Electrical conduction in dynamical disordered synthetic semiconductors

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Consequences of the structural modulation of DMM-TCNQ$_2$ on its magnetic behaviour

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Abstract. The triclinic modification of DMM-TCNQ$_2$ is a linear-chain antiferromagnet with an incommensurate modulation of the lattice. As a consequence the antiferromagnetic exchange constant is also modulated along the chain. The effect of this modulation on the magnetic properties is calculated and is found to be in agreement with experiment. At 1.7 K a transition occurs to a low-temperature phase, which in zero field has a modulation q = 0.54, a value that coincides with the fourth harmonic of the high-temperature modulation of the lattice. It is shown that this phase strongly resembles the field-induced phase of a regular spin-Peierls system.

1. Introduction

Triclinic dimethylmorpholinium-bis-tetracyanoquinodimethane (DMM-TCNQ$_2$) 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 cases the TCNQ molecules form one-dimensional (1D) stacks (van Bodegom 1979, Visser 1984). This stacking is reflected in the 1D nature of the electron structure; the wavefunction overlap between adjacent molecules, which is directly proportional to the transfer integral, is typically two orders of magnitude larger within the chain (*intra*-chain) than between neighbouring chains (*inter*-chain). The resulting 1D electronic system is usually described by a Hubbard Hamiltonian of the form

$$\mathcal{H} = \sum_{i,\sigma} t_{i,i+1}(c^{\dagger}_{i,\sigma}c_{i+1,\sigma} + c^{\dagger}_{i+1,\sigma}c_{i,\sigma}) + \sum_{i,\sigma}(-1)^{i}En_{i,\sigma} + \sum_{i} Un_{i,\uparrow}n_{i,\downarrow} \qquad (1.1)$$

where $c^{\dagger}$ is the fermion creation operator, c is the fermion annihilation operator and n is the occupation number operator. The *intra*-chain transfer integral t may alternate within the unit cell, which usually consists of two TCNQ molecules. E is the Madelung energy, which has opposite signs for the two crystallographically inequivalent TCNQ neighbours. U is the on-site Coulomb repulsion. t, E and U are all taken to be positive. For DMM-TCNQ$_2$, $U \simeq 1.4$ eV (Mazumdar and Zoos 1981) and $t < 0.2$ eV, which justifies the use of the large-U limit.

Within the class of morpholinium-TCNQ$_2$ compounds, DMM-TCNQ$_2$ has a rather special place; both its electronic and its magnetic behaviours are primarily determined by an anomalously large alternation of the Madelung potential between adjacent sites. Visser

(1984) has analysed the bond lengths within the two different TCNQ molecules, from which he estimated that the charge distribution within the unit cell is roughly 0.85 : 0.15. We have previously shown (Kramer and Brom 1985) that this implies that the ratio E/t equals 2, which in turn explains both the anomalously small value of the magnetic *intra*-chain exchange constant ($J_0/k \approx 10$ K† (Korving *et al* 1983)) and the high value of the semiconductor gap, found in conductivity measurements (Visser *et al* 1982). The magnetic behaviour of DMM-TCNQ$_2$ has been studied extensively in the past (Schwerdtfeger *et al* 1982, Korving *et al* 1983, Hijmans and Brom 1986). At high temperatures, the system is paramagnetic with a Curie–Weiss θ of -7.5 K. From this, one expects for temperatures lower than θ to find the behaviour of a 1D Heisenberg antiferromagnet. This is not the case; marked deviations from the prediction of Bonner and Fisher (1964) for the susceptibility of a 1D antiferromagnet were found. At 1.7 K a transition occurs, which at first has been interpreted as a spin-Peierls (SP) transition, i.e. a dimerisation transition of the magnetic system, which introduces a gap for magnetic excitations (a review of the SP problem has been given by Bray *et al* (1982)). Later, Korving *et al* (1983) observed that the susceptibility does not drop to zero as required for an SP system, and therefore a three-dimensional (3D) AF ordering was suggested. Recently, on the basis of electron spin resonance (ESR) data obtained in the low-temperature phase, it was shown (Hijmans and Brom 1986) that the resonance data are in conflict with a 3D AF ordered phase but instead indicate that the low-temperature phase is similar to the (field-induced) incommensurately modulated phase of an SP system. This conclusion was later supported by the observation that the ESR spectra are remarkably similar to those obtained in the high-field phase of the well known SP system TTF-AuBDT (Hijmans and Beyermann 1987). Despite the success of the modulated SP hypothesis in explaining the experimental data from microscopic techniques, it does not yet offer an explanation for the macroscopic quantities, such as the magnetic susceptibility.

It is the purpose of this paper to show that the magnetic properties of DMM-TCNQ$_2$ can be understood if one assumes that the magnetic exchange is strongly modulated in real space. Such an approach is plausible, since below 200 K DMM-TCNQ$_2$ is incommensurately modulated with a wavevector (Visser and de Boer 1983)

$$q = -0.046a^* - 0.535b^* + 0.385c^* \tag{1.2}$$

where a^*, b^* and c^* are the reciprocal lattice vectors, defined as

$$a^* = (b \times c)/[a \cdot (b \times c)]. \tag{1.3}$$

This convention (differing by 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 c axis, the only component of the modulation that is relevant to our discussion is that along the c axis. The modulated structure is reflected in satellite peaks in the Bragg reflection pattern. The intensity of these satellite peaks saturates at low temperatures (figure 1). Recently, details of the modulated structure at 99 K were published (Steurer *et al* 1987). The DMM units appear to alternate periodically between two possible configurations and within the TCNQ chain a small displacive modulation is found. In the following, we shall assume that the modulation of the magnetic exchange integral is entirely due to the modulation of the Madelung potential. The neglect of the modulation of the transfer integrals is justified since it gives only a small correction to the above effect.

† Throughout this paper, we adopt the '1J' convention (equation (2.7)) and positive J denotes antiferromagnetic (AF) exchange.

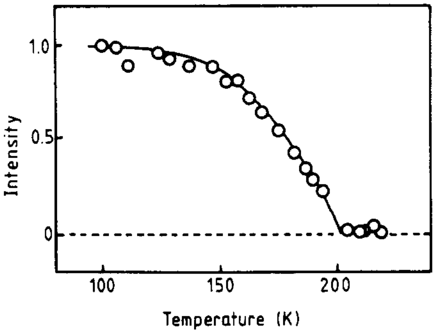

Figure 1. Intensity of the satellite peaks, resulting from the incommensurately modulated DMM chain, against temperature: ———, a guide to the eye. The intensity saturates at low temperatures (after Visser and de Boer (1983)).

The outline of the paper is as follows. In § 2, we show how a modulation of the Madelung potential produces an exchange modulation and we outline how the magnon spectrum of a modulated exchange system is calculated in an effective *XY* model. In § 3 the high-temperature ($T > 1.7$ K) phase of DMM-TCNQ$_2$ is dealt with. Both the magnetic susceptibility and the magnetic specific heat can be explained by assuming a highly modulated exchange along the chain with a modulation vector $\boldsymbol{q}$ as observed by Visser. In § 4 the effect of modulation in the low-temperature ($T < 1.7$ K) phase is examined. We show that the magnetic behaviour is best understood if one assumes that a structural phase transition takes place in which an additional modulation (tentatively associated with $4\boldsymbol{q}$) is developed. We devote § 5 to a discussion of our findings and comparison is made with earlier proposals. Special attention is paid to the similarities between the exchange modulation model advocated in this paper and the field-induced incommensurate phase of an SP system, suggested by Hijmans and Brom (1986). Finally, the field dependence of the transition is discussed.

2. Theory of a magnetic linear chain with modulated exchange

In this section, we outline how we have calculated the magnon spectrum of a linear chain for which the exchange parameter is harmonically modulated in space. As our aim is primarily to gain understanding of the magnetic phenomena in DMM-TCNQ$_2$, we shall start by establishing a relation between the magnetic exchange and the alternation of the Madelung potential E, since this is the cause of the exchange modulation in a 1D semiconductor described by equation (1.1).

2.1. Relation between potential alternation and exchange

As an alternating potential along a chain will, at low temperatures, tend to localise electrons on sites with a favourable energy (even-numbered sites), it is appropriate to consider a basis set either with wavefunctions (ψ^{L}) localised around even-numbered sites or with wavefunctions ($\bar{\psi}^{\mathrm{L}}$) localised around odd-numbered sites:

$$|\psi^{\mathrm{L}}_{2i}\rangle = (1-\rho)^{1/2}|\psi_{2i}\rangle + (\rho/2)^{1/2}(|\psi_{2i-1}\rangle + |\psi_{2i+1}\rangle) \tag{2.1}$$

$$|\bar{\psi}^{\mathrm{L}}_{2i+1}\rangle = (1-\rho)^{1/2}|\psi_{2i+1}\rangle - (\rho/2)^{1/2}|\psi_{2i}\rangle + |\psi_{2i+2}\rangle) \tag{2.2}$$

where ρ denotes the electron density of odd-numbered sites in the ground state and $|\psi_i\rangle$ are normalised valence orbital wavefunctions for TCNQ. This basis set is orthonormal to order ρS, where S is the *intra*-chain overlap, defined as

$$S = \langle \psi_i | \psi_{i+1} \rangle. \tag{2.3}$$

If we restrict ourselves to the limit that $E \gg t$, we have that the energy of the states $|\bar{\psi}^{\mathrm{L}}\rangle$ is roughly E, whereas the energy of $|\psi^{\mathrm{L}}\rangle$ is $-E$. We recall that for DMM-TCNQ$_2$ $U \gg t$, which implies that the band is effectively half filled. This means that at low temperatures ($T < E$) only the states $|\psi^{\mathrm{L}}\rangle$ are occupied. The transfer integral, defined as

$$t = \langle \psi_i | \mathcal{H} | \psi_{i+1} \rangle \tag{2.4}$$

reduces for the relevant states $|\psi^{\mathrm{L}}\rangle$ to

$$t^* = \langle \psi^{\mathrm{L}}_{2i} | \mathcal{H} | \psi^{\mathrm{L}}_{2i+2} \rangle = [2\rho(1-\rho)]^{1/2} t. \tag{2.5}$$

The magnetic exchange for a Hubbard system is usually taken to be $4t^2/U$ (Pincus 1972). For a system with large Madelung potential variations, this becomes, according to equation (2.5),

$$J = 8\rho(1-\rho)t^2/U. \tag{2.6}$$

This equation has the same functional ρ dependence of J as found previously by the present authors on the basis of finite-chain calculations (Kramer and Brom 1985). In the same paper the relation between ρ and E is derived in the $U \to \infty$ limit. For values of E/t exceeding unity, ρ is roughly inversely proportional to E.

In the above, we have derived a relation between exchange and potential alternation in the limit of high E/t-values. We stress that in this limit the electrons can be considered to be effectively localised (at least for temperatures low compared with the transfer integral) on low-energy sites and the exchange between neighbouring spins depends mainly on the electron population of the high-energy sites in between.

2.2. The magnon spectrum of a chain with modulated exchange

At low temperatures, the system which is described by equation (1.1) with $E/t > 1$ and $U/t > 1$ becomes a magnetic chain with isotropic exchange. The Heisenberg spin Hamiltonian reads

$$\mathcal{H}_m = \sum_j (J_{j,j+1} \boldsymbol{S}_j \cdot \boldsymbol{S}_{j+1} - \tfrac{1}{4}) \tag{2.7}$$

and $J_{j,j+1}$ is modulated by the wavevector $\boldsymbol{q}$; the lattice constant is set equal to unity, yielding

$$J_{j,j+1} = J_0 + J_q \cos(2\pi q j). \tag{2.8}$$

In the following, we use the approach of Pytte (1974) in his treatment of the SP problem. We first transform the spin operators to fermion operators of the form (Schultz *et al* 1964)

$$\psi_j = (-2)^{j-1} S_1^z S_2^z \ldots S_{j-1}^z S_j^- . \tag{2.9}$$

These operators satisfy the fermion anti-commutation relations

$$\{\psi_j, \psi_{j'}\} = \delta_{j,j'}. \tag{2.10}$$

Then, with the help of the relations

$$S_j^+ S_{j+1}^- = \psi_j^\dagger \psi_{j+1} \qquad (2.11)$$

$$S_j^z = \tfrac{1}{2} - \psi_j^\dagger \psi_j \qquad (2.12)$$

the spin Hamiltonian (equation (2.7)) is written, using the Hartree–Fock approximation, as

$$\mathcal{H}_m = \sum_k pJ_0 \cos k\, \psi_k^\dagger \psi_k + \sum_k \frac{pJ_q}{2} [\exp(-\mathrm{i}\pi q) \cos(k + \pi q) \psi_k^\dagger \psi_{k+2\pi q} + \exp(\mathrm{i}\pi q) \cos(k - \pi q) \psi_k^\dagger \psi_{k-2\pi q}]. \qquad (2.13)$$

The parameter p is determined by the Hartree–Fock self-consistency equation

$$p = 1 - 2 \sum_k n_k \cos k \qquad (2.14)$$

where

$$n_k = \langle \psi_k^\dagger \psi_k \rangle = [\exp(\beta E_k) + 1]^{-1}. \qquad (2.15)$$

Although p varies slightly with temperature, it is approximately constant at $1 + 2/\pi \simeq 1.64$ for temperatures lower than J_0/k. Since we shall later be dealing mainly with low-temperature behaviour, we neglect the temperature dependence altogether and incorporate p in J. Note that this formally corresponds to an XY exchange model.

The calculations in the following sections are simplified by setting q to a higher-order commensurate value m/n (DMM-TCNQ$_2$, the $\boldsymbol{q}$ component along the stacking axis is $0.385 \simeq 5/13$). The task of finding the magnon spectrum reduces to the numerical solution (for an appropriate number of k-values) of the $m \times m$ Hamiltonian matrix with elements

$$\mathcal{H}_{i,i}(k) = J_0 \cos k \qquad (2.16)$$

$$\mathcal{H}_{i,i+n}(k) = \mathcal{H}^*_{i+n,i}(k) = (J_q/2) \exp(\mathrm{i}n\pi/m) \cos(k + n\pi/m). \qquad (2.17)$$

Once the magnon spectrum is known, the magnetic susceptibility χ is easily calculated from it. The fermions introduced in equation (2.9) are magnetic excitations; an empty band corresponds to ferromagnetic spin alignment, whereas a half-filled band corresponds to a non-magnetic state. A magnetic field changes the chemical potential. For a more extensive discussion, the reader is referred to the paper by Pytte (1974). This leads to an expression for χ of the form

$$\chi(T) = \frac{g^2 \mu^2 N}{4kT} \int \mathrm{d}\varepsilon\, N(\varepsilon) \frac{\partial f(\varepsilon/kT)}{\partial \varepsilon} \qquad (2.18)$$

where $N(\varepsilon)$ is the magnon density of states (DOS) and $f(\varepsilon/kT)$ is the Fermi–Dirac distribution function (equation (2.15)).

The consequence of exchange modulation with a certain wavevector ($2\pi q$) is to introduce a coupling between states with $\Delta k = 2\pi q$. This interaction causes the opening of a gap at vector $\bar{k}$, for which

$$\varepsilon(\bar{k}) = \varepsilon(\bar{k} + 2\pi q). \qquad (2.19)$$

The effect is completely analogous to the gap occurring in charge-density wave condensates (Grüner and Zettl 1985).

3. DMM-TCNQ$_2$ above the 1.7 K phase transition

In this section, we shall show that the temperature dependence of the magnetic susceptibility of DMM-TCNQ$_2$ can be understood by assuming exchange modulation along the magnetic chain with $q = 0.385$, which is the observed discommensuration of the DMM system. As we have seen in § 2, it is computationally advantageous to set q equal to $\frac{5}{13}$, which means that we approximate the system by a supercell consisting of 13 simple unit cells, containing two TCNQ molecules and one (localised) spin†. We emphasise at this point that there is no essential difference (with respect to the magnon spectrum) between an incommensurate system with modulation vector q_i and a system which is incommensurately modulated with q_c as long as q_c does not differ too much from q_i. In both cases a gap is opened at k-values satisfying $\varepsilon(k) = \varepsilon(k + 2\pi q)$.

As we have seen before, the functional relation between E and J is *via* the occupation density ρ:

$$J = C\rho(1 - \rho) \tag{3.1}$$

where $C = 8t^2/U$ and for large E/t (Kramer and Brom 1985)

$$\rho \simeq 0.16t/E. \tag{3.2}$$

Combined, this gives for $J(E)$

$$J \simeq C(0.16t/E)(1 - 0.16t/E). \tag{3.3}$$

As a simplification, we shall assume that the modulation of the DMM positions along the chain is directly proportional to the variation in E, yielding

$$E_j = E_0 + E_q \cos(2\pi qj). \tag{3.4}$$

Since the relation between E and J is not linear, we expect higher harmonics in J to occur, especially when E_q is large compared with E_0. Therefore, J_j will have the general form

$$J_j = J_0 + \sum_n J_{nq} \cos(2\pi nqj). \tag{3.5}$$

J_0 and the modulation amplitudes J_q, J_{2q}, etc, can be evaluated as a function of E_q by a series expansion around E_0. We have taken $E_0/t = 2$, the estimated value in earlier work and have calculated terms up to J_{4q}. Their relative strengths are shown in figure 2. One observes that the amplitudes of higher harmonics decrease rapidly and that J_q and J_{2q} are by far the most important for all relevant values of E_q.

With the above-mentioned simplification (linearity in E), we are left with only two independent parameters for the description of the magnetic system: J_0, the average exchange value and E_q, the energy variations introduced by the modulation of the donor system. Figure 3 shows the magnetic susceptibility as a function of temperature together with the prediction for a regular 1D Heisenberg chain and the results of our model with $J_0/k = 15$ K and $E_q/t = 1.2$. We should remark that the value for the exchange should be divided by 1.64 before a comparison is made with earlier estimates. The resulting value (9 K) is quite close to the value of 7 K estimated by Korving *et al* (1983). As can be seen, our approach accounts satisfactorily for the magnetic behaviour above the 1.7 K

† It is also just possible that q is truly commensurate with the lattice and that $q = \frac{5}{13}$ is exact.

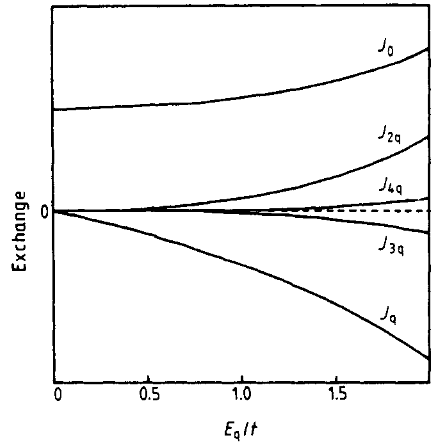

Figure 2. The average exchange value J_0 and the amplitude of the exchange modulation J_q, J_{2q}, etc, as a function of the modulation amplitude of the Madelung energy E_q alternation scaled to the transfer integral t.

phase transition, especially if one considers the fact that we have made an approximation to the Heisenberg Hamiltonian. The marked improvement to the Bonner and Fisher curve is not surprising since the modulation E_q is quite strong; if one calculates the various exchange values within the magnetic supercell, one finds them ranging from 6 to 25 K. We must finally mention that the agreement between theory and experiment is less if one leaves out the higher harmonics of the exchange modulation.

The magnon spectrum of the appropriately modulated chain is shown in figure 4. The magnon band is highly fragmented, except for a small band around the Fermi level ($\varepsilon_F = 0$). One may think of the latter as a magnetic subsystem with a small effective exchange ($J^{eff}/k \simeq 2$ K) in which $\frac{3}{13}$ of all spins partake. This explains the recent findings

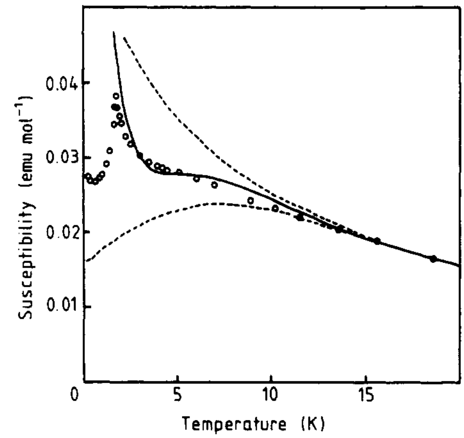

Figure 3. The magnetic susceptibility of DMM-TCNQ$_2$ in a zero external field: ———, susceptibility found from the calculations described in the text for a modulated magnetic chain; – – –, predictions of Bonner and Fisher (1964) for a Heisenberg linear chain with J/k = 10 K (lower curve) and a Curie–Weiss dependence with $\theta = -7.5$ K (upper curve).

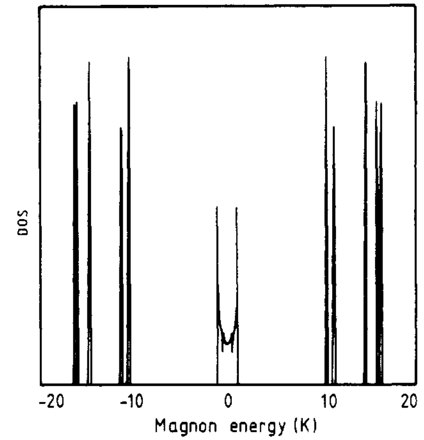

Figure 4. Calculated magnon DOS for DMM-$TCNQ_2$ above 1.7 K.

of Korving *et al* (1988) that both susceptibility and specific heat are remarkably similar to that of a finite Heisenberg chain of only five spins; 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 $\frac{1}{5}$ of the total spin. This situation is similar to the small-J magnon band with relative strength $\frac{3}{13}$ ($\simeq\frac{1}{5}$) as found here.

To end this section, we mention that our assumption for the magnon spectrum also explains the other thermodynamic properties of DMM-$TCNQ_2$: the specific heat and the magnetisation. As regards the first, the present authors have previously shown on thermodynamic grounds that the excess specific heat is of magnetic origin, which means that a fit of the susceptibility ensures a fit of the specific heat (Kramer and Brom 1985). The 'missing entropy' (Korving *et al* 1988) arises because the entropy of the mid-gap band is still present at 1.7 K. The magnetisation at 4 K shows a steep incline at low fields but, as the field is increased further, the slope decreases although no sign of saturation is seen, even in fields as high as 6 T. This is precisely the behaviour which one expects for a split band with a high overall exchange and a narrow mid-gap band.

4. DMM-$TCNQ_2$ below the 1.7 K phase transition

Schwerdtfeger *et al* (1982) were the first to observe that the ESR spectrum of DMM-$TCNQ_2$ shows a drastic change at 1.7 K. The intensity of the high-temperature ESR line decreases rapidly below this temperature, which suggested a transition to an SP dimerised non-magnetic state. Later it was found by Korving *et al* (1983) that below 1.7 K a new broad ESR line develops, causing a non-zero susceptibility in this phase. This was confirmed by direct measurements of the magnetic susceptibility by Korving *et al*; below 1.7 K the AC susceptibility decreases only slightly and reaches a finite value as the temperature is lowered. Superimposed on this is a Curie tail, caused by a small amount of impurities.

Another prominent feature of the low-temperature phase is a phase boundary at about 0.2 T, which manifests itself in a maximum in the field dependence of the susceptibility. The transition temperature is the same in the high-field phase as in zero field; in fact, no change is observed for fields up to 5 T (Korving *et al* 1988). We shall return to this point in § 5.

As remarked earlier, the analysis of the ESR data suggests a phase which is similar to the incommensurately modulated field-induced phase of an SP system. In this section we show that the magnetic behaviour can be explained if one assumes that a new structural modulation is developed in the phase transition. We shall see that the best description is obtained if the wavevector of the new distortion coincides with the fourth harmonic of the high-temperature discommensuration. A comparison of this proposal with earlier ones, especially the incommensurate SP phase is reserved for § 5. Before starting our description of the low-temperature phase, we should remark that the results are necessarily less unambiguous than above the phase transition since there are no low-temperature structural data.

Without any modification in the magnon spectrum of DMM-TCNQ$_2$, the susceptibility would have saturated as T approaches zero at a value corresponding to that of a spin chain with an AF exchange of 2.4 K and $\frac{3}{13}$ of the normal intensity. However, below 1.7 K the susceptibility drops to a lower plateau. Phenomenologically, this implies that the low-temperature phase is characterised by a reduced (but non-zero) magnon DOS at the Fermi level (as seen from equation (2.18)). Such a modification is accomplished by a lattice deformation with a wavevector that is close, but not equal, to the dimerisation vector $q_{SP} = 0.5$.

We have therefore assumed that below 1.7 K a low-temperature distortion vector q_{LT} develops, which opens a new gap Δ' for which we assumed the following dependence:

$$\Delta'(T) \propto [1 - (T/T_c)^2]^{1/2} \tag{4.1}$$

which has a Bardeen–Cooper–Schrieffer form just below the transition temperature:

$$\Delta'(T)/\Delta'(0) \simeq 2^{1/2}(1 - T/T_c)^{1/2}. \tag{4.2}$$

The precise form of the temperature dependence of equation (4.1) is not important; it merely reflects the fact that the phase transition has a second-order character. In our calculations, we have considered the case where the initial magnon spectrum consists of a narrow band with relative intensity $\frac{3}{13}$. The functional form is taken to be that of a one-dimensional tight-binding band. The other part of the spectrum is captured in two peaks with a separation Δ from the Fermi level (figure 5(a)). For the magnon spectrum at $T = 0$, we assume, as indicated above, that a gap splits the magnon band into a still narrower band around ε_F and two side peaks at energies $\pm\Delta'$ as in figure 5(b). The relative

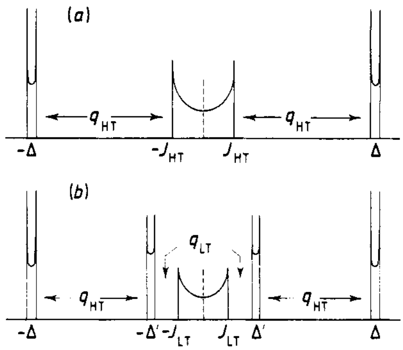

Figure 5. (a) The simplified magnon spectrum of DMM-TCNQ$_2$ above 1.7 K, and (b) the assumed magnon spectrum below the phase transition: – – –, the Fermi level. Details are explained in the text.

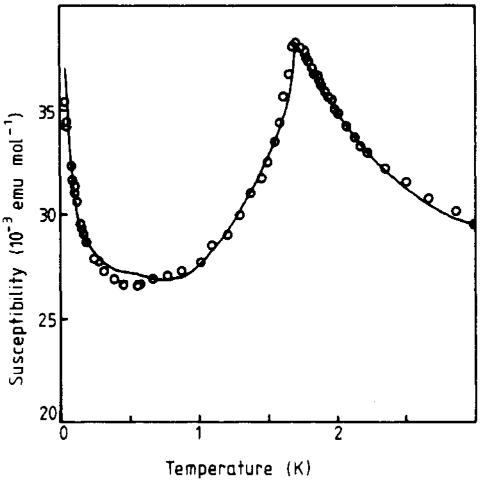

Figure 6. The low-temperature magnetic susceptibility of DMM-TCNQ$_2$ in a zero external field: ———, susceptibility resulting from the magnon spectra in figure 5, with the values in table 1.

intensities of bands and side peaks are determined by q_{LT}. We have neglected all internal structure of the bands except for that at the Fermi level. This is a fair approximation since the susceptibility is a convolution of the magnon DOS with the derivative of the Fermi–Dirac distribution function (equation (2.18)). Hence the susceptibility is most sensitive to details close to the Fermi energy. The susceptibility was best described (figure 6) by the set of parameters listed in table 1.

Table 1. Magnon spectrum parameters for DMM-TCNQ$_2$.

J_{HT}/k	2.4 K	($T > 1.7$ K)
Δ/k	13 K	(all temperatures)
q	0.385	(all temperatures)
q_{LT}	0.54	($T < 1.7$ K)
J_{LT}/k	1.7 K	($T < 1.7$ K)
$\Delta'(0)/k$	4 K	($T < 1.7$ K)

Superimposed on this is a Curie tail corresponding to one magnetic impurity per 1000 unit cells. The fit produced in this way is in satisfactory agreement with the experiments. The wavevector q_{LT} coincides with $4q$ ($=1.54 \equiv 0.54$), where q is the high-temperature incommensurate distortion of the donor system. The implications of this are discussed in § 5.

5. Discussion

We have seen that the concept of exchange modulation is very successful in explaining the magnetic behaviour of triclinic DMM-TCNQ$_2$. In the high-temperature phase the qualitative agreement between theory and experiment is particularly satisfying since we have used explicitly the known discommensuration. Also in the low-temperature regime, the experimental data can be explained by assuming a modulated exchange structure. Below, we shall argue that our model for the low-temperature phase can be regarded in many respects as a modification of an SP system.

There are two essentially different ground states known for a linear antiferromagnet with finite *inter*-chain and spin–phonon coupling. The first, most commonly occurring ground state is a 3D, magnetically ordered phase, which arises as a consequence of a small coupling between spins on neighbouring chains. Such a coupling is always present in real systems. A second possibility is that, when the spin–phonon coupling is large, an SP transition occurs, rendering the system non-magnetic in the ground state. With regard to the first option, we refer the reader to the paper by Hijmans and Brom (1986), who have shown that 3D magnetic order conflicts with the ESR data in this compound. Still, the ground state remains magnetic down to 40 mK, the lowest temperature reached in the susceptibility experiments. This sets an upper bound to the *inter*-chain exchange: $J^{\text{inter}}/k \leqslant 0.04$ K. One may question whether or not such a low value can still be considered reasonable. We feel that this is indeed the case; the *inter*-chain transfer integrals are calculated to be smaller by a factor of 30 compared with the *intra*-chain ones (Oostra 1983). This ensures that the *inter*-chain exchange is a factor of 10^3 smaller than the average *intra*-chain exchange found in XYM-TCNQ$_2$ salts ($J^{\text{intra}}/k \simeq 100$ K (Oostra *et al* 1983)) which would mean that J^{inter}/k is of the order of 10^{-1} K†. In the specific case of DMM-TCNQ$_2$, it may be even smaller; recall that the modulation of the exchange causes $\frac{10}{13}$ of the spin system to be effectively non-magnetic. The remaining spin excitations are strongly localised within the supercell as a consequence of the large donor modulation. As the modulation vector $\boldsymbol{q}$ also has components in the directions perpendicular to the stacking axis (equation (1.2)), the spin excitations in neighbouring chains may be quite far apart, which would reduce the *inter*-chain exchange value below the above-cited value of 10^{-1} K.

We now turn to the central part of the discussion: the resemblance between the incommensurate SP phase and our model. The reason for paying special attention to this point is, of course, the fact that the description given by Hijmans and Brom was quite satisfactory with regard to the microscopic spin structure.

The principal feature of the incommensurately modulated high-field phase of an SP system is the existence of mid-gap states (solitons) in the dimerised magnon band. These solitons are localised spin structures, bridging two different realisations of the ground state (see, e.g., the review by Bishop *et al* 1980). In the SP case, the solitons form a 3D lattice. The spin configuration within the soliton is coupled to the lattice and produces a high expectation value of the staggered magnetisation within the soliton, which is crucial in the explanation of nuclear magnetic resonance and ESR data in a regular SP system such as TTF-AuBDT (Hijmans *et al* 1985) and of the otherwise puzzling ESR data in DMM-TCNQ$_2$ (Hijmans and Brom 1986). This incommensurately modulated state resembles our model for the low- as well as the high-temperature phase; the proposed magnon spectra (figure 5) are quite similar to the excitation spectrum of a dimerised system with a mid-gap soliton band. 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 § 4 in which the low-temperature phase is dealt with, we saw that a good description of the experiments in zero field is possible if one assumes a lattice distortion, which coincides with the fourth harmonic of the high-temperature discommensuration vector.

† This low value agrees with the fact that, within the XYM-TCNQ$_2$ series, no examples of 3D, magnetically ordered systems are known.

The proper SP distortion vector q_{SP} is 0.5. However, in DMM-TCNQ$_2$, one has to expect a (strong) coupling between the dimerisation of the lattice and the modulation of the donor system†. As we have seen, the supercell consists of 13 unit cells. If the dimerisation locks to the modulation, there is a mismatch every 13 unit cells, giving rise to one soliton per supercell. If we were to describe this by a distortion vector, this would be $\tilde{q}_{SP} = \frac{1}{2}(1 + \frac{1}{13}) = 0.54$, precisely the modulation found in our fit of the susceptibility.

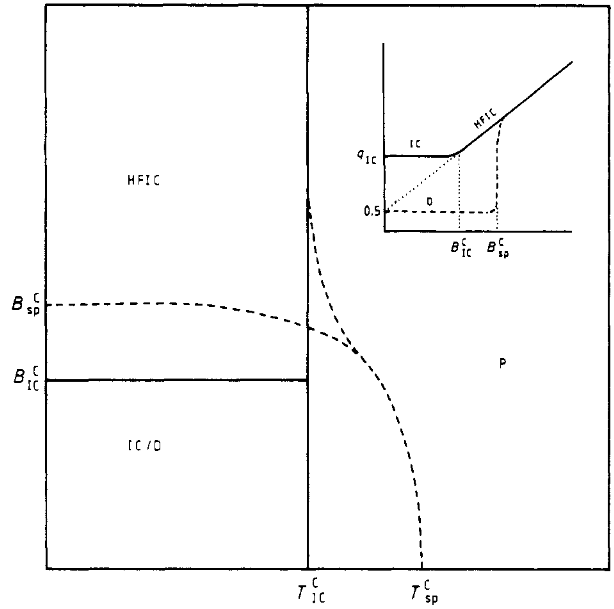

Figure 7. Proposed phase diagram of an SP system in the presence of an incommensurate modulation (———) compared with that of a regular SP system (- - -). The inset shows the magnetic field dependence of the low-temperature distortion vectors. Note that the high-field incommensurate phase is the same in both cases.

So far we have restricted ourselves to the zero-field case. We now turn to the field dependence of the transition. As remarked above (§ 4), the application of an external field induces a transition at 0.2 T. The transition temperature is field independent. An important experimental observation was recently made by Korving *et al* (1988) who showed that the magnetisation curves for fields exceeding 0.2 T are almost identical above and below the phase transition temperature. This situation is also encountered in SP systems for fields above the critical field, where the number of mid-gap states increases linearly in the field (Korving *et al* 1987). From this, one may infer that also the high-field phase of DMM-TCNQ$_2$ has an SP character. With these considerations in mind, we have drawn a tentative phase diagram for DMM-TCNQ$_2$ (figure 7). For comparison, we have also drawn the SP phase diagram; the high-field phases are identical and characterised 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 =

† Since the exchange is dominated by the E-term in equation (1.1) rather than by the transfer integrals, the most likely origin of magnetic dimerisation is a suitable modulation of the Madelung energy term.

0.5), DMM-TCNQ$_2$ is magnetic, because the SP distortion vector is slightly off its commensurate value owing to the coupling with the incommensurate superstructure. This phase diagram is probably appropriate in general for the SP transition in the presence of a structural incommensurate modulation.

6. Conclusions

We have obtained a microscopic understanding of both the high- and low-temperature phase of DMM-TCNQ$_2$. Above 1.7 K the 1D AF Heisenberg chain is strongly disturbed by a structural modulation of this lattice, which modulates the exchange values with the same periodicity. The phase transition which takes place at 1.7 K resembles closely an SP transition. However, the transition is not precisely a dimerisation, but the new superstructure is locked to the high-temperature superstructure. This makes the zero-field spin structure of DMM-TCNQ$_2$ analogous to the field-induced spin structure of a normal SP system. To confirm our picture of the low-temperature phase, it is useful to undertake a neutron diffraction study, which enables one to verify the existence of the low-temperature distortion vector.

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