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SPIN-PEIERLS TRANSITION IN AN INCOMMENSURATELY MODULATED SYSTEM

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P.O. Box 9506, 2300 RA Leiden, The Netherlands**ABSTRACT**

Under certain conditions uniform magnetic chains are known to be unstable for a lattice dimerization modulating the exchange integral, i.e. the spin-Peierls (SP) transition. In sufficiently high fields a SP system enters a magnetic discommensuration (MD) state incommensurate with the underlying lattice, characterized by the presence of midgap states. The question is raised, what happens in those magnetic systems that are not uniform from the beginning. Based on experimental evidence obtained in triclinic DMM-TCNQ₂, it will be argued that in zero field there is an instability for a lattice modulation, that approaches the dimerization wave vector via a multiple of the original modulation vector. In sufficiently high fields the so created midgap band becomes magnetic field dependent, like the MD-phase of a regular SP-system.

INTRODUCTION

The spin-Peierls (SP) transition is an intrinsic lattice instability in a system of quantum-mechanical antiferromagnetic chains where the spins are interacting via a Heisenberg or XY exchange interaction and the chains are coupled to a 3-dimensional (3-d) phonon lattice. At the critical temperature, T_{SP} , a second order transition occurs to a state where the chains become dimerized. The dimerization increases progressively as the temperature is lowered and reaches a maximum at zero temperature.

The SP transition is the magnetic analogue of the regular Peierls instability in a quasi 1-d metal, where dimerization of the lattice introduces a gap in the electronic spectrum, thereby lowering the electronic energy and turning the metal into a semiconductor. One of the most interesting aspects of the SP transition is the correspondence between the applied magnetic field in the SP problem and the chemical potential in the Peierls problem: changing

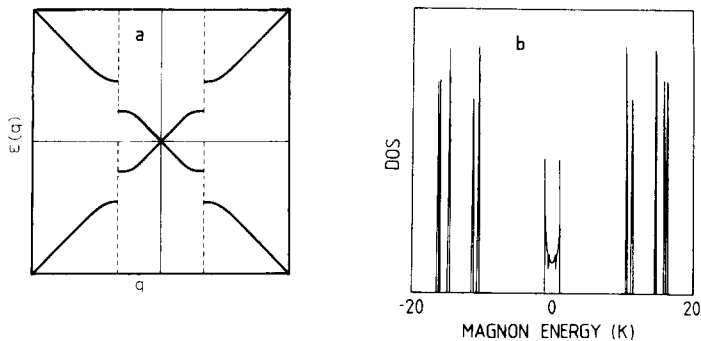


Fig. 1. Midgap states in the MD phase of a spin-Peierls system (a), as obtained in a pseudo-fermion representation. In (b) the magnon spectrum for a magnetic chain with modulated exchange is shown. The parameter values used for this calculation are appropriate for the high-temperature (HT) phase of DMM-TCNQ₂.

the magnetic field corresponds to the reduction of the number of fermions, that is the band filling of the Peierls system.

An applied magnetic field will lower the gain in magnetic energy upon dimerization and reduce the critical temperature. Due to Umklapp processes the wavevector describing the dimerization will remain fixed, up to a critical field B_c . Above this value an intermediate phase is predicted at sufficiently low temperatures, separating the dimerized and uniform phases. Several proposals for the nature of the intermediate state have been made. Recent theories conclude that it is incommensurate with the underlying lattice and will be in the form of a soliton lattice, i.e. the envelope of the ion displacements has a soliton lattice character. The associated wave vector will change continuously as a function of field. Literature on the theory of the SP transition is already quite vast. We mention two earlier review articles by Bray et al. [1] and by Buzdin and Bulaevskii [2] as extensive introductions, and the review on the phase Hamiltonian approach by Fukuyama and Takayama [3]

Of the few compounds, in which a spin-Peierls transition is well established: TTF-AuBDT, TTF-CuBDT [4,5], MEM-TCNQ [6], and (TMTTF)₂PF₆ [7], especially TTF-AuBDT is a suitable candidate to study the intermediate phase. Its low zero-field critical temperature of 2 K implies a critical field of only 2 T, hence large values of B/B_c are within reach. Especially by NMR [8] and ESR [9] convincing evidence for the soliton lattice or magnetic discommensuration (MD) state was obtained. A characteristic of this MD state is the presence of midgap states (in the pseudo fermion representation illustrated in fig. 1a and a staggered magnetization along the fixed direction fig. 1b). The question we address in this paper is, what happens in those magnetic systems that are modulated from the beginning. The discussion will be based on experimental evidence, obtained in triclinic DMM-TCNQ₂ [10]. First we will derive the magnon spectrum for a Hubbard chain with modulated exchange, as appropriate for DMM-TCNQ₂. Thereafter, it is shown that the structure below the transition

temperature can be described by a new modulation wave vector and how the new modulation is related to a dimerization. In a magnetic field the excitation spectrum in this low temperature state is argued to evolve into that of the MD-phase of a regular SP-system [11].

THEORY OF A MAGNETIC LINEAR CHAIN WITH MODULATED EXCHANGE

Let us consider a one-dimensional (1D) electronic system, e.g. a TCNQ chain, described by a Hubbard Hamiltonian of the form

$$\mathcal{H} = \sum_{i,\sigma} t_{i,i+1} (c_{i,\sigma}^\dagger c_{i+1,\sigma} + c_{i+1,\sigma}^\dagger c_{i,\sigma}) + \sum_{i,\sigma} (-1)^i E n_{i,\sigma} + \sum_i U n_{i,\uparrow} n_{i,\downarrow} \quad (1)$$

where c^\dagger (c) are fermion creation (annihilation) operators and n is the occupation number operator. The intrachain transfer integral t may alternate within the unit cell, which consists of two TCNQ-molecules. E is the Madelung energy, which has opposite sign for the two crystallographically inequivalent TCNQ-neighbours. U is the on-site Coulomb repulsion. Both t , E and U are taken positive. The alternating potential tends to localize electrons on sites with favourable energy leading to an effective transfer integral or effective exchange integral $J \approx 8\rho(1 - \rho t^2/U)$ with ρ the density at e.g. an even site. In the limit $E/t > 1$, ρ is roughly proportional to E :

$$\rho \approx 0.16t/E \quad (2)$$

If the potential E is modulated according to

$$E_j = E_0 + E_q \cos(2\pi qj) \quad (3)$$

the pair exchange integral $J_{j,j+1}$ will have the approximate form

$$J_{j,j+1} = J_0 + J_q \cos(2\pi qj) \quad (4)$$

So, in the limit $U > t$ and $E > t$ the system described by equation 1 with modulate E is equivalent to a magnetic chain with modulated exchange described by the Heisenberg spin Hamiltonian

$$\mathcal{H}_m = \sum_j (J_{j,j+1} \vec{S}_j \cdot \vec{S}_{j+1} - \frac{1}{4}) \quad (5)$$

in which $J_{j,j+1}$ is given by eq. 4.

In the following we use the approach of Pytte [12] in his treatment of the spin-Peierls problem. We first transform the spin operators to fermion operators of the form [13]:

$$\psi_j = (-2)^{j-1} S_1^+ S_2^+ \dots S_{j-1}^+ S_j^- \quad (6)$$

The operators satisfy the fermion anticommutation relations

$$\{\psi_j, \psi_{j'}\} = \delta_{j,j'} \quad (7)$$

Then, with the help of the relations

$$S_j^+ S_{j+1}^- = \psi_j^\dagger \psi_{j+1} \quad (8)$$

$$S_j^z = \frac{1}{2} - \psi_j^\dagger \psi_j \quad (9)$$

the spin Hamiltonian equation (5) is written, using the Hartree-Fock approximation as

$$\mathcal{H}_m = \sum_k p J_o \cos(k) \psi_k^\dagger \psi_k + \sum_k \frac{p J_q}{2} \{ e^{-i\pi q} \cos(k + \pi q) \psi_k^\dagger \psi_{k+2\pi q} + e^{i\pi q} \cos(k - \pi q) \psi_k^\dagger \psi_{k-2\pi q} \} \quad (10)$$

For temperatures lower than J_o/k , $p \approx 1.64$ and can be incorporated in $J \rightarrow pJ$.

As an illustration, in fig. 1b we show the magnon spectrum calculated with $J_o/k = 15$ K and $E_q/t = 1.2$ (these values are appropriate for DMM-TCNQ₂, see below).

TRICLINIC DMM-TCNQ₂

Triclinic dimethylmorpholinium-bis-tetracyanoquinodimethane (DMM-TCNQ₂) belongs to a class of organic (semi)conductors in which one or two of the *N*- protons of the morpholinium molecule are substituted by alkyl groups. In the majority of case the TCNQ-molecules form one-dimensional stacks [14,15]. This stacking is reflected in the one-dimensional nature of the electron structure: the wave function overlap between adjacent molecules, which is directly proportional to the transfer integral, is typically two orders of magnitude larger within the chain (intrachain) than between neighbouring chains (interchain). The resulting one-dimensional (1-D) electronic system is usually described by eq.(1) with $U \approx 1.4$ eV and $t < 0.2$ eV, which justifies the use of the large U limit

Below 200 K DMM-TCNQ₂ is incommensurately modulated with a wave vector

$$\vec{q} = -0.046\vec{a}^* - 0.535\vec{b}^* + -.385\vec{c}^* \quad (11)$$

where \vec{a}^* , \vec{b}^* and \vec{c}^* are the reciprocal lattice vectors, defined as:

$$\vec{a}^* = \frac{\vec{b} \wedge \vec{c}}{\vec{a} \cdot (\vec{b} \wedge \vec{c})} \quad (12)$$

This convention (differing 2π from the usual one) is chosen in such a way that a higher-order commensurate structure is described by the quotient of two integers. Since the stacking of the TCNQ-molecules is along the \vec{c} - axis, the only component of the modulation that is relevant to our discussion is the one along the \vec{c}^* -axis. For the ease of calculation this \vec{q} -component is set equal to the higher order commensurate value 5/13. Modelling of the system along the

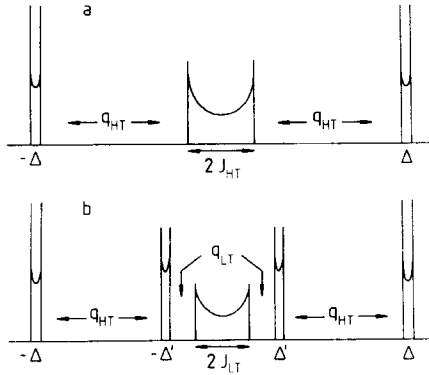


Fig. 2. Simplified magnon spectrum above (a) and below (b) 1.7 K. The Fermi-level is in the centre of the figure.

Table 1

Magnon spectrum parameters for DMM-TCNQ₂

J_{HT}/k	= 2.4 K	($T > 1.7$ K)
Δ/k	= 13 K	(all temperatures)
q	= 0.385	"
q_{LT}	= 0.54	($T < 1.7$ K)
J_{LT}/k	= 1.7 K	"
Δ'/k	= 4 K	"

theoretical lines indicated in the previous section, results in the magnon spectrum of fig. 2.

The magnon band is highly fragmented, except for a small band around the Fermi-level ($\epsilon_F = 0$). One may think of the latter as a magnetic subsystem with a small effective exchange ($J^{eff}/k \approx 2$ K) in which 3/13 of all spins partake. This explains the recent findings that both susceptibility and specific heat are remarkably similar to that of a finite Heisenberg chain of only five spins [10]: in that case, there is a magnetic ($S = \frac{1}{2}$) ground state which gives rise to a diverging susceptibility at low temperatures with a relative strength of 1/5 of the total spin. This situation is similar to the small-J magnon band with relative strength 3/13 ($\approx 1/5$) as found here. Mainly based on the susceptibility it is assumed that at $T = 1.7$ K the magnon band splits into a still narrower band around ϵ_F and two side peaks at energies $\pm\Delta'$ as in figure 2. The relative intensities of bands and side peaks are determined by q_{LT} . The data are summarized in table 1.

INCOMMENSURATE PHASE COMPARED TO SPIN-PEIERLS PHASE

The principle feature of the incommensurately modulated high-field phase of a SP-system is the existence of mid-gap states (solitons) in the dimerized magnon band. These solitons

are localized spin structures, bridging two different realizations of the ground state (see e.g. the review by Bishop et al. [16]). In the SP-case, the solitons form a 3-D lattice. The spin configuration within the soliton is coupled to the lattice and produces a high expectation value of the staggered magnetization within the soliton, which is crucial in the explanation of the NMR- and ESR-data in a regular SP-system such as TTF-AuBDT [8,9] as well as in explaining the "otherwise puzzling ESR-data" in DMM-TCNQ₂ [17]. This incommensurately modulated state resembles our model for the low- as well as the high-temperature phase: the proposed magnon spectra (fig. 2) are quite similar to the excitation spectrum of a dimerized system with a mid-gap soliton band (fig 1a). Moreover, in both cases the mid-gap spin excitations are coupled to the lattice, which makes both models equivalent in the explanation of the resonance data.

In the previous section we mentioned that below 1.7 K a good description of the experiments in zero field is possible if one assumes a lattice distortion, which coincides with the 4th harmonic of the high-temperature discommensuration vector. The proper spin-Peierls distortion vector (q_{SP}) is 0.5. But in DMM-TCNQ₂ one has to expect a (strong) coupling between the dimerization of the lattice and the modulation of the donor system. As we have seen the supercell consists of 13 unit cells. If the dimerization locks to the modulation, this implies that there is a mismatch every 13 unit cell giving rise to one soliton per supercell. If we were to describe this by a distortion vector, this would be $\tilde{q}_{SP} = 0.5 + 1/26 = 0.54$, precisely the modulation found in our fit of the susceptibility.

So far we have restricted ourselves to the zero-field case. We now turn to the field-dependence of the transition. As remarked above, the application of an external field induces a transition at 0.2 tesla. The transition temperature is left unchanged. An important experimental observation was recently made by Korving et al. [10] who showed that the magnetization curves for fields exceeding 0.2 tesla are almost identical above and below the phase transition temperature. This situation is also encountered in spin-Peierls systems for fields above the critical field, where the number of mid-gap states increases linearly in the field [18]. From this one may infer that also the high-field phase of DMM-TCNQ₂ has spin-Peierls character. With these considerations in mind we have drawn a tentative phase diagram for DMM-TCNQ₂ fig. 3. For comparison, we have also drawn the spin-Peierls phase diagram: the high-field phases are identical and characterized by magnetic excitations, the number of which increases linearly in the field. The low-field phases however are different: whereas the SP-ground state is non-magnetic ($q = 0.5$), DMM-TCNQ₂ is magnetic, due to the fact that the SP-distortion vector is slightly off its commensurate value due to the coupling with the incommensurate super structure. This phase diagram is probably appropriate in general for the spin-Peierls transition in the presence of a structural, incommensurate modulation.

A complication in DMM-TCNQ₂ arises from the small exchange anisotropy. In low fields the anisotropy becomes dominant and there will be a tendency of the spins to align along the easy axis i.e. perpendicular to the magnetic field, when it is oriented along the c' (hard) axis. Indications of this were seen in ESR around 0.2 T; the same value associated with a

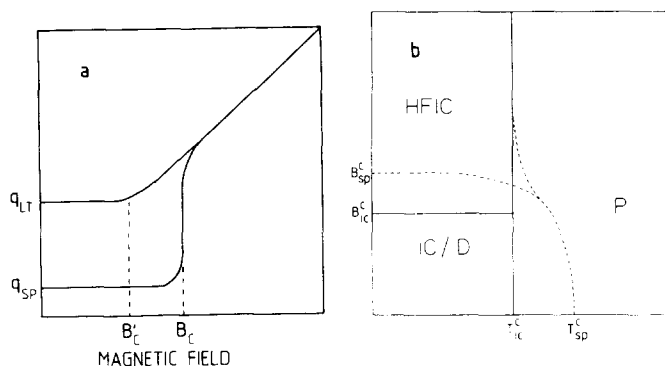


Fig. 3. Proposed field-dependence of the modulation wave vector (a) and tentative phase diagram for an IC modulated AF chain (b). Below T_c in low fields the IC-phase competes with the SP-dimerization (IC/D); at higher fields there is no difference with the MD-phase of a spin-Peierls system (HFIC). Above T_c the system is paramagnetic (P).

critical field in the susceptibility measurements. In high fields (> 0.2 T) the anisotropy can be neglected.

CONCLUSION

Triclinic DMM-TCNQ₂ in its low temperature phase presumably is an incommensurately modulated system, which has the same advantages as TTF-AuBDT: only moderate fields are needed to overcome the effective exchange constant. Like in the MD phase of a SP system for fields $B > B_c$ the number of discommensurations grows with magnetic field strength. For $B < B_c$ a mixed phase exists where the incommensurate wave vector q changes from its zero field value to $q(B_c)$. In the near future neutron studies will be performed to verify parts of this model.

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