

A MODEL FOR PHASE TRANSITIONS IN  
TETRATHIAFULVALENE–TETRACYANOQUINODIMETHANE (TTF–TCNQ)

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The observed phase transitions in Tetrathiafulvalene–Tetracyanoquinodimethane (TTF–TCNQ) are discussed using a simple model for the inter-chain coupling of charge density waves. Estimates based on Coulomb energies show that for  $38\text{ K} < T < 49\text{ K}$  the components  $q_x = \pi/a + q'_x$  and  $q'_z$  of the wave vector associated with the charge density wave satisfy  $q_z c/q'_x a \approx 0.1$ , with  $q'_x a \sim (T_2 - T)^{1/2}$  and  $T_2 = 49\text{ K}$ . A possible mechanism for the first order transition at  $38\text{ K}$  is proposed. The results are compared with neutron and X-ray scattering and with isotope shifts of the transition temperatures.

THE PHASE TRANSITIONS occurring in TTF–TCNQ have been studied extensively in recent years. The various phases are characterized by the wavevector  $q$  of a charge density wave (CDW). At  $T_1 = 54\text{ K}$  [1–3] a second order Peierls transition occurs with  $q = (0.5a^*, 0.295b^*, 0)$ , involving CDW's on one type of chains [4, 5] (probably on the TCNQ [5]). The component  $q_y = 0.295b^*$  is usually identified as  $2k_F$ , twice the Fermi momentum. As pointed out by Bak and Emery [4] another transition is expected to take place at a temperature  $T_2 < T_1$  in which the other set of chains orders. Below  $T_2$  the  $q_x$  component of the CDW is expected to satisfy  $q_x = 0.5a^* + \lambda_c(T_2 - T)^{1/2}$ . A careful analysis of the original experimental data and further measurements performed with higher precision support these predictions with [4]  $T_2 = 49\text{ K}$ . Finally, as was first observed by Jerome, Muller and Weger [6] a first order transition takes place at  $T_3 = 38\text{ K}$  [2, 3, 6] below which the wave vector  $q$  is locked at  $q = (0.25a^*, 0.295b^*, 0)$ . Recently [7] symmetry considerations have been used to analyze the  $T_2$  transition. It has been shown that owing to a coupling between the  $q_x$  and  $q_z$  components in the Landau–Ginzburg free energy, the  $q_z$  component of the CDW is expected to be non-zero for  $T_3 < T < T_2$  with  $q_z = \lambda_c(T_2 - T)^{1/2}$ . This behavior of the component  $q_z$  has not yet been observed experimentally. The observability of this effect depends on the value of the parameter  $\lambda_c$ . This value cannot be

determined by symmetry considerations alone; a more detailed microscopic model is needed.

In the present note we consider a simple model for possible interaction energies between CDW's on different chains. Taking into account Coulomb energies we find that  $\lambda_c/\lambda_a \approx 0.1$  which together with the experimental value [4]  $\lambda_a \approx 0.4$  yields  $\lambda_c \approx 0.04$ . Our model certainly does not represent a complete microscopic description of TTF–TCNQ. The numerical results should therefore be considered only as a guide to the order of magnitude of various quantities.

The model also suggests a possible mechanism for the first order transition at  $T_3 = 38\text{ K}$ .

A detailed study of the various lattice modes and their interchain couplings was made by Weger and Friedel [8]. They emphasize mainly the interchain couplings within the  $(a, b)$  plane where TTF and TCNQ chains alternate. In the present work we look for additional effects which may arise due to interchain couplings in the  $c$  direction.

Suppose that the CDW's are localized on chains along the  $b$  axis, and let  $R_{ij}$  be the vector in the  $(a, c)$  plane which connects the  $i$ th and  $j$ th chains. We assume that the charge density along the chain takes the form  $\rho_i \cos(2k_F y + \phi_i)$  where  $\rho_i = \rho_Q$  on a TCNQ chain and  $\rho_i = \rho_F$  on a TTF chain. The Coulomb interaction between the  $i$ th and  $j$ th chains then takes the form [9]

$$E_{ij}^{\text{coul.}} = \rho_i \rho_j \cos(\phi_i - \phi_j) K_0(2k_F R_{ij}), \quad (1)$$

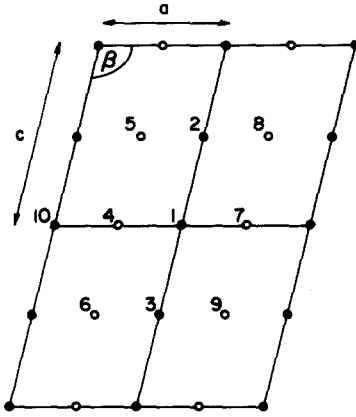


Fig. 1. A cross-section of the chain system in the  $(a, c)$  plane. The chain direction  $b$  is perpendicular to the  $a$  and  $c$  axis. A full circle is a TCNQ chain and an open circle is a TTF chain.  $a = 12.2 \text{ \AA}$ ,  $c = 18.3 \text{ \AA}$  and the  $(a, c)$  angle  $\beta$  is  $104.5^\circ$ .

where

$$K_0(x) = \int (t^2 + x^2)^{-1/2} \cos t \, dt$$

is the modified Bessel function of the third kind. A cross-section of the chain system in the  $(a, c)$  plane is shown in Fig. 1. For the parameters [1, 10] of TTF-TCNQ  $2k_F a \approx 6$  and  $k_F c \approx 4.5$ . Since  $K_0(x) \sim e^{-x}/\sqrt{x}$  for  $x \geq 2$  the Coulomb energy is dominated by the nearer neighbor terms, and the interchain couplings of the  $4k_F$  instability [3, 11] (or those of higher harmonics) can be neglected. The Coulomb interaction (1) between two chains favours a phase difference  $\phi_i - \phi_j = \pi$ . The hopping term also favours a phase difference of  $\pi$  since a density maximum on one chain tends to be close to a density minimum on the other chain. More explicitly, it has been shown [12] that within a single band approximation and to lowest order in the interchain coupling, the hopping term takes the same form as the Coulomb term, namely

$$E_{ij}^{\text{hop}} = \rho_i \rho_j t_{ij}^h \cos(\phi_i - \phi_j). \quad (2)$$

We therefore assume that the interaction between chains is given by

$$E_{ij} = \rho_i \rho_j t_{ij} \cos(\phi_i - \phi_j) \quad (3)$$

with

$$t_{ij} = t_{ij}^h + K_0(2k_F R_{ij}). \quad (4)$$

Since the interaction energy falls off quite rapidly with distance we consider only interaction between chains which are not too far apart. Define now the following interaction parameters (see Fig. 1):

$$\alpha \equiv t_{1,10} = t_{4,7},$$

$$\beta \equiv t_{1,2} = t_{4,5},$$

$$\gamma \equiv t_{1,4},$$

$$\delta \equiv \frac{1}{2}(t_{1,5} + t_{1,6}), \quad (5)$$

$$\epsilon \equiv t_{1,5} - t_{1,6}.$$

Here we assume that the hopping term  $t_{ij}^h$ , like the Coulomb term, depends only on the distance between the chains  $i$  and  $j$  and therefore we take  $t_{1,10} = t_{4,7}$  and  $t_{1,2} = t_{4,5}$ . We also assume that for the ground state  $\phi_i - \phi_j = \mathbf{q} \cdot \mathbf{R}_{ij}$ , except for an additional phase difference  $\phi$  between the TTF and TCNQ sublattices. Indeed higher harmonics were seen only below  $T_3$  with relatively low intensity [3]. The free energy of the system, now, has the form:

$$f(q_x, q_z) = \alpha \cos q_x a + \beta \cos \frac{1}{2} q_z c + \mu \cos \phi [\gamma \cos \frac{1}{2} q_x a + 2\delta \cos \frac{1}{2} q_z c \cos \frac{1}{2} q_x a + \epsilon \sin \frac{1}{2} q_z c \sin \frac{1}{2} q_x a] \quad (6)$$

where  $\mu = 2\rho_F \rho_Q / (\rho_F^2 + \rho_Q^2)$ . This expression is minimized by  $\phi = \pi$  or  $\phi = 0$ . We can choose  $\phi = \pi$ , while  $\phi = 0$  yields equivalent solutions with  $q_x$  replaced by  $q_x + 2\pi/a$ .

If  $\mu = 0$  the absolute minimum of (6) is at  $q_x = \pi/a$ ,  $q_z = 2\pi/c$ . Note that neighbouring CDW's in the  $c$  direction are out of phase. This maintains the original lattice periodicity, since there are two TCNQ chains per unit cell in the  $c$  direction. This configuration describes TTF-TCNQ for  $T_2 < T < T_1$ . Below  $T_2$  the ratio  $\mu$  grows linearly [4] with  $(T_2 - T)^{1/2} / \rho_Q(T)$ , and  $\rho_Q(T)$  depends weakly on temperature. To first order in  $\mu$  the minimum of (6) is given by

$$\begin{aligned} \sin \frac{1}{2} q'_x a &= \mu(\gamma - 2\delta)/4\alpha \\ \sin \frac{1}{2} q'_z c &= \mu\epsilon/\beta \end{aligned} \quad (7)$$

where  $q'_x = -q_x + \pi/a$ ,  $q'_z = -q_z + 2\pi/c$ . Thus  $q'_x$  and  $q'_z$  are both nonzero for  $T < T_2$  and their ratio,

$$q'_z c \approx \frac{4\alpha\epsilon}{\beta(\gamma - 2\delta)} q'_x a \quad (8)$$

is temperature independent. This behaviour has been predicted by Mukamel [7] using symmetry considerations. The parameter  $\epsilon$ , which measures the deviation of the unit cell from being orthorhombic is responsible for the variation of  $q_z$ . If the Coulomb terms dominate in (4) then  $\alpha/\gamma \approx 0.04$ ,  $\beta/\gamma \approx 0.2$ ,  $\delta/\gamma \approx 0.1$ ,  $\epsilon/\gamma \approx 0.1$ , and  $q'_z c \approx 0.1 q'_x a$ . From the known values [4] of  $q'_x a$  we obtain  $0.13 \geq q'_z c \geq 0$  for  $T_3 < T \leq T_2$ , and the periodicity in the  $c$  direction deviates by up to  $0.13/2\pi \approx 2\%$ . This should be a lower bound since the transfer integral between molecules 1 and 4 is zero [10] (Fig. 1) while hopping does contribute to other  $t_{ij}$  terms [12].

The postulated free energy (6) suggests a possible mechanism for the first order transition at 38 K. The

solution (7) is associated with one minimum of  $f(q_x, q_z)$ . As the temperature is lowered, the parameter  $\mu$  grows and another minimum of  $f(q_x, q_z)$  may yield a lower energy, thus giving rise to a first order transition. Let us study the minima of the expression (6), assuming for simplicity  $\epsilon = 0$ . The extrema are

$$\cos \frac{1}{2}q_x a = \mu(\gamma + 2\delta)/4\alpha, \quad \cos \frac{1}{2}q_z c = +1, \quad (9)$$

$$\sin \frac{1}{2}q_x a = 0, \quad \cos \frac{1}{2}q_z c = \pm 1, \quad (10)$$

And the previous solution (7)

$$\cos \frac{1}{2}q_x a = \mu(\gamma - 2\delta)/4\alpha, \quad \cos \frac{1}{2}q_z c = -1. \quad (11)$$

The first derivatives of equation (6) vanish also for

$$\cos \frac{1}{2}q_x a = \beta/2\mu\delta, \quad \cos \frac{1}{2}q_z c = \alpha\beta/(\mu\delta)^2 - \gamma/2\delta. \quad (12)$$

Checking the second derivatives it is easy to verify that the solution (12) is not a local minimum for any value of the parameters  $\alpha, \beta, \gamma, \delta$  and  $\mu$ , and therefore need not be considered. Hence, the solution (9) is the only one which could account for the first order transition to  $q^* \equiv (0.25a^*, 0.295b^*, 0)$ . For (9) to be the absolute minimum one needs:

$$\mu(\gamma + 2\delta)/4\alpha < 1, \quad (13)$$

and

$$2\alpha\beta < \mu^2\gamma\delta. \quad (14)$$

Thus when  $\mu$  becomes large enough to satisfy (14), and (13) is also satisfied, a first order transition takes place in which the CDW's are described by (9), instead of (7). If the parameters then satisfy  $q_x \simeq q_x^* = \pi/2a$  and  $q_z \simeq q_z^* = 0$  (when  $\epsilon \neq 0$ ) umklapp terms [4, 13] would pin the CDW at  $q = q^*$ . Thus it is sufficient to have weak Umklapp terms since the phase transition itself is driven by other forces.

It has been suggested that the phase transition at  $T_3$  is due entirely to umklapp terms [4, 13] which are of fourth order in the order parameters. The solution (9) illustrates an alternative mechanism – the transition is driven by second order terms in the order parameter, but involves higher order terms in the wavevectors  $q'_x, q'_z$ .

Taking into account only the Coulomb contributions to (5) one finds that (13) and (14) cannot be simultaneously satisfied. However a solution is possible if the hopping contributions and the  $\epsilon$  term is included. In fact even the original form (6) may not be sufficiently realistic. It should certainly be modified to allow for CDW's which are not localized on linear chains, by adding more complicated hopping terms [12] and other types of interchain couplings [8, 12]. However, the correct  $f(q_x, q_z)$  can still develop a minimum, distinct from the solution for  $T_3 < T$ , which for large  $\mu$  would cause a first order transition.

Thus we expect, rather generally, that the transition temperature  $T_3$  is the solution of

$$\rho_F(T)/\rho_Q(T) = \text{const.} \quad (15)$$

The constant is determined by interchain couplings, which can be taken as temperature independent in the relevant temperature range.

An interesting feature of the solution (9) is that the relative phase of neighbouring CDW's in the  $c$  direction  $\Delta\phi_z = q_z c/2$  jumps from close to  $\pi$  for  $T > T_3$  [equation (7)] to zero for  $T < T_3$ . This can be understood easily if  $\beta \sim \delta \ll \gamma$ . For small  $\mu(T > T_3)$  the chain 1 (Fig. 1) is coupled strongly only with the chains 2 and 3, hence  $\Delta\phi_z = \pi$ . For larger  $\mu$ , the  $\gamma$  term favours nearest TTF and TCNQ to be out of phase. Also the interactions between the chain 1 and the chains 2, 3, 5, 6, 8, 9 become comparable. If  $\Delta\phi_z = \pi$  then only two of these interactions are attractive, while if  $\Delta\phi_z = 0$  then four of them are attractive. The condition  $\beta \sim \delta \ll \gamma$  seems reasonable in view of the shape and orientation of the various molecules [10] and is indeed satisfied for the Coulomb terms in (4). Thus for large enough  $\mu$  a transition from  $\Delta\phi_z \simeq \pi$  to  $\Delta\phi_z = 0$  is possible.

We discuss now the available neutron and X ray scattering data. The scattering intensity associated with the orderings given by (7) and by (9) can be estimated if the structure factor of each molecule is slowly varying within one zone [3, 14]. Since we are interested in the  $q_z$  component of the CDW consider the measured scattering intensity at  $q_1 = (ha^* \pm q_x, kb^* \pm q_y, lc^*)$ , where  $q_x, q_y$  are the  $x, y$  components of the CDW wavevector. Thus we eliminate complications due to the relative phases in the  $(x, y)$  directions. The scattering intensity is then given by

$$\begin{aligned} S(q_1) &= |b_1 + b_2(-)^l e^{iq_z c/2}|^2 \\ &= (b_1 - b_2)^2 + 2b_1 b_2 [1 - (-)^l \cos \frac{1}{2}q'_z c]. \end{aligned} \quad (16)$$

Here the scattering amplitudes  $b_i(h, k, l) = b_i^Q + b_i^F = b_i$  corresponds to the TCNQ molecules 1, 2 ( $b_1^Q, b_2^Q$ ) and the TTF molecules 4, 5 ( $b_1^F, b_2^F$ ) of Fig. 1. The factor  $\exp[iq_z c/2]$  accounts for the relative phases on these chains ( $b_i$  can be taken as positive numbers).

Experimentally it is found (see Fig. 4 of reference [2]) that for  $T_2 < T < T_1$  no scattering intensity is observable for  $(h, k, l) = (1, 3, 0)$  while one finds  $S(q_1) \sim (T_1 - T)$  for  $(h, k, l) = (0, 1, 3)$ . Below  $T_2$  the  $(1, 3, 0)$  scattering grows like  $(T_2 - T)$  while the  $(0, 1, 3)$  scattering exhibits a weak dependence on temperature. Theoretically we expect for  $T > T_2$   $q'_z = -q_z + 2\pi/c = 0$  and  $b_i^F = 0$  (i.e. no order on the TTF chains), and so  $S(q_1) = [b_1^Q - (-)^l b_2^Q]^2$ . Hence experiment implies  $b_1^Q(l=0) = b_2^Q(l=0)$ . If the  $2k_F$  mode

polarized in the  $c^*$  direction [3] then  $b_i^Q(l=0) = 0$ . The growth of order on the TCNQ chains is described by  $S(q_1) = (b_1^Q + b_2^Q)^2 \sim \rho_Q^2 \sim T_1 - T$ , and corresponds to the  $l = 3$  data. Below  $T_2$ , a temperature dependence associated both with  $b_i^F$  and  $q_z' \neq 0$  may appear. The factors  $b_i$  are dominated by  $b_i^Q$  so that  $b_i$  and  $S(q_1)$  for odd  $l$  are expected to depend weakly on temperature if  $T < T_2$ . This is consistent with the  $l = 3$  data. For  $l = 0$  the experiment is consistent with the increase of the first term in equation (16) (if  $b_1^F \neq b_2^F \neq 0$  and  $b_1^Q = b_2^Q$ ) since  $(b_i^F)^2 \sim \rho_F^2 \sim T_2 - T$ . It is also consistent with the second term of equation (16), since  $(q_z')^2 \sim T_2 - T$  from equation (7). If  $b_1^l = b_2^l$  for all  $l$ ,  $S(q_1)$  is expected to have the same pattern for all even  $l$ , namely  $S(q_1)$  is zero for  $T > T_2$  and grows linearly with  $T_2 - T$  for  $T < T_2$ . If  $b_1^l \neq b_2^l \neq 0$  for  $l \neq 0$  then this pattern will be smeared. X-ray data for  $l = 0$  and  $l = 12$  seem to be consistent with this pattern, although not as nicely as the  $l = 0$  neutron scattering data. Thus the predicted  $q_z' \neq 0$  for  $T_3 < T < T_2$  does not contradict the available experimental data. These conclusions do not depend on the details of the model (6), since they can be derived from a Landau-Ginzburg expansion [4, 7].

At the transition  $T_3$ ,  $S(q_1)$  increases by [2]  $\sim 20\%$  for  $l = 3$  and by  $\sim 60\%$  for  $l = 0$ . A quantitative analysis of this increase depends on the actual values of  $b_i$ . However, the large difference in the increase of the  $l = 0$  and  $l = 3$  intensities suggests a change in the order within the unit cell, in addition to the growth of the amplitudes  $b_i$ . In the model proposed here,  $\cos \frac{1}{2} q_z' c$  is close to  $+1$  for  $T > T_3$  [equation (7)] and jumps to  $-1$  for  $T < T_3$  [equation (9)]. Thus the last term of (16) causes a larger increase in scattering with even  $l$  than with odd  $l$ , in agreement with the neutron scattering data [2]. The X-ray data [3] shows a different pattern: the  $l = 0$

intensity increases very slightly at  $T_3$ , while  $l = 1$  and  $l = 12$  intensities increase by a factor of two. The difference between the X-ray and neutron scattering data is probably due to the higher sensitivity of X-ray scattering from the sulfur atoms in the TTF chains. Thus  $(b_1^F - b_2^F)^2$  in the first term of (16) is larger and the effect of the second term in (16) is smaller.

Finally, we comment on the recently measured isotope shifts [15] of  $T_1$  and  $T_3$ . Deuteration of TCNQ increases  $T_1$  while  $T_3$  is decreased. On the otherhand deuteration of TTF instead of TCNQ does not affect  $T_1$ , while  $T_3$  is increased. These results imply a Peierls instability on the TCNQ chains at  $T_1$ . The positive isotope shift is in agreement with theory [16] and its magnitude determines the electron-phonon coupling of the C-H mode. Deuteration of TCNQ increases  $T_1$  and  $\rho_Q(T)$ , so that the solution  $T_3$  of equation (15) is indeed decreased. Since  $T_2$  corresponds to a Peierls instability on the TTF chain, the same theory [16] predicts that deuteration of TTF would increase  $T_2$ . Thus, for a given  $T$   $\rho_F(T)$  is larger and  $T_3$  from (15) is increased. Therefore, the relation (15) which determines  $T_3$  is in good agreement with the isotope shift measurements.

In conclusion, a simple model for the interchain coupling is able to account for the phase transitions in TTF-TCNQ. It yields previous results concerning the second order phase transition and suggests a novel mechanism for the first order phase transition at  $T_3 = 38$  K.

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