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The Landau theory of phase transitions in TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane)

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The observed low-temperature charge-density-wave (CDW) transitions in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) are analyzed in the framework of the Landau theory of second-order phase transitions. A careful treatment of the symmetry requirements is given. It is found that the (commensurate) transition at 54 K involves CDW distortions on both TCNQ and TTF chains. The possibilities for the subsequent (noncommensurate) transition near 49 K are analyzed. A continuous transition involving a phase modulation of the first transition may happen for a range of values of the Landau parameters. The next (commensurate) transition, at 38 K is discontinuous. The formulation requires a thorough group-theoretical analysis: We discuss the validity of the usual practice of using only a simple basis set for an irreducible representation associated with a transition. A discussion of the absence or presence of commensurability energies of the various transitions is also given.

I. INTRODUCTION

The discovery of high and strongly anisotropic conductivity and strong one-dimensional fluctuations[1] in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and related compounds have prompted intensive study of these materials. In particular, neutron-scattering experiments[2-4] have revealed that the charge-density waves (CDW's) which appear as a consequence of the one-dimensional fluctuations are stabilized at about 54 K, where three-dimensional ordering sets in. The same experiments show that in the direction of alternating sheets of TTF and TCNQ molecules, there is a definite relative phase between the CDW's which run along the chains. From one TTF (or TCNQ) sheet to the next TTF (or TCNQ) sheet the phase difference is π at and somewhat below 54 K. Below 38 K the phase difference is $\frac{1}{2}\pi$. According to recent interpretations of the data, as the temperature is lowered below about 49 K, the phase difference varies continuously away from π toward $\frac{1}{2}\pi$, but there is a small discontinuous jump locking the phase to $\frac{1}{2}\pi$ at 38 K.

All theories dealing with TTF-TCNQ are based on the assumption that the material consists of more or less independent chains which have one-dimensional metallic character. The CDW susceptibility of such a system exhibits a $T = 0$ divergence at wave vector $2k_F$ and it is generally accepted that the 54-K transition is driven by these one-dimensional CDW fluctuations which are stabilized at finite temperature through the residual three-dimensional Coulomb interactions between chains. In this way, a new phase with a periodic lattice distortion and an associated electronic CDW develops[5-7] with wave-vector component along the chains equal to $2k_F$. The other wave-vector component transverse to the chain direction is determined by the crystal structure and the interchain interactions and appears to vary as described by the relative phase changes given in the previous paragraph.

Šaub, Barišić, and Friedel[8] mentioned an explanation of the phase sliding below 54 K. This effect was discussed by Bak and Emery[9] who elaborated a similar explanation and developed a Landau-type theory to explain the phase transitions. Bak and Emery pointed out that in addition to the commensurate transitions at 54 K (lattice doubling transverse to the chain direction) and at 38 K (lattice quadrupling) there appeared to be an intermediate transition near 49 K below which the phase sliding sets in.[4,10]

In the calculation of Bak and Emery,[9] the conclusions are as follows: (i) At 54 K there is a second-order phase transition involving CDW's on *only one* set of chains (either TTF or TCNQ) with the phase difference π. (ii) Another second-order transition occurs near 49 K. Here, CDW's on the second set of chains order and the phase differences begin to shift toward $\frac{1}{2}\pi$. (iii) There is a first-order transition at 38 K at which a discontinuous locking of the phase at $\frac{1}{2}\pi$ occurs. Recent experimental work[4,11] appears to confirm this picture.

In this paper we present a calculation from a similar point of view. We use the Landau theory of second-order phase transitions to analyze the possible symmetry changes and the order of the transitions. This theory, as is well known, neglects fluctuations and hence gives the wrong critical exponents. In addition, fluctuations may drive a Landau second-order transition to a first-order one. These caveats are especially significant when the transitions are dominated by fluctuations as in the present case where there is evidence of quasi-one-dimensional behavior. However, the Landau theory is useful as a guide and can elucidate the symmetry changes which are allowed.

Our conclusions partly agree with those of Bak and Emery[9,10] but differ in certain respects. We find, for example, that there is no reason to suppose that only one set of chains orders at 54 K. It is, however, possible that the CDW's have a large amplitude on the TCNQ chains and a much smaller amplitude on the TTF's. This seems likely in view of the experimental situation.[11,12] Our description of the transition proposed by Bak and Emery at 49 K differs from theirs as well and includes a discussion of commensurability effects.[13] Finally, we describe the 38-K transition in a manner consistent with that of Bjeliš and Barišić[14] and Bak.[10]

In order to give a full description we present a rigorous treatment in the framework of the Landau theory.[15] In Sec. II, we recapitulate the crystal symmetry, the details of which are basic ingredients in the analysis. In Sec. III, we review the Landau theory[16] and apply it to the phase transition at 54 K. In Sec. IV, we consider the next transition, near 49 K and the 38-K transition is described in Sec. V. We discuss our own results in Sec. VI and compare them to earlier work.

II. CRYSTAL SYMMETRY OF TTF-TCNQ

The elementary cell of TTF-TCNQ is shown in Fig. 1.[17] The TTF and TCNQ molecules are arranged in chains along the b direction and these chains form sheets in the bc plane. The TTF and TCNQ sheets alternate in the a direction. There are two sublattices of chains: As one goes along the c direction, for example, adjacent chains have molecules displaced by one-half a lattice constant along b and they are tilted in the opposite direction. This is indicated in Fig. 1 and is the reason why the relevant space group is nonsymmorphic (contains screw axis and glide plane).

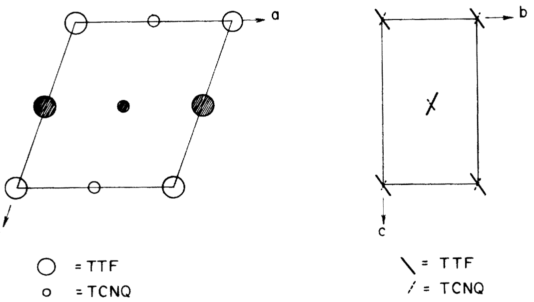

FIG. 1. Views along b and a directions in the TTF-TCNQ showing the tilted molecules. The shaded molecules are displaced out of the ac plane and are centered at $\frac{1}{2}b$. The (dotted) TCNQ molecules are displaced out of the bc plane and are centered at $\frac{1}{2}a$.

The symmetry elements of the space group (and hence of the high-temperature phase) of the crystal are the translations, the identity E, the inversion I, a twofold screw axis C_2^* around b: $C_2^* = \{\frac{1}{2}b + \frac{1}{2}c \,|\, C_2\}$, and a glide plane (the ac plane): $\sigma^* = C_2^* I = \{\frac{1}{2}b + \frac{1}{2}c \,|\, \sigma\}$. The notation for the mixed elements is due to Seitz[18] and is of the form $\{t\,|\,R\}$, where R indicates a pure rotation or reflection and t denotes the fractional lattice translation associated with it. The rule for combining such elements is $\{t_2 | R_2\}\{t_1 | R_1\} = \{t_2 + R_2 t_1 | R_2 R_1\}$. The symmetry is monoclinic with space group C_{2h}^5 ($P2_1/b$).

It is known from the experiments[2-4] that at 54 K, the wave vector of the CDW distortion is $k_0 = \frac{1}{2}a^* + \mu b^*$, where a^*, b^* are the reciprocal-lattice vectors (times 2π). That is, we have lattice doubling along a and a CDW distortion locked to the Fermi wave vector $\mu = 2k_F$ along b^*. Below 38 K, the wave vector is $k_2 = \frac{1}{4}a^* + \mu b^*$; between, denote the wave vector by $k = (\frac{1}{2} - q)a^* + \mu b^*$ and q varies from 0 to $\frac{1}{4}$.

In what follows, we consider the wave vector to be given by the experiment and we study the possible CDW's with that wave vector, the symmetry change at the formation of the CDW distortion, and the order of the transition. As we shall see, we need then to enumerate the irreducible representations (IR's) of the space group associated with the given wave vector.

III. PHASE TRANSITION AT 54 K

The starting point of a Landau treatment is the choice of order parameter and the expansion of the free energy in terms of it. In the present case it is the charge density. The structure of the order parameter, the number of its components, is determined by the symmetry of the system. Following the well-known procedure,[16,19] we expand the change $\delta\rho$ in the actual charge density as one moves away from the phase-transition line in terms of basis functions of the IR's of the space group of the high-temperature phase. The IR's may be characterized by their behavior under translations: To each IR is associated a certain star K of wave vectors. We have

$$\delta\rho(r, P, T) = \sum_{K\alpha i} c_{Ki}^{\alpha} \Phi_{Ki}^{\alpha}(r) , \tag{3.1}$$

where $\Phi^{\alpha}_{Ki}(r)$ is the ith basis function (belongs to the ith row) of the αth IR belonging to the star K. The expansion coefficients are functions of pressure and temperature eventually to be determined by minimizing the free energy. If the transition is second order, or weakly first order, then $\delta\rho$ and hence the c's are small near the transition and the free energy may be expanded in terms of the c's. The c's are then taken as order parameters. Only those combinations of the c's which are invariant under the symmetry operations of the space group may enter. These combinations are easily constructed from the known transformation properties of the corresponding basis functions of the IR's. The coefficients of the various invariants in this expansion consist of spatial integrals over certain products of the basis functions. Since $\delta\rho$ depends on P, T the precise form of the basis functions depends on P, T, and so do the coefficients in the free-energy expansion. The values of the c's are determined by minimizing the expression for the free energy and these values determine the symmetry of $\delta\rho$ in the low-temperature phase. In general, the phase transition occurs when the coefficient of the bilinear invariant involving a particular IR passes through zero. The number of components of the order parameter is equal to the dimensionality of the IR which is involved in the transition.

The usual assumption is that in the expansion (3.1) each IR appears only once and that, as remarked, the basis functions are P and T dependent. This comes about as follows. When one first expands the charge density, a complete set of functions must be used. A given IR has an infinite set of orthogonal basis functions[20] so that each IR appears infinitely many times and another index ("band index") appears in the sum (3.1). This extremely complicated situation may in principle be resolved by a further minimization which will pick out, for each row of the IR in question, that (P- and T-dependent) linear combination of the complete set of functions for that row which minimizes the energy at the given P, T. The number of times the IR in question enters the $\delta\rho$ expansion depends on the form of the resulting linear combinations and in the case that the ratios of the coefficients of the different rows are the same for all occurences of the IR then it is possible to use a single P-, and T-dependent basis for the IR. For the cases we consider, it has been shown by one of us (FW) that it is possible to use a single basis for each IR. The details of the argument will be given elsewhere. In any case, the use of a single basis gives complete information about the symmetry, but not the details of the charge distribution.

The IR's associated with the star to which $k_0 = \frac{1}{2}a^* + \mu b^*$ belongs are easily constructed. The star contains only k_0 and $-k_0$ since C_2 transforms k_0 into $k_0 - a^*$ which is equivalent to k_0, and σ transforms k_0 into $-k_0 + a^*$, equivalent to $Ik_0 = -k_0$. The group of the wave vector contains only E, C_2 and has therefore only two one-dimensional small representations. The relevant IR's of the space group are constructed in the usual manner.[18,19,21] There are two two-dimensional IR's T_+ and T_- belonging to this star and the matrices may be written as follows:

$$T_\pm(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad T_\pm(C_2^*) = \pm \begin{pmatrix} e^{-i\pi\mu} & 0 \\ 0 & e^{i\pi\mu} \end{pmatrix},$$
$$T_\pm(I) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad T_\pm(\sigma^*) = \pm \begin{pmatrix} 0 & e^{-i\pi\mu} \\ e^{i\pi\mu} & 0 \end{pmatrix}. \tag{3.2}$$

The basis functions of these IR's are of Bloch type

$$\phi_1^\pm = e^{i\vec{k}_0\cdot\vec{r}}[u_\pm(r) \pm e^{-i\vec{a}^*\cdot\vec{r}} u_\pm(C_2^{*-1}r)],$$
$$\phi_2^\pm = e^{-i\vec{k}_0\cdot\vec{r}}[u_\pm(-r) \pm e^{i\vec{a}^*\cdot\vec{r}} u_\pm(-C_2^{*-1}r)], \tag{3.3}$$

where $u_+(r)$ and $u_-(r)$ are functions periodic in the lattice with $u_\pm(r) = u_\pm^*(-r)$ (in order that $\delta\rho$ be real), but otherwise arbitrary. Whatever the $u_\pm$, however, in every case the expressions (3.3) may be replaced by

$$\Phi_1^\pm = e^{i\vec{k}_0\cdot\vec{r}} V^\pm(r), \quad \Phi_2^\pm = e^{-i\vec{k}_0\cdot\vec{r}} V^\pm(-r), \tag{3.4}$$

where the $V^\pm(r)$ are periodic in the lattice and have the property

$$V^\pm(r) = \pm e^{-i\vec{a}^*\cdot\vec{r}} V^\pm(C_2^{*-1}r). \tag{3.5}$$

This form of the basis functions will be used in Sec. IV.

As we have remarked above, the transition will be associated with a particular IR, either T_+ or T_-. Therefore the CDW within a unit cell is either even (T_+) or odd (T_-) under C_2^*. The amplitudes will be determined by the precise form of $V^\pm(r)$, but only two symmetries are possible. In what follows, to analyze the symmetry, we only need consider one T_+ and one T_- and their associated $\phi_i^\pm$ functions.

The expansion of the charge density (3.1) has the form

$$\delta\rho = c_1^+\phi_1^+ + c_2^+\phi_2^+ + c_1^-\phi_1^- + c_2^-\phi_2^-. \tag{3.6}$$

Since the $\phi^{\alpha}_{Ki} = \phi_i^\pm$ transform among themselves for given K, α under the operations of the space group in the high temperature phase, the c's may be considered as basis functions for the matrices of the IR's instead of the ϕ's. The c's, being small near the transition, are the order parameters in terms of which the free energy F is expanded. The invariant combinations which appear are easily found. We have

$$F=F_0+A_+c_1^+c_2^+ +A_-c_1^-c_2^- +B_+(c_1^+c_2^+)^2+B_-(c_1^-c_2^-)^2+Cc_1^+c_2^+c_1^-c_2^- +D(c_1^+c_2^- +c_1^-c_2^+)^2+\dots\,, \tag{3.7}$$

where all terms through fourth order are indicated explicitly. It is customary to assume that above T_c all coefficients A, B, C, $D\dots$ are positive. In fact, for stability in the absence of higher-order terms, one needs $A_\pm$, $B_\pm$ all positive and $4B_+B_- \geqslant C^2$ if $D>0$ and for $D<0$, $4B_+B_- > (C-4|D|)^2$. Then F is minimal for all c's $=0$. The phase transition takes place when A_+ or A_- becomes negative. Assume it is A_+. Then the condition that F be at an extremum yields

$$c_1^+=c_2^{+*}=c_+e^{i\theta},\quad c_+^2=-A_+/2B_+\,,$$
$$F=F_0-A_+^2/4B_+\,, \tag{3.8}$$

with $c_{1,2}^-=0$. The phase θ is undetermined as a consequence of the incommensurability along b. If it is A_- which goes negative, the result is like (3.8) with the obvious notational change. In any case, only one of the two IR's, T_+ or T_-, is activated and only the even or odd (under C_2^*) CDW is established. It may be shown that, for a certain behavior of the A, B, C, D coefficients, this solution becomes unstable at a lower temperature and a new CDW appears in which both IR's are activated. We do not discuss this possibility since the CDW wave vector is unchanged.[22]

Having found the c's, we may write the charge density for the two possibilities from (3.8):

$$\delta\rho_\pm(r)=c_\pm\{e^{i\theta_\pm}[u_\pm(r)\pm e^{-i\vec{a}^*\cdot\vec{r}}u_\pm(C_2^{*-1}r)]e^{i\vec{k}_0\cdot\vec{r}}+e^{-i\theta_\pm}[u_\pm(-r)\pm e^{i\vec{a}^*\cdot\vec{r}}u_\pm(-C_2^{*-1}r)]e^{-i\vec{k}_0\cdot\vec{r}}\}\,. \tag{3.9}$$

It is now possible to find the values of $\delta\rho$ on the various chains. In the elementary cell (l,m,o), there are two inequivalent TTF sites $f=(l,m,o)$ and $f'=(l,m+\frac{1}{2},\ o+\frac{1}{2})$ and two TCNQ sites $q=(l+\frac{1}{2},m,o)$ and $q'=(l+\frac{1}{2},\ m+\frac{1}{2},\ o+\frac{1}{2})$. Here, l, m, and o are integers. We write the charge density $\delta\rho$ at the positions of the various molecules. For the $T_\pm$ transitions, we have

$$\begin{aligned}&\delta\rho_\pm(f)=2(-1)^l c_\pm\cos(\theta_\pm+2\pi m\mu)[u_\pm(f)\pm u_\pm(f')]\,,\quad \delta\rho_\pm(f')=\pm 2(-1)^l c_\pm\cos[\theta_\pm+2\pi(m+\tfrac{1}{2})\mu][u_\pm(f)\pm u_\pm(f')]\,,\\ &\delta\rho_\pm(q)=-2(-1)^l c_\pm\sin(\theta_\pm+2\pi m\mu)[u_\pm(q)\mp u_\pm(q')]\,,\quad \delta\rho_\pm(q')=\pm 2(-1)^l c_\pm\sin[\theta_\pm+2\pi(m+\tfrac{1}{2})\mu][u_\pm(q)\mp u_\pm(q')]\,.\end{aligned} \tag{3.10}$$

In deriving these results we have used the fact that C_2^* shifts from f or q sites to f' or q', respectively. We illustrate these CDW's schematically in Fig. 2 where we have taken $u_\pm$ constant along b.

The symmetry makes no requirements on the values of $u_\pm$ at the sites f, f', q, q' and therefore, from (3.10) there is no symmetry reason to suppose that $\delta\rho$ vanishes on any of the chains. This can be understood also from consideration of the Coulomb interaction between the chains if we take proper account of the symmetry. It is important to note that the molecules do not lie in the ac plane, but are tilted out of it. If we ignore this, the net Coulomb potential on a TTF molecule f coming from its neighboring TCNQ molecules is zero.[23] In this case the symmetry would be C_{2h}^1 and the TTF's will be decoupled from their TCNQ neighbors. With the actual C_{2h}^5 symmetry, on the other hand, the tilted TCNQ molecules always give a nonzero potential at TTF sites and the two sets of chains order at the same temperature. However, the amplitude of the TTF CDW may be much smaller than that of the TCNQ CDW.

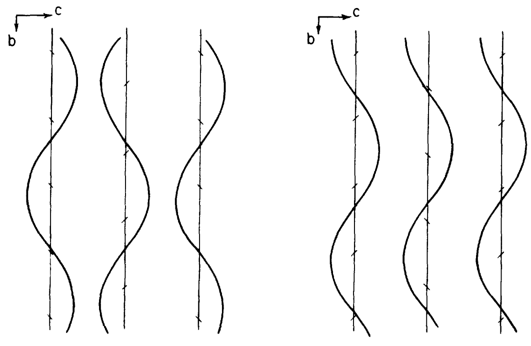

FIG. 2. Schematic illustration of CDW's for each type of molecule when the T_+ (T_-) representation is activated at 54 K. For simplicity, unit amplitude is chosen on both sets of chains.

From (3.10) and Fig. 2 we see that the CDW distortion on the two inequivalent TTF chains in the elementary cell have the same sign ("in-phase") for the T_+ transition, while on the TCNQ molecules the CDW's are "out of phase." The phase shift $\pi\mu$ in (3.10) comes from the difference in the b coordinate of the f and f' sites. For the T_- transition, the situation is reversed. There is no solution for which both types of molecules have the same phase relation between their inequivalent chains. Since the Coulomb forces favor the "out-of-phase" situation, the CDW amplitude on the "in-phase" chains is probably small.

IV. PHASE TRANSITION AT 49 K

The experiments indicate that the T_+ or T_- CDW described in Sec. III persists from 54 K down to about 49 K where, as pointed out by Bak and Emery,[9] the wave vector changes from $k_0=\frac{1}{2}a^*+\mu b^*$ to $k=(\frac{1}{2}-q)a^*+\mu b^*$ and q varies continuously from zero. We are going to apply the Landau theory in this situation. There is an important difference between the phase transitions of 54 K and 49 K. In the former case, a lower-symmetry structure (the CDW) is superimposed on the high-symmetry structure of the high-temperature phase; therefore the free energy had to be invariant with respect to the space group of the high-temperature phase. However, at 49 K, the situation is different. The CDW of wave vector k is *not* superimposed on that of wave vector k_0. It is not appropriate then to analyze the situation at 49 K in the same way as before, i.e., to construct a free energy which is invariant under the symmetry elements of the structure just above the transition point. It is possible, however, to work with the symmetry of the phase above 54 K and to study the shift in the CDW wave vector. It must be kept in mind that the order parameter, the CDW amplitude, is not necessarily small at the 49-K transition and therefore a low-order expansion may not be sufficient. However, the higher-order invariants will not change the results qualitatively since, due to the low symmetry, the higher-order invariants can all be obtained from products of the low-order ones.

We repeat the steps of Sec. III, but for a general $0<q<\frac{1}{4}$. The group of the wave vector contains only the unit element and the star contains four vectors

$$k_1=(\tfrac{1}{2}-q)a^*+\mu b^*,\quad k_2=-(\tfrac{1}{2}-q)a^*-\mu b^*=Ik_1\,,$$
$$k_3=-(\tfrac{1}{2}-q)a^*+\mu b^*=C_2k_1\,,$$
$$k_4=(\tfrac{1}{2}-q)a^*-\mu b^*=\sigma k_1\,.$$

The space group C_{2h}^5 has only one four-dimensional IR for this star whose basis functions and matrices are easily found

$$\begin{aligned}
\chi_1&=u_q(r)e^{i\vec{k}_1\cdot\vec{r}}\,,\\
\chi_2&=T(I)\chi_1=u_q(-r)e^{i\vec{k}_2\cdot\vec{r}}\,,\\
\chi_3&=T(C_2^*)\chi_1=u_q(C_2^{*-1}r)e^{-i\pi\mu}e^{i\vec{k}_3\cdot\vec{r}}\,,\\
\chi_4&=T(\sigma^*)\chi_1=u_q(-C_2^{*-1}r)e^{i\pi\mu}e^{i\vec{k}_4\cdot\vec{r}}\,,
\end{aligned}\tag{4.2}$$

where $u_q(r)$ is an arbitrary lattice-periodic function and

$$\begin{aligned}
T(E)&=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{bmatrix},\\
T(C_2^*)&=\begin{bmatrix}0&0&e^{-2\pi i\mu}&0\\0&0&0&e^{2\pi i\mu}\\1&0&0&0\\0&1&0&0\end{bmatrix},\\
T(I)&=\begin{bmatrix}0&1&0&0\\1&0&0&0\\0&0&0&e^{2\pi i\mu}\\0&0&e^{-2\pi i\mu}&0\end{bmatrix},\\
T(\sigma^*)&=\begin{bmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{bmatrix}.
\end{aligned}\tag{4.3}$$

The charge-density change associated with this IR is

$$\delta\rho_q=\sum_{i=1}^{4}d_i\chi_i\,.\tag{4.4}$$

The invariant combinations of the d_i are easily found and the free-energy change has the form

$$\Delta F_q=A_q(d_1d_2+d_3d_4)+B_q(d_1d_2+d_3d_4)^2+C_q(d_1d_2d_3d_4)\,.\tag{4.5}$$

If $\Delta F_q<0$, then finite values of the d_i minimize ΔF. If we carry out the minimization, we find two types of solutions:

$$d_1=d_2^*=de^{i\theta}\,,\quad d_3=d_4=0\tag{4.6a}$$

or

$$d_1=d_2=0\,,\quad d_3=d_4^*=de^{i\theta}\,,\quad d^2=-A_q/2B_q$$

$$d_1=d_2^*=de^{i\theta},\quad d_3=d_4^*=de^{i\theta'},\quad d^2=-A_q/(4B_q+C_q)\,.\tag{4.6b}$$

In the two cases, the minimum values of the free energy are:

$$\text{(a)}\quad \Delta F_q=-A_q^2/4B_q\,,\tag{4.7a}$$

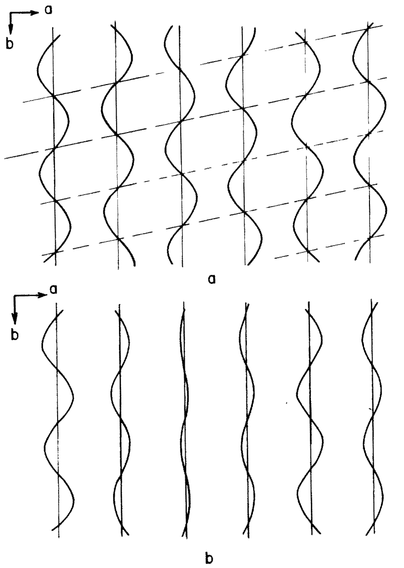

FIG. 3. Illustration of CDW's on TCNQ (or TTF) chains when $q \neq 0$ for case (a) phase sliding and case (b) amplitude modulation.

$$\text{(b)}\ \Delta F_q = -A_q^2/(4B_q + C_q)\,. \tag{4.7b}$$

In case (a), only two elements of the star are activated and $\delta\rho_q(r)$ has only two wave vectors, either k_1, k_2 or k_3, k_4. In case (b), all four wave vectors appear in $\delta\rho_q(r)$. The two cases correspond to different charge distributions as seen in Fig. 3.[14]
In case (a), the phase of the CDW's on the chains of the same type of molecule varies along the a direction; it slides with respect to the $q = 0$ solution of Sec. III. In case (b), the phase is constant, but the amplitude is modulated.

In the above calculation, we have used only one set of basis functions. Our conclusions concerning the possible symmetries which can occur if one of the free energies of (4.7) becomes lower than that of (3.8) are correct, but we have no information about the actual charge distribution or the continuity properties of the transition. As we have emphasized earlier, we must either use a complete set of basis functions for the IR in question or choose the single basis, if possible, which minimizes the free energy. If we want to look in more detail at the nature of the transition to $q \neq 0$, we need to proceed by one of these methods. Our main object is to find whether the transition to $q \neq 0$ is continuous or not and which of the two cases is realized. These questions depend on the nature of the A, B, C coefficients, hence on the basis functions. In addition, we shall be able to describe the relation of the basis functions or small q to those for $q = 0$.

In either approach, we assume that the change in free energy when $\delta\rho(r)$ appears can be expanded as follows:

$$\Delta F = \int d^3r_1\, d^3r_2\, F^{(2)}(r_1 r_2)\,\delta\rho(r_1)\,\delta\rho(r_2) + \int d^3r_1\, d^3r_2\, d^3r_3\, F^{(3)}(r_1 r_2 r_3)\,\delta\rho_1\,\delta\rho_2\,\delta\rho_3 + \cdots\,, \tag{4.8}$$

where $F^{(n)}$ is the nth functional derivative of ΔF with respect to $\delta\rho$. The $F^{(n)}$ are assumed to be symmetric in their n arguments and invariant under the operations of the space group applied to all arguments simultaneously. As we shall see, the Landau coefficients A, B, $C\ldots$ may be found from the integrals which appear in (4.8).

A. Complete set of basis functions

If we choose to proceed using a complete set of basis functions, we choose them as follows: In the $q = 0$ case (Sec. III) we took even and odd bases with V^+ and V^- [cf. (3.4) and (3.5)] for the IR's T_+ and T_-. There is a complete orthogonal set of V^+'s and one of V^-'s. We can choose the u_q functions in (4.2) in such a way that as $q \to 0$ they tend continuously to the functions $V^\pm(r)$. If we use the property (3.5), we see from (4.2) that such a choice of the u_q leads to basis functions $\chi_i^\pm$, which, when $q \to 0$, go over to basis functions for $T_\pm$(3.4), as follows:

$$\begin{aligned} &\chi_1^\pm \to \phi_1^\pm\,, \quad \chi_2^\pm \to \phi_2^\pm\,, \\ &\chi_3^\pm \to \pm e^{-i\pi\mu}\phi_1^\pm\,, \quad \chi_4^\pm \to \pm e^{i\pi\mu}\phi_2^\pm\,. \end{aligned} \tag{4.9}$$

If we use this complete set there will be infinitely many coefficients d_i in the expansion of the charge density (4.4) and the problem is too complex. Let us illustrate the procedure with two sets of basis functions. We suppose that we know the forms of $V^\pm$ which give the lowest free energy. The other orthogonal $V^\pm$ functions of the complete sets belong to "higher bands." We discard the higher band functions and restrict our u_q functions to those that go, as $q \to 0$, to the lowest band $V^\pm$ functions for the $q = 0$ IR's $T_\pm$. With these simplifications we are ready to establish relations between the Landau coefficients A, B, $C, \ldots$ for $q \neq 0$ and $q = 0$.

The next step is to insert the charge-density expansions into the free-energy expansion (4.8). When $q = 0$, we use (3.6) and when $q \neq 0$ we use, instead of one basis as in (4.4), two basis sets:

$$\delta\rho_q \sum_{i=1}^{4} (d_i^+\chi_i^+ + d_i^-\chi_i^-)\,, \tag{4.10}$$

where these $\chi_i^\pm$ are those basis functions which go over, as $q \to 0$, to the lowest band bases for $T_\pm$.
If we insert (4.10) into (4.8) we find a variety of

terms involving the various invariants which may be formed from the $d_i^{\pm}$. Instead of (4.5), valid for one basis set, we now obtain a free energy of the form

$$\begin{aligned}\Delta F_q = {} & A_q^+(d_1^+d_2^+ + d_3^+d_4^+) + A_q^-(d_1^-d_2^- + d_3^-d_4^-) + A_q'(d_1^+d_2^- + d_1^-d_2^+ + d_3^+d_4^- + d_3^-d_4^+) + B_q^+(d_1^+d_2^+ + d_3^+d_4^+)^2 + B_q^-(d_1^-d_2^- + d_3^-d_4^-)^2 \\ & + B_q(d_1^+d_2^- + d_1^-d_2^+ + d_3^+d_4^- + d_3^-d_4^+)^2 + C_q^+(d_1^+d_2^+d_3^+d_4^+) + C_q^-(d_1^-d_2^-d_3^-d_4^-) + D_q(d_1^+d_2^+ + d_3^+d_4^+)(d_1^-d_2^- + d_3^-d_4^-) \\ & + H_q^+(d_1^+d_2^+ + d_3^+d_4^+)(d_1^+d_2^- + d_1^-d_2^+ + d_3^+d_4^- + d_3^-d_4^+) + H_q^-(d_1^-d_2^- + d_3^-d_4^-)(d_1^+d_2^- + d_1^-d_2^+ + d_3^+d_4^- + d_3^-d_4^+) \\ & + P_q(d_1^+d_2^+d_3^-d_4^- + d_1^-d_2^-d_3^+d_4^+) + Q_q(d_1^+d_2^-d_3^+d_4^- + d_1^-d_2^+d_3^-d_4^+) + R_q(d_1^+d_2^-d_3^-d_4^+ + d_1^-d_2^+d_3^+d_4^-) \\ & + E_q^+(d_1^+d_2^+d_3^+d_4^- + d_1^+d_2^+d_3^-d_4^+ + d_1^+d_2^-d_3^+d_4^+ + d_1^-d_2^+d_3^+d_4^+ + E_q^-(d_1^+d_2^-d_3^-d_4^- + d_1^-d_2^+d_3^-d_4^- + d_1^-d_2^-d_3^+d_4^- + d_1^-d_2^-d_3^-d_4^+) ,\end{aligned} \qquad (4.11)$$

where, for example, from (4.8) we find

$$\begin{aligned} A_q^{\pm} &= 2\int\int d^3r_1\, d^3r_2\, F^{(2)}(r_1r_2)\chi_1^{\pm}(r_1)\chi_2^{\pm}(r_2) , \\ A_q' &= 2\int\int d^3r_1\, d^3r_2\, F^{(2)}(r_1r_2)\chi_1^{+}(r_1)\chi_2^{-}(r_2) , \end{aligned} \qquad (4.12)$$

and the other Landau coefficients are found similarly.

As $q \to 0$, according to (4.12) and (4.9) we have

$$\begin{aligned} A_{q\to 0}^{\pm} &= 2\int\int d^3r_1\, d^3r_2\, F^{(2)}(r_1r_2)\phi_1^{\pm}\phi_2^{\pm} = A_{\pm} , \\ A_{q\to 0}' &= 2\int\int d^3r_1\, d^3r_2\, F^{(2)}(r_1r_2)\phi_1^{+}\phi_2^{-} , \end{aligned} \qquad (4.13)$$

where $A_{\pm}$ is the Landau coefficient for $q=0$ appearing in (3.7). Note that, from (3.2), $C_2^*\phi_1^+ = e^{-i\pi\mu}\phi_1^+$, $C_2^*\phi_2^- = -e^{i\pi\mu}\phi_2^-$ so that $\phi_1^+\phi_2^-$ changes sign, while $F^{(2)}$ is of course invariant. Therefore, when $q=0$, A_q' as given by (4.13) vanishes. Similar arguments for other mixed coefficients give the results

$$A_q', H_q^{\pm}, E_q^{\pm} \text{ all} \to 0 \text{ as } q \to 0 . \qquad (4.14)$$

At the same time, we can find the relations between the other Landau coefficients as $q \to 0$ and those of (3.7) for $q=0$. The latter may be found by inserting (3.6) into (4.8). We compare the results with the limit as $q \to 0$ of expressions like (4.12), using (4.9). We find

$$\left.\begin{aligned} & A_q^{\pm} \to A_{\pm} , \quad B_q^{\pm} \to B , \quad C_q^{\pm} \to 2B_{\pm} , \\ & B_q \to D , \quad P_q \to 2D , \quad D_q \to C , \\ & Q_q \to -6D , \quad R_q \to -(C+4D), \end{aligned}\right\} \text{as } q \to 0 . \qquad (4.15)$$

The analysis of the free energy (4.11) is prohibitively complicated. However, it is clear from (4.14) that the mixing of two basis sets is small for small q. The mixed invariants with coefficients B_q, D_q, P_q, Q_q, R_q do not modify this conclusion because, unlike the terms with A_q', $H_q^{\pm}$, $E_q^{\pm}$, in the minimization of ΔF_q for finite d_i^+, they do not necessarily produce a finite d_i^-. Then, if we neglect the mixing and use the continuity properties (4.15), we are led to consider, for small q, a free energy which is the sum of two terms of the form (4.5): one with superscript + on the A_q, B_q, C_q and d_i, and one with superscript −. Suppose that at 54 K, A_+ vanished with $A_- > 0$. Then we need to minimize only the terms with superscript "+."

We can now decide between alternatives (a) and (b) for the minimum free energy [cf. (4.6), (4.7)]. We can find the limit of ΔF_q when $q \to 0$ by using the relations (4.15). We find case (a) has lower energy (by a factor $\frac{3}{2}$) when $q=0$ and hence also for small q. Thus the transition to finite q involves phase slippage along the chains.

In our argument, supposing that T_+ is activated at 54 K, we have finally kept only the band which goes over to the actual distortion as $q \to 0$ (lowest band for T_+). The basis for this assumption is that if only the lowest band counts for $q=0$, the mixing must be small for small q and should not change the qualitative results. We have seen explicitly how the mixing of the higher band represented by the d_i^- vanishes in the $q \to 0$ limit.

B. Single set of basis functions

We now discuss the second approach for finding the charge distributions in the transition to $q \to 0$. We use the single basis set (4.2) and choose it to minimize the free energy. This is carried out as follows: We insert the charge density (4.4) into the free-energy expansion (4.8) in order to find the Landau coefficients A_q, B_q, C_q of (4.5) in terms of the basis functions (4.2). We then examine the limit $q \to 0$ and compare to the case $q=0$. We expect that the free energies for $q \to 0$ and $q=0$ do not necessarily agree since the latter case (commensurable in the a direction) admits umklapp terms in the free energy, i.e., terms involving invariant combinations of order parameters in which the wave vectors add up to a reciprocal lattice vector.[13] For example, when $q=0$, in the star of k[cf.(4.1)], $k_1(k_2)$ and $k_3(k_4)$ become equivalent (differ by a reciprocal-lattice vector) and new invariants

$$U(d_1d_4e^{i\pi\mu}+d_2d_3e^{-i\pi\mu})+V(d_1d_2+d_3d_4)(d_1d_4e^{i\pi\mu}+d_2d_3e^{-i\pi\mu})+W[(d_1d_4e^{i\pi\mu})^2+(d_2d_3e^{-i\pi\mu})^2] \tag{4.16}$$

need to be added to the free energy. Thus, we first look at the possibilities for having a continuous free energy as q leaves zero. We shall find that for certain properties of the Landau coefficients there is the possibility of a continuous transition, that these properties are a consequence of a particular choice of basis (4.2), and that any other choice leads to a higher free energy.

The first step is to calculate the free energy for a particular choice of basis functions. Supposing again that T_+ is activated for $q=0$ at 54 K, we choose a basis χ_i for $q\neq 0$ which goes over, as $q\to 0$, to the T_+ basis $\phi^+_{1,2}$ as in (4.9). The free-energy expression valid for both $q\neq 0$ and $q=0$ is the sum of (4.5) and (4.16), the latter contributing for $q=0$ only.

If we let $q\to 0$ in (4.5) and perform the transformation

$$c_1^\pm=d_1\pm e^{-i\pi\mu}d_3\,,\quad c_2^\pm=d_2\pm e^{i\pi\mu}d_4\,, \tag{4.17}$$

then from the sum of (4.5) and (4.16) we recover the free energy of (3.7) with the following identification of the Landau coefficients:

$$\begin{aligned}&A_q\pm U\to 2A_\pm\,,\quad 4B_q+C_q\pm 4V+2W\to 16B_\pm\,,\\ &B_q-W\to 2(C+2D)\,,\quad C_q+2W\to 16D\,.\end{aligned} \tag{4.18}$$

The coefficients in (4.5) and (4.16) are given by expressions like (4.12) in terms of our single basis χ_i:

$$\begin{aligned}&A_q=2\int\int F^{(2)}\chi_1\chi_2\,,\quad U=2\int\int F^{(2)}\chi_1\chi_4e^{-i\pi\mu}\,,\\ &C_q+2B_q=24\int\int\int\int F^{(4)}\chi_1\chi_2\chi_3\chi_4\,,\\ &B_q=6\int\int\int\int F^{(4)}\chi_1\chi_1\chi_2\chi_2\,,\\ &V=12\int\int\int\int F^{(4)}\chi_1\chi_1\chi_2\chi_4e^{-i\pi\mu}\,,\\ &W=6\int\int\int\int F^{(4)}\chi_1\chi_1\chi_4\chi_4e^{-2\pi i\mu}\,.\end{aligned} \tag{4.19}$$

We determine the $q\to 0$ values of these coefficients by replacing the χ_i by $\phi^+_{1,2}$ as in (4.9). We find

$$A_{q=0}=U\,,\quad C_{q=0}+2B_{q=0}=4B_{q=0}=2V=4W\,. \tag{4.20}$$

We put these relations into (4.17) and find

$$\begin{aligned}&A_+=A_{q=0}\,,\quad A_-=0\,,\\ &B_+=B_{q=0}\,,\quad B_-=0\,,\\ &C=0\,,\quad D=0\,.\end{aligned} \tag{4.21}$$

Thus only the terms corresponding to the basis for T_+ remain and A_q and B_q go continuously over to A_+ and B_+.

Having established the form of the free energy and its $q\to 0$ behavior, we need to minimize it for $q\neq 0$. Thus, we are going to minimize (4.5). We can use the results (4.6) and (4.7). For the present choice of basis,[24] $C_{q=0}>0$ and case (a) has lower free energy for small q and since A_q and B_q go continuously to A_+ and B_+, the free energy (4.7a) of this solution goes continuously to the $q=0$ free energy of (3.8). Thus we have shown that there is a possible choice of basis for which q shifts continuously from $q=0$ and that the corresponding charge density corresponds to phase sliding with respect to the $q=0$ case.

We now show that any other choice of basis yields higher free energy for $q\neq 0$. We consider first the case that $C_q<0$ for small q. Then the solution case (b) of (4.6, 4.7) obtains. If we carry this solution continuously to $q=0$ and use it in the free energy, then the umklapp terms (4.16) appear and make a negative contribution to the free energy which means that the free energy $F_{q=0}$ is always less than the free energy $F_{q\to 0}$ as given by (4.7b). Another way of seeing this is by an examination of how the basis functions enter the Landau coefficients A_q, B_q, C_q of (4.5) and U, V, W of (4.16). One finds that there is no choice of basis which allows $F_{q\to 0}$ of case (b) to go over continuously to $F_{q=0}$ of the T_+ or T_- transition.

The situation is different when $C_q>0$. Now case (a) obtains for small q and $d_3=d_4=0$. It may pay, however, to introduce some d_3, d_4 at $q=0$ if one can lower the energy via umklapp by doing so. If we set $d_1=d_2^*=de^{i\theta}$, then the linear umklapp terms in d_3, d_4 will vanish if $U=-Vd^2$ [cf.(4.16)]. The quadratic terms of (4.5) and (4.16) are of the form

$$\begin{aligned}&[A_q+(B_q+C_q)d^2]d_3d_4\\ &\qquad+Wd^2\{d_4^2\exp[2i(\theta-\pi\mu)]+d_3^2\exp[-2i(\theta-\pi\mu)]\}\,.\end{aligned} \tag{4.22}$$

If we can have these always positive and $U=-Vd^2$ with the solution $d^2=-A_q/2B_q$ of (4.6), then at $q=0$ the lowest energy still has $d_3=d_4=0$. On the other hand, if (4.22) gives a negative contribution, or if $U\neq -Vd^2$, then finite values of d_3, d_4 can lower the free energy at $q=0$ compared to $q\to 0$. Thus, for $F_{q=0}$ not to be lower than $F_{q\to 0}$ we require, as $q\to 0$

$$\begin{aligned}&C_q>0\,,\quad A_q<0\,,\quad U=VA_q/2B_q\,.\\ &2|W|\leq C_q\,,\quad 2B_qW\geq V^2-B_qC_q\,.\end{aligned} \tag{4.23}$$

We have added a fifth condition; it insures that the minimum of $F_{q=0}$ is an absolute minimum. If (4.17) obtains, then the same solution (4.6a) minimizes both $F_{q\to 0}$ and $F_{q=0}$ and the charge density is continuous in q. These conditions are satisfied by our particular choice of basis, as can be seen from (4.20). In this case there is no commensurability energy.

Let us summarize our conclusion. We suppose T_+ is activated at 54 K. According to (3.9) and (3.3), the charge density has the form

$$\delta\rho_{q=0}=(-A_+/2B_+)^{1/2}(e^{i\theta}\phi_1^+ + e^{-i\theta}\phi_2^+)\,, \qquad (4.24)$$

where A_+, B_+ are the Landau coefficients of Sec. III and depend on the $\phi_{1,2}^+$. In the case $C_{q\to 0}>0$ we know that for small q, it remains true and the solution (4.6a) obtains. The charge density is

$$\delta\rho_{q\to 0}=(-A_q/2B_q)^{1/2}(e^{i\theta}\chi_1 + e^{-i\theta}\chi_2)\,. \qquad (4.25)$$

If now we pick for our basis set χ, the one satisfying (4.9), then since (4.23) is satisfied the umklapp does not contribute to the free energy which is therefore continuous as q leaves zero. Furthermore, the Landau coefficients A_q, B_q go over, as $q\to 0$, to A_+, B_+, just as in (4.15), from which it follows that the charge density is also continuous since (4.25) goes to (4.24) as $q\to 0$. Finally we note that since the basis $\phi_{1,2}^+$ has been chosen to give an absolute minimum $F_{q=0}$, we have shown that the choice (4.9) leads to an F_q which tends to a minimum as $q\to 0$. Any other choice of basis would yield a higher $F_{q\to 0}$. In any case, if the conditions (4.23) are violated, then $F_{q\to 0}>F_{q=0}$.

We have discussed the continuity of charge density and free energy near $q=0$ by two methods. Let us now elucidate the possible behavior for the transition away from $q=0$. We shall plot the free energy as a function of q. Note that the Landau coefficients are even in q,[25] since the wave vectors $k_1=(\frac{1}{2}-q)a^* + \mu b^*$ and $k'=(\frac{1}{2}+q)a^* + \mu b^*$ belong to the same star and hence the same IR. This is because k' is equivalent to k_3 (see 4.1); it differs from it by the reciprocal-lattice vector a^*. Therefore A_q and F_q are even in q and since the CDW at 54 K has $q=0$ it follows that both A_q and F_q have a minimum at $q=0$. From continuity arguments it follows that below 54 K the minimum of F is still at $q=0$ and the relative phase of the CDW's on successive TTF or TCNQ sheets is unchanged. It may happen, however, that at a certain temperature below 54 K, this minimum starts to shift symmetrically from $q=0$. Another possibility is that a new minimum develops at a finite q value. We show the possibilities in Fig. 4. In the first case [Fig. 4(b)], the wave vector of the CDW begins at T_2 to vary continuously away from $q=0$, while in the second case [Fig. 4(c)], the new structure appears abruptly at T_2 with a discontinuous change in the wave vector from zero to a finite value. Still another possibility [Fig. 4(d)] occurs if a CDW corresponding to [4.6(b)] is activated; it has a higher free energy for small q but may have a lower one at some temperature for a larger q. In the case shown in Fig. 4(b), the transition is continuous in q and second order, while in the other two cases there is an abrupt change in wave vector and a first-order transition. We conjecture that the experimental results[3,4] at 49 K reflect the behavior shown in Fig. 4(b).

We have pointed out earlier[15] that once the wave vector moves away from $q=0$, there is no symmetry reason to suppose that CDW wave vector has no component along c^*. In the absence of experimental evidence of a c^*-component of $\vec{q}$, we have not included that possibility. However, it would make no substantive changes anywhere in our discussion. From symmetry considerations, Mukamel[26] has reached the conclusion that a c^* component should be present and Horowitz and Mukamel[26] have estimated the ratio $q_c/q_a \approx 0.1$.

We have shown in the above analysis that in spite of the fact that the transition from $q=0$ is from a commensurate to a noncommensurate (in the a direction) state, it does not follow that a finite commensurability energy is involved. To analyze this question in the general case one can follow the procedure we have used, namely, to compare the commensurate to the nearby noncommensurate state via the expansion (4.8) and the subsequent analysis of the Landau coefficients. In this respect, the argument of Ref. 13 is incomplete. We will find a finite commensurability energy for the 38-K transition in Sec. V.

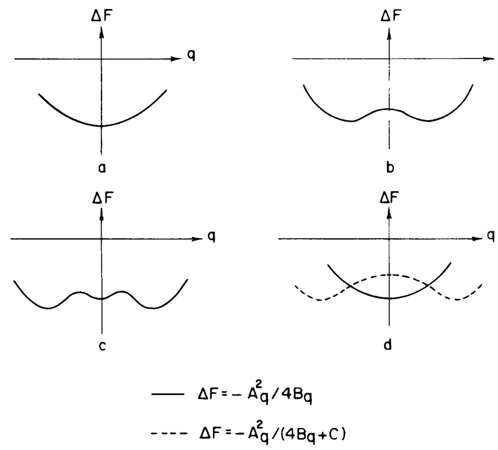

FIG. 4. Plots of free energy illustrating possible phase transitions associated with change of wave vector q.

V. PHASE TRANSITION AT 38 K

When $q=\frac{1}{4}$ the CDW distortion is again commensurate in the a direction, with a lattice spacing four times the original. It can be expected then that a commensurability energy may be involved in the transition from $q\neq\frac{1}{4}$ to $q=\frac{1}{4}$ at 38 K. To see how this enters we follow the same line of reasoning we used in Sec. IV. The star of k consists now of the four vectors

$$\begin{aligned} &k_1=\tfrac{1}{4}a+\mu b^*\,, \quad k_2=-\tfrac{1}{4}a-\mu b^*\,,\\ &k_3=-\tfrac{1}{4}a+\mu b^*, \quad k_4=\tfrac{1}{4}a-\mu b^*\,, \end{aligned} \tag{5.1}$$

and there is again a four-dimensional IR with basis

$$\begin{aligned} &\psi_1=v(r)e^{i\vec{k}_1\cdot\vec{r}}\,, \quad \psi_2=v(-r)e^{i\vec{k}_2\cdot\vec{r}}\,,\\ &\psi_3=v(C_2^{*-1}r)e^{i\vec{k}_3\cdot\vec{r}}e^{-i\pi\mu}\,,\\ &\psi_4=v(-C_2^{*-1}r)e^{i\vec{k}_4\cdot\vec{r}}e^{i\pi\mu}\,. \end{aligned} \tag{5.2}$$

The matrices of the IR are the same as (4.3). We may expand the charge density in terms of these functions with coefficients f_i. Treating the f_i as basis functions in the usual way, we find the following second- and fourth-order invariants

$$\begin{aligned} &(f_1f_2+f_3f_4), \quad (f_1f_2+f_3f_4)^2, \quad (f_1f_2f_3f_4)\,,\\ &(e^{-i\mu}f_1^2f_4^2+e^{i\mu}f_2^2f_3^2)\,. \end{aligned} \tag{5.3}$$

The last, umklapp, one is new, it only appears for $q=\frac{1}{4}$ and arises, as $q\to\frac{1}{4}$, continuously from the following mixed fourth-order invariants for $q\neq\frac{1}{4}$:

$$\begin{aligned} &e^{-2\pi i\mu}d_1d_4d_1'd_4'+e^{2\pi i\mu}d_2d_3d_2'd_3'\,,\\ &e^{-2\pi i\mu}[(d_1d_4')^2+(d_1'd_4)^2]+e^{2\pi i\mu}[(d_2d_3')^2+(d_2'd_3)^2]\,, \end{aligned} \tag{5.4}$$

where d_i, d_i' are the basis functions for IR's with $q=\frac{1}{4}+p$, $q'=\frac{1}{4}-p$, respectively. In a free-energy expansion, the sum of the Landau coefficients of the invariants in (5.4) would go continuously, as $p\to 0$, to the coefficient of the new invariant for $q=\frac{1}{4}$ in (5.3). We have not included (5.4) in our discussion of general q since it mixes two stars with different wave vectors. In the absence of any experimental evidence of a structure having two different wave vectors one can neglect the mixed terms.[27]

We now write the free energy using (5.3):

$$\begin{aligned} F=F_0&+A_{1/4}(f_1f_2+f_3f_4)+B_{1/4}(f_1f_2+f_3f_4)^2\\ &+C_{1/4}(f_1f_2f_3f_4)+G(e^{-2\pi i\mu}f_1^2f_4^2+e^{2\pi i\mu}f_2^2f_3^2)\,. \end{aligned} \tag{5.5}$$

Minimizing the free energy again leads to two types of solutions (i) and (ii):

(i) $f_1=f_2^*=fe^{-i\theta}\,,\ f_3=f_4=0$

or

$$f_1=f_2=0\,,\ f_3=f_4^*=fe^{i\theta}\,,\qquad f^2=-A_{1/4}/2B_{1/4}\,, \tag{5.6a}$$

(ii) $f_1=f_2^*=fe^{i\theta}\,,\ f_3=f_4^*=fe^{i\theta'}$

$$f^2=-A_{1/4}/(4B_{1/4}+C_{1/4}-2|G|)\,,\qquad \cos 2(\theta-\theta'+\pi\mu)=\operatorname{sgn}G\,. \tag{5.6b}$$

In the two cases, the minimum value of the free energy is

(i) $F_{1/4}=F_0-A_{1/4}^2/4B_{1/4}\,,$ (5.7a)

(ii) $F_{1/4}=F_0-A_{1/4}^2/(4B_{1/4}+C_{1/4}-2|G|)\,.$ (5.7b)

Case (i) corresponds to a phase modulation as in Sec. IV (cf. Fig. 3) and is just the continuation of the solution found there to $q=\frac{1}{4}$. It is continuous in q, there is no transition as q shifts through the value $q=\frac{1}{4}$. In case (ii), we have amplitude modulation and, due to the umklapp term G, a discontinuous transition from general q to $q=\frac{1}{4}$. Whether or not the transition is continuous at $q=\frac{1}{4}$ depends on the value of G.

Our description of the 38-K transition is as follows: Below 49 K, we assert that a CDW of the form (4.6a) exists since experimentally, the 49-K transition is continuous. As the temperature is lowered the q shifts toward $\frac{1}{4}$ and the free energy varies with q according to (4.7a). At 38 K, the free energy (5.7b) becomes lower and a discontinuous transition takes place with an abrupt change in q. This is illustrated in Fig. 5. Our description is similar to that of Bjeliš and Barišić.[14]

Finally, we remark that in the solutions of case (i), the umklapp terms play no role. This would be true also at other commensurability points (e.g.,

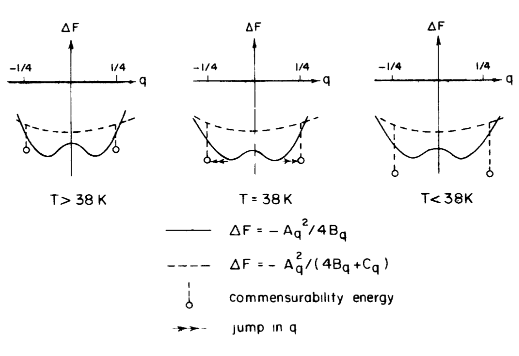

FIG. 5. Plots of free energy illustrating phase lock-in at 38 K.

$q=\frac{1}{8}$, $\frac{1}{6}$, etc.) and the CDW form and the free energy would be continuous as is observed. If the solution of (4.6b) took over at any intermediate temperature, then as q varied, the commensurability energies present in case (ii) would cause discontinuous transitions between commensurate states. Thus the experiment shows that case (i) is appropriate from $q=0$ at 49 K to the sudden jump to $q=\frac{1}{4}$ at 38 K.

VI. DISCUSSION

We have described the possible successive phase transitions in TTF-TCNQ in terms of the Landau theory of second-order phase transitions. The theory can be applied not only to the first transition which is of second order, but also to the other transitions where the CDW amplitude is not small. In the latter cases, it is probably not sufficient to terminate the free-energy expansion at the fourth-order invariants. However, due to the low symmetry, the higher-order invariants can all be obtained from products of the low-order ones. Therefore higher-order terms will have quantitative effects, but will not change the qualitative features which we have elucidated since these are based on symmetry alone.

We now summarize our results. The 54-K transition is a continuous one with simultaneous ordering of both TTF and TCNQ chains. Two possibilities for the structure are allowed by the symmetry. Either the CDW's on the inequivalent TTF chains have similar amplitude and are essentially in phase while the CDW's on the TCNQ chains are essentially out of phase, or the relative phase relations are reversed [cf. (3.10) and Fig. 2]. It may be seen in a classical calculation that the coupling causing the simultaneous ordering of both TTF and TCNQ is a consequence of the tilting of the molecules out of the *ac* plane and of the mono-clinic structure. In quantitative terms, the coupling may be small and the CDW ordering may be predominantly on the TCNQ chains.

In our description, the second transition, near 49 K, can be either a continuous shift in q away from $q=0$ or a discontinuous jump to a finite value of q. There is no way to tell which occurs without a quantitative treatment of the Landau coefficients. The various possibilities are shown in Fig. 4. The free energy is continuous in and symmetric in q and has a local minimum at and below 54 K at $q=0$. This minimum can become a local maximum in the case of a continuous change in q [Fig. 4(b)] from $q=0$ and the experiments indicate that this possibility is what occurs. It then follows that the CDW for finite q has the form of case (a) in Sec. IV and the change in q represents phase sliding as shown in Fig. 3(a).

Our description differs from previous theories[9,10] both in the mathematical formulation and the physical basis of the onset of phase sliding. In contrast to earlier work, our analysis shows that although the first transition, at 54 K, may be primarily on TCNQ, the small amplitude CDW which *must be present* on TTF already removes the $T=0$ divergence of the TTF susceptibility, which therefore cannot drive the 49-K transition. However, if the TCNQ-TTF coupling is small, then the CDW susceptibility on TTF may remain large enough for it to be favorable for the system to develop an additional CDW, predominantly on TTF, whose phase structure is favorable for TTF and unfavorable for TCNQ. The two CDW's do not couple at $q=0$, but coupling between them which can lower the free energy will develop if the phase slides to finite q. Thus, we conclude that if the TCNQ-TTF coupling is not small enough, then the TTF susceptibility will not be large enough for this mechanism to develop. This may be the reason why other systems having the same structure (e.g., TSeF-TCNQ) do not behave in the same way.

The transition at 38 K interrupts the phase sliding due to the commensurability energy associated with the umklapp invariant which enters for $q=\frac{1}{4}$. The physical basis of this transition is the same as that of Bjelis and Barišić,[14] but the formulation is somewhat more general since we do not restrict the couplings which enter the calculation.

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