more global method must be found.

Finally, it is worth noticing that atom-phonon coupling is usually described by means of atoms displacements which modify the electronics interactions (see magnetoelastic coupling [14–16], or relaxation studies [17]). This corresponds to the first term in the development of the crystal potential energy considered as a function of atoms displacements. In this study we do not take into account this term but only the following term in the development.

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Appendix: Chain thermodynamic functions in the mean field approximation

In the mean field approximation, F, the chain free-energy is

$$F = -NkT\ln A + 3kT\sum_{\alpha}\ln\left(2\sinh\beta\frac{\hbar\omega_\alpha}{2}\right) + N\left(\frac{\varDelta}{2}+h\right)m \qquad (41)$$

where $\beta = \frac{1}{kT}$, m verifies equation (18), $\sum_\alpha$ is the sum over phonon normal modes and

$$A = g_{\mathrm{b}}\exp\beta h + g_{\mathrm{a}}\exp-\beta h \qquad (42)$$

$$h = -\frac{\varDelta}{2} + \frac{3(\lambda-\nu)}{4NK}\langle H_{\mathrm{ph}}(K)\rangle_T \qquad (43)$$

$$K = \frac{2(\lambda+\nu)}{4} - \frac{(\lambda-\nu)m}{2}\cdot \qquad (44)$$

Taking the infinitesimal variation of F, we find

$$\mathrm{d}F = -S\mathrm{d}T + Nm\mathrm{d}\frac{\varDelta}{2} \qquad (45)$$

where S, the chain entropy, is given by

$$S = S_{\mathrm{spin}} + S_{\mathrm{ph}} \qquad (46)$$

with

$$S_{\mathrm{spin}} = -N\frac{h\,m}{T} + Nk\ln A \qquad (47)$$

and

$$S_{\mathrm{ph}} = \frac{3\langle H_{\mathrm{ph}}(K)\rangle}{T} - 3k\sum_{\alpha}\ln\left(2\sinh\beta\frac{\hbar\omega_\alpha}{2}\right). \qquad (48)$$

The spin entropy is that of N independent spin (±1) interacting with the applied field h. The phonon entropy is that of a periodic chain with elastic force of constant K.

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