A simple model of spin transitions in polymeric materials

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Abstract. Recent experiments have shown that first-order spin transitions can occur in polymeric Fe^{II} compounds. In such materials the metal ions are linked by ligand groups to form polymeric chains. Existing theories of the spin transition in crystalline materials are discussed, but we argue that the physical justification of these theories may be inappropriate for polymeric compounds. We describe a possible mechanism in which local strain in the ligand network can drive the transition. A model Hamiltonian is presented and solved, and the effects of pressure and dopant concentration on the spin transition are investigated. We also point out that the model describes many of the effects observed in experiments on crystalline materials.

1. Introduction

Various transition metal compounds exhibit so-called spin transitions, in which the metal ions undergo transitions from low-spin (LS) to high-spin (HS) states upon a change in the temperature or pressure, or upon irradiating the sample [1]. This phenomenon occurs typically for $3d^n$ metal ions with $n = 4$–8. Fe^{II} ($3d^6$) in an octahedral coordination environment is probably the most common example. The electronic transition occurs between the $S = 0$ (LS) and $S = 2$ (HS) states, which are separated by a positive energy difference $\Delta = E_{HS} - E_{LS}$. The HS level actually comprises fifteen electronic states, but since the splitting of these states is small compared to Δ, it can be viewed as being fifteen-fold degenerate. The order parameter for the transition is the fraction of ions in HS states, which can be inferred from magnetic susceptibility measurements or Mössbauer spectroscopy [1]. When the temperature is raised to the order of Δ/k_B, where k_B is Boltzmann's constant, the HS fraction rises steeply. Depending on the compound and the experimental conditions, the change in HS fraction is either continuous or apparently discontinuous. For the case of non-interacting and isolated ions the HS fraction is driven solely by thermal excitation, and one would expect the curve to be continuous. This is found to be the case experimentally in systems where ion–ion interactions are negligible— for instance, in samples doped with large concentrations of metal ions which cannot undergo a spin transition, such as Zn^{II} [2, 3]. As the dopant concentration is increased, the transition is shifted to lower temperature and becomes less sharp [2, 3]. A discontinuous jump in HS fraction indicates a first-order transition. In this case, on decreasing the temperature the HS fraction falls again but there may be a large temperature hysteresis as well as a residual HS fraction. These effects can be magnified by increasing the pressure [4]. For a first-order transition to occur there must be significant effective ion–ion interactions which disfavour LS–HS mixtures, and it is the source of these interactions which will form the core of our discussion.

There is an extensive body of literature regarding the cause of the effective ion–ion interaction. Although the ideas are varied, the theoretical implementations are similar; an approximate form for the free energy is presented which contains terms linear and quadratic in the HS fraction, as well as an ideal-mixing contribution. This functional form gives rise to continuous and first-order transitions, and hysteresis, depending on the coefficients. The earliest examples of this approach are those of Chestnut [5] and Slichter and Drickamer [6]. The work of Slichter and Drickamer is based on solution theory, but the resulting expression for the free energy contains the essential ingredients. The linear term in the HS fraction arises from the single-ion energy, i.e. the crystal-field splitting. The coefficient of the quadratic term arises from the effective ion–ion interaction. In references [3, 5, 7–9] the respective authors attribute all or some of this interaction to lattice strains, caused either by phonon–ion interactions giving rise to attractive HS–HS interactions [5, 7], or by different elastic energies associated with crystals of LS or HS ions [3, 8]. The coupling of molecular (Jahn–Teller) distortion and lattice strains has also been investigated [9]. In references [4, 10–12] the possibility of HS (or LS) domains is explored. Direct ion–ion and phonon-assisted interactions lead to a spin cooperativity over domains of a characteristic size, thus giving a sharp transition. The interpretation of experimental data using this domain model can lead to estimates of the characteristic domain size of anywhere between three [10] and a hundred [11] ions. Hysteresis is explained once the rôle of lattice defects as domain nucleation sites is considered [10, 12]. An increase in pressure raises the density of defects and so magnifies the hysteresis [4]. Lastly, some authors have simply mapped the problem onto Ising-type models [8, 13], which leads to an appropriate form for the free energy. The origin of the effective ion–ion interaction is not addressed, however, but merely mapped onto the (anti-) ferromagnetic interaction of the Ising model.

In all of these approaches the LS–LS and HS–HS interactions are necessarily more favourable than LS–HS interactions, although the explanations for this are varied and approximate. The current status of the theory of spin transitions in crystalline Fe^{II} compounds is therefore largely phenomenological, but perhaps the likely sources of the effective ion–ion interactions have been identified.

Recently, first-order transitions have been observed in some polymeric Fe^{II} compounds [14–16]. In these compounds, chains of Fe^{II} ions are bonded together by large ligand groups, but there is not necessarily a well-defined crystal structure. In the experiments it proved impossible to grow a large single crystal of the compound, and the crystal structure is not known. EXAFS data in reference [15] show no major structural changes accompanying the spin transition, but only a lengthening of the Fe^{II}–ligand bonds by 0.18 Å. This may be due, in part, to the fact that HS ions have a larger radius than those in the LS state. The spin transition in these materials shows appreciable hysteresis, and in some work [14] the metastable limits lie about 10 K either side of typical room temperatures. There was seen to be almost no residual HS fraction on cooling the sample, other than that due to small traces of Fe^{III} ions formed by atmospheric oxidation of the sample in the course of the experiments. In a recent study, Cantin *et al* [16] note that the effect of doping polymeric materials with ions such as Cu^{II} or Mn^{II} on the spin transition is similar to that in crystalline materials, i.e., the transition shifts to lower temperature and becomes less sharp.

It is not clear whether ideas developed about crystalline compounds are applicable to polymeric materials without a well-defined crystal structure. Firstly, the treatment of proper vibrations in perfect crystals, such as the Debye theory [8], or the study of lattice expansion via the Grünheisen approximation [3], cannot be carried over to such polymeric compounds. Secondly, the formation of HS (or LS) domains in a system of polymeric chains with steric

interactions seems unlikely, and this is supported by the absence of residual HS fractions in experiments [14–16]. Some experimental data suggest that magnetic or dispersion interactions, which can lead to spin cooperativity, are weak even in some crystalline materials [10]. In reference [7] Bari and Sivardière studied an Ising-type Hamiltonian with ferromagnetic interactions. They found that the spin transition, on increasing the temperature, is always accompanied by a magnetic transition to an ordered state. We have confirmed this for a variety of spin Hamiltonians with ferromagnetic and antiferromagnetic interactions. A magnetic transition is not observed in experiments, however.

The task, therefore, is to find an alternative explanation for the first-order spin transition in polymeric Fe^{II} compounds. In this paper we present a simple model Hamiltonian for such materials. Although the model is one dimensional, thus mimicking the polymeric structure of the compounds, the physical mechanism through which the effective ion–ion interactions arise is three dimensional.

In section 2 we describe and justify the model, and then proceed to derive its exact free energy. In section 3 we present some experimentally relevant results, and section 4 concludes the paper.

2. The model

The central idea of our approach to the spin transition in polymeric materials is the presence of strain in the ligand network. Imagine a chain of Fe^{II} ions, with each ion bridged to its neighbour by a large ligand group. This is the case in the experiments of reference [15]. In the bulk material each chain will interact with its nearest neighbours largely through steric interactions. It is reasonable to assume that there is considerable resistance towards a particular region of a given chain sliding freely against the neighbouring chains. The Fe^{II} ions are therefore constrained to particular positions relative to the ligand network. As the temperature is increased, ions undergo thermal excitations to HS states at random, assuming that no domains of cooperative spins can develop. The HS ionic radius is greater than that of a LS ion, and so the equilibrium separation between metal ions in a chain also increases. In a mixture of LS and HS ions, the ion–ion distance in a particular chain is constrained by the ligand network to be commensurate with its neighbouring chains. As a result, elastic strain develops, mainly in the pairs of ligand bridges attached to each HS ion. The only way that the resulting strain can be relieved is if the equilibrium ion–ion separation along a chain is roughly equal for all chains. This is achieved if the majority of ions are either in the LS state or in HS states. Consequently, mixtures of LS and HS ions are disfavoured. A similar argument holds for the cooling of a sample where the majority of ions are initially in HS states.

On the basis of this argument, we define our model system as follows. Consider N particles of equal mass m, free to move along a line of length L. We will wish to investigate the effect of dopant concentration on the spin transition and so we will include it at the outset. Each particle is labelled with either 0, 1 or d corresponding to whether it is a LS ion, a HS ion or an inert dopant ion, respectively. A LS ion can undergo a transition to any of ν HS states at random, and vice versa, where ν is the HS level degeneracy. We define the system Hamiltonian as

$$\mathcal{H} = N_1 \Delta + \sum_{k=1}^{N} (p_k^2/2m + u_{k,k-1}) \tag{1}$$

where N_1 is the number of ions in HS states and p_k is the momentum of particle k. $u_{k,k-1}$

is the pair interaction potential which is a function of the particle positions, q_k and q_{k-1}:

$$u_{k,k-1} = \begin{cases} \infty & |q_k - q_{k-1}| < \sigma_{k,k-1} \\ 0 & |q_k - q_{k-1}| \geqslant \sigma_{k,k-1}. \end{cases} \tag{2}$$

The interaction potential is therefore defined by a set of six numbers, namely σ_{00}, σ_{01}, σ_{11}, σ_{0d}, σ_{1d}, and σ_{dd}. Actually, in demanding that the dopant be inert, we can set $\sigma_{0d} = \sigma_{1d} = \sigma_{dd} = 0$. The model is therefore defined by only three parameters. On the basis of the argument outlined above, $\sigma_{k,k-1}$ is greatest between a LS ion and a HS ion. Since the HS radius is larger than that of the LS radius, the following inequalities must therefore be satisfied:

$$\sigma_{01} > (\sigma_{11} + \sigma_{00})/2 > \sigma_{00}. \tag{3}$$

The model so defined is a non-additive one-dimensional version of the Widom–Rowlinson model [17], where non-additivity implies the first inequality in equation (3).

　　This model is clearly oversimplified, but we argue that it is physically relevant. The dominant interactions of a given ion on a given polymer chain are with its nearest neighbours on the *same* chain, and these can be accounted for, at least approximately, in a one-dimensional model. In the physical picture described above, the unfavourable LS–HS interactions arise from chain–chain interactions. These are *effectively* accounted for by the non-additivity of our one-dimensional Hamiltonian. One could think of an explicit model for the polymer chains which included intra- and inter-chain coupling, but it would probably not admit an exact solution, nor would it be a simple model with only a few parameters. The present model has the merits of an exact solution, which we shall show in the next section, and identifying the physically relevant parameters.

2.1. The free energy at constant pressure

In this section we derive the Gibbs free energy at constant pressure from the Hamiltonian defined in equations (1) and (2). Of the N particles, N_0 are LS ions, N_1 are HS ions, and N_d are inert dopant ions. The concentration of species α is given by $c_\alpha = N_\alpha/N$ and $\sum_\alpha c_\alpha = 1$. In the canonical ensemble, N_0, N_1, N_d, L, and T are constant, and the configurational integral is given by

$$Z = \nu^{N_1} \exp(-\beta N_1 \Delta) \sum_{\mathcal{P}} \int_0^L dq_1 \cdots \int_0^L dq_N \ \exp\left(-\beta \sum_{k=1}^N u_{k,k-1}\right) \tag{4}$$

where ν is the HS level degeneracy, $\beta = 1/k_B T$, and the sum is performed over all distinguishable permutations of the N particles along the line. By defining new coordinates $r_k = q_k - q_{k-1} - \sigma_{k,k-1}$, equation (4) can be written as

$$Z = \nu^{N_1} \exp(-\beta N_1 \Delta) \sum_{\mathcal{P}} \int_0^\infty dr_1 \cdots \int_0^\infty dr_N \ \Theta\left(L - \sum_{k=1}^N (r_k + \sigma_{k,k-1})\right) \tag{5}$$

where $\Theta(x)$ is the Heaviside function, the argument of which constrains the chain of particles to the line of length L. Following the approach of Ibsen *et al* [18], by inserting the complex integral representation for $\Theta(x)$ into equation (5) and integrating over the particle coordinates, we obtain

$$Z = \nu^{N_1} \exp(-\beta N_1 \Delta) \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \frac{dz}{z^{N+1}} \ \exp(zL) \sum_{\mathcal{P}} \exp\left(-z \sum_{k=1}^N \sigma_{k,k-1}\right). \tag{6}$$

To evaluate the sum in equation (6) we note that it is related to an average over all $N!/N_0!N_1!N_d!$ possible particle arrangements. Since we assume that all arrangements of LS and HS ions are equally likely in the absence of domains, and that the system is doped at random, we can write in the limit of large N, with c_0, c_1, and c_d constant,

$$\sum_{\mathcal{P}} \exp\left(-z\sum_{k=1}^{N} \sigma_{k,k-1}\right) = \frac{N!}{N_0!N_1!N_d!}\overline{\exp\left(-z\sum_{k=1}^{N} \sigma_{k,k-1}\right)} = \frac{N!}{N_0!N_1!N_d!}\exp(-zN\bar{\sigma}) \quad (7)$$

where

$$\bar{\sigma} = c_0^2\sigma_{00} + 2c_0c_1\sigma_{01} + c_1^2\sigma_{11} \qquad (\sigma_{0d} = \sigma_{1d} = \sigma_{dd} = 0). \quad (8)$$

The bars in equations (7) and (8) denote averages over all distinguishable permutations of ion identities. Substituting equation (7) into equation (6) and performing the integral by parts, we obtain the configurational integral in the canonical ensemble,

$$Z = \frac{\nu^{N_1}\exp(-\beta N_1\Delta)}{N_0!N_1!N_d!}(L - N\bar{\sigma})^N \Theta(L - N\bar{\sigma}). \quad (9)$$

The canonical partition function, Q, is given by

$$Q = \frac{Z}{\Lambda^N} \quad (10)$$

where Λ is the de Broglie thermal wavelength. To transform the canonical partition function to the constant-pressure (N_0, N_1, N_d, P, T) partition function, ζ, the integral required is

$$\zeta = \int_0^\infty dL \ \exp(-\beta PL)Q = \frac{N!}{N_0!N_1!N_d!}\frac{\nu^{N_1}}{(\beta P)^{N+1}\Lambda^N}\exp(-\beta N_1\Delta - \beta PN\bar{\sigma}). \quad (11)$$

Finally, the Gibbs free energy per particle, G/N, is given in the thermodynamic limit by

$$\frac{\beta G}{N} = -\frac{1}{N}\ln\zeta = c_0\ln c_0 + c_1\ln c_1 + c_d\ln c_d + c_1(\beta\Delta - \ln\nu) + \ln\beta P\Lambda + \beta P\bar{\sigma}. \quad (12)$$

The pressure, P, in equation (12) is strictly a force in one dimension, but we use pressure here to highlight the link with experiments. This is the central result of our analysis, and it contains all of the necessary terms to predict a spin transition. It is also the exact solution of the Hamiltonian described and justified above. In the next section we present numerical results for the spin transition.

3. Numerical results

In this section we investigate the effects of pressure and dopant concentration on the spin transition. We study the model defined in section 2 with the parameters

$$\begin{aligned}
\sigma_{00} &= \sigma \\
\sigma_{01} &= 3\sigma \\
\sigma_{11} &= 2\sigma \\
\sigma_{0d} &= \sigma_{1d} = \sigma_{dd} = 0 \\
\nu &= 15
\end{aligned} \quad (13)$$

where σ defines the unit of length. The $\sigma_{k,k-1}$-parameters satisfy equation (3) but are otherwise arbitrary. The degeneracy of the HS level, ν, is set to that of the $S = 2$ level of Fe^{II}.

For a given pressure, temperature and dopant concentration, the equilibrium HS concentration is that which minimizes the Gibbs free energy, i.e.

$$\left. \frac{\partial(\beta G/N)}{\partial c_1} \right|_{c_1=c_1^{eq}} = 0. \tag{14}$$

In experiments, the *fraction* of ions in HS states, x_1, is reported, and this is given by

$$x_1 = \frac{c_1}{c_0 + c_1}. \tag{15}$$

In the case of non-interacting ions, minimization of equation (12) with $\sigma = 0$ leads directly to

$$x_1 = \frac{\nu \exp(-\beta\Delta)}{1 + \nu \exp(-\beta\Delta)} \tag{16}$$

yielding the high-temperature HS fraction, $x_1 = \nu/(\nu + 1)$. Equation (16) is expected to hold in heavily doped systems, whilst the high-temperature HS fraction will hold at all dopant concentrations. In general, the free energy in equation (12) was minimized by solving equation (14) using the Newton–Raphson method. For each pressure, temperature, and dopant concentration, two minimizations were performed, with the initial value of c_1 set to 0.0001 and $0.99(1 - c_d)$. The two solutions of equation (14) will be different only for those temperatures inside the metastable region which brackets the equilibrium transition temperature. This reflects the fact that there is a free-energy barrier between the LS and HS 'phases' in the metastable region, which manifests itself in temperature hysteresis. The equilibrium transition temperature is determined by the equality of the Gibbs free energy per particle in the two phases, one predominantly LS and the other predominantly HS.
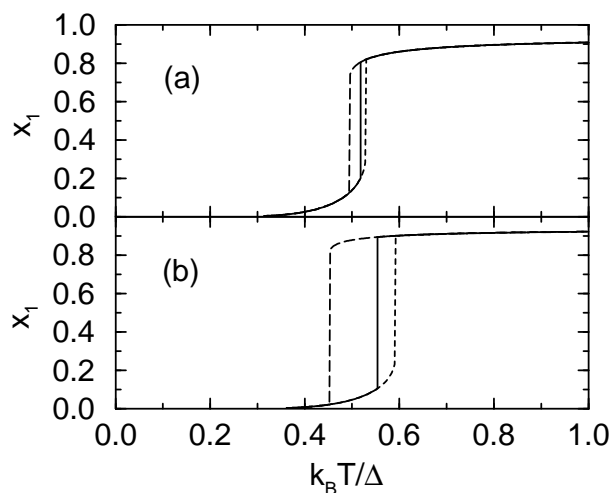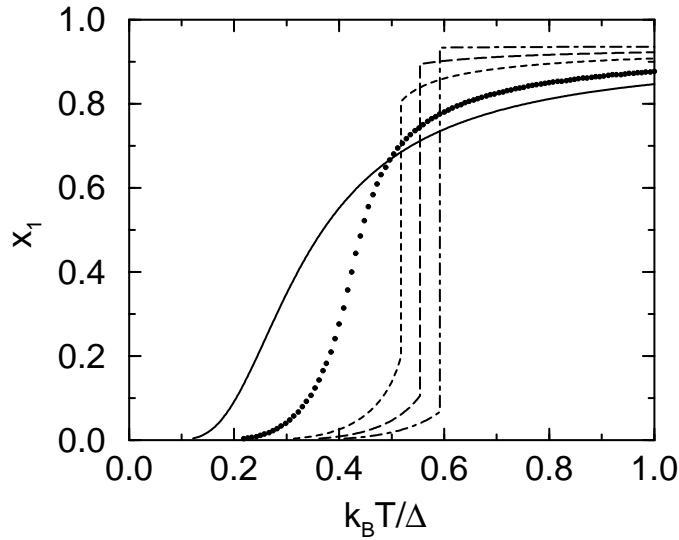

Figure 1. The high-spin fraction as a function of temperature for (a) $P\sigma/\Delta = 0.4$ and (b) $P\sigma/\Delta = 0.5$: the heating curve (short-dashed line); the cooling curve (long-dashed line); the equilibrium curve (solid line). $c_d = 0$ in both cases.

We report results in dimensionless units reduced by σ and Δ. In figure 1, x_1 is shown as a function of temperature at two pressures $P\sigma/\Delta = 0.4$ and $P\sigma/\Delta = 0.5$, with no dopant. For each pressure the warming curve (low initial c_1), cooling curve (high initial c_1), and equilibrium curve are shown. The main point is that the width of the hysteresis loop

increases with increasing pressure, in qualitative agreement with experiments on crystalline materials [4]. This reflects the fact that as the pressure is raised, the free-energy barrier between LS and HS phases increases, i.e. mixtures of LS and HS ions are increasingly disfavoured.

In figure 2, we show the equilibrium x_1-curves against temperature for a series of pressures in the range $P\sigma/\Delta = \{0, 0.6\}$, with no dopant. As the pressure is increased the transition shifts to higher temperature and becomes discontinuous. In the experiments of König *et al* on crystalline materials [4], a slight increase in transition temperature with pressure was recorded, in agreement with our results. Also observed in these experiments was an increase in the residual HS fraction upon cooling the material, which does not occur in our model. This is consistent with the formation of domains, but as we pointed out in section 1, the formation of domains in polymeric materials seems unlikely. Indeed, no such residual HS fraction was observed in references [14, 15], other than that due to small traces of Fe^{III} ions.

Figure 2. The equilibrium high-spin fraction as a function of temperature at various pressures: $P\sigma/\Delta = 0$ (solid line); $P\sigma/\Delta = 0.2$ (dotted line); $P\sigma/\Delta = 0.4$ (short-dashed line); $P\sigma/\Delta = 0.5$ (long-dashed line); $P\sigma/\Delta = 0.6$ (dot–dashed line). $c_d = 0$ in all cases.

The pressure at which the transition becomes discontinuous, P^*, can be determined from equation (12). For $P > P^*$ there exists, at the transition temperature, a maximum in the free energy corresponding to the top of the barrier between LS and HS phases. Therefore, at P^*,

$$\left.\frac{\partial(\beta G/N)}{\partial c_1}\right|_{P^*,T^*,c_1^*} = 0$$
$$\left.\frac{\partial^2(\beta G/N)}{\partial c_1^2}\right|_{P^*,T^*,c_1^*} = 0 \tag{17}$$

where T^* and c_1^* are the corresponding transition temperature and HS concentration

respectively. From the free energy in equation (12), some algebra yields

$$\frac{k_B T^*}{\Delta} = \left(\ln \nu + \frac{2(\sigma_{00} - \sigma_{11})}{2\sigma_{01} - \sigma_{00} - \sigma_{11}} \right)^{-1}$$

$$\frac{P^* \sigma}{\Delta} = \frac{2\sigma}{2(\sigma_{00} - \sigma_{11}) + (2\sigma_{01} - \sigma_{00} - \sigma_{11}) \ln \nu} \tag{18}$$

$$c_1^* = \frac{1}{2}.$$

From equation (18) it is clear that if $\sigma_{00} = \sigma_{11}$, then for there to be a discontinuous transition at finite pressure, $\sigma_{01} > (\sigma_{00} + \sigma_{11})/2$ and $\nu > 1$. Hence, the sharp transition is driven by the non-additivity of the ion interactions, and the degeneracy of the HS level. For the parameters used in this study, $P^* \sigma / \Delta \simeq 0.3266$ and $T^* \simeq 0.4899$.

In figure 3 we show the equilibrium x_1-curves against temperature for a series of dopant concentrations at a pressure $P \sigma / \Delta = 0.5$. As the dopant concentration is increased the transition shifts to lower temperatures and becomes less sharp, in qualitative agreement with experiments on polymeric Fe^{II} compounds [16] and crystals [2, 3]. In the most heavily doped system, $c_d = 0.99$, the curve is indistinguishable from equation (16). This is due to the dilution of interacting pairs of ions by the dopant.
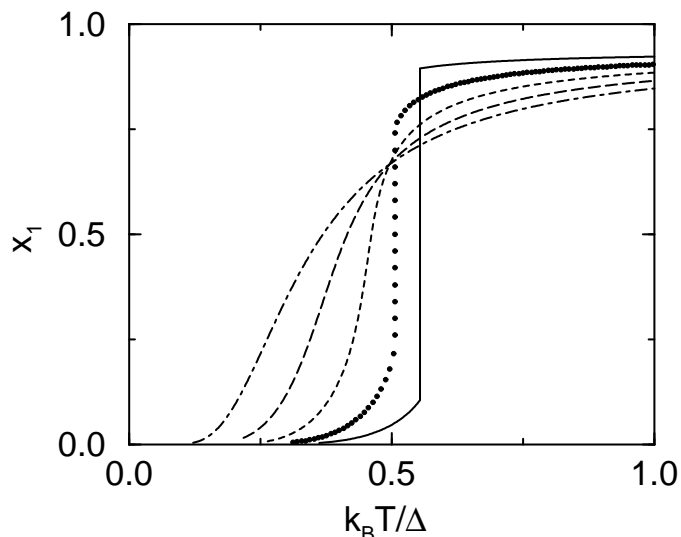
Figure 3. The high-spin fraction as a function of temperature for $P\sigma/\Delta = 0.5$ and various dopant concentrations: $c_d = 0.0$ (solid line); $c_d = 0.25$ (dotted line); $c_d = 0.50$ (short-dashed line); $c_d = 0.75$ (long-dashed line); $c_d = 0.99$ (dot–dashed line).

It should be noted that at the time of writing there is very little published literature regarding spin transitions in polymeric Fe^{II} compounds [14–16]. Hence the effect of pressure on the spin transition in polymeric Fe^{II} is not yet known from experiments. Our simple model does predict the effect of doping seen in reference [16], i.e., the transition occurs at a lower temperature and becomes less abrupt. Our theoretical predictions are in agreement with experiments on crystalline Fe^{II} compounds, although the physical justification of our model does not necessarily carry over to such materials.

4. Discussion

In this paper we set out to describe the mechanism by which sharp spin transitions can occur in polymeric Fe^{II} compounds. We have discussed the theories of the transition in crystalline materials, but we have pointed out that the application of such ideas to the case of polymeric materials might be inappropriate. We have described a possible mechanism in which the transition is driven by a strain developed in the ligand network due to HS ions having a larger radius than those in the LS state. The only way to relieve the strain is by a cooperative transition to HS states. From these ideas, we conceived of a model Hamiltonian which contains the effective ion–ion interactions required by our suggested mechanism. The model was solved exactly, allowing us to investigate the spin transition. The effects of pressure and dopant concentration on the spin transition, and the hysteresis of the transition, were studied. On increasing the pressure, we find that the spin transition shifts to higher temperature and becomes sharper. In addition, the associated hysteresis grows with increasing pressure. Although, to date, there are no published experimental data on the effect of pressure in polymeric materials, the trends that we found are similar to those observed in experiments with crystalline materials. We anticipate that the effect of pressure on the spin transition in polymeric materials will be captured by our model. Adding an inert dopant at fixed pressure reduces the transition temperature and makes the transition less sharp, in agreement with recent experiments.

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