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SPIN ANISOTROPY EFFECTS ON THE
DIMERIZATION OF THE MAGNETOSTRICTIVE
ONE-DIMENSIONAL XY MODEL

by

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ABSTRACT

We consider in the one-dimensional first-neighbour spin- $\frac{1}{2}$ magnetostrictive XY model (with crystalline degrees of freedom assumed three-dimensional) different X and Y spin coupling constants. This anisotropy leads to a quite rich phase diagram for the dimerizing spin-Peierls instability; in particular it provides the possibility of a first-order phase transition at vanishing external magnetic field, thus constituting a convenient theoretical framework for the discussion of substances like the alkali-TCNQ salts.

Since Chestnut's discussion^[1] in 1966 of the connection between the metallic Peierls instability and what is now called the "spin-Peierls instability" (SPI), a certain amount of experimental^[2-9] and theoretical^[10-23] effort has been dedicated to the study of structural phase transitions in systems which are magnetically quasi-one-dimensional although three-dimensional in what concerns crystalline interactions. The system typically presents at high temperatures an uniform (or disordered) phase (equidistant atoms along the chain) and, at low temperatures, a more complex (or ordered) phase (a structurally dimerized or even polymerized chain if a non vanishing magnetic field is present). As we shall see further on, if we include spin anisotropy in the system the picture becomes quite more complex than just outlined. Among the substances which present SPI (or supposed so) we can mention^[2-9] TTF-BDT and several alkali-TCNQ salts; in what concerns the latter, the K, Rb and NH₄ salts present^[2], at vanishing external magnetic field, a latent heat thus characterizing a first order phase transition (whereas the Na and C₅ salts present a second order one). This feature is, to the best of our knowledge, absent from all the theoretical frameworks that have been proposed until now for the SPI in the standard magnetostrictive XY^[10,11,13,15,16,20,23] model; the same holds for the SPI in the magnetostrictive Heisenberg model^[12,14,17,18,21,22] with the possible exception of the (Hartree-Fock) approximate treatment of Takaoka and Motizuki^[22] who disagree with Beni's conclusions^[12]. Herein we exhibit on the spin- $\frac{1}{2}$ XY model (which presents the advantage of being exactly solvable in what concerns the magnetic degrees of freedom) that spin coupling anisotropy is a mechanism which provides the possibility for the phase transition to be a first order one.

We assume in the present paper that the ordered phase is (at least infinitely close to the critical frontier) a purely dimerized one, in spite of the possible spin coupling anisotropy.

This point is a delicate one and deserves further comments. Pincus^[10] discussed the isotropic magnetostrictive spin - $\frac{1}{2}$ XY antiferromagnetic linear chain and showed that, at vanishing temperature, the system becomes unstable with respect to dimerization. Beni and Pincus^[11] exhibited next that this instability leads to a second order phase transition between the uniform and dimerized phases, under the assumption that those two phases are the only ones to be considered. Dubois and Carton^[13] proved next (for both ferro and antiferromagnetic cases) that this assumption was right at least immediately below the critical temperature T_c (more precisely they proved that coming from high temperatures the order which appears at T_c is indeed a dimerization). The validity of the assumption was recently^[23] concluded by exhibiting that for all temperatures below T_c , no other contribution to the structural order appears than the pure dimerization one. The whole picture is drastically altered in the presence of an external magnetic field (which plays the role of the chemical potential for a fermionic gas): in this case complex polymerizations occur^[15,16] which can even be incommensurate with the crystalline parameter and whose origin is the energetic displacement (as a whole) of the relevant fermionic spectrum with respect to the chemical potential. As we shall see further on no such energetic displacement occurs in the presence of spin coupling anisotropy (let us stress that this anisotropy privileges a direction but not a sense in the spin space, whereas a magnetic field privileges both), therefore the central assump-

tion of this work becomes very plausible if not proved (the complete proof along the lines of Ref. [23] is almost impracticable because of its operational length).

The magnetic contribution to the Hamiltonian of the spin - $\frac{1}{2}$ XY cyclic linear chain (with unitary crystalline parameter) is given by

$$H_m = -\sum_{j=1}^N \{J_0 [(1+\gamma)S_{2j-1}^x S_{2j}^x + (1-\gamma)S_{2j-1}^y S_{2j}^y] + \bar{J}_0 [(1+\gamma)S_{2j}^x S_{2j+1}^x + (1-\gamma)S_{2j}^y S_{2j+1}^y]\} \quad (1)$$

where, for future convenience, we have separated the interactions into odd and even ones and $\gamma \geq 0$ by convention. We remark that the isotropic XY ($\gamma=0$) and the Ising ($\gamma=1$) models are recovered as particular cases. Let us recall at this point a conclusion due to Dubois and Carton^[13] concerning vanishing temperature and $\gamma \leq 1$: the system is in its ordered phase (presumably dimerized) if $\gamma < \gamma_c$, and is in its disordered phase (uniform) if $\gamma > \gamma_c$, γ_c being a critical anisotropy. The present extension (to all values of γ and all temperatures) will confirm their conclusion. Before going on let us indicate an interesting relation between the models with $\gamma < 1$ and those with $\gamma > 1$. If we perform on the even sites the following canonical transformation:

$$\begin{aligned} S_{2j}^x &= S'_{2j}^x \\ S_{2j}^y &= -S'_{2j}^y \\ S_{2j}^z &= -S'_{2j}^z \end{aligned} \quad (2)$$

we immediately verify that

$$H_m(J_0, \bar{J}_0, \gamma) = H_m(\gamma J_0, \gamma \bar{J}_0, 1/\gamma) \quad (3)$$

We shall come back to this later on; however we can right now state that if γ_c is a critical anisotropy then $1/\gamma_c$ is critical as well.

Let us now go back to Hamiltonian (1): through the standard Jordan-Wigner transformation followed by a Fourier transformation and a final diagonalization we may rewrite the Hamiltonian as follows:

$$\frac{H_m}{J} = -\sum_k \epsilon_k' U_k^+ U_k + \sum_k \epsilon_k'' V_k^+ V_k + \frac{1}{2} \sum_k (\epsilon_k' - \epsilon_k'') \quad (4)$$

where k runs in the first Brillouin zone associated to a dimerized chain (i.e. $-\pi/2 < k \leq \pi/2$), U_k^+ and U_k (V_k^+ and V_k) are creation and annihilation operators associated to fermionic quasi-holes^[24] (quasi-particles), and

$$\epsilon_k' \equiv -(1 + \gamma \eta_0) \left[\cos^2 k + \left(\frac{\gamma + \eta_0}{1 + \gamma \eta_0} \right)^2 \sin^2 k \right]^{1/2} \quad (5)$$

$$\epsilon_k'' \equiv (1 - \gamma \eta_0) \left[\cos^2 k + \left(\frac{\gamma - \eta_0}{1 - \gamma \eta_0} \right)^2 \sin^2 k \right]^{1/2} \quad (6)$$

$$J \equiv \frac{|J_0 + \bar{J}_0|}{2} \quad (7)$$

$$\eta_0 \equiv \frac{J_0 - \bar{J}_0}{J_0 + \bar{J}_0} \quad (8)$$

We remark that $\epsilon_k'(\gamma, \eta_0) = \epsilon_k'(-\gamma, -\eta_0) = -\epsilon_k''(-\gamma, \eta_0) = -\epsilon_k''(\gamma, -\eta_0)$ and also that Eqs.(5) and (6) remain invariant under the trans-

formation $\gamma \leftrightarrow \eta_0$, i.e. the influence of γ on the spectra is indistinguishable from the influence of η_0 (thus supporting the assumption of dimerization). The magnetic free energy F_m is given, at vanishing temperature, by

$$F_m = \frac{J}{2} \sum_k (\epsilon_k' - \epsilon_k'') = - \frac{NJ}{\pi} \int_0^{\pi/2} dk (-\epsilon_k' + \epsilon_k'') \quad (9)$$

and, for finite temperature T , by the general expression

$$F_m = - \frac{2Nk_B T}{\pi} \int_0^{\pi/2} dk \left[\ln \left(2 \cosh \frac{J\epsilon_k'}{2k_B T} \right) + \ln \left(2 \cosh \frac{J\epsilon_k''}{2k_B T} \right) \right] \quad (10)$$

To the magnetic contribution we must add the elastic free energy F_e which, contrarily to F_m , is going to be treated only approximately (within the adiabatic approximation [25,26] which roughly takes into account the crystalline three-dimensionality of the real substance); we have that

$$F_e = F_e(\eta=0) + 2N \left[\frac{C}{2} (2\eta)^2 + \frac{D}{4} (2\eta)^4 \right] \quad (C, D > 0) \quad (11)$$

where η is the dimerization or order parameter (the distances between spins are now alternatively $(1+2\eta)$ and $(1-2\eta)$) and where higher order terms have been neglected (there is no η^3 term because of symmetry). The total free energy F is given, through Eqs. (10) and (11), by

$$F = F_m + F_e \quad (12)$$

If the exchange integral (between nearest neighbours) de

pendes smoothly on distance we will have (by neglecting higher order terms)

$$J_0 = J(0) + 2J'(0)\eta + 2J''(0)\eta^2 + \frac{4}{3}J'''(0)\eta^3 + \frac{2}{3}J^{IV}(0)\eta^4 \quad (13.a)$$

$$\bar{J}_0 = J(0) - 2J'(0)\eta + 2J''(0)\eta^2 - \frac{4}{3}J'''(0)\eta^3 + \frac{2}{3}J^{IV}(0)\eta^4 \quad (13.b)$$

and, by using Eqs. (7) and (8),

$$\eta_0 = \frac{2J'(0)}{J(0)} \eta \left\{ 1 + \left[\frac{2J'''(0)}{3J'(0)} - \frac{2J''(0)}{J(0)} \right] \eta^2 \right\} \quad (14)$$

and

$$j \equiv \frac{J}{J(0)} = 1 + \frac{2J''(0)}{J(0)} \eta^2 + \frac{2}{3} \frac{J^{IV}(0)}{J(0)} \eta^4 \quad (15)$$

By introducing the reduced free energies per site

$$f_i \equiv F_i/N|J(0)| \quad (i = m, e) \quad (16)$$

we obtain the total reduced free energy per site

$$\begin{aligned} f = & - \frac{2t}{\pi} \int_0^{\pi/2} dk \left[\ln \left(2 \operatorname{ch} \frac{j\varepsilon_k^I}{2t} \right) + \ln \left(2 \operatorname{ch} \frac{j\varepsilon_k^{II}}{2t} \right) \right] + \\ & + f_e(\eta = \eta_0 = 0) + K\eta_0^2 + \left\{ K \left[\frac{J(0)J''(0)}{(J'(0))^2} - \frac{(J(0))^2 J'''(0)}{3(J'(0))^3} \right] + \right. \\ & \left. + \frac{D|J(0)|^3}{2(J'(0))^4} \right\} \eta_0^4 \quad (17) \end{aligned}$$

where

$$t \equiv k_B T / |J(0)| \quad (18)$$

and

$$K \equiv C |J(0)| / [J'(0)]^2 \quad (19)$$

If we expand f in (even) powers of η and vanish the coefficient of η^2 we obtain the critical surface in the space t - γ - K (see Fig.1). In particular in the plane $\gamma=0$ [23], K monotonically decreases with increasing t ($K \sim \frac{1}{\pi} \ln \frac{1}{t}$ if $t \rightarrow 0$ and $K \sim 1/8t$ if $t \rightarrow \infty$). In the plane $t=0$, K presents a minimum at $\gamma=1$ ($K \sim \frac{2}{\pi} \ln \frac{1}{\gamma}$ if $\gamma \rightarrow 0$, $K \sim (1-\gamma)^2/4$ if $\gamma \rightarrow 1$ and $K \sim \frac{2}{\pi} \gamma \ln \gamma$ if $\gamma \rightarrow \infty$); in the neighbourhood $\gamma \approx 1$ (checked numerically as well) we are in disagreement with the result obtained by Dubois and Carton [13] ($K \propto 1-\gamma$); in any case these results hold only if the transition is a second order one, which is not necessarily the case for $\gamma \approx 1$ (see Fig. 1).

We remark in Fig.1 an interesting feature: the phase diagram presents two branches for a given value of the reduced harmonic elastic constant K . Furthermore according to if $K > K^*$ or $K < K^*$ (where $K^* \approx 0.20$) we have different types of phase diagram: if $K > K^*$ and γ increases at fixed reduced temperature t we have the sequence $\eta \neq 0$, $\eta = 0$ and $\eta \neq 0$ if t is sufficiently low and the sequence $\eta = 0$ and $\eta \neq 0$ if t is sufficiently high; if $K < K^*$ and γ increases at fixed t we have the sequence $\eta \neq 0, \eta = 0$ and $\eta \neq 0$ if t is sufficiently low, $\eta \neq 0$ if t takes intermediate values, and we have the sequence $\eta = 0$ and $\eta \neq 0$ if t is sufficiently high. The same type of richness appears if we operate with increasing t at fixed γ ; in any case in the limit $t \rightarrow \infty$ we always obtain $\eta = 0$ in accordance with the principles of Ther-

modynamics. For vanishing temperature and $\gamma < 1$ we recover Dubois and Carton^[13] critical anisotropy γ_c ; however a second critical anisotropy is exhibited at $\gamma = 1/\gamma_c > 1$; at the point ($\gamma = 1$, $t = 0$) we have $\eta = 0$ for any finite value of K (if the transition is a second order one). As a consequence of Eq.(3) if the point (t, γ, K) belongs to the critical surface then the point $(t/\gamma, 1/\gamma, K/\gamma)$ also belongs to it (this property is numerically verified in Fig.1); remark that this transformation does not transform the lower branch associated to a given value of K into its upper branch, therefore there is no reason for the special point which connects both types of phase diagrams (and is associated to K^*) to belong to the invariant critical line associated to $\gamma = 1$; as a matter of fact the coordinates of that point are $(t^*, \gamma^*, K^*) \approx (0.52, 0.75, 0.20)$.

Let us now turn back to the expansion of f in (even) powers of η the sign of the coefficient of η^4 determines whether the transition is a first or second order one, and its zero determines the equation of the tricritical line. Contrarily to what happens to the whole set of critical lines, the location of the tricritical line depends on the values of the parameters such as D , $J''(0)$, $J'''(0)$, and $J^{IV}(0)$; in Fig.1 we have represented (dash-dotted line) the tricritical line associated to $D = J''(0) = J'''(0) = J^{IV}(0) = 0$, and it is clear that the eventual presence of a non vanishing value for D dislocates the tricritical line towards higher values of γ . We verify that the particular tricritical line of Fig.1 contains the point (t^*, γ^*, K^*) as well as the particular points $(0, \gamma_T, K_T)$ and $(0, 1/\gamma_T, K_T/\gamma_T)$ with $\gamma_T \approx 0.08$ and $K_T \approx 0.6$. For γ sufficiently low (and

also sufficiently high) the transitions are of the second order thus recovering the well known result [11,13,15,16,20,23]; but for intermediate γ and sufficiently low K and t the transitions are of the first order: this could well be the case of several alkali-TCNQ salts. We have numerically calculated one such example ($K=0.255$ and $\gamma < 1$) by solving the equation $f(t, \gamma, K; n=0) = f(t, \gamma, K; n(t, \gamma, K))$: see Fig.2.

Let us conclude by saying that the spin coupling anisotropy appears to be, for the XY spin-Peierls instability (possibly for the Heisenberg case as well, at least as long as the Hartree-Fock type approximations [12] are qualitatively correct), an extremely relevant parameter which is at the origin of considerable richness in the temperature-anisotropy-(harmonic) elastic constant phase diagram. In particular it appears (for the first time as far as we know) to be a mechanism for the XY spin-Peierls instability connecting the uniform and dimerized phases through first order phase transition (alkali-TCNQ salts).

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CAPTION FOR FIGURES

- Fig.1 - Phase diagram in the (reduced) temperature-anisotropy space; the lines are parametrized by the corresponding values of the reduced elastic constant K (—second order phase transition; ---- metastability frontier of the disordered phase; -.-.- tricritical line corresponding to the harmonic (linear) approximation for the elastic potential (exchange integral)).
- Fig.2 - An example (associated to the harmonic and linear approximations for the elastic potential and exchange integral respectively) of phase diagram including the second (—) and first (...) order critical lines, the metastability frontier (---) of the disordered phase ($\eta=0$ i.e. uniform chain) and the tricritical point (o); $\eta \neq 0$ means dimerized chain.