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A LANDAU THEORY FOR THE DISPLACIVE PHASE TRANSITIONS IN TTF-TCNQ (*)

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Résumé. — Les modes de translation et de libration des molécules de TTF et de TCNQ ont été examinés dans le cadre de la théorie de Landau classique. Les divers paramètres sont estimés à partir de la structure cristallographique. Dans l'hypothèse de forces coulombiennes entre atomes de soufre du TTF et atomes d'azote du TCNQ, on établit une suite d'interactions qui sont à l'origine d'une suite de transitions displacives en excellent accord avec les résultats expérimentaux. On attribue le changement de la période de la distorsion périodique transverse de $2a$ à $4a$ entre 48 K et 38 K au positionnement incliné des molécules de TCNQ et de TTF. Les réflexions des rayons X de vecteur d'onde $4k_F$ sont attribuées à des librations possédant un plan de glissement comme élément de symétrie, supprimant ainsi les réflexions au vecteur d'onde $2k_F$. La symétrie empêche ces librations d'être couplées (au premier ordre) à la distorsion de Peierls sur la même chaîne, mais elles se couplent fortement à la distorsion de Peierls sur les chaînes voisines.

Abstract. — Translational and librational modes of TTF and TCNQ molecules are treated within the framework of classical Landau theory. The various parameters are estimated from the crystalline structure. The Coulomb forces between TTF sulphurs and TCNQ nitrogens are assumed to be dominant, and this approximation establishes a hierarchy of interactions, which in turn gives rise to a cascade of displacive transitions, in excellent agreement with experiment. The change in transverse period of the periodic lattice distortion from $2a$ to $4a$ between 48 K and 38 K is accounted for, and found to be due to the staggered placement of the nitrogens with respect to the sulphurs. The X-ray reflections with wavevector $4k_F$ are attributed to librations possessing a glide-plane symmetry element, which suppresses the $2k_F$ reflections. Symmetry prohibits these reflections from being coupled (in first order) to the Peierls transition on the *same* chain, however they couple strongly to the Peierls distortion on the neighbouring chains.

1. Introduction. — The organic charge-transfer metal TTF-TCNQ (tetra-thio-fulvalene tetra-cyanoquino-dimethanide) consists of molecules which possess internal structure. Therefore the Peierls transition in this quasi-one-dimensional system is more complicated than the simple type of longitudinal distortion originally considered by Peierls [1] and Frohlich [2]. This point was emphasized quite some time ago [3]. Thus, the richness of the crystallographic transitions discovered at 54 K, 48 K, and 38 K is not surprising. At 54 K, anomalies in the resistivity [4, 5] specific heat [6], and other electronic properties occur, and a periodic lattice distortion (PLD) starts to build up [7], with a longitudinal period of $A = 3.6b$ and a transverse period of $2a$. At 48 K, the transverse period

of the PLD starts to increase [8], and the susceptibility of the TTF chains seems to display an anomaly [9]. At 38 K, there is an anomaly in the resistivity [10, 11], and the transverse period of the PLD jumps [7] to $4a$. The transitions appear to be displacive ones, associated with motions of the molecules.

The motions of the molecules can be classified into : Translations, which can : be longitudinal or transverse ; internal distortions, such as changes in the length or angle of the bonds, and librations (rigid rotations of the molecules).

The internal motions can contribute significantly to the energetics of the process [12, 13] but because of the large force constants involved, the displacements of the atoms are probably small and hard to see by X-ray or neutron diffraction. Therefore, we shall not consider them here. Thus, we shall consider six types of modes (table I). Translations parallel to the b -axis (longitudinal) and parallel to the molecular ζ and ξ axes (transverse), and rotation [14, 15] of the

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TABLE I
The various rigid modes of TTF, TCNQ molecules

Property	Mode	Translations			Librations		
		longitudinal b	transverse ξ ζ		rotation around axis η ζ ξ		
1 Notation		ρ	E		χ		
2 Space group of distorted chain		P2/m	P2/b	P2/m	P2/b	P2/b	P2/m
3 Couples with Peierls distortion on same chain ?		Yes	No	No	No	No	No
4 $2 k_F$ reflections allowed ? (for $h = 0$)		Yes	No	Yes	No	No	Yes
5 $4 k_F$ reflections allowed ? (for $h = 0, l = 0$)		No	No	No	Yes	No	Yes
6 Spatially easy ? (small restoring force)		No	Yes	Yes	Yes	moderately	No
7 N-S distance affected ?		Little	Yes	Yes	Yes	Little	Little
8 Couples with Peierls distortion on neighbour chain, via N-S bonds, for $1/4$ filled band ($A = 4 b$) ?		No	No	Yes	Yes	No	No

The η -libration is considered in detail in this work because of the *No* of (4) and *Yes* of (8) (in addition to *Yes* of (5, 6, 7)). The longitudinal phonon is considered because of the *Yes* of (3).

molecule around the molecular ξ , η , and ζ axes. (The ξ axis is along the crystallographic a -axis, while the η and ζ axes are somewhat tilted from the b and c axis ; see figure 1.)

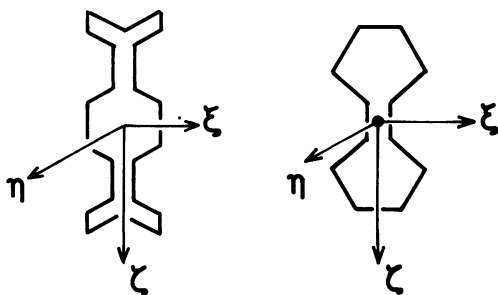


FIG. 1. — Definition of the molecular axes.

Formally, the crystallographic transformations can be described by Landau theory. However, it is clear that a very large number of order parameters is needed in such a theory (24 degrees of freedom for the unit cell of TTF-TCNQ, which contains 4 molecules), and since the various order parameters are coupled non-linearly, the number of adjustable parameters needed in a strictly formal Landau theory is clearly prohibitive. Thus we need some simplifying assumptions. Fortunately, the structure of TTF-TCNQ is known from the excellent work of Kistenmacher *et al.* [16] and the molecular electronic wavefunctions are also known reasonably well [17, 18, 19, 20]. The negative charge on the TCNQ⁻ ions resides mainly on the CN groups, while the positive charge of the

TTF⁺ ions resides mainly on the sulphurs and edge-carbons. The TCNQ nitrogens are particularly close to the TTF sulphurs [16] (3.2 Å apart, which is smaller than the sum of the Van-der-Waals radii of 3.35 Å), and therefore the Coulomb attraction between these charges should be a dominant factor in the interaction ; the high polarizability of the sulphurs also contributes to their attraction to the nitrogens. Moreover, rigid motions of the molecules which are sterically easy, such as a libration of the TCNQ molecule around an axis perpendicular to its plane, are extremely effective in changing the N-S distances. Experiment shows [7] that the direction of the N-S bonds, namely the a -direction, is where the interesting changes of the period of the lattice distortion take place.

Therefore, the simplifying assumption we make in this work is the following : *The N-S bonds play the major role in the lattice distortions, due to the small separation (3.1-3.2 Å), strong Coulomb interaction, and large polarizability of these atoms.* It will be shown that this reasonable assumption is sufficient to provide a rather detailed microscopic theory of the various complicated lattice transformations in this highly interesting system.

An immediate consequence of this simplifying assumption is the following : The distance between the N and S atoms is given by [16] : 2.94 Å in the a -direction, 0.87 Å in the b -direction, and 1.935 Å in the c -direction. Thus, a displacement in the b -direction can at most reduce the distance between the atoms from 3.2 Å to 3.1 Å, which is a negligible effect.

Thus, we shall ignore the modes which mainly change the b -coordinates of the atoms, namely the librations around the molecular ξ and ζ axis. (The longitudinal mode is important because it is coupled to the Peierls transition).

Two of the three modes left, namely the translation along the ξ -axis and the libration around the η axis, possess a glide-plane symmetry element consisting of a translation by $\Lambda/2$ where Λ is the period of the CDW, or lattice distortion wave, $\Lambda = 2\pi/2k_F$, followed by a reflection in the bc plane. The translation along the c -axis does not possess this symmetry element, but the bc plane remains a symmetry plane for simple reflections for this mode. *The glide-plane symmetry element has the property that reflections at*

$$\mathbf{q} = (q_a, q_b, q_c) = (0, 2k_F, q_c)$$

are strictly forbidden [21].

For non-vanishing q_a , these reflections do not vanish entirely, but by continuity, they are expected to be weak. On the other hand, reflections with $\mathbf{q} = (0, 4k_F, q_c)$ are allowed. Thus, the strong reflections at $4k_F$ observed experimentally [22] are accounted for. Probably, the actual displacements contain contributions from several modes. Such modes have been observed independently in TSeF-TCNQ [23].

The importance of the strong $4k_F$ reflections for establishing the nature of the physical processes occurring in organic metals cannot be overemphasized. One way to account for them is by postulating an extremely strong electron-electron Coulomb repulsion U [24]. Here we propose an alternative explanation, more in line with classical crystallography, attributing them to distortions with glide-plane symmetry. A careful study of the intensities of the $2k_F$ and $4k_F$ reflections in various regions of the reciprocal space in TTF-TCNQ, as well as in similar systems, may be required to establish (or refute) the present theory.

The lack of a first-order interaction between librations and the CDW due to the Peierls distortion, is intimately related to the absence of $(0, 2k_F, q_c)$ reflections due to these librations. This is because the selection rule forbidding $2k_F$ reflections applies to all waves, the conduction electrons as well as the X-rays and neutrons [21].

A glide plane causes the gap at the Brillouin Zone of the PLD at $2k_F$ associated with the libration of this wavevector to vanish. This is a particular case of a general argument given by Jones [21]. Note that librations which do *not* have this selection rule (here, librations around the ξ -axis), do have a first-order coupling with the CDW on the same chain. In this work however, we restrict ourselves to librations around the η -axis.

We may note in passing that in another metallic chain system, namely the A-15's, the individual chains also possess a glide-plane symmetry element [25]. The presence of this element gives rise to a potential instability in which this symmetry is broken as the

temperature is lowered, and a weak first-order transition takes place; this may account for the martensitic transformation observed in V_3Si , Nb_3Sn [26, 27]. The Landau theory for this special instability has been given in detail recently [28]. Note that this is only one of several possibilities [29], but it indicates that perhaps in TTF-TCNQ too, the glide-plane symmetry may give rise to a potential instability that may account for the transition observed at 48 K [8], or possibly for the weak first-order transition observed at 38 K [7, 10, 11].

In section 2, we shall show that the staggered placement of the molecules, associated with the nearly $\frac{1}{4}$ filled band, gives rise to special symmetry properties which are responsible for the change in period between $2a$ and $4a$ observed experimentally [7].

In section 3, we shall consider the interaction between a libration around the η -axis of the TCNQ chain (say) and the Peierls distortion on a neighbouring TTF chain. This coupling gives rise to strong librations with wavevector $2k_F$, which give rise to X-ray reflections with wavevector $4k_F$.

In section 4, we shall consider the interaction between two librations around the η -axis, on TCNQ and TTF chains. This coupling plays an important role in inducing the transitions at 48 K and 38 K.

In section 5, we shall show how these interactions give rise to a cascade of displacive transitions, which account for the transitions observed at 54 K, 48 K, 38 K.

2. The change in transverse period from $2a$ to $4a$.

— Comes [7] found that the transverse period of the lattice distortion in TTF-TCNQ changes from $2a$ to $4a$ as the temperature is lowered from 54 K to 38 K. In order to account for this change, let us first consider Coulomb interactions between the chains [30, 31]. Formally [32] such behaviour can be attributed to a term V_{QQ} , describing an interaction between TCNQ chains. The problem is that due to the large distance (12.3 \AA), the short wavelength of the lattice distortion in the b -direction ($\lambda/2 = 7 \text{ \AA}$), and the intervening highly polarizable TTF chain which screens the Coulomb interaction, this interaction should be rather weak; much weaker than in the c -direction, where the distance between TCNQ chains is 9.2 \AA and there are no intervening TTF chains.

Thus, it may be more likely that the coupling between chains proceeds via polarization of the TTF molecules, since according to Heeger and Garito [5] and Jérôme [33] this polarization is strong and vital in reducing the intra-molecular Coulomb interaction U , and the TCNQ nitrogen to TTF sulphur distance is 3.2 \AA , which is rather small (the sum of the Van der Waals radii is 3.35 \AA). Therefore let us assume that a CDW associated with a longitudinal PLD on the TCNQ chain polarizes the TTF chain, which in turn interacts with the next TCNQ chain. We consider two types of polarization: intra-molecular charge transfer, and inter-molecular charge transfer (within a chain).

2.1 THE INTRA-MOLECULAR CHARGE TRANSFER MECHANISM. — Let us consider first, for simplicity, a hypothetical case in which the planes of the TCNQ and TTF molecules are parallel, as shown in figure 2. Let the CDW make the left TCNQ molecule more positive than average. Then the two sulphurs on the Left of the TTF molecule will be polarized more negatively. Remembering that in the present mechanism the total charge on the TTF molecule does not change, the two Right sulphurs will become more positive, inducing a Negative charge in the TCNQ molecule to the right (Fig. 2). Thus we have an effective (rather than direct [32]) V_{QQ} term via the TTF which is negative, and we can account for the observed $2a$ period. The magnitude of this term is given, for unity charge e , by

$$V_{QQ} \simeq (e^2/r_{NS})^2/E_{\text{excitation}}(\text{TTF}) \quad (1)$$

where $E_{\text{excitation}}(\text{TTF})$ is the excitation energy of TTF to a state of molecular symmetry b_{3g} (antisymmetric between right and left).

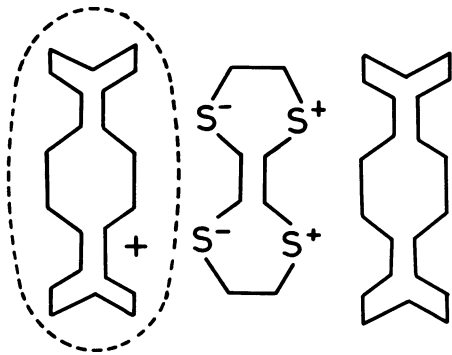


FIG. 2. — Interaction between TCNQ chains by intra-molecular polarization of intermediate TTF molecules.

The interaction energy through this V_{QQ} is of order $(\Delta/E_F)^2 V_{QQ}$, vs. an energy Δ for the PLD (Δ is the gap); thus the ratio of the two is $(\Delta/E_F) (V_{QQ}/E_F)$, and for $\Delta \simeq 450$ K (from the conductivity activation energy [11], or some infra-red measurements [34]), $E_F \simeq 2000$ K $\simeq 1/4$ eV (from the plasma frequency [5], or the thermopower [35]), $V_{QQ} \simeq 2-3$ eV (assuming a molecular excitation energy of 2 eV, from molecular orbital calculations [17, 18, 19] or photoemission experiments [18]), this ratio is of order unity and the effect could be strong.

In TTF-TCNQ, the planes of the TCNQ and TTF molecules are tilted oppositely with respect to the ac plane ($+24^\circ$ for TTF, -34° for TCNQ) [16]. Therefore, the main interaction of a TCNQ molecule at (u, v, w) is with TTF molecules at $(u + \frac{1}{2}, v \pm 1, w)$ which in turn interact with TCNQ molecules at $(u + 1, v \pm 2, w)$ and $(u + 1, v, w)$. Note that there are two TTF bridges to the neighbour at $(u + 1, v, w)$ and only one to each neighbour at $(u + 1, v + 2, w)$ and $(u + 1, v - 2, w)$. See figure 3.

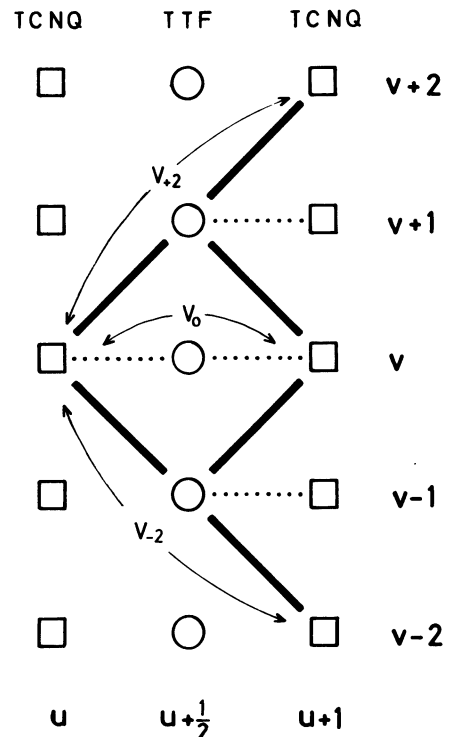


FIG. 3. — Elements of the effective interaction between neighbouring TCNQ chains in the a -direction, mediated by polarization of the intermediate TTF chain. Note that for TCNQ molecules at the same height, there are two TCNQ-TTF-TCNQ bridges, while for TCNQ molecules displaced by $2b$, there is only one such bridge. This gives rise to a very important symmetry property for a quarter-filled band.

Thus, we have the following model :

Let $\rho_Q(u, v)$ be the amplitude of the CDW on molecule (u, v, w) (ρ_Q is assumed independent of w). The CDW is proportional to the strain, so it is shifted by 90° ($A/4$) from the molecular displacement due to the longitudinal PLD on that chain. Then the CDW is given by

$$\rho_Q(q_a, q_b) = \sum_{u,v} \exp(iq_a ua) \exp(iq_b vb) \rho_Q(u, v)$$

and the energy is given by

$$E(q_a, q_b) = [V_0 \cos aq_a + V_{+1} \cos (bq_b + aq_a) + V_{-1} \cos (bq_b - aq_a) + V_{+2} \cos (2bq_b + aq_a) + V_{-2} \cos (2bq_b - aq_a)] \cdot [\rho_Q(q_a, q_b)]^2. \quad (2)$$

Here, V_i is the effective Coulomb interaction (mediated by the TTF's) between TCNQ molecules at (u, v, w) and $(u + 1, v + i, w)$.

For TTF-TCNQ, $q_b \simeq 0.55 \pi/b$. Near T_p (54 K), the TTF chains are probably not distorted, and due to symmetry, $V_{+1} = V_{-1} = V_1$; $V_{+2} = V_{-2} = V_2$. Then

$$E(q_a) = [V_0 \cos aq_a + 2 V_1 \cos 0.55 \pi \cos aq_a + 2 V_2 \cos 1.1 \pi \cos aq_a][\rho_Q(q_a)]^2. \quad (3)$$

If the coefficient of $\cos aq_a$ is positive, $q_a = \pi/a$ for minimum energy, and the period is $2 a$, as observed [7]. The V_1 term is due to polarization of the TTF double bond at the center of the molecule, by the TCNQ ring, and thus probably weaker than the V_0, V_2 terms.

Assume now that below some temperature the TTF chains become distorted, due to a transverse motion, or libration. (The most likely distortion is a libration around the η -axis, as will be discussed later. The temperature could be 48 K [8, 24].) Then, the symmetry between V_{+1} and V_{-1} and between V_{+2} and V_{-2} , may be destroyed. Let $V_{+1} = V_1 + \delta_1$, $V_{-1} = V_1 - \delta_1$, $V_{+2} = V_2 + \delta_2$, $V_{-2} = V_2 - \delta_2$. Then

$$E(q_a) = \{ [V_0 + V_1 \cos 0.55 \pi + 2 V_2 \cos 1.1 \pi] \cos aq_a + [2 \delta_1 \sin 0.55 \pi + 2 \delta_2 \sin 1.1 \pi] \sin aq_a \} \rho_Q(q_a)^2 \quad (4)$$

and a minimum of energy is obtained for

$$\tan aq_a = \frac{2 \delta_1 \sin 0.55 \pi + 2 \delta_2 \sin 1.1 \pi}{V_0 + 2 V_1 \cos 0.55 \pi + 2 V_2 \cos 1.1 \pi}. \quad (5)$$

We notice that the term in the energy causing the change in transverse period is a third order term ($\rho_Q^2 \delta$). The physical origin of the δ terms will be discussed in sections 4, 5. (This result is different from that of refs. [24, 30].)

Up to here, everything is straightforward and *geometrical*, and the analysis depends only upon the well-known structure of TTF-TCNQ. Now we see that the behaviour of the system depends upon the relative ratios of the various parameters, the knowledge of which requires some *physics*. We saw that generally, we may expect $2 V_2$ to be of the same order as V_0 because V_0 is due to *two* TCNQ-TTF-TCNQ bridges, and V_2 is due to one, as illustrated in figure 3.

Since $\cos 0.55 \pi = -0.16$, which is small, we can probably neglect the V_1 term in the denominator. Thus, it is mainly the magnitude and sign of the ratio $2 V_2/V_0$ which determine the behaviour of the system; if it is 1, the denominator nearly vanishes ($\cos 1.1 \pi = -0.95$) and thus $\tan aq_a$ is large, even for rather small values of δ . Otherwise, the denominator will be large and a value of aq_a close to zero (or π) is to be expected.

The ratio $2 V_2/V_0$ should depend mainly upon the mode of polarization of the TTF molecule, which depends upon the excited molecular states. The ground state of TTF^+ is [17, 18] $4 b_{1u}(\pi)$. In this state, an appreciable fraction of the wavefunction rests on the sulphurs. If the excited state has b_{3g} symmetry, admixture of it into the ground state (due to polarization by the TCNQ nitrogen) creates a polarized state as in figure 4a and $2 V_2 \simeq V_0$. If it has b_{2g} symmetry (Fig. 4b), $2 V_2 \simeq -V_0$. If it has a_u symmetry (Fig. 4c), $2 V_2 \simeq -V_0$ with reversed sign for both V_0 and V_2 . According to Gleiter *et al.* [18], there are $b_{2g}(\pi)$, $b_{3g}(\pi)$, and $a_u(\pi)$ states (with ψ appreciable on the sulphurs) 1.86 eV, 3.35 eV, and 2.93 eV respectively below the $4 b_{1u}(\pi)$ ground state (thus they are excited states for the hole in the $4 b_{1u}$ shell). However, the assignment

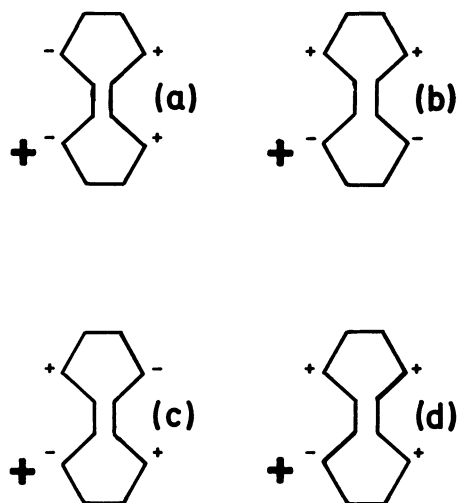


FIG. 4. — Polarization of TTF molecule by a neighbouring *positive* TCNQ molecule (at the site of the *positive* sign). (a) Nearest excited state of TTF having b_{2g} symmetry. (b) Nearest excited state of TTF having b_{3g} symmetry. (c) Nearest excited state of TTF having a_u symmetry. (d) Nearly degenerate b_{3g}, b_{2g}, a_u excited states. The small +, - signs indicate the excess of charge at the given site.

of Gleiter *et al.* is only tentative. Based on this tentative assignment, we could conceive of a model in which all these three states are nearly degenerate, contributing equally to the polarization. In that case, we get the configuration of figure 4d (the charge of the sulphur polarized by the nitrogen comes equally from all other sulphurs), and again $2 V_2 \simeq V_0$.

Summarising, if the excited state nearest to the ground state has b_{3g} symmetry, or the three states with b_{3g}, b_{2g} and a_u symmetry are nearly degenerate,

one may expect $2V_2 \simeq V_0$, a small denominator, and a large shift of aq_a from π (or zero) even for rather small δ , just as observed experimentally.

Note that the presence of factors like

$$\cos 2k_F b = \cos 2\pi b/\Lambda$$

indicates a special symmetry property for

$$k_F b = \pi/4 \quad (\Lambda = 4b)$$

corresponding to a quarter-filled band. While symmetry properties of half-filled bands have been investigated in detail [38], those of quarter-filled bands with staggered interaction have not. These seem to be most important in TTF-TCNQ.

2.2 THE INTER-MOLECULAR CHARGE TRANSFER MECHANISM. — A CDW on the TCNQ chain polarizes the TTF chain adjacent to it, giving rise to a CDW on it. The CDW on the TTF chain may exist either on its own, with only its phase determined by the CDW on the TCNQ chains [30, 24], or it may be induced by the TCNQ CDW.

According to this mechanism, we might expect naively that the CDW on the TCNQ chain at $x = 0$ should polarize the TTF chain at $a/2$ in antiphase with it, which in turn should polarize the TCNQ chain at a in phase with the CDW at $x = 0$, resulting in a period of a , rather than $2a$, as observed. However, the staggering of the N-S bonds alters the situation radically. The charge induced on the TTF molecule at $a/2$ due to the N-S bonds, $\rho_F(u, v, w)$, is given by

$$\alpha_F[\rho_Q(u+1, v, w) + \rho_Q(u-1, v, w)]$$

where α_F is the polarizability. Thus

$$\begin{aligned} \rho_Q(u, v+1, w) = & \alpha_F \alpha_Q [\rho_Q(u+2, v, w) + 2\rho_Q(u, v, w) + \\ & + \rho_Q(u-2, v, w)] = 4\alpha_F \alpha_Q \cos^2 2\pi b/\Lambda. \end{aligned} \quad (6)$$

Since $\cos^2 2\pi b/\Lambda = 1/40$, we see how strongly this interaction between TCNQ chains, mediated by the TTF chains, is attenuated. Because of this attenuation, interactions not via N-S bonds (V_1 terms, in the language of the preceding section) may play a role. But a more important aspect of the attenuation is that a slight libration of the TTF (or TCNQ) molecule changes the N-S distances, so that the near-cancellation will no longer take place. Whether the interaction between a TCNQ molecule at (u, v, w) and one at $(u, v+1, w)$, or, $(u \pm 2, v+1, w)$ will be stronger, and $V_0 - 2V_2$ is positive (in the first case) or negative (in the second), depends on the type of motion; a rotation of the TTF molecule around the η -axis should make the interaction with the neighbours at $u \pm 2$ stronger (because of the shortening of the corresponding N-S distances), and thus cause the CDW's on the TCNQ chains to be in antiphase; i.e. $V_0 - 2V_2$ is negative as observed experimentally. These rotations will be discussed in detail in the following sections.

Such rotations will be shown to be present permanently below 48 K, but we do not expect them to be present permanently at 54 K. However, a fluctuating rotation, with mean value zero, may be sufficient to bring about the negative sign of $V_0 - 2V_2$. Consider such librations around the molecular η -axis. For a restoring force of $K = 3$ eV (as estimated in section 3), the amplitude of thermal vibrations near 50 K is about 0.05 rad. For librations of TCNQ molecules, this changes the N-S distance by more than 0.15 Å. For librations of TTF molecules, the effect is smaller (because of geometrical considerations), but even for the potential on the nitrogens due to a charge of 0.1 e on the TTF ring carbons (whose distance from the nitrogens is strongly modulated by the libration), there is a contribution of order 10 meV to $2V_2 - V_0$, which is rather larger in comparison with the other contributions.

2.3 SUMMARY. — Thus, some differences between the *intra* and *inter* charge-transfer mechanisms are:

(i) In the *inter* mechanism, for neighbouring TCNQ chains having CDW's in antiphase, there is no polarization of the TTF chain between them for a rigid lattice. In the *intra* mechanism there is. Therefore, for a perfectly ordered lattice, the energy of a state with period a is always smaller for the *inter* mechanism than that of a state with period $2a$. For the *intra* mechanism, either period is possible, depending on which molecular excited state is closest to the ground state.

(ii) In the *inter* mechanism, there is more cancellation of the interchain interaction. First, the equivalents of V_0 and $2V_2$ are equal, yielding the $\alpha_F(\text{S-N}) 2 \cos 2\pi b/\Lambda$ term. Second, the polarization due to the TCNQ rings, $\alpha_F(\text{ring})$, yields a correction $\alpha_F(\text{S-N}) 2 \cos 2\pi b/\Lambda + \alpha_F(\text{ring})$.

Since $\alpha_F(\text{ring})$ is about half an order weaker than $\alpha_F(\text{S-N})$ (because the distance is somewhat larger, and somewhat less charge resides on the ring), and both have the same sign, and $2 \cos 2\pi b/\Lambda \simeq -0.3$, there is a further cancellation.

(iii) α_F should be expected to be large because the TTF chains, even if they don't undergo a Peierls transition at 54 K, undergo one several degrees lower.

Therefore, and because of the large uncertainty in the values of the various parameters, we cannot say at present which mechanism dominates. Both can account for the change in period from $2a$ to $4a$, and both show clearly that the coupling between the chains is much weaker than e^2/r (where r is the interchain distance, 6 Å).

We should point out that the pictures of refs. [30] and [32], and the present work are different. There, the direct Coulomb repulsion between TCNQ chains in the a -direction is assumed dominant in TTF-TCNQ and partially screened by the donor chains in TSeF-TCNQ, thus accounting for the lower T_p (29 K) of this compound.

In addition to Coulomb interactions between the chains, we must also consider the interaction due to electron tunnelling [39]. The tunnelling time has been measured recently [40] and corresponds to an energy of 6-10 meV for incoherent tunnelling to all four neighbouring chains, or about 3-5 meV for tunnelling to an individual neighbouring chain. Since tunnelling and Coulomb interactions have different effects on the Peierls transition, a direct comparison of this tunnelling energy to the Coulomb energy between chains is not very meaningful. Rather, following Barisic [30], we should compare transverse correlation lengths. The TTF-TCNQ tunnelling energy gives rise to an effective transverse correlation length [39]

$$\xi_{\perp} \simeq a(t_{\perp}/t_{\parallel}) (2 E_F/k_B T_P) \simeq 1 \text{ to } 2 a$$

(t_{\parallel} is the transfer integral along the chain).

The direct Coulomb energy between CDW's on TCNQ chains gives rise to a transverse correlation length of order [30]

$$\xi_{\perp} \simeq a[2 n(E_F) e^2/b]^{1/2} \cdot \ln 2 E_F/k_B T_P \cdot (2 \pi a/\Lambda)^{-1/2} \exp(-\pi a/\Lambda) \simeq 0.3 a$$

which is seen to be smaller than that due to the TTF-TCNQ tunnelling, and also too small to create transverse order. This supports our neglect of the direct Coulomb interaction between TCNQ chains in this work. The transverse correlation length due to the Coulomb energy between a CDW on the TCNQ chain and one on the neighbouring TTF chain (inter-molecular charge-transfer mechanism) may be expected to be about an order larger, because of the small distance between TCNQ nitrogens and TTF sulphurs replacing a ; however the factor $\cos^2 2 \pi b/\Lambda$ of expression (6) reduces this correlation length, so that order-of-magnitude-wise it is not very different from that due to tunnelling. The intra-molecular charge-transfer mechanism was also seen to be of the same order. Therefore, order-of-magnitude estimates alone cannot determine which mechanism dominates.

Note that the total interaction of a chain with its four neighbouring chains is of order 30 meV, which is about one tenth of the transfer integrals along the chains. This is sufficient to suppress the one-dimensional fluctuations and validates the present Landau-theory approach [39], but not sufficient to affect the mean-field properties of individual chains significantly. The effect of the tunnelling interaction of the coupling between chains depends on the nesting of Fermi surfaces. For one type of chain, and simple transverse coupling, there is complete nesting, and the CDW's of neighbouring chains are in antiphase [39]. In TCNQ-TTF, there are two types of chains and several transverse transfer integrals, and therefore the shape of the Fermi surface is complex and there need not be complete nesting [41]. In this work we shall follow our postulate of the dominance of S-N Coulomb interactions and not consider this mechanism further.

3. Coupling between an η -libration and the Peierls distortion. — As mentioned in the introduction, $-4 k_F$ reflections are caused by librations around the η -axis with wavevector $2 k_F$. In this section we show how such librations are excited by coupling with the CDW on a neighbouring chain.

A Peierls transition caused by molecular librations was first proposed by Morawitz [14]. Merrifield and Suna [15] pointed out that due to symmetry, the effect of a libration on the electronic energy spectrum of a non-degenerate band of an isolated linear chain is a second-order process. Therefore, for an *isolated* chain we may expect an interaction term $\cos^2 q_b y \rho(y)$, where $\rho(y)$ is the amplitude of the CDW due to the Peierls distortion, and the amplitude of the libration is proportional to $\cos q_b y$. Such a coupling term may give rise to a libration with $2 q_b = 2 k_F$, or $q_b = k_F$. (Rather than $2 k_F$.) Such a distortion has not been observed in TTF-TCNQ (though it may very well be present in other charge-transfer complexes, in particular ones with very small molecules which may be expected to execute large-amplitude librations [42]). Here, the term *libration* denotes a permanent distortion by rotation around a molecular axis.

For a three-dimensional system of coupled chains, however, the situation is more complicated. For a libration possessing a wavevector in the direction of the chain, $\mathbf{q} = (0, q_b, 0)$, the symmetry argument will still hold. For TTF-TCNQ, the symmetry of a longitudinal phonon (as well as a CDW) with wavevector along the chain is P2/m (table I), while that of a libration around the ζ or η axis (same \mathbf{q}) is P2/b, therefore they do not mix. (A libration along the ξ -axis has the same symmetry as that of a longitudinal phonon, therefore it mixes with it even for \mathbf{q} along the chain direction, and even for an isolated chain.) However, this argument no longer holds for a wavevector in a general direction in the Brillouin zone. For such a wavevector, very strong mixing between longitudinal phonons and librations is present in molecular crystals. Such coupling has been studied extensively by Ostertag [43] for the case of anthracene. When such mixing is present, we may talk of a first-order coupling between the libration and the CDW characteristic of the Peierls transition. The mixing between the various modes is brought about by the interatomic forces. In the present work, we restrict ourselves to the Coulomb forces between the TCNQ nitrogens and the neighbouring TTF sulphurs, and attempt to demonstrate that these forces account qualitatively, and even semi-quantitatively, for many of the features of the various phase transitions. However, it is clear that the forces between many other pairs of atoms should be considered in a complete quantitative theory.

For this reason, we have to regard the composite Peierls-Frohlich transition as a complex process in which many phonon branches participate and soften. In this work, we use the term *Peierls distortion* in a restricted sense for the longitudinal CDW.

When the electronic conduction band is *degenerate* (or nearly degenerate), the librations couple directly with the Peierls transition, and the longitudinal phonon (or longitudinal CDW) mode is not essential as an intermediary. This case has been studied recently by Morawitz [44]. We shall not consider it here.

As a special case of a composite Peierls-Frohlich transition, consider a first-order coupling between a libration around the η -axis on a TCNQ stack, and a (longitudinal) CDW on an adjacent TTF stack (Fig. 5). The one-electron potential of the TTF is modulated by the alternatively close and distant sulphurs of the librating TCNQ stack. Since this interaction is brought about by the N-S bonds, we may expect it (following our basic postulate) to be strong. A numerical estimate is as follows :

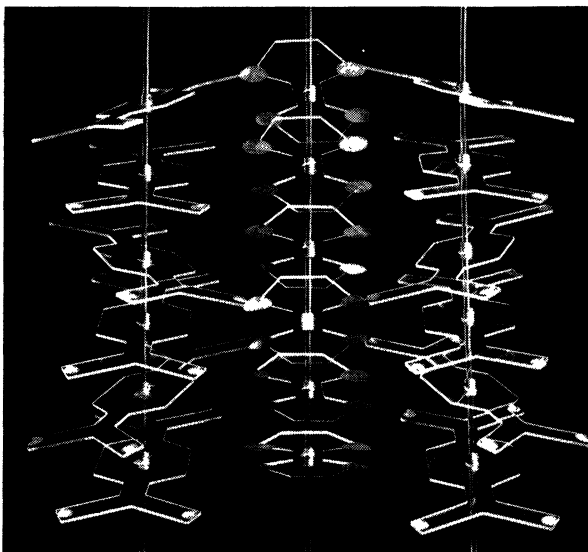


FIG. 5. — Effect of an η -libration on TCNQ chains on the one-electron potential of the TTF chain. The TTF molecule third from the bottom has the potential of all four sulphurs *Lowered* by the approaching nitrogens ; the TTF molecule second from top has the potential of all four sulphurs *Raised* by the receding nitrogens.

Consider an η -libration of amplitude χ_Q . The displacement of the nitrogens is given by

$$\delta r = \alpha \chi_Q \quad \alpha \simeq 4 \text{ \AA/rad.}$$

Thus the change in potential energy at the nitrogen site is given by $Ze^2/R^2 \delta r$, where Z is the charge on the nitrogens. There are 2 TTF stacks neighbouring each TCNQ stack, but only half of the sulphurs of each stack are affected by a libration of a single TCNQ stack.

The dimensionless electron-phonon coupling constant is given by $\lambda = g^2 n(E_F)/K$, where K is the force constant ; $K = \omega^2 I$ where ω is the libration frequency and I the moment of inertia. The frequency of libration (for modes with a large moment of inertia) is [36] in the range 20-40 cm^{-1} . Thus, let us tentatively assume that $\omega \simeq 30 \text{ cm}^{-1}$. $I_\eta = 1.3 \times 10^{-37} \text{ gm cm}^2$ for TCNQ, so $K \simeq 3 \text{ eV}$. For TTF $n(E_F) \simeq 2 \text{ eV}^{-1}$ and $g \simeq Ze^2/R^2 \alpha \simeq 0.3 \text{ eV}$ (for $Z \simeq 1/8$).

Thus we get a value $\lambda_{\text{lib}} \simeq 0.06$ for this mode. For a Peierls transition at 54 K, with

$$T_P \simeq 2 E_F \exp(-1/\lambda),$$

we get $\lambda_{\text{tot}} \simeq 0.18$ [3] (see also Seiden [45]). Thus we see that we can account for something like one third of the electron-phonon coupling leading to the Peierls transition by a libration mechanism like this. Clearly this estimate is very crude, and we cannot hope at this stage for something better than an order of magnitude estimate of the contribution of this mechanism to the electron-phonon coupling constant.

Note that the potential energy on the TTF chain is given by

$$V(\text{TTF}) = g \cos(2\pi y/\Lambda) \sin(2\pi b/\Lambda) \sin(k_a a/2) \chi_Q;$$

thus this coupling is maximum for a quarter filled band, $\Lambda = 4b$. This is a particular property of the η -libration. See table I.

For an η -libration of amplitude χ_F on the TTF stacks, the displacement of the sulphurs towards the nitrogens is given by $\delta r = \beta \cdot \chi_F$, $\beta \simeq 0.3 \text{ \AA/rad}$. This small value of β is an accident, occurring because the centre of the TTF molecule, the sulphur, and the nitrogen are nearly colinear and thus a rotation of the TTF molecule does not bring the sulphur closer to the nitrogen. Because of this small value of β , we may have to relax our assumption of the exclusivity of the N-S interactions somewhat, and consider also the interaction between the TTF ring carbon and the TCNQ nitrogen (say). This will give rise to a larger value of β , though not quite as large as α , where the libration on the TCNQ moves the nitrogen straight ahead towards the sulphur (Fig. 5).

In conclusion, we suggest that the coupling between η -librations on the TCNQ chains and the CDW on the TTF chains is considerably stronger than the complementary process. Therefore, the $4k_F$ reflections could be due to the librations on the TCNQ stacks.

4. Interaction between η -librations on TTF and TCNQ chains. — In the previous section we considered the coupling between librations and the CDW on the neighbouring chains. In this section, we treat the coupling between librations on neighbouring chains, and show how this coupling plays a major role in determining the temperatures of the transitions at 48 K and 38 K, as well as providing an origin for the term δ_1 introduced in section 2.

Since the close N-S neighbours belong to molecules that are displaced a distance b along the stacking axis, and the period of the CDW is close to 4 ($\Lambda/b = 3.55$), the bilinear interaction between librations on adjacent TTF and TCNQ chains nearly vanishes, while the bi-quadratic interaction is very strong. This can easily be seen from figure 5 : Since the phase of the libration changes by nearly 180° on advancing a distance $2b$,

the net torque on the TTF molecule nearly cancels out. Let us formulate this simple observation somewhat more quantitatively.

The 4 nitrogens of the TCNQ are close to 4 sulphurs of 4 different TTF molecules, centered at

$$+ a/2, + b (N_1); + a/2, - b (N_2); \\ - a/2, + b (N_3); - a/2, - b (N_4).$$

Let δr_i be the change in distance of nitrogen i from its sulphur. The interaction energy is proportional to

$$\sum_{i=1}^4 (R + \delta r_i)^n;$$

$n = -1$ for a monopole-monopole interaction, $n = -4$ for a monopole-induced dipole interaction, etc.

$$\begin{aligned} \delta r_1 &= \alpha \chi_Q(y) - \beta \exp(ik_a a/2) \chi_F(y+b) \\ \delta r_2 &= -\alpha \chi_Q(y) + \beta \exp(ik_a a/2) \chi_F(y-b) \\ \delta r_3 &= -\alpha \chi_Q(y) + \beta \exp(-ik_a a/2) \chi_F(y+b) \\ \delta r_4 &= \alpha \chi_Q(y) - \beta \exp(-ik_a a/2) \chi_F(y-b) \end{aligned} \quad (7)$$

$\chi_Q(y)$ is the amplitude of the libration on the TCNQ stack (measured in radians) at height y : $\chi_F(y) \exp(ik_a x)$ that on the TTF stack at x, y . $\alpha \simeq 4 \text{ \AA}$ per rad and β is somewhat smaller (section 3). The bilinear term originates from the coefficient of $\chi_Q(y) \chi_F(y)$ of the term $\sum_i \delta r_i^2$ in the expansion, and is seen to contain the small term $\cos(2\pi b/\Lambda) = -0.15$, while the bi-quadratic term originates from the coefficient of $\chi_Q^2(y) \chi_F^2(y)$ of the term $\sum_i \delta r_i^4$ in the expansion, and is seen to contain the large term $\cos(4\pi b/\Lambda) = -0.96$.

If the phase of the CDW on the TTF is displaced by φ , $\chi_F(y) = \chi_F \cos(2\pi y/\Lambda + \varphi)$ with respect to that on the TCNQ, $\chi_Q(y) = \chi_Q \cos(2\pi y/\Lambda)$, the interaction energy is given by :

$$- A \cos(k_a a/2) \cos(2\pi b/\Lambda) \cos \varphi \chi_F \chi_Q + \\ + B \cos(k_a a) \cos(4\pi b/\Lambda) \cos 2\varphi \chi_F^2 \chi_Q^2 \quad (8)$$

(A, B positive). This contribution to the free energy is a minimum when

$$\cos \varphi = \frac{A \cos(2\pi b/\Lambda) \cos(k_a a/2)}{4 B \cos(4\pi b/\Lambda) \chi_F \chi_Q \cos(k_a a)} \quad (8')$$

as long as the absolute value of the right hand side does not exceed 1.

Note that the *basic* factor in B is $z_1 z_2 e^2/R$, with $R = 3.2 \text{ \AA}$ and z_1, z_2 are the charges on the nitrogen and sulphur. The α and β coefficients actually increase the value of B considerably, as does the high-order of the expansion (this is particularly true for monopole-induced dipole forces, with $n = -4$). Thus, a term B considerably larger than 5 eV is to be expected, which can overcome the restoring force of order 3 eV

(estimated in section 3 for TCNQ, but probably similar for TTF), even if χ_F^2 is somewhat small. This restoring force is, moreover, reduced by the tendency of the TTF chains to undergo a Peierls transition independently.

In an *ab initio* calculation, we have to let the bilinear term, which tends to minimize the energy for $k_a = 0$, compete with the polarization term of section 2 which tends to minimize the energy for $k_a a = \pi$. Since at the present stage we cannot estimate the numerical values of the various coefficients sufficiently accurately, we do not attempt an *ab initio* calculation, but use the experimental observation [8] that for $48 \text{ K} < T < 54 \text{ K}$, $k_a a = \pi$. Thus, the bilinear term vanishes,

$$\cos k_a a = -1, \quad \cos 4\pi b/\Lambda \simeq -1$$

too, so the energy is minimum for $\cos 2\varphi = -1$, $\varphi = \pi/2$.

The argument that the bilinear term vanishes for the $2a$ period has been made before [32]. Here we point out that even if the period is not $2a$, this term is small, because of the smallness of $\cos(2\pi b/\Lambda)$ (nearly quarter-filled band). This is one reason for the stability of the $2a$ period, since the bilinear term energetically favours a period a .

Formula (8) is symmetric in χ_Q, χ_F . Therefore it describes both a buildup of a libration on TTF chains by the librations on TCNQ chains, and the reverse process. Following the spirit of refs. [8, 24] we would say that a Peierls transition ρ_Q takes place on the TCNQ chains at 54 K; following section 3, ρ_Q induces a libration χ_F on the TTF chains at that temperature. From formula (8), at 48 K where χ_F^2 is large enough, it induces a second-order transition in which a libration χ_Q builds up on the TCNQ chains, which by the mechanism of section 3 induces (or helps in inducing) a Peierls transition ρ_F on the TTF chains. Thus at 48 K, when the bi-quadratic term overcomes the restoring force, a libration builds up on the TCNQ chains displaced by $\pi/2$ (i.e. $\Lambda/4$) with respect to that on the TTF chains. In the next section we shall expand on this picture somewhat.

However, the question of whether a second Peierls transition takes place at 48 K is not quite so simple, and will be discussed elsewhere [46].

5. Systematic description of the cascade of displacive transitions. — Broadly speaking, the various transitions in TTF-TCNQ (at 54 K, 48 K, 38 K, and probably a few more temperatures) can be regarded as Jahn-Teller transitions in which symmetry elements are lost. Let us try to see systematically which are the symmetry elements lost in each transition, and what is the driving force causing the loss of symmetry.

It is worthwhile to consider the symmetry of an individual chain (stack) of TTF (and TCNQ) molecules [25]. This symmetry is to be distinguished from the space group of the whole lattice [16],

$P2_1/c$ (C_{2h}^5 , No. 14), and the point group of individual molecules, $\bar{1}$ (Ci). This symmetry is $P1$ (C_1^1 , No. 2). This low symmetry occurs because the molecules are slightly distorted due to the monoclinic stacking. See figure 6.

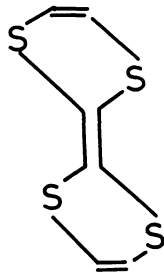


FIG. 6. — Distortion of a TTF molecule due to the monoclinic stacking, greatly exaggerated. This small distortion is ignored in this work and point symmetry mmm is assumed.

In the figure, the distortion is greatly exaggerated. Actually, it amounts to less than 0.5 % (0.1 % for the inside CS bonds, 0.4 % for the outside ones). Also, the molecules are not perfectly planar. However, these distortions are small, and probably do not affect the Peierls transition appreciably. Therefore, let us make the approximation that the molecules keep their (mmm) symmetry, and consequently the chains have $P2/m$ (C_{2h}^1 , No. 10) symmetry. Thus, in addition to the inversion symmetry, there is a twofold axis $xyz \rightarrow x\bar{y}\bar{z}$, and a reflection plane $xyz \rightarrow \bar{x}yz$. The xyz axes are along the crystalline abc axes, while the molecular principal axes are denoted by $\xi\eta\zeta$ (Fig. 1); ξ coincides with x , while $\eta\zeta$ are tilted by 24.5° and 32° with respect to the yz axes respectively for TTF and TCNQ.

Note that the monoclinic symmetry axis of this group is along the crystalline a -axis, not the b -axis. For a single stack of TCNQ (or TTF) molecules, the stacking axis is *not* a symmetry axis. The monoclinic symmetry of the space group of the whole crystal is brought about by the screw-axis $xyz \rightarrow \bar{x}, y + \frac{1}{2}b, \bar{z} + \frac{1}{2}c$ in which stacks at $z = 0$ and $z = \frac{1}{2}c$ are interchanged. This symmetry element clearly does not exist when we consider a single stack only. Moreover, in the crystal, the a -axis is not a true symmetry axis, because of the tilted stacking along the c -axis. Only if we consider a single ab plane, and neglect the neighbouring ab planes at distances $\pm \frac{1}{2}c$, does the a -axis become a symmetry axis. But following our procedure of considering *approximate* symmetries, neglecting the distortion of the molecule brought about by the tilted stacking along the c -axis, and considering only interactions of N-S neighbours (as well as between molecules along the b -axis) thus neglecting the interaction in the c -direction, this procedure is self-consistent.

Thus, above 54 K, both TTF and TCNQ stacks have (approximately) $P2/m$ symmetry, and an array (ab plane) of stacks possesses the same symmetry.

However, fluctuations reduce this symmetry instantaneously giving rise to a diffuse X-ray scattering characteristic of the distortion that exists permanently below 54 K, and which will be discussed now.

When a Peierls distortion takes place, both a longitudinal displacement and a libration around the η -axis of the neighbouring chain are excited. For the libration, the reflection plane $xyz \rightarrow \bar{x}yz$ is lost, but instead a glide-plane $xyz \rightarrow \bar{x}y + \frac{1}{2}Az$ exists. Thus, the symmetry is $P2/b$ (C_{2h}^4 , No. 13) [47]. Note that if y is a lattice point, $y + A/2$ will not be one, so we have to take $y + A/2 + kb$ and choose a value of k so that this point is as near as we please to a lattice point; or we have to regard the libration as a modulation of the lattice. However, this point of quasi-periodicity already applies to the CDW itself, and is not a new concept here. For $(0kl)$, $P2/b$ has the selection rule $k = 2n$ for allowed reflections [47] (due to the glide plane [21]). Thus for $h = 0$ only reflections with wavevector $4k_F$ ($8k_F$, etc.) will be allowed, and $2k_F$ ($6k_F$, etc.) are strictly forbidden. If $h \neq 0$ but is small, we may expect by continuity that the $2k_F$ reflections will be weak.

Following this general argument, let us turn to the specific case of TTF-TCNQ, where a Peierls transition takes place at 54 K. We do not know whether it occurs on the TCNQ chain, or the TTF chain, or both. Following current practice [9, 24], let us assume that it takes place on the TCNQ chains, associated with a libration on the TTF ones; and following ref. [24], that the Peierls transition of the TTF chains takes place at 48 K.

While the symmetry of the TTF chain is $P2/b$ due to the libration, that of the TCNQ chain, which has a Peierls distortion and thus a longitudinal phonon associated with it, is $P2/m$, but with a period A (rather than b). Thus the TCNQ chain should provide reflections with $2k_F$ (since there are no selection rules for $P2/m$) and the TTF chain should provide reflections at $4k_F$ (because of the selection rule of $P2/b$). The strong scattering of X-rays by the TTF sulphurs can make these $4k_F$ reflections strong. This explanation ($2k_F$ due to TCNQ, $4k_F$ due to TTF) is in line with that of Pouget *et al.* [22]. However, it may be an oversimplification, since strong η -librations exist on the TCNQ chains as fluctuations, and X-rays do not distinguish between dynamic and static displacements. The amplitude of the motion of the CN groups in the b -direction is very large, because of the large distance of these groups from the center of the molecule, and the large tilt of the TCNQ molecules from the ac plane. This large amplitude may compensate for the smaller atomic number. Therefore, the presence of $4k_F$ reflections is no *proof* that it is the TTF molecules that librate.

This explanation applies to reflections at $T > 54$ K, where there is no long-range order perpendicular to the chains. In the temperature range $48 \text{ K} < T < 54 \text{ K}$, where such a long-range order exists and moreover

$k_a a = \pi$, i.e. the CDW's on adjacent TCNQ chains are displaced by $A/2$; the $2 k_F$ reflections of adjacent TCNQ chains cancel each other (for miller index $h = 0$) (since the CDW's are 180° out of phase). The space group of an array of TTF and TCNQ chains in an ab plane is $C2/m$ (C_{2h}^3 , No. 12, $C2/m$ 11) [47]. For this symmetry we have the selection rules : for (hkl) , $h + k = 2n$; for $(0kl)$, $k = 2n$; and for $(h00)$, $h = 2n$. Thus, $2 k_F$ reflections are again forbidden for $h = 0$.

Note that the symmetry of the η -libration is such that for two TTF chains at $+a/2$ and $-a/2$ and with opposite phase of libration (i.e. period $2a$ in the a

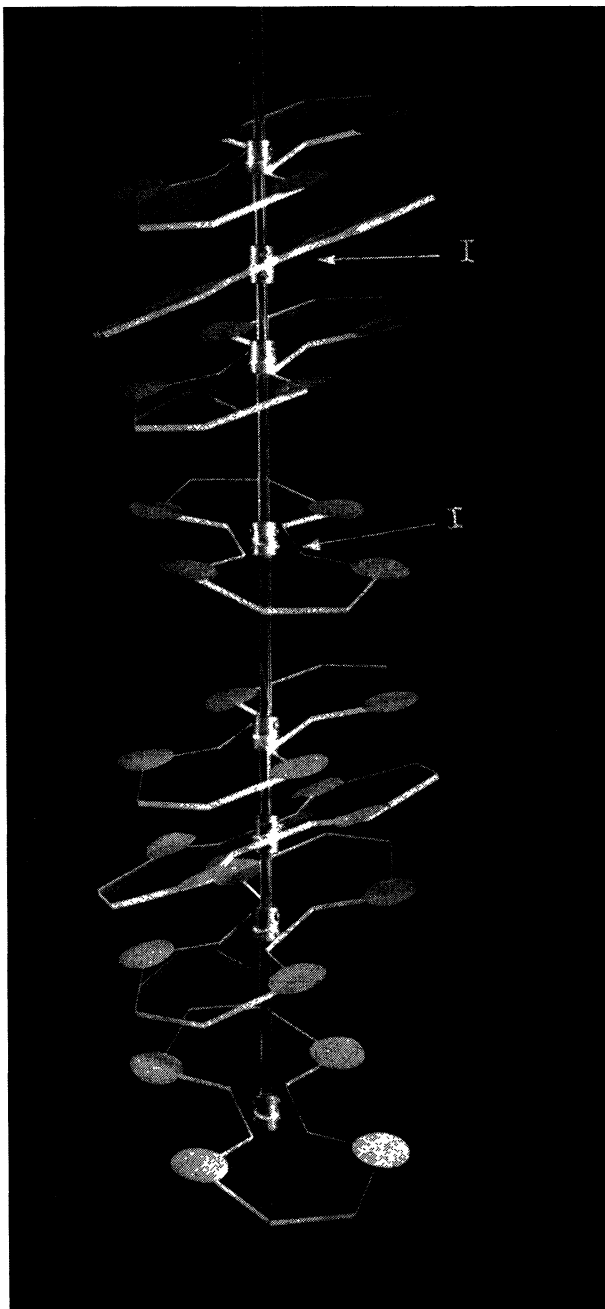


FIG. 7. — A longitudinal phonon and an η -libration on a TTF chain, ρ_F and χ_F being in phase. There is inversion symmetry around the marked points. (In these photographs $A = 4b$ for simplicity).

direction, as observed experimentally [8] between 48 K and 54 K) the one-electron potentials induced on the TCNQ chains *add*. This is in contrast to coupling between modes of the same type (librations on both types of chains, longitudinal phonons on both types of chains) where the interactions *cancel* for the $2a$ transverse period [32].

When the symmetry drops, other modes consistent with the lower symmetry (such as transverse phonons or librations around other axes, as shown in table I) will be excited too, but probably only weakly.

At 48 K, the TCNQ chain undergoes a second-order transition in which an η -libration builds up (section 4), displaced by $A/4$ from the longitudinal phonon already existing on this chain. Thus, the longitudinal displacement vanishes for TCNQ molecules with extremum libration, and vice versa (Fig. 7). The only symmetry remaining is inversion around the center of the molecule at the extrema of the libration (zeros of the longitudinal displacement). This leaves symmetry $P\bar{1}$. As for the TTF's, the libration of the TCNQ's should induce a Peierls distortion on them (unless such a distortion has already been produced by some other mechanism), so their symmetry should not be higher either.

Because of the loss of the two-fold axes, there is no longer up-down symmetry, and thus the period in the a -direction starts to increase (section 2). This breakdown in symmetry is proportional to χ_Q^2 , which increases linearly with decreasing T according to Landau theory, hence the linear decrease of k_a below 48 K [7, 8].

The change in period along the a -direction reduces the term $\cos k_a a$ in the biquadratic term which induces the libration on the TCNQ chains (section 4), while the bilinear term no longer vanishes. One effect this has is to change φ from its value of $\pi/2$ to the value given by formula (8'), where $\cos \varphi$ no longer vanishes, since now $\cos k_a a/2 \neq 0$.

Thus the longitudinal phonon and the libration are no longer displaced by $A/4$, and as a result, no more symmetry elements are left on the chain (space group $P1$) below 48 K, see figure 9. Also, as the temperature is lowered the reduction of $\cos k_a a$ will eventually offset the increase in χ_F^2 , and the biquadratic term will no longer be able to overcome the restoring force of the libration on the TCNQ chain. Assuming $\chi_F^2 \propto 1 - T/T_P$ (first-order Landau theory), then χ_F^2 increases by a factor of 2.7 from 48 K to 38 K ($T_P = 54$ K); using the experimental value at 38 K of $k_a a \simeq 0.6$, so $\cos k_a a = -0.3$, we see that the reduction in $\cos k_a a$ just offsets the increase in χ_F^2 at 38 K. This will give rise to a first-order transition in which φ jumps to π (or zero) and the value of χ_Q also changes discontinuously. For $\cos \varphi = \pm 1$ a two-fold symmetry axis exists on the chains at the zeros of ρ_Q , χ_Q (space group $P2$; see figure 8). A first-order transition is indeed observed experimentally at just that temperature. Thus the simple and naive expression

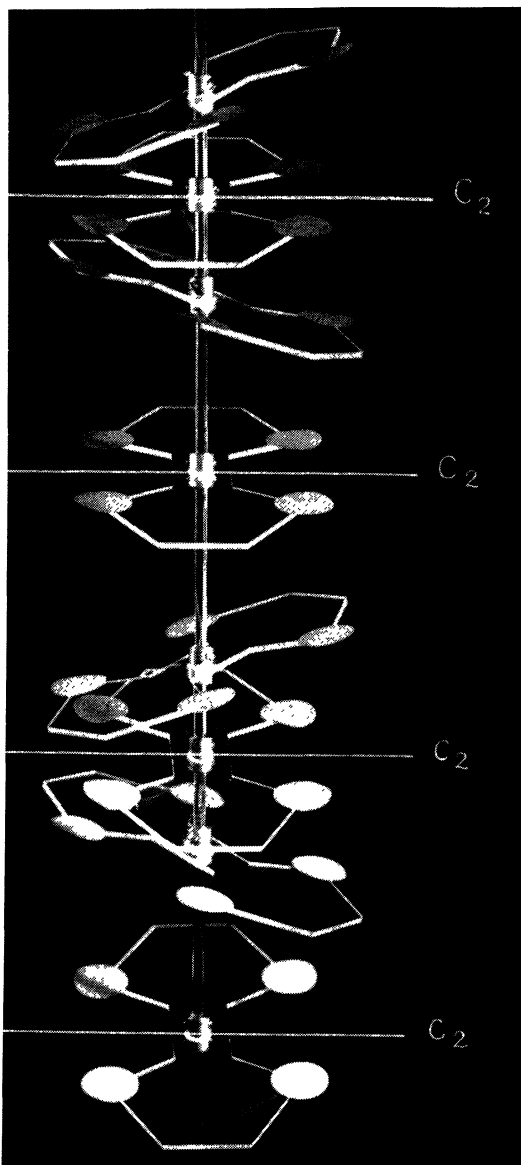


FIG. 8. — A longitudinal phonon and an η -libration on a TTF chain. ρ_F and χ_F are displaced by $\Lambda/4$. There is a two-fold axis around the lines marked « C_2 ».

(section 4) predicts the transition at 38 K to an astonishing accuracy.

Because of the importance of this point, let us discuss it in somewhat more detail. The bi-quadratic coupling between the librations on the two chains is given by [from equation (8)] $B \cos(k_a a) \cos(4\pi b/\Lambda) \cos 2\varphi \chi_F^2 \chi_Q^2$. In this term, k_a , χ_F , and χ_Q are strong functions of temperature. If this is the only term driving the χ_Q libration (i.e. neglecting the bilinear term, and the $\chi_Q \rho_F$ coupling), and the restoring force of this mode is temperature independent, the two transition temperatures at which χ_Q instabilities occur, $T_I = 48$ K and $T_L = 38$ K, are related by :

$$\cos[k_a(T_L) a] \chi_F^2(T_L) = \cos[k_a(T_I) a] \chi_F^2(T_I) \quad (9)$$

with $\chi_F^2(T) \propto 1 - T/T_P$, where $T_P = 54$ K is the temperature at which χ_F starts to build up. Since $k_a(T_I) a = \pi$, we are left with a relationship between $k_a(T_L)$, T_L , T_I , and T_P , which seems to be fulfilled experimentally [8] to a very high accuracy (much higher than one would expect for such a crude approximation). This may be regarded as an argument for simple Landau theory (rather than a theory with a mean-field transition temperature much higher than T_P [24, 32, 48]).

However, this simple model would predict that $k_a a$ falls at 38 K to zero (or rises to π), and not just to $\pi/2$ (since the two-fold symmetry axis implies up-down symmetry, while the breakdown of it is necessary to obtain $k_a a \neq 0$, see section 2). The $4a$ transverse period observed experimentally can be accounted for by coupling to some additional degree of freedom. Clearly, the system possesses many more order parameters (due to transverse phonons, additional librations, distortions of the molecules, etc.) which are expected to be strongly coupled to the 4 order parameters treated up to now, and a first-order transition can thus make such modes appear. While this simple theory tells us that there is an instability causing a

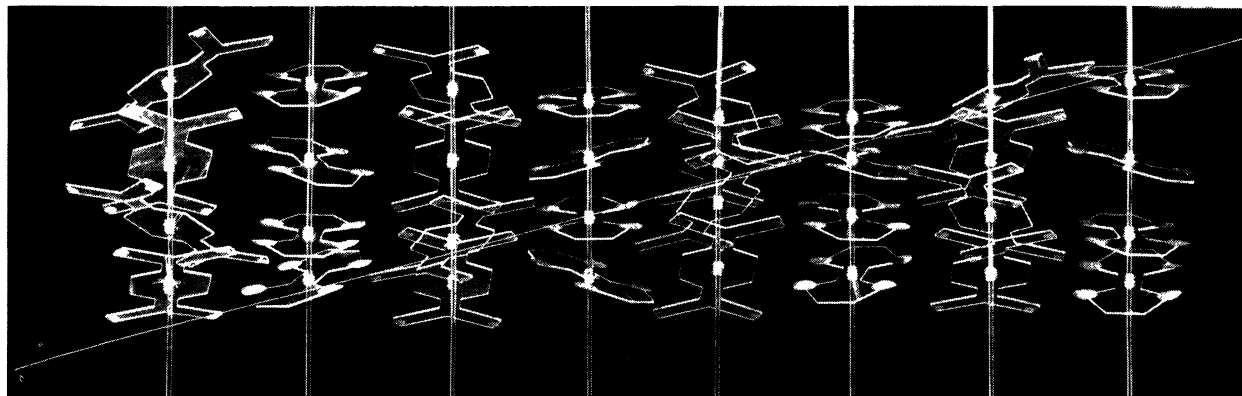


FIG. 9. — Typical state between 48 K and 38 K. There are librations and Peierls CDW's on both families of chains. In the vicinity of the sloping white line, nitrogens and sulphurs approach. Notice the absence of up-down symmetry, necessary for a transverse period changing continuously between $2a$ and $4a$.

first-order transition at 38 K, it does not tell us to what state this instability will lead us.

Let us summarize the situation. At 54 K, ρ_Q builds up with a transverse period $2a$, inducing χ_F by the bilinear $\rho_Q \cdot \chi_F$ coupling. Below 54 K χ_F builds up, until at 48 K it is strong enough to create χ_Q by the biquadratic $\chi_F^2 \cdot \chi_Q^2$ coupling. χ_Q in turn induces ρ_F by the bilinear $\chi_Q \cdot \rho_F$ coupling. The induced ρ_F is large because the *bare* TTF Peierls transition is nearby. The presence of all four $\rho_Q, \chi_F, \chi_Q, \rho_F$ with the phase φ following (8') destroys the up-down symmetry (2-fold axis), increasing the transverse period from $2a$ [following (5)]. As the transverse period increases sufficiently, the biquadratic $\chi_F^2 \cdot \chi_Q^2$ coupling is broken at 38 K. By that time both ρ_F and ρ_Q are large and exist independently of coupling to other modes. What modes they induce (χ_Q, χ_F or \mathcal{E}_F , etc.) cannot be established with certainty at this stage, but the number of alternatives is small. This (admittedly complicated) cascade of displacive transitions, caused by the hierarchy of interatomic interactions, is summarized in table II.

Some guidance may be provided by the pressure dependence of the transition temperatures. The librational modes in TTF-TCNQ are extremely soft. Mook and Watson [36] list (from neutron diffraction) such modes with frequencies around $20\text{-}30\text{ cm}^{-1}$, and Coleman's [49] far-infrared spectroscopic data seem to substantiate these values. Such soft modes may be expected to harden considerably under pressure (i.e. to possess a large Gruneisen constant). On the other hand, the longitudinal phonon along the chain direction is not particularly soft; its energy at the zone boundary is about 200 cm^{-1} [36, 50]. From the thermal expansion, Thomas *et al.* [51] find a rather *regular* value of the Gruneisen constant (about 4) for these modes, so their frequency does not change significantly under pressure of order 5 kbar. Therefore we may expect the electron-phonon coupling, which is inversely proportional to the force constant, to fall

much more rapidly under pressure for the librational modes than for the longitudinal phonon. Thus the transition temperature for the sliding motion of the molecules may be expected to fall with increasing pressure, while the Peierls transition temperature may even rise (due to increased electron-phonon matrix element g with the increased overlap) [10]. T_P (at 54 K) rises slightly under pressure [18, 52] ($d \ln T_P/dP = 1.3\% \text{ kbar}^{-1}$) but much less than [24] in ⁽¹⁾ TSeF-TCNQ ($7\% \text{ kbar}^{-1}$). This may be due to some compensation between the longitudinal phonon (giving a positive effect) and librations, or intra-molecular distortions (giving a negative effect). The transition at 38 K falls with pressure [10] ($d \ln T_L/dP = -2.6\% \text{ kbar}^{-1}$), suggesting above-mentioned libron hardening (*disc-brake* effect), impeding the additional libration, or sliding motions. The very strong effect of TSeF impurities in suppressing T_L [11] is also in line with this interpretation, since the transition is due to a disappearance of χ_F and appearance of \mathcal{E}_F [for pattern (10), figure 10; or the disappearance of χ_F for one type of TTF chains, for pattern (11) see section 6.4] as the temperature is lowered. Clearly modes on the TTF chains should be affected more by impurities on the TTF chains than by ones on the TCNQ chains [53].

6. Some additional structural considerations. —

In this section, we discuss for completeness a few additional problems related to symmetry and structure. The reader is advised to skip this section at first reading.

6.1 THE POSSIBLE EXISTENCE OF TWO PEIERLS TRANSITIONS. — Several authors have suggested that there may be two Peierls transitions in TTF-TCNQ, one associated with the TCNQ chains and the second with

⁽¹⁾ COOPER, J. R. (private communication).

TABLE II

Effect of the cascade of displacive transitions on the approximate symmetries of the chains

Approximate symmetry	Temperature				
	$T > 54\text{ K}$	$48\text{ K} < T < 54\text{ K}$	48 K	$38\text{ K} < T < 48\text{ K}$	$T \leq 38\text{ K}$
TTF chain	P2/m	P2/b	$\overline{P1}$	P1	$\begin{pmatrix} \overline{P2/m} \\ \overline{P2/b} \end{pmatrix}$
TCNQ chain	P2/m	P2/m	$\overline{P1}$	P1	P2
ab plane (array of TTF and TCNQ chains)	P2/m	C2/m	$\overline{P1}$	P1	C2/m
Period	(a, b)	$(2a, A)$	$(2a, A)$	(na, A) $2 < n < 4$	$(4a, A)$
Figure	5		7	9	10
Notes	Figure shows the fluctuating state			Up-down symmetry of pattern is destroyed due to the absence of up-down symmetry of individual chains.	One of several possibilities. See text. There are two types of TTF chains, P2/b symmetry of one is only average. See text.

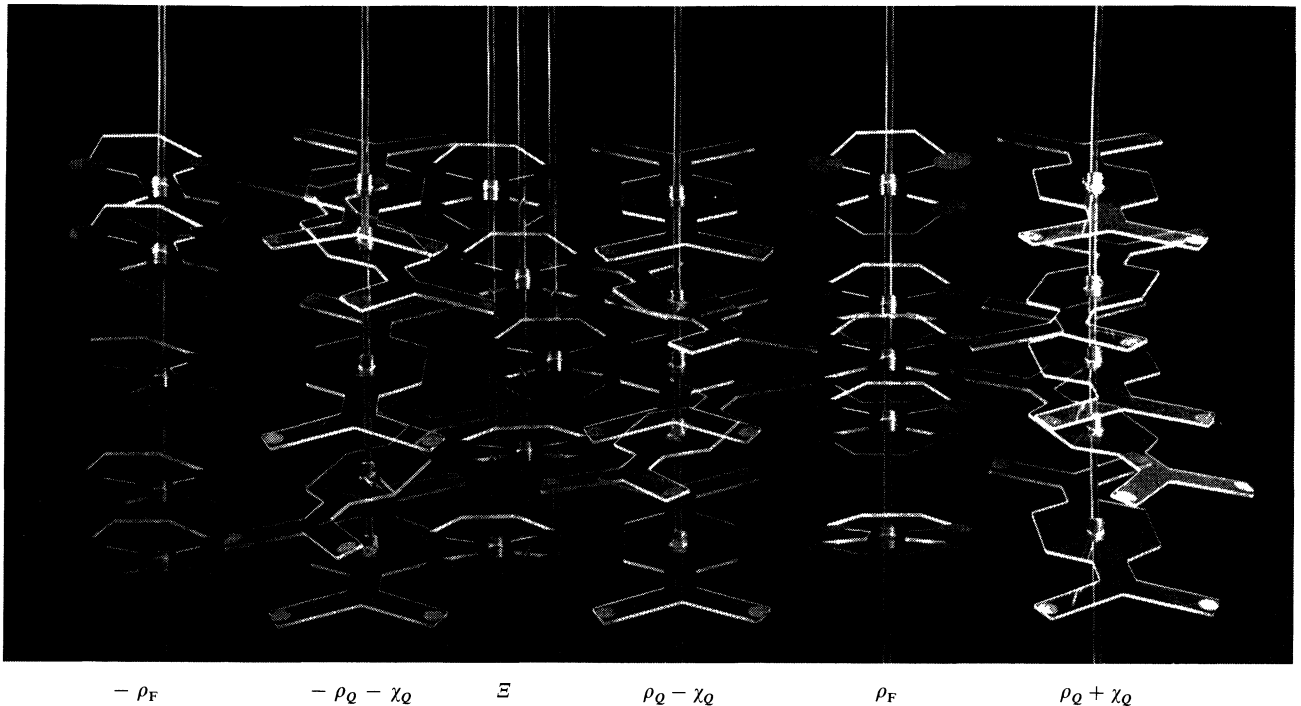


FIG. 10. — Possible state below 38 K. Note that there are two types of TTF chains, one (I) with a transverse phonon and the other (II) without. The distances between type I and type II TTF chains and the neighbouring TCNQ chains need not be equal. There should be a Peierls distortion on « type I » chains too, but its sign ($+\rho_F$ or $-\rho_F$) is random, and not shown on this figure. The exact state depends on the relative strength of the various interactions, and this is only one of several possibilities.

the TTF chains [9, 10, 24, 30, 32, 52, 53]. The present work is related to this question (a transition at 54 K on the TCNQ chains, and 48 K on the TTF chains being implied, following current literature [9, 24]) but a comprehensive discussion of this point is outside the scope of the present publication [46].

6.2 THE BEHAVIOUR IN THE c -DIRECTION. — Experimentally, TTF-TCNQ crystals are usually twinned, so that the a -axis is common to the twins but the c -axis isn't. This makes it hard to investigate the behaviour in the c -direction by diffraction methods. From the point of view of this work, the N-S bonds are in the a -direction, so they cannot account for what happens in the c -direction. Both the electron tunnelling [39] and Coulomb interactions [30] should change the phase of the PLD on alternate planes, which are displaced a distance $c/2$, by 180° . (These alternate planes are related by a glide-plane symmetry element of the space group $P2_1/c$ of undistorted TTF-TCNQ.) Thus, the phase of the CDW on chains separated by a distance c should be the same. The η -libration should have a similar effect (Fig. 11). Thus we may expect $k_c = 0$.

The stacking along the c -axis destroys the approximate symmetries we are considering in this work. Thus, we have two alternatives :

(i) Consider isolated ab planes, but remember that the interaction along the c -direction slightly destroys the symmetry, and forbidden reflections may become allowed, though rather weak ; and reverse the phase of the PLD's on alternate planes in an *ad hoc* way.

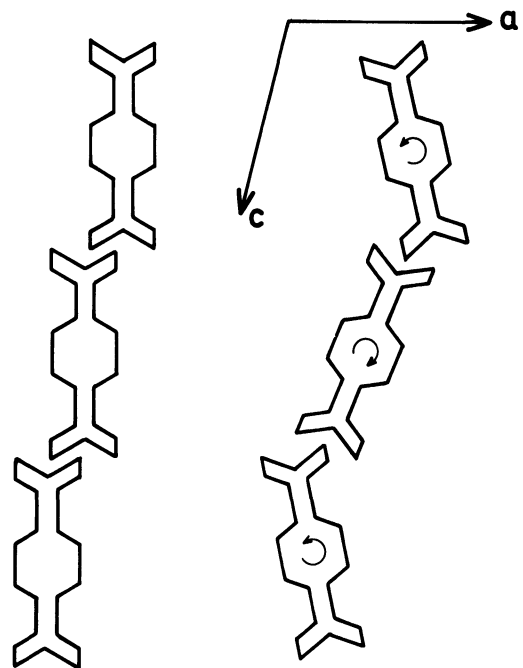


FIG. 11. — The stacking of TCNQ molecules projected on the ac plane, and an η -libration, greatly exaggerated. The phase on alternate chains reverses, thus the period in the c -direction is c and $k_c = 0$. Other factors involved are discussed in text.

(ii) Ignore the deviation of β ($\beta = 104^\circ$) from $\pi/2$, and thus consider a case where $\beta = \pi/2$ and we have orthorhombic symmetry. In that case, we can describe the symmetry properties along the c -axis as well, by orthorhombic space groups. Again, the deviation of β

from $\pi/2$ will cause forbidden reflections to be allowed, though weak. For this case, when for example the ab plane has approximate C2/m symmetry, the whole structure will have approximate Cmca (No. 64) [47] symmetry. We do not recommend this second approach, since we lose a lot in complication without gaining much in information.

6.3 FORM FACTORS OF THE $2k_F$ AND $4k_F$ REFLECTIONS. — Perhaps the most crucial experimental check of the present theory is the determination of the intensities of the $2k_F$ and $4k_F$ reflections throughout reciprocal space.

The intensities of the reflections depend on three factors (besides spurious factors like crystalline disorder, etc.)

- (i) The amplitude of the given mode.
- (ii) The form factor of the given mode, which, for example, prohibits some $2k_F$ reflections for modes with a glide-plane symmetry element.
- (iii) The molecular form factor.

Consider for example χ_Q . Most of the reflection is probably due to the $C(CN)_2$ groups, because the amplitude of their motion is the largest. The motion is mainly in the a -direction, but this motion has a period $2k_F$, and should give rise to reflections $(h, 2k_F, l)$ for large values of h . The component of motion responsible for the $4k_F$ reflections is that along the b -direction, which is proportional to $r \cdot \chi_Q^2 \sin \varphi$, where φ is the angle of tilt (34°) and r is the distance from the centre of the molecule to the $C(CN)_2$ groups (3.5 Å). There is also motion in the c -direction proportional to $r \cdot \chi_Q^2 \cos \varphi$. Note that for χ_F , r of the sulphurs is only 1.5 Å and φ is smaller too (24°); this compensates in part for the larger scattering factor of the sulphurs due to their larger atomic number. These motions should increase the intensity of reflections of large k and l indices. (Following Pouget [22] the intensity should go like

$$\langle u_a^2 \rangle h^2 + \langle u_b^2 \rangle k^2 + \langle u_c^2 \rangle l^2,$$

where u_i are the displacements). However, we have to modulate these intensities by the molecular form factor [23]. In the present case, this is the component of the length of the $C(CN)_2$ groups along the relevant axis, which is about 4.4 Å along the a -axis and about 1.8 Å along the c -axis. When this length is large (as along the a -direction in the present case), this molecular form factor may cause a fast decrease of amplitude with increasing miller index (h in the present case).

Note that \mathcal{E} is not associated with any movement in the b -direction, therefore it should not give rise to reflections with $(0, 4k_F, 0)$ in spite of the glide-plane symmetry element.

The longitudinal phonon should yield motion mainly along the b -direction, but the molecular tilt should cause some motion in the c -direction too. Thus we should expect motion for $2k_F$ reflections in the b

and c directions due to the ρ_Q, ρ_F modes, and in the a -direction due to the χ_Q, χ_F modes, and motion of the $4k_F$ reflections in the b and c directions, due to χ_Q, χ_F .

Correlation between the motions of adjacent chains should also have an effect on the intensities.

Up to now, the motion of the $4k_F$ reflections along the c -direction has not been observed (perhaps due to the large distance between the $C(CN)_2$ groups in that direction, causing the form factor to drop rapidly), nor has the $2k_F$ motion in the a -direction. Clearly a more quantitative calculation of the combined form factors is necessary, as has been done, for example, for KCP [54].

6.4 THE STRUCTURE BELOW 38 K. — In section 5 it was suggested that the structure below 38 K, possessing C2/m symmetry, is complicated, and several alternative structures possessing this symmetry are in principle possible. Therefore, detailed determination of the structure below 38 K may be an extremely powerful (and perhaps decisive) means to determine the hierarchy of interactions between the different degrees of freedom. For this reason, we now elaborate on this question. The material of this section is not essential for the understanding of the rest of this text, and the reader who feels that reading this work is difficult is advised to skip it.

At 38 K, a first-order transition takes place. At this low temperature, due to the large amplitude of ρ_Q and ρ_F the molecules at the dilatation of the longitudinal phonon are spaced far apart and thus can easily slide out of the stack, or librate around the ξ or ζ axes. Another possibility is that the interaction between the CDW's ρ_Q on neighbouring TCNQ stacks is modulated so that

$$V_0 + 2V_1 \cos 2\pi b/A + 2V_2 \cos 4\pi b/A$$

which is small (section 2), alternates in sign, causing the phase shifts between neighbouring TCNQ chains to alternate between 0 and π , following the pattern $++--++--$. Clearly this gives rise to a $4a$ period. Such an alternation could be due to sliding of TCNQ molecules (or chains) in the ξ direction, or to sliding of TTF molecules on alternate stacks in the ζ direction, or to alternation in the amplitude χ_F on *odd* and *even* TTF chains (since the libration on the TTF chain changes the N-S distances in such a way as to increase V_2 and decrease V_0). For example, we could have a pattern

$$\begin{aligned} & -\rho_F, \quad -\rho_Q - \chi_Q, \quad \mathcal{E}_F \pm \rho_F, \quad \rho_Q - \chi_Q, \\ & \rho_F, \quad \rho_Q + \chi_Q, \quad -\mathcal{E}_F \pm \rho_F, \quad -\rho_Q + \chi_Q, \quad -\rho_F \end{aligned} \quad (10)$$

where \mathcal{E}_F describes a transverse phonon in the ξ direction (see table I, and in particular Fig. 10). The $\pm \rho_F$ indicates that the phase of the Peierls distortion on these chains is not determined by the interaction with

the neighbouring chains, and could be random. An alternative pattern is :

$$-\rho_F, -\rho_Q + \chi_Q, \chi_F \pm \rho_F, \rho_Q + \chi_Q, \rho_F, \\ \rho_Q - \chi_Q, -\chi_F \pm \rho_F, -\rho_Q - \chi_Q, -\rho_F. \quad (11)$$

The first pattern makes use of the $\Xi_F \chi_Q$ and $\Xi_F \rho_Q$ interactions, while the second makes use of the $\chi_F \chi_Q$ and $\chi_F \rho_Q$ interactions. We cannot say at this stage which are stronger. For these patterns, the TTF and TCNQ chains behave rather differently, and moreover, there are TTF chains of two types. Clearly, these are not the only possibilities (we chose them because they make use of the $\rho_F \rho_Q$ and $\rho_F \chi_Q$ interactions, which we believe to be the strongest), and the situation may look hopelessly complicated. However, note that the space group of this pattern is C2/m, and this symmetry restricts the number of alternatives severely. Simple molecular models, like that shown in figure 10, may also prove valuable.

These two patterns assume that the primitive cell of the periodic lattice distortion (a term that we use for the ensemble of translations, librations, CDW's, etc.) has the principal axes $(4a, 0)$ and $(0, A)$. In principle, a primitive cell with principal axes $(a, \frac{1}{4}A)$ and $(a, -\frac{3}{4}A)$ also gives a $4a$ period; however, in the first case there is a symmetry reason for the $4a$ period (namely, C2/m), while in the second there isn't, and therefore we would not expect the period $4a$ to be stable over the whole temperature range below 38 K.

Although the proposed space groups at $48 \text{ K} < T < 54 \text{ K}$ and below 38 K are both C2/m, the symmetries of the two patterns are entirely different. At 48 K, the maxima of ρ_Q are at points of type [47] a , i.e. the points $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ of the unit cell describing the distorted state, while the minima are at points of type b , i.e. $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, 0)$; both these points have local symmetry 2/m. The extrema of χ_F are at points of type e , i.e. $(\frac{1}{4}, \frac{1}{4}, 0)$, $(\frac{1}{4}, \frac{3}{4}, 0)$, $(\frac{3}{4}, \frac{1}{4}, 0)$ and $(\frac{3}{4}, \frac{3}{4}, 0)$. These points have local symmetry 1 (as in figure 7, but without the longitudinal displacement). Below 38 K, the extrema of ρ_Q are at points of type g , i.e. $(x, 0, 0)$, $(\bar{x}, 0, 0)$, $(\frac{1}{2} + x, \frac{1}{2}, 0)$, and $(\frac{1}{2} - x, \frac{1}{2}, 0)$. These points have local symmetry 2 (as in figure 8, but with TCNQ instead of TTF molecules; see also figure 10). The nodes of Ξ_F [for pattern (10), or the extrema of χ_F for pattern (11)] for one type of TTF chains are at points of type e (local symmetry $\bar{1}$), and the maxima and minima of ρ_F for the second type of TTF chains are at points of type a and b respectively, i.e. with local symmetry 2/m. Therefore the point-symmetries, and the symmetries of the chains, are entirely different at both temperatures. Note that the coordinates of the points g , in which x is variable (and not determined by symmetry), immediately suggest the possibility of the TCNQ chains sliding sideways.

We suggest that a Ξ mode may exist below 38 K. This mode is invoked, because (a) it is very effective in

modulating S-N distances, (b) it is allowed by symmetry, (c) it is easy to accommodate specially, and (d) it can explain the alternation in the sign of the effective interaction between TCNQ chains. The interaction between χ_Q and Ξ_F is given by :

$$-C \sin 2\pi b/A \cos k_a a/2 \Xi_F \chi_Q \sin \theta \quad (12)$$

where θ is the phase shift between Ξ_F and χ_Q .

Thus it is driven by two χ modes on neighbouring chains of the same phase (and two ρ modes of opposite phase). (See Fig. 10.) The $\sin 2\pi b/A$ term is also instrumental. The jump of χ_F down at 38 K may be very conducive to the buildup of these modes, for the following steric reason. In the undistorted state, two TTF molecules can slide relatively easily along the ξ axis or twist around the η -axis; but once they are twisted, sliding along the ξ -axis is constrained due to sulphur-sulphur steric interference. Thus, just above 38 K the χ mode may prevent the Ξ mode from being excited. Formally, such an effect is described by a $\nu \chi_F^2 \Xi_F^2$ term with positive ν .

7. Conclusion. — The description of the structural transitions in TTF-TCNQ is a rather complicated subject. Each molecule has 6 degrees of freedom for rigid motion, there are 2 molecules per formula unit and 4 per unit cell, and each degree of freedom must be described by a complex order parameter. Within Landau theory, the interactions are not local and the dependence of the interaction energy upon the molecular separation is complicated, yet very important (section 2). Also, the fourth-order terms must be included in the free-energy functional. Therefore, at first sight one would expect a Landau theory, with evaluation of the parameters of the free-energy functional from microscopic theory, to be unmanageable. In this work, we show that with the simplifying assumption of the dominance of N-S interactions, such a description is possible, and is only moderately complicated. Clearly the ultimate test for such a theory is its accord with experiment. In this work, we focus on two experimental properties: The continuous change in transverse period from $2a$ to $4a$, and the $4k_F$ reflections.

The change in transverse period is shown to be due to three factors: (i) The staggered structure, in which close N-S neighbours belong to molecules displaced by a distance b along the chain direction; this makes the interaction between TCNQ molecules on neighbouring chains, at distances $\pm 2b$ along the chain, nearly equal to the interaction with the TCNQ molecule at the same b -coordinate (section 2, figure 3 in particular). (ii) The fact that the conduction band is nearly $\frac{1}{4}$ filled (0.275 filled). This causes the phase of the CDW to change by nearly 180° upon displacement by $2b$, and thus the interactions with TCNQ neighbours at $\pm 2b$ and zero, nearly to cancel (section 2, formula (5), in particular). (iii) The breakdown of up-down symmetry, due to the buildup

of a Peierls distortion on the TTF chains and a libration on the TCNQ chains below 48 K (in addition to the Peierls distortion on the TCNQ chain, and libration on the TTF chain, existing between 48 K and 54 K. Section 5, table II, figure 9, in particular). This establishes a difference between the interaction in the upward direction, V_{+1} , and in the downward direction, V_{-1} , which in turn gives rise to a transverse period between $2a$ and $4a$ [formula (5)].

The experimentally observed approximately linear change of the transverse period with temperature, and the temperature of the jump to $4a$ (38 K), are precisely given by the theory, and the temperature of the commencement of the change in period (48 K) is also reasonably well accounted for by this theory. (Section 5, formula (9) in particular).

The $4k_F$ reflections, observed by X-rays and neutron diffraction, are in the present theory the *fingerprints* of the librations around the axis perpendicular to the molecular plane (or possibly, but less likely, the axis along the molecule). These librations possess a glide-plane symmetry element (section 1, and table I) for which the $2k_F$ reflections are forbidden. (Other modes, such as longitudinal phonons, can account for the observed, but relatively weak, reflections at $2k_F$.)

The dependence of the amplitude of these reflections upon the region in k -space predicted by the present theory (section 6, (c)) has not yet been verified experimentally. In this context, we should be aware that an alternative theory exists [24], which attributes these reflections to very strong correlations caused by intramolecular electron-electron interactions U . (Large U compared with the electronic bandwidth.) Detailed structural work is required to decide between these two competing theories. The importance of the question whether TTF-TCNQ should be described by a *small U* theory [5] (like the present one) or a *large U* theory [55], cannot be overemphasized.

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