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2007 J. Phys.: Condens. Matter 19 106201

(http://iopscience.iop.org/0953-8984/19/10/106201)

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J. Phys.: Condens. Matter **19** (2007) 106201 (12pp) doi:10.1088/0953-8984/19/10/106201

Theoretical investigations on an axial next nearest neighbour Ising-like model for spin crossover solids: one- and two-step spin transitions

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Received 23 October 2006, in final form 19 January 2007
Published 15 February 2007
Online at stacks.iop.org/JPhysCM/19/106201

Abstract
We investigate the thermodynamical properties of an adapted ANNNI-like (axial next nearest neighbour Ising-like) model for 1D spin crossover solids. We performed an exact treatment within the framework of the well known transfer matrix method and derived the thermal evolution of the high spin fraction, the correlation function and the heat capacity. We show that a model of competition of the interactions between similar spin state ions reproduces qualitatively the main features of experimental data: gradual, abrupt and two-step spin crossover transitions. In addition, we found that the intermediate region of the two-step transition exhibits two types of spatial organization, according to the sign of the interactions. Indeed, antiferro-like and 'antiphase' (called the phase $\langle 2 \rangle$ in the ANNNI model) structures are obtained. We also found that these two configurations can be distinguished through the thermal evolution of their corresponding correlation functions.

The existence of the phase $\langle 2 \rangle$, predicted by the present model, is in good agreement with recent observations on a spin crossover sample of $[\{Fe(CNBH_3)(4phpy)\}_2(\mu\text{-bpypz})_2]$ for which this phase was evidenced for the first time, in these materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, there has been growing interest in the field of 1D spin crossover (SC) materials, which may constitute good examples for investigating the DOMINO effect in [1], under light. It is now well established that SC systems have potentialities as switchable materials for information storage [2] and for ultrafast switching [3–5]. Indeed, intensive chemical [6–8], and theoretical [9–16] activities have concerned 1D spin crossover solids, carried out in order to find new properties associated with their low dimensionality. Among them, theoretical investigations [10, 17, 18] in which elastic and magnetic interactions coexist and compete have been developed recently. Such a phenomenon is already present in photomagnetic Prussian blue analogues [19, 20] for which the synthesis of 1D materials constitutes a formidable challenge. The present work concerns the study of the effect of the interaction on the thermodynamical properties of 1D SC solids. In this field of research, it is important to mention that pioneering works on the statics and dynamics of SC solids have pointed out the role of interactions on the shape of thermal spin transition and relaxation curves [12, 14, 21–23]. Both phenomenological mean field models [22] and dynamic Monte Carlo simulations [24] have been reported to describe the experimental data. As regards the dynamical properties, the typical feature of a self-accelerated relaxation giving the relaxation curves a sigmoidal shape was assigned as an effect of interactions. In addition, 'tail' effects observed in experiments have been attributed to the transient onset of correlations, i.e. to the existence of short range interactions [25]. This effect cannot, of course, be explained using mean field theory.

In an SC transition, a cooperative distortion of the lattice occurs, that is associated with a large change in the metal–ligand distance. Indeed it increases by $\sim$10% at the molecular level in the conversion from the low spin (LS) to the high spin (HS) state, which causes a volume expansion of the molecules. Thus, the SC phenomenon at the microscopic scale originates from the coupling between the electronic and vibrational structures [13, 26] of the molecules. That is the intramolecular vibronic coupling, which plays a crucial role in the existence of the intramolecular energy barrier which gives a long lifetime to the photo-induced metastable HS state at low temperature [23, 27]. The coupling between the lattice distortion and the change of the electronic states of the molecules induces cooperativity of SC solids. That is the microscopic origin of the elastic interaction, which is responsible for the SC transition. From the experimental point of view, optical and magnetic property changes upon the SC transition can be followed by magnetic or optical (absorption, reflectivity) techniques.

To make clear what is new in the present theoretical contribution, it is necessary to rapidly review Ising-like models used to describe SC and Prussian blue analogues [28]. One model widely used to describe SC systems, and more generally bistable systems, is an Ising-like model proposed by Wajnflasz and Pick [29] in the 1970s. This model is based on interacting two-level units (HS, LS), the energy levels of which have different energies and degeneracies. The degeneracy ratio of the HS and LS states, $g = g_{\mathrm{HS}}/g_{\mathrm{LS}}$, is related to the molar entropy change upon the total conversion, $\Delta S = k_{\mathrm{B}} \ln g$ [30], and therefore can be derived from calorimetric measurement at the transition temperature. Because of the electronic, vibrational (intramolecular) and phonon contributions, the entropy change $\Delta S > 0$ ($\Delta S \approx$ 30–70 J K^{-1} mol^{-1}), and therefore $g \gg 1$. In this simple model, each level is associated with an eigenvalue of a fictitious spin operator $\hat{s}$ ($s = \pm 1$), and the ligand field energy of the two states is written as $\Delta/2 \sum_i s_i$. It is worth noting that the interaction in SC solids originates from elastic strength [31]; however in the Ising-like model it takes place through the following phenomenological contribution: $-J \sum_{i \neq j} s_i s_j$, written as in magnetism. Therefore, the parameter J is not an exchange magnetic coupling, but has to be viewed as an effective phenomenological elastic interaction. The HS fraction n_{HS} is expressed as a function of the 'fictitious magnetization' $\langle s \rangle$, such as $n_{\mathrm{HS}} = (\langle s \rangle + 1)/2$. Despite the drastic simplification of the realistic vibronic level scheme, as a two-level system, this model permits one to describe, even in the mean field version, with amazing success, most of the quasi-static properties of the SC solids. For example, it explained consistently the change from a smooth transition to the first-order transition [29, 32] of spin conversion between the LS and HS states as a function of material parameters, and also the two-step SC transition in 3D solids, reflecting the lattice structure [33–35].

Such a two-state model with different degeneracies is equivalent to, i.e. it has the same equilibrium properties as, the original Ising model under a temperature dependent field [32, 36]. Its dynamical extension [32] led exactly to the phenomenological formula given by Hauser *et al* [22] for the sigmoidal relaxation in the mean field approximation.

In previous investigations [12, 14], a static 1D Ising-like model combining nearest neighbour (NN) short range interaction and infinite long range interaction was solved exactly, using the transfer matrix method. It was found that thermal hysteresis may occur due to the competition of short and long range interactions. In addition, the hysteresis loop becomes square shaped when the short range interaction parameter is increased. However, the width of the latter closely depends on the long range order parameter. Unfortunately, this model is not able to explain new experimental observations [6, 7] of a two-step transition in dinuclear 1D SC solids, in which an unexpected type of spatial organization (HS–HS–LS–LS–HS–HS) was found in the plateau region.

These recent experimental results have motivated the present study, which is devoted to probing the role of short range interactions in 1D SC systems. Here, we present a general model for 1D SC, with which we aim to reproduce as much as possible the various experimental data. In particular, we focus on the two-step SC transition and on the microscopic nature of the transition plateau obtained in the experiments. Many works have concerned this aspect, and all of them were based on the competition between a negative (antiferro-like) short range interaction and a positive (ferro-like) long range interaction. In addition, all of these studies have been performed in the mean field (MF) approximation. It is well known that the MF approach introduces many artefacts, such as phase transitions, infinite lifetime for the metastable states, etc. Recently [35], we demonstrated using MC simulations that a 3D Ising-like model accounting for NN and next nearest neighbour (NNN) short range interactions in a two-sublattice system is able to produce a thermal double-step transition. However in that study, we considered only the case of negative (positive) NN (NNN) interaction, which is in the spirit of the previous studies based on MF models.

Here, we realize an exact treatment, i.e. beyond the MF approximation, of an adapted ANNNI Ising-like model describing the thermal properties of 1D SC solids, and investigate all the configurations of the signs of the interaction parameters. As an additional point justifying the present study for SC systems, it should be remarked that analytical treatments are strongly needed to simulate the thermodynamic properties of systems possessing macroscopic energy barriers; Monte Carlo simulations would require tremendous computer times, especially in the low temperature regime.

The present work is organized as follows. Section 2 is devoted to the brief presentation of the ANNNI-like model for SC solids, that is the 1D Ising-like model including NN and NNN interactions. Then, we use the transfer matrix technique, and we derive the exact partition function and its associated free energy. In section 3, we analyse the exact thermodynamical properties of the system, obtained for different configurations (ferro-like, antiferro-like) of the interactions present in the model. In the same section, we show the related thermal behaviours of the HS fraction: gradual, steep and two-step SC transition behaviours are evidenced. There, we also develop a comparative study on the two possible microscopic configurations produced by the model in the plateau region of the two-step spin transition, according to the sign of the coupling parameters. These configurations are then discussed in relation to the experimental data available in the literature. In section 4, we end with a short discussion and our conclusions.

2. Model and method

We study the thermodynamic properties of the 1D Ising-like model which includes the respective NN and NNN interactions J and K, under a ligand field Δ.

The effective degeneracy ratio g of the HS and the LS states comes from the differences in the angular momentum, the spin momentum and the phonon degrees of freedom [37, 38]. In the case of Fe(II) complexes, the degeneracy of the spin part is 5 and that of the angular momentum is 3 in the octahedral symmetry. Taking into account the lattice degrees of freedom and intramolecular vibration change during the transition, the degeneracy ratio increases to 100–1000 and becomes temperature dependent. Here, for reasons of simplicity, the parameter g is taken as a constant equal to 100; therefore it should be considered as an effective degeneracy ratio. Accounting for the isomorphism [32, 36] between the Ising model with degenerate states and the pure Ising model under a temperature dependent field, the degeneracy g results as an additional entropic term $-k_B T \ln g$ in the Hamiltonian. Therefore, the Hamiltonian of a 1D SC system including these two types of interaction can be written as

$$H = -J \sum_i s_i s_{i+1} - K \sum_i s_i s_{i+2} + \tfrac{1}{2}(\Delta - kT \ln g) \sum_i s_i . \tag{1}$$

It is important to note the similarity between this Hamiltonian and the ANNNI model under a field, which has been extensively studied in the past [39–41]. In particular, a complete review made by Selk [39] on one-, two-, and three-dimensional ANNNI models shows that the Ising model with competing interactions exhibits a rich variety of spatially modulated structures. Therefore, we expect this model to be well adapted to describing SC solids in which intermediate phases appear during the thermal transition from the LS to the HS state.

In the Hamiltonian (1), the spin s is in fact a fictitious spin. Its two eigenvalues $s = +1$ and -1 are respectively associated with the HS and the LS states of the SC molecules. We also recall that in the SC problem, the two interaction parameters J and K have an elastic origin [31]. Moreover, in the present study, we assume periodic boundary conditions, $s_{N+1} = s_1$, where N is the number of spins in the chain.

With the notation $\beta = 1/k_B T$, where k_B is the Boltzmann constant, the partition function is written as

$$Z = \mathrm{Tr}[\mathrm{e}^{-\beta H}] = \sum_{\{s_i\}} \mathrm{T}\,(s_1, s_2; s_3, s_4) \times \mathrm{T}\,(s_3, s_4; s_5, s_6) \cdots \mathrm{T}\,(s_{N-1}, s_N; s_1, s_2) . \tag{2}$$

The kernel T is defined by

$$\begin{aligned} \mathrm{T}(s_1, s_2; s_3, s_4) = \exp\!\left(\beta \frac{J}{2}(s_1 s_2 + 2 s_2 s_3 + s_3 s_4)\right) \exp(\beta K (s_1 s_3 + s_2 s_4)) \\ \times \exp\left(\frac{\beta\,(\Delta - kT \ln g)}{4}(s_1 + s_2 + s_3 + s_4)\right) . \end{aligned} \tag{3}$$

Following previous studies, where a similar four-point, real non-symmetric kernel $(\mathrm{T}(s_1, s_2; s_3, s_4) \neq \mathrm{T}(s_3, s_4; s_1, s_2))$ was obtained in the 1D ANNNI model, the partition function can be written as $Z = \mathrm{Tr}[\mathrm{T}]^{N/2}$. In the thermodynamic limit (i.e. for $N \to \infty$) the partition function becomes the maximum eigenvalue of T to the power $N/2$. Let us denote by λ_0 the largest eigenvalue of T and by φ_0 and ψ_0 the respective eigenfunctions of the matrix T and its transpose. The correct Gibbs free energy, including the degeneracy of the spin states, is given by

$$F = -\frac{N}{2} k_B T \ln \lambda_0 - \frac{N}{2} k_B T \ln g . \tag{4}$$

The heat capacity is then obtained as $C_v = -T \frac{\partial^2 F}{\partial T^2}$. In the expression (4), the contribution $-\frac{N}{2} k_B T \ln g$ results from the transformation of the Ising model with degenerate states into an Ising model under a temperature dependent ligand field [32]. However, this term does not play any role when we derive the thermodynamical properties.

From the experimental point of view, the relevant quantity describing the thermal properties of SC solids is the HS fraction, n_{HS}, which is the fraction of molecules in the HS state at a given temperature, that is the fraction of up spins in our model, which is related to the average magnetization $\langle s\rangle$ per site through $n_{\mathrm{HS}} = (1+\langle s\rangle)/2$. It is given in the present formalism by the following expression:

$$n_{\mathrm{HS}} = \frac{1}{2}\left(1+\frac{\sum_{s_1}\sum_{s_2} s_1\varphi_0\left(s_1,s_2\right)\psi_0\left(s_1,s_2\right)}{\sum_{s_1}\sum_{s_2}\varphi_0\left(s_1,s_2\right)\psi_0\left(s_1,s_2\right)}\right). \tag{5}$$

Despite the rather simple procedure for obtaining the partition function and the average magnetization in the previous calculations, the two-spin correlation functions require the knowledge of both eigenvalues and eigenfunctions of the whole spectrum. In our study two kinds of pair correlation functions, to be precise $\langle s_1 s_2\rangle$ and $\langle s_1 s_3\rangle$, corresponding to NN and NNN spin correlations, are derived. They are given [42, 40, 41] by

$$\lim_{N\to\infty}\langle s_1 s_j\rangle_N = \sum_{i=1}^{4}\left(\frac{\lambda_i}{\lambda_0}\right)^{j}\sum_{\{s_1\}}\sum_{\{s_j\}}\langle\varphi_0(s_1,s_j)s_1\psi_i\left(s_1,s_j\right)\rangle\langle\varphi_i\left(s_1,s_j\right)s_j\psi_0\left(s_1,s_j\right)\rangle. \tag{6}$$

3. Transfer matrix results

We now derive the thermodynamical properties of the ANNNI model under an effective temperature dependent ligand field.

To study the effect of the NNN contribution, we calculate the thermal behaviour of the HS fraction and its associated heat capacity for different parameter values of the model. To check the accuracy of our results, standard Monte Carlo (MC) Metropolis simulations have been performed on the same Hamiltonian. We have considered a periodic chain with a size $L = 300$. We have used 10 000–50 000 MC steps as the waiting time to make the system reach the equilibrium state, and we have taken 10 000–50 000 MC steps for measuring the statistical average of the thermodynamical quantities. In all our calculations the transfer matrix results have exactly reproduced MC simulations with a computer time at least ten times smaller.

3.1. Case $J > 0$ and $K \geqslant 0$

Here we limit our study to the case where both interactions are 'ferro'-like, and we investigate the effect of the NNN short range interaction on the shape of the thermal behaviour of the HS fraction.

In the restricted case $J \neq 0$ and $K = 0$, the HS fraction can be obtained analytically. It is given by [14]

$$n_{\mathrm{HS}} = \frac{1}{2}\left[1-\frac{\sinh\beta\left(\frac{\Delta}{2}-\frac{\mathrm{k_B}T\ln g}{2}\right)}{\sqrt{\sinh^2\beta\left(\frac{\Delta}{2}-\frac{\mathrm{k_B}T\ln g}{2}\right)+\mathrm{e}^{-4\beta J}}}\right]. \tag{7}$$

The thermal dependence of the HS fraction, calculated using equation (7), for the parameter values $K = 0$, $J = 100$ K, $g = 100$ and $\Delta = 1300$ K, is depicted in figure 1. It shows a gradual spin conversion from LS to HS states, with a transition temperature $T_{\mathrm{eq}} = \frac{\Delta}{k_{\mathrm{B}}\ln g}$, for which $n_{\mathrm{HS}} = 1/2$. It is worth noting that the transition temperature is independent on the coupling parameters J and K, when both interactions are positive. Increasing the NNN coupling parameter K results in a change in the shape of the HS fraction curve. The NNN interaction sharpens the transition curve (see also the heat capacity in the inset of figure 1),

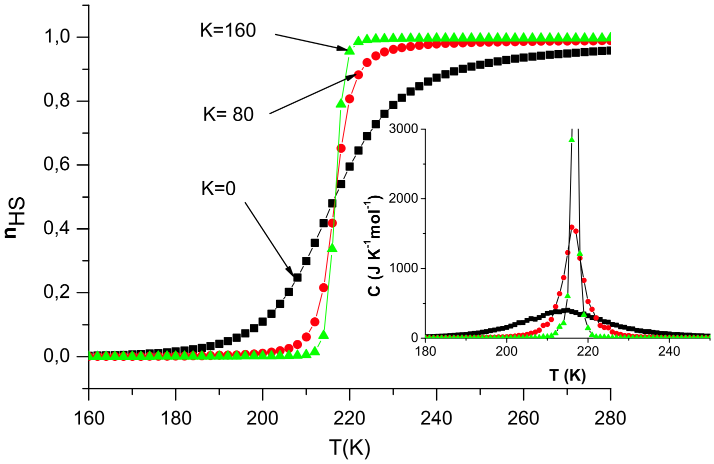

Figure 1. Thermal evolution of the HS fraction for $J > 0$ and for different positive values of the interaction parameter K. The conversion is gradual for $K = 0$ K (squares) and becomes abrupt for $K = 80$ (circles) and $K = 160$ K (triangles). In the inset, we show the corresponding thermal variation of the heat capacity. A sharp peak is obtained for $K = 160$ K, while a small broad Schottky anomaly is observed for $K = 0$, in agreement with the evolution of the HS fraction. The other parameter values are $\Delta = 1300$ K, $\ln g = 6$, and $J = 160$ K.

indicating that the chain approaches a 'first-order' phase transition-like behaviour for realistic values of the NNN interaction K, which are of the same order of magnitude as that of J. It is known that there is no true first-order transition with NN and NNN interaction in 1D systems. However, the tendency observed in figure 1 when $K \neq 0$ strongly supports the idea of the existence of a true phase transition at higher dimension.

It is worth mentioning that keeping $K = 0$ and increasing J leads also to sharpening of the transition curve. However, this procedure needs 'unrealistic' values of the NN interaction J ($J \approx 500$ K, as in [12]). The main difference between this procedure and that of the present section (fixing J and increasing K) will also come from the thermal behaviour of the two-spin correlation functions associated with the NN and NNN sites. It is also expected that these fluctuations will lead to different effects on the thermal behaviour of the heat capacity. However, it is rather difficult from the experimental point of view to distinguish between these two situations.

In addition, and in contrast with the model where only NN interactions exist [12], here due to the existence of the NNN interaction, a very weak long range ferro-like interaction $(-G\langle s\rangle \sum_i s_i)$ produces a true first-order transition. Indeed, including this term makes the system tridimensional, due to the infinite range of the interaction. This long range effect can be due to the existence of interchain interactions. This is actually the case in SC triazole chain compounds [8], in which non-coordinated water molecules and counter-anions were found between the polymeric chains. They introduce steric and/or electrostatic interactions between the chains, which finally allows the existence of a true first-order phase transition, accompanied with a hysteresis loop.

3.2. The two-step SC transition

Many examples of SC systems show a two-step spin transition, attributed to the competition between long and short range interactions [14, 43, 33, 34]. Very recently [35, 44], MC

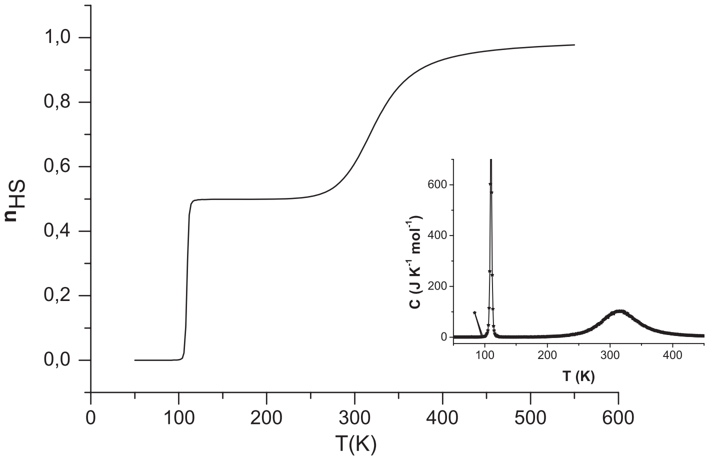

Figure 2. Thermal evolution of the HS fraction in the case of $J < 0$ and $K > 0$. A two-step transition behaviour is observed: the first steep transition occurs at 110 K from the ordered LS to the antiferro-like LS–HS–LS–HS state. It is followed by a gradual transition at 330 K from the intermediate state (plateau) to the ordered HS state. In the inset, we show the corresponding temperature dependence of the heat capacity. A double peak is obtained, reflecting the two-step nature of the spin transition. The parameter values are $J = -160$ K, $K = 190$ K, $\Delta = 1300$ K and $\ln g = 6$.

simulations performed on a three-dimensional fcc lattice, using only NN and NNN short range interactions, have shown that two-step and first-order spin transitions may be derived.

It is straightforward to see that there are only two possible ways to obtain a two-step spin transition with the present ANNNI model with competing interactions. They correspond to the following cases: (i) $J < 0$ and $K > 0$; (ii) $J > 0$ and $K < 0$.

Here we want to study the difference between these two cases and to demonstrate the existence of an intermediate state during the transition. In addition, we want to investigate the microscopic nature of the intermediate state that relates to the plateau region in the thermal dependence of the HS fraction.

3.2.1. Case $J < 0$ and $K > 0$.

We analyse the case of 'antiferro'-like NN ($J < 0$) and 'ferro'-like NNN ($K > 0$) interactions. In figure 2, we summarize the thermal evolution of the HS fraction and that of the associated heat capacity for the following parameter values: $J = -150$ K, $K = 190$ K, $\Delta = 1300$ K and $\ln g = 6$. It is found that a two-step spin crossover transition, with a large plateau region, can be obtained using only short range interactions. Long range interactions are then not needed, when there is no phase transition. The two peaks found in the thermal behaviour of the corresponding heat capacity, shown in the inset of figure 2, clearly confirm the two-step character of the transition. To elucidate the microscopic nature of the plateau, we follow the thermal evolution of the two-spin correlations $\langle s_i s_{i+1}\rangle$ and $\langle s_i s_{i+2}\rangle$. However, for SC systems, we found that the relevant parameters are the HS–LS pairs, of NN and NNN, denoted here respectively by $n^{\mathrm{HL}}_{i,i+1}$ and $n^{\mathrm{HL}}_{i,i+2}$. These two quantities are simply related to the correlations $\langle s_i s_{i+1}\rangle$ and $\langle s_i s_{i+2}\rangle$ through the relations $n^{\mathrm{HL}}_{i,i+1} = (1 - \langle s_i s_{i+1}\rangle)/2$ and $n^{\mathrm{HL}}_{i,i+2} = (1 - \langle s_i s_{i+2}\rangle)/2$.

We report in figure 3 the thermal evolution of the quantities $n^{\mathrm{HL}}_{i,i+1}$ and $n^{\mathrm{HL}}_{i,i+2}$. In the plateau region, corresponding to the interval of temperature [115 K, 250 K], we found $n^{\mathrm{HL}}_{i,i+1} \approx 1$ and $n^{\mathrm{HL}}_{i,i+2} \approx 0$, which denotes a strong ordering of the system in the configuration HS–LS–HS–LS–

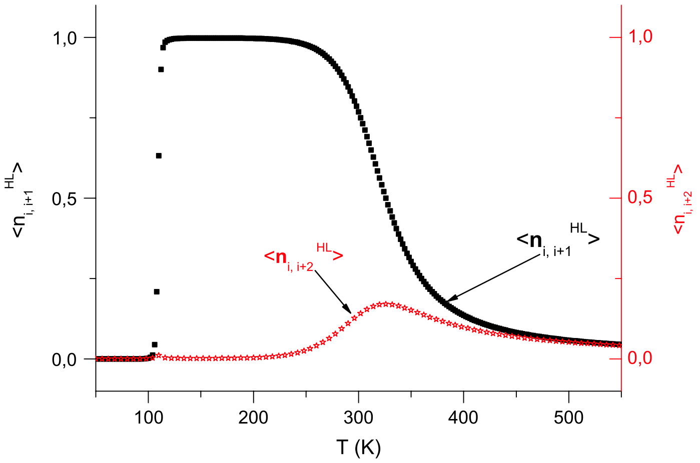

Figure 3. Thermal dependence of the fraction of HS–LS, NN ($n^{\mathrm{HL}}_{i,i+1}$) and NNN ($n^{\mathrm{HL}}_{i,i+2}$) pairs, in the case of figure 2. In the plateau region $n^{\mathrm{HL}}_{i,i+1} \approx 1$ and $n^{\mathrm{HL}}_{i,i+2} \approx 0$, which indicates that the system organizes as an antiferro-like (HS–LS–HS–LS) state (see the text for more explanation).

HS–LS–HS–$\cdots$ which is the antiferro-like ordering. This is well confirmed by the evolution of the heat capacity which drops drastically in this region, as seen in the inset of figure 2. One can follow the entropy of the system and make the same remark. This 'ordered' intermediate state is lost at higher temperature, due to thermal fluctuations, which induce a disordered phase in a small interval of temperature. Consequently, the fraction of $n^{\mathrm{HL}}_{i,i+2}$ increases in the region [250 K, 300 K], and finally it drops again at a higher temperature due to the presence of the ordered HS state. Finally, we can summarize that the chain undergoes the following scenario with temperature: LS ordered state → (abrupt transition) HS–LS–HS–LS–HS–LS–HS (antiferro-like state) ⟶ disorder ⟶ HS ordered state. From the experimental point of view, this behaviour is observed in some of two-step SC compounds [12].

3.2.2. Case $J > 0$ and $K < 0$. A 'ferro'-like NN interaction ($J > 0$), combined with an 'antiferro'-like NNN interaction ($K < 0$), favours the HS–HS–LS–LS configuration with respect to symmetric quartets. At low temperature, the ligand field energy stabilizes the LS state. On the other hand, at high temperature, the ligand field energy decreases drastically due to the effect of entropy ($-kT \ln g$), and finally with the help of the NN interaction, the system converts into the HS state. This behaviour is illustrated in figure 4. In the intermediate phase, that is the temperature region [175 K, 250 K], a competition occurs between the 'ferro'-like and the 'antiferro'-like interactions, leading to a new macroscopic state in which the system is partially in the configuration HS–HS–LS–LS–HS–HS–LS–LS–HS–HS, that is the so-called 'antiphase' (or phase $\langle 2 \rangle$) structure, already reported in the literature on the ANNNI model for Ising models [39].

The double-step transition on the HS fraction, is also confirmed by the heat capacity behaviour (in inset) which shows two peaks. To investigate the nature of the intermediate phase, we study the thermal variation of the NN and NNN HS–LS pairs: $n^{\mathrm{HL}}_{i,i+1}$ and $n^{\mathrm{HL}}_{i,i+2}$. The results obtained are depicted in figure 5. In the plateau region, corresponding to the temperature interval [175 K, 250 K], the HS–LS pairs reach the maximum values $n^{\mathrm{HL}}_{i,i+1} \approx 0.25$ and $n^{\mathrm{HL}}_{i,i+2} \approx 0.75$. We consider this result as a clear indication of the existence of a macroscopic phase of the system in the configuration HS–HS–LS–LS–HS–HS–LS–LS–HS–HS. This phase,

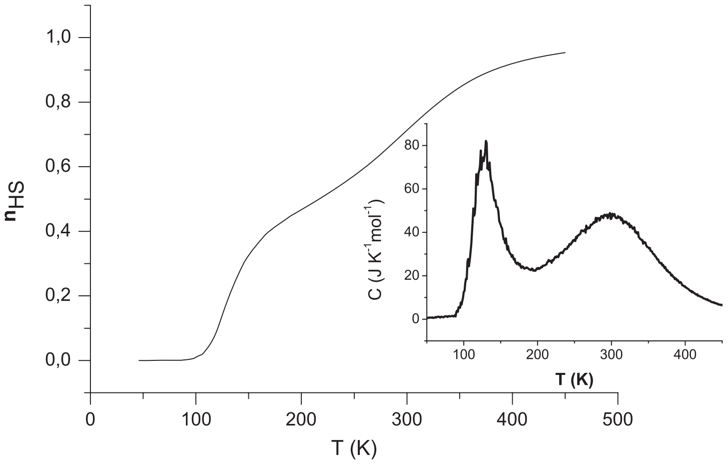

Figure 4. The HS fraction as function of temperature in the case $J > 0$ and $K < 0$. A two-step spin transition is again obtained, where both transitions are gradual. The investigations on the nature of the plateau are shown in figure 5. In the inset, the temperature dependence of the heat capacity also shows two peaks, as in figure 2. The parameter values are $J = 290$ K, $K = -250$ K, $\Delta = 1300$ K and $\ln g = 6$.

which has never been predicted theoretically in the SC literature, is in good agreement with recent experimental results evidencing a direct two-step SC through the [HS–HS] $\cdots$ [LS–LS] plateau in the '1D' dinuclear complex $[\{Fe(CNBH_3)(4phpy)\}_2(\mu\text{-bpypz})_2]$ [6]. In that experimental study, the authors were able to characterize the microscopic spin states (HS or LS) of NN and NNN molecules using Raman spectroscopy, leading to discrimination of the present phase $\langle 2 \rangle$ from the 'antiferro'-like phase (HS–LS–HS–LS). Indeed, Raman spectroscopy is a very sensitive technique, which probes local distortions. It is widely applied to differentiate the HS and LS states and to estimate the entropy contributions [45, 46] due to vibrational degrees of freedom.

4. Discussion and conclusion

At the beginning of this paper, we said that the real interaction in SC is elastic; however we used an Ising-like model to describe the thermal properties of these systems. Let us discuss the real origin of the competing interaction observed in SC materials.

In real crystals, as in SC solids, the elastic interactions can be complicated. As an example, the interaction may decay slowly, as $1/r^3$, and, most importantly, it can have different signs in different directions [47]. One example of this complexity was recently evidenced by Burgi *et al* [48] in their structural investigations of the $[Fe(2\text{–}pic)_3]Cl_2\cdot EtOH$ (2-pic stands for 2-picolylamine) [49] SC solid, which is a 3D compound showing a two-step spin transition. The structural investigations in the intermediate phase, that is the plateau region, have shown the existence of a cell doubling. The superstructure obtained is made up of successive planes, predominantly HS and LS, showing that long range correlations play a crucial role in this material. In addition, this result indicates that the interactions inside this crystal are anisotropic, which is a characteristic of the elastic interactions. On the other hand, kinetic investigations on the same system, that is studies of the relaxation of the photo-induced metastable HS state at low temperature, have clearly established the presence of a long tail effect attributable to the existence of predominant short range correlations [50] between the SC species. This discrepancy between the dynamic and the static experimental results shows the key role of the

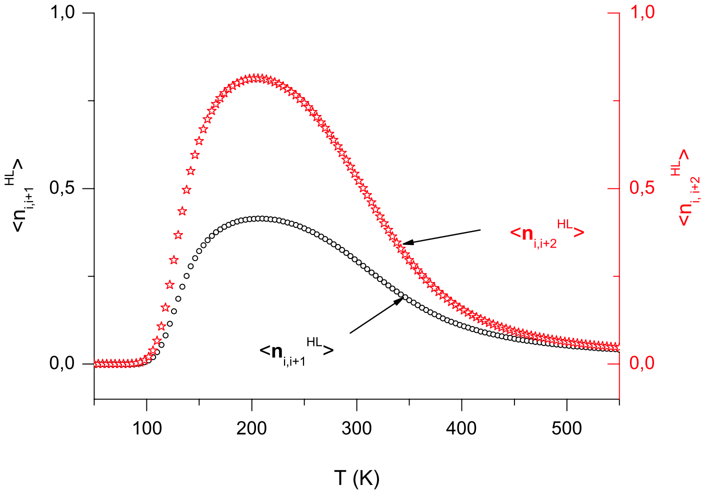

Figure 5. Thermal evolution of the fraction of HS–LS of NN ($n^{\mathrm{HL}}_{i,i+1}$) and NNN ($n^{\mathrm{HL}}_{i,i+2}$) pairs in the case of figure 4, indicating that the major microscopic configuration in the plateau is now the phase ⟨2⟩ (HS–HS–LS–LS–HS–HS–LS–LS). The intermediate state is not ordered, due to thermal fluctuations. This result is in agreement with the heat capacity behaviour (see the inset of figure 4), which drops partially in the plateau region.

temperature in the interactions. Indeed, the true interaction between SC units proceeds through the phonon field [9, 16] which is temperature dependent. In particular, the interaction between the phonon field, which contributes to thermal driving of the spin transition, and the electronic system may explain the discrepancy between the equilibrium thermodynamic properties and the out of equilibrium behaviours.

In the present study, we have performed an exact examination of an accurate 1D ANNNI-like model describing the various spin crossover transitions observed in 1D SC solids. Our model includes both NN and NNN interactions and shows that in the case of competing interactions, the nature of the plateau depends on the interaction parameter signs. In the framework of the present Hamiltonian, we have identified two microscopic configurations for the intermediate phase: (i) an antiferro-like organization HS–LS–HS–LS–HS, and (ii) an 'antiphase' state HS–HS–LS–LS–HS–HS. The former configuration was already reported [33] in the SC literature several years ago for 3D systems. In contrast, for the latter configuration, recent experiments on a new 1D two-step SC solid [7], based on Raman investigations [6], have evidenced an organization of type (ii) in the plateau. Our model predicts this behaviour and explains it as a consequence of a thermodynamic competition between an antiferro-like NNN interaction and a ferro-like NN interaction.

A possible extension of the present work would be as regards its dynamical aspects. This development could be possible using the stochastic formalism of the master equation, introduced by Glauber [51]. In particular, it becomes interesting to investigate the relaxation of the metastable HS fraction at low temperature in the case of a two-step transition for both situations studied here, and to evaluate the impact of the antiphase and antiferro-like organization on the shape of the relaxation curves.

Acknowledgments

The authors wish to acknowledge the Université de Versailles Saint-Quentin en Yvelines (UVSQ), CNRS, the ECONET programme, the MAGMANet Network of Excellence of the European Union (Contract: NMP3-CT-2005-515767-2) and PAI (Tournesol programme: 10883PD), for financial support. Professor Y Garcia is also acknowledged for his reading of the manuscript and for valuable discussions.

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