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Abstract. — Several parameters of the Landau Free Energy Function of TTF-TCNQ are calculated from the crystal structure taking into account the atomic positions and realistic charge distributions. In particular, the parameters that determine the coupling between charge density waves and rotations (librons) on neighbouring chains are evaluated. The Free Energy Function is solved, and good agreement with the experimental observation of the $2 \alpha$ period between 53 K and 48 K and its variation below this temperature, is obtained. The CDW-libron interaction seems to be responsible for this transverse period. The behaviour of $C_p$ in the vicinity of the two close phase transitions is studied. The Free Energy should possess several (up to four) Lifshitz points, for appropriate values of the parameters.

1. Introduction. — It is known that the organic charge-transfer metal TTF-TCNQ (tetrathiofulvalene tetracyanoquinodimethanide) undergoes a cascade of three nearby phase transitions [1-10]. The first two are second order and occur at the transition temperatures $T_{pl} = 53$ K and $T_{p2} = 48$ K, the third is a first order phase transition and occurs at 38 K. It is believed that the two first transitions can be made to coincide by changing the stoichiometric coefficients in $\text{TTF}_{(1-x)}\text{TSeF}_x\text{TCNQ}$.

In TSeF-TCNQ both transitions apparently coincide at 29 K [11].

In TTF-TCNQ, a charge density wave (CDW) builds up at $T_{pl}$ with a longitudinal period of $\Lambda = 3.39 \text{\textit{b}}$ and a transverse period of $2 \alpha$. At $T_{p2}$ a second CDW appears and the transverse period begins to increase continuously. At the temperature of 38 K, TTF-TCNQ undergoes the third phase transition, where the transverse period jumps to the commensurate value $4 \alpha$ [12].

In this study we discuss only the phase-diagram and other features which are connected with the two nearby higher temperature phase transitions. The Landau theory of the phase transitions was applied to TTF-TCNQ first by Bak and Emery [13], Schultz and Etemad [14], Bjelis and Barisic [15] and more recently by several authors [16, 17, 18, 19]. These authors make use of the symmetry properties of the lattice, and derive those properties that are an essential consequence of this symmetry; namely, the existence of two transition temperatures, $T_{pl}$ and $T_{p2}$, and the change in the transverse period only below $T_{p2}$. However, the amount of information that can be derived from symmetry alone is limited. For example, TSeF-TCNQ which has the same symmetry as TTF-TCNQ, has only one phase transition, and application of small pressure to TTF-TCNQ, which does not change the lattice symmetry, has a drastic effect on the phase diagram. Therefore, symmetry properties alone are not sufficient to give a complete description of these complicated systems, and numerical calculations of the various parameters in the LFEF are necessary. A first step in that direction was made in a previous paper [21] where some of the parameters were estimated from the lattice structure, and the importance of the librational degrees of freedom, already introduced by Morawitz [20], was stressed.

Weger and Friedel [21] showed that the CDW-Libron interaction between nearest chains in the $\alpha^*$-direction should provide the main contribution to the
effective interaction between nearest similar chains; especially when it is realized that the direct Coulomb interaction (DCI) between nearest similar chains should be screened by the interposing chains of the other type.

In ref. [21], 4 order parameters were employed; $\rho_Q$ and $\chi_Q$ for the TCNQ's, and $\rho_F$ and $\chi_F$ for the TTF's. The $\rho_Q(\rho_F)$ parameter describes a distortion which has the symmetry of a longitudinal phonon, namely symmetry group $P2/m$ for an isolated TCNQ(TTF) chain; the $\chi_Q(\chi_F)$ parameter describes a distortion with the symmetry of a libration in the molecular plane, or around the long molecular axis, namely symmetry group $P2/b$ for an isolated TCNQ(TTF) chain.

When we have a LFEF with a given number of order parameters: $F(x_1 \ldots x_n)$, we can always reduce the number of order parameters by algebraic elimination; i.e. solve the equations:

$$\frac{\partial F}{\partial x_i} = 0 \ (i = 1, \ldots, m)$$

and derive from them the $x_i$'s ($i = 1, \ldots, m$) as function of the $x_j$'s ($j = m + 1, \ldots, n$), put the values of the $x_i$ back into $F$, and thus obtain a function $F(x_{m+1}, \ldots, x_n)$ with less variables.

In the present case, we can, for example, eliminate the order parameters $\chi_Q$ and $\chi_F$, and be left with a function $F(\rho_Q, \rho_F)$ which appears to be equivalent to the function used by several authors [13, 14, 15, 16]. If we wish we can go further and eliminate $\rho_F$, obtaining a function $F(\rho_Q)$, or even further, and eliminate $\rho_Q$, obtaining just a number $F$.

The question here is not whether such an elimination is mathematically correct, but whether it is useful and fruitful. When we perform a partial elimination we obtain a function of less variables, which looks at first sight simpler. However, we also lose in the process.

First, the coefficients of the bare LFEF can be calculated (or at least estimated) from first principles. We calculate a few parameters in this work. In contrast, the coefficients of the reduced LFEF must be fitted to experiment, and be regarded as no more than a representation of experimental results, or, alternatively, be calculated from the coefficients of the bare LFEF as we do here. Thus, for any linkage with an ab-initio consideration, the bare coefficients are essential.

Second, the coefficients of the reduced LFEF become complicated functions of temperature, pressure, and the other variables. They may even be non-analytic functions. The coefficients of the bare LFEF are much more nearly constant. Thus, if we try to take into account the complicated temperature, pressure, etc., dependence of these coefficients, say by some power series expansion, we actually end up with more adjustable parameters than there are in the bare LFEF, and the description is much more complicated.

Third, the order parameters of the bare LFEF are very simply related to measurable quantities such as molecular translations and rotations, phonon frequencies [22], etc. Thus we can make use of available experimental data, and we can make predictions that could not be made from the reduced LFEF. For example the detailed theory of the conductivity in the metallic state [23] is a direct outcome from the bare LFEF, which demonstrated the importance of the libron degree of freedom.

Because of the very large number of order parameters, the LFEF contains, in principle, a very large number of terms. Even if only nearest neighbour chain interactions within the a-b plane are included (Fig. 1), and only one type of translation and one type of rotation in each chain are considered, there are about 50 terms up to the 4th order. Therefore, by appropriate choice of the parameters, just about any result can be obtained. In order that the results be meaningful, the parameters in the LFEF must be estimated from ab-initio considerations (i.e. the crystal structure, the various microscopic constants, etc.) rather than arbitrarily fitted by experiment. Of course, it is a very hard task to fulfill such a program for as complicated a system as TTF-TCNQ in a rigorous way. Here we limit ourselves to the monopole-monopole electrostatic interactions and the simple mean field (MF) approach as the first step to more comprehensive ab-initio calculations.

The shaded molecules have their centroids at $x = a/2$ (from Kistenmacher et al. [56]).

**Fig. 1.** — a) A view of the crystal packing in TTF-TCNQ. The shaded molecules have their centroids at $x = a/2$ (from Kistenmacher et al. [56]). b) Definition of the molecular axes.

In our preliminary short report [24] we used the CDW-libron interaction model of Weger and Freidel [21] in which the extra charge of the TCNQ$^{-0.6}$ (TTF$^{+0.6}$)

$$\text{TCNQ}^{-0.6} \ (\text{TTF}^{+0.6})$$
molecule was located only on the nitrogens (the sulphur and end carbon) atoms. In this paper we also use another model with the more realistic picture of the charge distribution, based on the charge distribution calculations of Ladik et al. [25] for the TCNQ, TCNQ\(^-\), TTF\(^+\) and TTF molecules. The two models are compared in section 5 and the importance of the intramolecular screening for the case of the second model is discussed.

The paper is organized as follows:

In section 2 we discuss the elementary solutions of the LFEF and show the temperature dependence of the order parameters, the transverse period and the heat capacity for various sets of the LFEF interaction parameters.

In section 3, we estimate the value of the LFEF parameters for the CDW-libron [21] model and the direct Coulomb interaction parameters are considered in section 4. In section 5 the values of the parameters used in the numerical calculations are compared with the estimates of the preceding sections. The validity of these estimates is discussed. In section 6 we show that two (or four) Lifshitz points [26] may appear on the phase diagram of the TTF-TCNQ system and discuss some features of this phase diagram. Details of the calculations are presented in Appendices I and II.

It is worthwhile to note that TTF-TCNQ is one of the several systems in which phase transitions occur at very nearby temperatures. For example, in V\(_3\)Si, a displacive phase transitions occurs at \(T_M = 22\) K and a superconducting one at \(T_s = 17\) K [27]. Under pressure, \(T_M\) and \(T_s\) approach until they coincide at about 35 kbar [28, 29]. \(T_M\) is, strictly speaking, a first order transition, however, its latent heat is very small, and it is close to a second-order one.

In dichalcogenides, like NbSe\(_2\), a CDW builds up at \(T_p = 26\) K and superconductivity at \(T_c = 7\) K, under pressure, \(T_p\) and \(T_c\) can be made to coincide [30]. In all these systems, we deal with two order parameters which are weakly coupled. In the two above-mentioned cases, this is because they characterize different physical properties. The closeness of the two transition temperatures may either be accidental (due to appropriate choice of external parameters-like pressure, for instance), or due to some complicated physical reason, such as the degeneracy of \(T_p\) and \(T_c\) in quasi-1d-systems suggested by Bychkov et al. [31]. The closeness of the two phase-transitions \(T_{p1}\) and \(T_{p2}\) in TTF-TCNQ and their interdependence is discussed here.

2. Elementary solution of the free energy function.

In this section we discuss the general picture of the phase transitions in TTF-TCNQ as it follows from the solutions of the LFEF suggested by Weger and Friedel [21] and completed here with the nearest similar chains DCI.

The simplified LFEF has the form:

\[
F = A_{11}(T) \rho_Q^2 + C_{11} \rho_Q^2 + A_{22}(T) \rho_F^2 + C_{22} \rho_F^2 + A_{33} \lambda_Q^2 + A_{44} \lambda_F^2 - 2 A_{12} u
\]

\[
- \rho_Q \rho_F - 2 A_{34} \sqrt{(1 - u^2)} \rho_Q \lambda_F
\]

\[
- 2 A_{23} \sqrt{(1 - u^2)} \rho_F \lambda_Q
\]

\[
- A_{14}[1 - 2 \sqrt{(1 - u^2)}] \rho_Q^2 - A_{22}[1 - 2 \sqrt{(1 - u^2)}] \rho_F^2
\]

(1)

where the indices 1, 2, 3 and 4 correspond to the order parameters \(\rho_Q\), \(\rho_F\), \(\lambda_Q\) and \(\lambda_F\) respectively.

\[
u = \cos \frac{q_a a}{2}
\]

where \(q_a\) is the wave number in the \(a\) direction transverse to the stack direction. \(A_{12}\) is the CDW-CDW coupling parameter between nearest chains, \(A_{14}\) and \(A_{23}\) are the coupling parameters of the CDW-libron interaction for nearest chains and \(A_{14}[a]\) and \(A_{22}[a]\) are the direct coupling parameters for nearest similar TCNQ and TTF chains respectively. The LFEF represents a two-dimensional model of quasi one dimensional conductors composed of weakly coupled chains. The order parameters fields are of the form

\[
\eta_i(x, y) = \eta_i \exp[i(2\pi y/A + q_a x + \phi_i)]
\]

where \(i = 1, 2, 3, 4\).

The interactions in the \(c^*-\)direction are neglected [21]. We do not include in eq. (1) the libron-libron interaction term \((\propto A_{34} \lambda_Q \lambda_F)\). Several fourth order terms are also neglected.

The second order phase transitions found in TTF-TCNQ are of the Peierls type [32-34] whose order parameter may be defined in several ways. It may be defined as the gap in the one-electron spectrum; it may be defined as the amplitude of the charge density wave, i.e., the variation in the charge of the molecules; or, it may be defined as some specific displacement of the molecules. All these definitions are equivalent, however, in order to assign well-defined numerical values to the parameters of the LFEF, we have to agree on some convention. In the present work, we define the order parameters \(\rho_Q\) and \(\rho_F\) as the molecular centre of gravity displacement in the \(b\)-direction in units of \(1/100\) Å. Some of the condensation energy of the Peierls transition is due to coupling with intramolecular modes, such as CN, CC, and CS stretching modes [35]. However, we still do not know the relative contribution of these modes to the condensation energy. Also, transverse phonons polarized in the \(c^*-\)direction, are coupled strongly to the Peierls distortion, in addition to longitudinal ones [36] (polarized in the \(b\)-direction). In an \textit{ab-initio} calculation of the Peierls transition temperature, all these modes must be taken into account. However,
here we use the experimental value of $T_{pi}$, $i = 1, 2$
and estimate from it the effective electron phonon
coupling constant $\lambda$. Therefore, we express the order
parameter of the Peierls transition in terms of one
mode only — say the longitudinal phonon — since
this is the mode that (probably) couples most strongly
with the conduction electrons. The actual amplitude
of displacement should not be too different (within a
factor of 2 or 3) from that calculated on the basis of
exclusive coupling with this mode. Since the definition
of the order parameter is a matter of convention, the
value of the free energy, its derivatives (i.e. specific
heat), etc., will not depend on this choice.

Weger and Friedel [21] pointed out that the $\eta$
liberations (i.e. librations in the molecular plane)
are most effective — from the geometrical point of
view — in producing the N-S and the N-C distance
modulation, but we show in section 3 that for TCNQ
molecules the $\zeta$-libration (i.e. a libration around the
long molecular axis) (see Fig. 1b) must also be taken
into account. Therefore in this paper $\chi_{pi}$ is a pure $\eta$
type libration and $\chi_{Q}$ is a linear combination of $\eta$ and $\zeta$
liberations, as defined in section 3.

To establish the appropriate phase diagram for
our system, we use here the usual mean field approach
and neglect the temperature dependence of all the
coefficients in eq. (1) except for $A_{11}(T)$ and $A_{22}(T)$.
(See, however, the discussion concerning the tempera-
ture dependence of the $A_{14}$ and $A_{23}$ parameters
in section 3 and section 5.) For these two coefficients we assume that in the vicinity of the unrenormalized
Peierls transition temperature $T_i (i = 1, 2)$ of the
uncoupled chains

$$A_{ii} = \alpha_0 (T - T_i)/T_i .$$

We use the minimum conditions

$$\frac{\partial F}{\partial \eta_i} = 0, \quad i = 1, 2, 3, 4, \quad \text{and} \quad \frac{\partial F}{\partial u} = 0$$

(3)

to find the transition temperatures $T_{pi}$ and $T_{p2}$ of the
weakly interacting subsystems $(\rho_{Q} \chi_{p})$ and $(\rho_{F} \chi_{Q})$
into which the LFEF naturally divides when $A_{12} = 0,$
and the temperature dependence of the order param-
eters $\eta_i = \eta_i(T)$ and of the transverse period
$u = u(T)$.

The solution of eq. (3) gives the following connec-
tion between the order parameters and the parameter $u$

$$\chi_{p} = (A_{14}/A_{44})^2 \rho_{Q}^2 (1 - u^2)$$

(4a)

$$\chi_{Q} = (A_{23}/A_{33})^2 \rho_{F}^2 (1 - u^2)$$

(4b)

$$u = A_{12} \rho_{Q} \rho_{F} [(A_{14}^2/A_{44} + 2 A_{11}[a]) \rho_{Q}^2 +
+ (A_{23}^2/A_{33} + 2 A_{22}[a]) \rho_{F}^2] , \quad u < 1 .$$

(4c)

Using eq. (4a) and eq. (4b) the libration order param-
eters may be eliminated from eq. (1) and eq. (1)
may be cast in the form

$$F_{eff} = [A_{11}(T) - A_{11}[a] - A_{14}^2/A_{44}] \rho_{Q}^2 +
+ [A_{22}(T) - A_{22}[a] - A_{23}^2/A_{33}] \rho_{F}^2
- 2 A_{12} u \rho_{Q} \rho_{F} + [2 A_{11}[a] + A_{14}^2/A_{44}] u^2 \rho_{Q}^2
+ [2 A_{22}[a] + A_{23}^2/A_{33}] u^2 \rho_{F}^2 + C_{11} \rho_{Q}^2 + C_{22} \rho_{F}^2$$

(1a)

which is valid when the conditions

$$\frac{\partial F}{\partial \chi_{p}} = \frac{\partial F}{\partial \chi_{Q}} = 0$$

are fulfilled (with $\partial^2 F/\partial \chi_{p}^2,$ $\partial^2 F/\partial \chi_{Q}^2 > 0$). Eq. (1a)
has the same form as the equation used, for instance,
by Bjelis and Barisic [15]. Thus, their formulae for the
phase temperature renormalization and for the phase
transition lines (see eqs. (6)-(10) in ref. [15]) apply also
here with the following correspondence between the
parameters of LFEF

$$A_{11}[a] \leftrightarrow A_{14}/A_{44} \leftrightarrow A_{11}[a] + A_{14}^2/A_{44}$$

(5a)

$$A_{22}[a] \leftrightarrow A_{23}/A_{33} \leftrightarrow A_{22}[a] + A_{23}^2/A_{33}$$

$$2 A_{11}[a] \leftrightarrow A_{14}/A_{44} \leftrightarrow 2 A_{11}[a] + A_{14}^2/A_{44}$$

$$2 A_{22}[a] \leftrightarrow A_{23}/A_{33} \leftrightarrow 2 A_{22}[a] + A_{23}^2/A_{33}$$

(5b)

Here the first column corresponds to the DCI between
nearest similar chains only, the second — to the
CDW-libron nearest different chains only and the
third column corresponds to the case when both
interactions are significant. Thus, we see that the
CDW-libron interaction between the nearest chains
provide an effective coupling between the next-nearest chains. The question arises: which coupling is dominant?

We show further that if the screening effect somewhat diminishes the DCI terms \( A_{11} \) and \( A_{22} \), the only mechanism which is responsible for the transverse ordering in TTF-TCNQ is the CDW-libron interaction. In any case, the renormalization of the next nearest chains interaction due to the CDW-libron coupling is an important factor in building up the transverse period (see section 5). The neglect of the interaction between the CDW in one type of chains with transverse phonons in the chains of the second type was justified by Weger and Friedel (see Table I of reference [21]). Transverse phonons polarized in the \( x \)-direction do not couple with a CDW in the neighbouring chain for a quarter filled band (the interaction coefficient includes a factor \( \cos(q_x b) \) that is zero for such a filling) and the coupling must be small for a 0.59 electron per atom filling. The opposite is true for the interaction between transverse phonons polarized in the \( z \)-direction with CDW in the neighbouring chains. Its interaction coefficient is proportional to \( \sin(q_x b) \), which is maximum for a quarter filled band. Moreover, the corresponding term in the LFEF contains a factor \( \sin(q_x a/2) \) instead of \( \cos(q_x a/2) \) appearing in the CDW-libron interaction terms. The former would lead to an \( \langle a \rangle \) period instead of a \( \langle 2a \rangle \) period in the 48 K-53 K temperature range. In order to fully justify the neglect of the transverse phonon (\( z \)-polarized)-CDW interaction we estimated its coefficient \( A_{1z} \) in the same way as we did with \( A_{14} \) and we obtained \( A_{1z} = 0.011 \text{ meV}/(10^{-2} \text{ Å})^2 \). The right comparison must be done between

\[
A_{1z}/A_{2z} = 0.002 \text{ meV}/(10^{-2} \text{ Å})^2
\]

\( A_{2z} = 0.062 \text{ meV}/(10^{-2} \text{ Å})^2 \) is the force constant obtained from reference [55] and (see Table VI)

\[
A_{14}^2/A_{44} = 0.060 \text{ meV}/(10^{-2} \text{ Å})^2.
\]

The former is 30 times smaller than the latter and its neglect is fully justified. This argument does not apply to coupling with the transverse phonon polarized in the \( cs^* \)-direction on the same chain since this phonon has the same symmetry as the longitudinal one, the coupling is strong, as seen by the diffuse X-ray and neutron diffraction work. For the sake of simplicity and because of the correspondence relation, eq. (5), in the following we shall use the second column of eq. (5) only.

For the temperature range \( T < T_{p2} \), we obtain

\[
\rho^2_b \approx \frac{\alpha_{22}}{2(C_{22} + \Delta C_{22})} \frac{(T_{p2} - T)}{T_2} \quad (7a)\]

\[
\Delta C_{22} = A_{11}^2 \left( \frac{A_{23}^2/A_{33}}{A_{11}^2/A_{44}^2} \right) \frac{1}{\rho_0^2(T_{p2})} \quad (7b)
\]

Eq. (7a) is only valid to first order in \( (T_{p2} - T) \). \( \Delta C_{22} \) is a renormalization of the fourth order term in \( \rho_F \). Eq. (4c) which is exact, shows us that the stabilization of the parameter \( u \) at zero in the temperature range \( T_{p2} \leq T \leq T_{p1} \) is due to the CDW-libron interaction (the \( A_{14} \) term in eq. (1)) and that the deviation of the parameter \( u \) from zero is caused by the inter-subsystem interaction (the \( A_{12} \) term in eq. (1)). The neglected bilinear libron-libron parameter (a \( A_{14} u_{Q1} T_F \) term in the energy) has the same role as the CDW-CDW parameter \( A_{12} \), thus it can be absorbed in this parameter, as long as it is not too strong.

The transition temperatures, for the region where \( T_{p1} > T_{p2} \) [15] are equal to:

\[
T_{p1} = T_1 + \Delta T_1, \quad \Delta T_1 = T_1 \frac{\alpha_{14}^2}{A_{14}/A_{44}} \quad (8a)
\]

\[
T_{p2} = T_2 + \Delta T_2 + \Delta T', \quad \Delta T_2 = T_2 \frac{A_{23}^2/A_{33}}{A_{11}^2/A_{44}^2} \quad (8b)
\]

\[
\Delta T' = T_2 \left( \frac{\alpha_{14}^2}{A_{14}/A_{44}^2} \right) \quad \Delta T' = T_1 T_2 W/\Delta T_1, \quad W = A_{12}^2/\alpha_{11}^2 \quad (8c)
\]

Eq. (8a) gives us the renormalization of the first transition temperature due to the CDW-libron interaction. This renormalization is always positive. Eq. (8b) contains, in addition to the CDW-libron renormalization \( \Delta T_2 \), a second renormalization \( \Delta T' > 0 \) due to the inter-subsystem coupling. From eq. (8)

\[
\Delta T_2 \propto \frac{A_{14}}{A_{44}^2} \quad (8c)
\]

and depends therefore upon the electron-libron renormalization in the first subsystem. Generalization of eq. (8) to the case of the \( A_{14}^2(A_{23})_p \) parameter depending upon \( T \) is discussed in section 3 (eq. 27)).

A feature of the phase diagram follows from the fact that \( u \) must be less or equal to one. If for some set of parameters of the LFEF \( u > 1 \) solution is obtained from eq. (3), those equations must be replaced by

\[
\frac{\partial F}{\partial n_i} \bigg|_{u=1} = 0 \quad i = 1, 2, 3, 4 \quad \frac{\partial F}{\partial u} \bigg|_{u=1} < 0 \quad (9)
\]

These equations may define a new phase for which \( u = 1, \alpha_Q = \alpha_F = 0 \) and the PLD amplitudes (\( \rho_D \) and \( \rho_F \)) are non-zero. The zero of the libron order parameters follows from eq. (1) in which the electron-libron coupling disappears for \( u = 1 \). We discuss this case in section 4.
The numerical solution of the LFEF for the CDW-libron interaction only (eq. (1) with $A_{11}[a]=A_{22}[a]=0$) is presented here for three sets of parameters $A_{12}$, $A_{14}$, and $A_{23}$. These three sets (see Table VI) fit the temperature dependence of the transverse period but they give different results for the order parameter amplitudes and for values of the specific heat jump at $T_{P}=53$ K. A more detailed comparison between these sets of parameters is made in section 5.

Figure 2 represents the temperature dependence of the longitudinal order parameters. $\rho_2^L$ behaves according to classical Landau theory. The experimental value, derived from the intensity of neutron diffraction lines, shows some saturation, probably due to higher order terms. We feel that these agreement with the present crude theory and experiment is about as good as could be expected. $\rho_2^L$ has a pronounced non-linear component near $T_{P2}$ due to the closeness of $T_{P2}$. Figure 3 illustrates the temperature dependence of the libron order parameters. We note that the value of $\gamma_F$ at 38 K means a linear deviation of the sulphur atom in the TTF-molecule $\delta R_s \approx 1 \times 10^{-2}$ Å which is comparable with the longitudinal displacement $\rho_F$. The magnitude of the rotation at 0 K is smaller by a factor of 10 from the values measured by Johnson and Watson [37] in TTF$_{1.5}$.

Figure 4 shows the good fit of the transverse period $q_a=2\pi/\lambda$ as function of temperature to the experimental points.

The heat capacity was also calculated and figure 5 shows its temperature dependence. Between 53 K and 48 K we have the usual mean field behaviour, but under 48 K $C_v$ increases with decreasing temperature and a broad maximum (Fig. 5c) appears. This unusual behaviour can be readily understood if eqs. (4a), (4b) and (4c) are used to rewrite the free energy of eq. (1a) in the following form:

$$F = F_1(\rho_2) + F_2(\rho_F) = \frac{A_{12}\rho_2^4}{A_{14}} + \frac{A_{23}\rho_F^4}{A_{33}}$$

where

$$F_1(\rho_2) = \alpha_{11} \frac{(T - T_1 - \Delta T_1)}{T_1} \rho_2^4 + C_{11} \rho_2^4$$

$$F_2(\rho_F) = \alpha_{22} \frac{(T - T_2 - \Delta T_2)}{T_2} \rho_F^4 + C_{22} \rho_F^4$$

are the classical free energies of the $(\rho_2 \chi_F)$ and $(\rho_F \chi_Q)$ subsystems respectively. The third term in eq. (10a) represents an effective interaction between those two subsystems. In the 48 K-53 K temperature range $\rho_F = 0$, $F = F_1(\rho_2)$ and the classical solution is obtained for the free energy. Below 48 K the series

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**Fig. 2.** — The longitudinal displacement amplitudes of the PLD in each type of chains versus temperature obtained by solving the minimum conditions for the LFEF with the corresponding sets of interaction parameters listed in table VI.
expansion of the free energy in powers of \((T_{p2} - T)\) may be obtained for the case

\[
(T_{p2} - T) \ll (T_{p1} - T_{p2})
\]

\[
F = F_0(T) - \frac{a}{2} (T - T_{p2})^2 + \frac{b}{3!} (T - T_{p2})^3 + \cdots
\]

\[
a, b > 0, \quad T < T_{p2}
\]  

(11)

where \(F_0(T)\) is the free energy for \(T \geq T_{p2}\). The coefficient of the quadratic term may be obtained with the help of eqs. (7) and (10b) and (10c). This coefficient is equal to

\[
a = \frac{\sigma_{22}^2}{2(C_{22} + \Delta C_{22}) T_{p2}^2}
\]  

(12)

and is small when \(T_{p1}\) and \(T_{p2}\) are close (see eq. (7b)) and the third order term becomes important. The specific heat below the second phase transition is

\[
C_p(T) = C_{p0}(T) + aT - bT(T - T_{p2}) + \cdots
\]  

(13)

where \(C_{p0}(T)\) is the specific heat above the phase transition.

---

Fig. 3. — The rotational (libronic) order parameters versus temperature for the corresponding three sets of interaction parameters.

Fig. 4. — Transverse period versus temperature. The experimental points are from Ellenson et al. [58]. The continuous curve corresponds to the parameters of the set \(a\) of table VI and the broken line to those of the set \(c\).
From eq. (13) we conclude that the heat capacity jump $\Delta C_p(T_{p2})$ at the second phase transition is equal to

$$\Delta C_p(T_{p2}) = a T_{p2} \propto (T_{p1} - T_{p2})$$  \hspace{1cm} (14)

and it is small when $T_{p2}$ is close to $T_{p1}$.

Below the second phase transition when the $a$-term in eq. (13) is sufficiently small the derivative of $C_p$ at $T_{p2}$ is negative and a broad maximum appears due to the third term in eq. (13). We note that two above-mentioned facts are not specific for our particular model but are the peculiar features of the MF model for two nearby second order transitions.

In the recent measurements of the heat capacity [38] an additional maximum was found at $T \approx 46$ K. The origin of the maximum may well be identified with the closeness of the two successive phase transitions in TTF-TCNQ (see Fig. 5). However, we were not able to obtain a maximum at 46 K by changing three interaction parameters only (see discussion in the end of section 5).

Recently, Craven et al. [3] noted that MF theory does not account quantitatively for the jump of the specific heat at $T = 53$ K. They measured

$$\Delta C_p = 0.3 \ k_F$$

while the MF theory predicted

$$\Delta C_p \approx 10 \ \frac{N(\epsilon_F)}{N}(k_B T_1) \ k_B \approx 0.08 \ k_B \text{ for } T_1 = 53 \text{ K}.$$  

The enhancement of $\Delta C_p$ can be readily understood if we note that the quartic coefficient $C_{11} \propto T^{-2}$, and that $T_{p1} = T_1 + \Delta T_1$ rather than $T_1$ must be used in its evaluation. When the corresponding changes are made in the $\Delta C_p$ formula, we get

$$\Delta C_p = 10 \ \frac{N(\epsilon_F)}{N}(k_B T_{p1}) \left( \frac{T_{p1}}{T_1} \right)^2 \ k_B$$  \hspace{1cm} (15)

and a bare transition temperature $T_1 \approx 27$ K can account for the $\Delta C_p$ enhancement.

3. Estimation of the parameters of the free energy function. — In this section we present the calculations of the parameters of the LFEF of eq. (1). As was already mentioned, the microscopic theory of the Peierls transition for the specific case of TTF-TCNQ must include the interaction between conduction electrons and at least four phonon modes.

We aim to express all the parameters in eq. (1) via a set of the microscopic quantities such as longitudinal phonon and libron frequencies $\omega_i$ ($i = 1, 2$ for the longitudinal phonons and $i = 3, 4$ for the librons), the electronic density of states $N(\epsilon_F)$, appropriate matrix elements of the interaction, etc. Up to now, however, such a theory has not yet been developed.
and we approach the problem using the mean field approximation \cite{33, 34, 39, 40, 41, 42} to estimate the parameters $a_{ij}, C_{ij}$ ($i = 1, 2$) and we generalize these theories to estimate the CDW-libron coupling $A_{14}$ and $A_{23}$ and the CDW-CDW $A_{12}$ coupling. The elastic libron parameters $A_{33}$ and $A_{44}$ are estimated using the experimental data on the X-ray Debye-Waller factor \cite{23}, the unrenormalized transition temperatures $T_1$ and $T_2$, eq. (2), are obtained from eqs. (8a), (8b) using the experimental values $T_{pi} = 53$ K and $T_{p2} = 48$ K.

To describe the high-temperature phase transition in TTF-TCNQ (an ordering of the $(\rho_{Q}, \chi_F)$ subsystem) we add to the Frohlich Hamiltonian the electron-libron interaction with the TTF $\eta$-libron mode \cite{21}.

The Hamiltonian which leads to the Peierls transition of the $(\rho_{Q}, \chi_F)$ subsystem has the form

$$H = H_e + H_{ph} + H_{e-ph}^{\text{lib}} + H_{e-ph}^{\text{long-lib}}$$

(16)

where the first two terms are the kinetic energy of the electrons and the energy of the phonons. The essential part of the last two terms may be written as follows

$$H_{e-ph}^{\text{lib}} + H_{e-ph}^{\text{long}} = \int dx \, dy \psi^*(x, y) \psi(x, y) \times \left[ g_{11}(q) \left( b_q + b^+_q \right) + g_{14}(q) \left( a_q + a^+_q \right) \right] e^{iq \cdot x}$$

(17)

where the $q$-components are $2 k_F$ along the chains and $q_a$ along the $x$-direction (alternating chains). $g_{11}$ and $g_{14}$ stand for the electron-longitudinal phonon and the electron-libron coupling constants, respectively. $\psi(x, y)$ is the electron wave fields, the operators $b_q$ and $a_q$ destroy a longitudinal phonon and a libron, respectively.

We define now the order parameter as half the gap in the electronic spectrum of the TCNQ chains

$$A_i = \left[ g_{11}(q) \left( b_q + b^+_q \right) + g_{14}(q) \left( a_q + a^+_q \right) \right] \times e^{iq \cdot x} = A_{11} + A_{14}.$$  

(18)

This order parameter replaces the ABB \cite{39} order parameter (our $A_{11}$). Further, we may follow the previous work \cite{39, 40} and obtain for the free energy the expression

$$F \approx \frac{N_1(\epsilon_F)}{\lambda_{11}} \left| A_{11} \right|^2 + \frac{N_1(\epsilon_F)}{\lambda_{14}} \left| A_{14} \right|^2 + \frac{N_1(\epsilon_F)}{\lambda_{11}} \left( a_{11} \left| A_{11} \right|^2 + 2 \text{Re} \left( A_{11} A_{14}^* \right) + \left| A_{14} \right|^2 \right) + b_{14} \left| A_{14} \right|^4 + \cdots$$

(19)

where the first two terms are the elastic energies and the other terms appear from the expansion of the electronic part of the free energy in powers of the order parameter. The dimensionless interaction parameters are

$$\lambda_{11} = 2 N_1(\epsilon_F) g_{11}^2(q)/h \omega(q) \quad i = 1, 4$$

(20)

and $\omega_i(q)$ is the phonon (libron) frequency, $N_1(\epsilon_F)$ is the density of states for one spin direction.

We assume that the conduction electron coupling to the longitudinal phonons is much larger than to librons so the longitudinal phonons go soft first and drive the Peierls transition. In the absence of librons the Peierls temperature $T_1$ would be the solution of the equation

$$\frac{1}{\lambda_{11}} = - \frac{1}{N_1(\epsilon_F)} a_q(T_1), \quad T_1 = K_{14} \epsilon_F \exp(-1/\lambda_{11})$$

(21)

where $K_{14} = 2/4$ depending upon the electron band model \cite{39, 40, 41, 42} ($K_{14} = 2.28$ for the one-half filled band and $K_{14} = 4$ for the free-electron model), and the interference term in eq. (19) renormalizes this temperature (see eq. (8a)). To compare eq. (19) with eq. (1) we note that the displacements $\rho_Q$ and $\chi_F$ are connected to the order parameters by the equations

$$\rho_Q = \frac{|A_{11}|}{g_{11}(q)} \left( \frac{\hbar}{2 M_1 N \omega_1(q)} \right)^{1/2}$$

$$\chi_F = \frac{|A_{14}|}{g_{14}(q)} \left( \frac{\hbar}{2 I_4 N \omega_4(q)} \right)^{1/2}$$

(22)

where $M_1$ is the TCNQ molecular mass and $I_4$ is the moment of inertia of the TTF molecule around the $\eta$-axis and $N$ is the number of cells along the $y$-axis. Noting that

$$N_1(\epsilon_F) / \lambda_{11} = - N_1(\epsilon_F) \ln T_1 / T_1$$

we obtain for the coefficients of the LFEF, eq. (1) :

$$\alpha_{11} = N M_1 \omega_1^2(q) \lambda_{11}$$

(23)

$$C_{11} = \frac{N}{2} K_2 \cdot \left( M_1 \omega_1^2(q) \lambda_{11} \right)^2$$

(24)

where the coefficient $K_2$ depends upon the electron band model. Eq. (24) follows from the explicit expression for $b_q$, eq. (17) in ref. \cite{39} where $K_2 = 0.106$. The $\rho_Q \chi_F$ term in eq. (1) appears in eq. (19) in the form $2 a_q(T) \text{Re} \left( A_{11} A_{14}^* \right)$. In the first approximation we put $a_q(T) \approx a_q(T_1) = - N_1(\epsilon_F) / \lambda_{11}$ (see eq. (19)). Using eq. (22) we obtain by comparison with eq. (1) :

$$|A_{14}| = N \omega_4(q) \omega_4(q) \left( \frac{\lambda_{14}}{\lambda_{11}} M_1 I_4 \right)^{1/2}$$

(25)

where $\lambda_{14} = \lambda_{14}(1 - u^2)$. 將這個方程式進行適當的簡化和約略後，可得到最優化的結果。
The parameter $A_{14}$ determines the renormalization of the transition temperature, eq. (8a). If the renormalization $\Delta T_1$ is large, the temperature dependence of $A_{14}$ in the interval $T_1 < T < T_{pl}$ cannot be neglected. In this case we obtain instead of the eq. (25) the following expression

$$A_{14}(T) = Na(T) \omega_1(q) \omega(q) \times \left( \frac{\lambda_{11} A_{14}}{\lambda_{11} M_{1} L_{D1}^{1/2} / N_{1}(\epsilon_{F})} \right)$$

(25a)

where $a(T)$ is a known function (essentially for $T \ll \epsilon_F$, $a(T) \sim \ln \epsilon_F / T$ [39, 40, 42]). For the phase transition temperature $T_{pl}$ we now have a transcendental equation

$$T_{pl} = T_1 + \frac{A_{14}^2(T_{pl})}{\lambda_{11} \alpha_{14}}$$

(26)

where $A_{14}(T_{pl})$ is defined in eq. (25a). For a given renormalization of the phase transition temperature $\Delta T_1$ we may make a crude estimate of the ratio where $A_{14}^0$ now is for the value of $A_{14}$ from eq. (25). With the approximation

$$a(T) \approx -\frac{N_{1}(\epsilon_{F})}{\lambda_{11}} + \frac{N_{1}(\epsilon_{F}) - T - T_1}{T_1}$$

we obtain the crude estimate

$$A_{14}(T_{pl}) / A_{14}^0 \approx 1 - \frac{\Delta T_1}{T_1}$$

(27)

and conclude that $|A_{14}(T_{pl})| < |A_{14}^0|$. We use eq. (27) in our discussion on the parameters of the LFEF in section 5.

For numerical estimates we use for $g_{14}$ the explicit expression

$$g_{14}(q) = \left( \frac{\hbar}{2 I_{m} \omega_4(q)} \right)^{1/2} M_{14}(q)$$

(28)

where $M_{14}(q)$ is the matrix element of the potential on one electron produced by the libration of a TTF molecule

$$M_{14}(q) = \int d^3r \psi_{1+q}^* \left( r \right) \frac{\partial V(r, \chi_F)}{\partial \chi_F} \bigg|_{\chi_F = 0} \psi(r).$$

(29)

The calculation of the matrix element $M_{14}$ was performed for the two above mentioned models of the charge distribution. In the first one we assumed the TCNQ molecular wavefunction of the conduction electron to be localized on the nitrogens, while the net charge of TTF$^{+0.6}$ molecule was concentrated at the sulphurs [21]. When the nearest neighbour interaction is taken into account the matrix element is given by

$$M_{14}(q) = 4 \sqrt{1 - u^2} \sin \left( \frac{2 \pi}{A} b \right) e |c_N|^2 \frac{\partial V}{\partial \chi_F}$$

(30a)

where

$$\frac{\partial V}{\partial \chi_F} = \sum_j e_j \frac{\partial R_{Nj}^{-1}}{\partial \chi_F}$$

is the electrostatic potential at the nitrogen atom due to the net charge of the sulphur atom, $c_N$ is the LCAO coefficient of each of the nitrogens atoms in the molecular wavefunction (I $c_N|^2 = 0.25$), $z_N$ is the net charge at the sulphur atoms ($z_N = 0.6 \times 0.25$), $R_{Nj}$ is the distance between nitrogen and sulphur atoms, $\sin \left( \frac{2 \pi}{A} b \right) \approx 1$ and the factor 4 appears when summing over the four bridges with the four nearest TCNQ molecules (see Fig. 12). This NS contribution leads to a rather small value of the $A_{14}$ interaction parameter because the centre of the TTF molecule, the N and the S atoms are almost colinear and the motion of the sulphur is almost perpendicular to the NS distance. Therefore, also the end carbon atoms must be included and the $A_{14}$ parameter is determined by the electrostatic potential

$$\frac{\partial V}{\partial \chi_F} = e \left( \frac{z_N}{\chi_F} \frac{\partial R_{NS}^{-1}}{\partial \chi_F} + z_c \frac{\partial R_{NC}^{-1}}{\partial \chi_F} \right).$$

The value of $A_{14}$ (NS only) appearing in table IV was calculated supposing that the net charge in TTF is equally distributed between sulphurs and end carbons ($z_N = z_c = 0.6 \times 0.125$).

We also calculated the $M_{14}(q)$ matrix element taking into account the interaction between the sulphurs and end carbons of the TTF molecule with all the nitrogens in the four nearest TCNQ chains. The summation along these chains diminishes the $A_{14}$ parameter in comparison with the nearest neighbour calculation scheme by 20-30 % (See Appendix I and table IV).

In the second model we allow the charge to be spread over the entire molecule. Eq. (30a) is readily generalized and it becomes

$$M_{14}(q) = 4 \sqrt{1 - u^2} \sin \left( \frac{2 \pi}{A} b \right) \sum_i e_i |c_i|^2 \frac{\partial V_i}{\partial \chi_F}$$

(30b)

where $c_i$ are the normalized expansion coefficients of each atomic function in the LCAO molecular wavefunction $\sum_i |c_i|^2 = 1$, and

$$\frac{\partial V_i}{\partial \chi_F} = \sum_j e_j \frac{\partial R_{ij}^{-1}}{\partial \chi_F}$$

is the electrostatic potential at the $i$-th atom of the TCNQ molecule due to net charges

$$z_j \left( \sum j z_j = \text{charge transfer} \right)$$

of the atoms of the TTF molecule. We note the difference between the orbital charge density, which is the
Table 1. — Physical constants appearing in different equations of this paper.

<table>
<thead>
<tr>
<th>Magnitude</th>
<th>Symbol</th>
<th>TCNQ</th>
<th>TTF</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal phonon frequency [55]</td>
<td>$\omega_l(2k_F)$</td>
<td>60</td>
<td>60</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>Molecular mass [56]</td>
<td>$M_i$</td>
<td>204</td>
<td>204</td>
<td>a.u.</td>
</tr>
<tr>
<td>Force constant</td>
<td>$1/2 M_i \omega_l^2(2k_F)$</td>
<td>0.14</td>
<td>0.14</td>
<td>meV</td>
</tr>
</tbody>
</table>

Electron-phonon interaction parameter | $\lambda$ | 0.2 | 0.2 | — |

Electron bandwidth [57] | $4t$ | 0.45 | 0.3 | eV |

Charge transfer [12] (electrons per molecule) | $\nu$ | 0.59 | 0.59 | — |

Density of states per spin per molecule | $N(\epsilon_F)/N$ | 1.8 | 2.7 | eV$^{-1}$ |

Fermi energy | $\epsilon_F$ | 0.09 | 0.06 | eV |

Scale factor ($I = \kappa/\rho$) | $I_i$ | 0.17 | 0.21 | $(10^{-2} \text{Å})^{-1}$ |

Moment of inertia (*), $\eta$ axis | $I^\eta$ | 2140 | 1175 | a.u. Å$^2$ |

Moment of inertia (*), $\zeta$ axis | $I^\zeta$ | 300 | — | a.u. Å$^2$ |

Libron frequency (**), $\eta$ axis | $\omega_l^\eta$ | 52 | 47 | cm$^{-1}$ |

Libron frequency (**), $\zeta$ axis | $\omega_l^\zeta$ | 51 | — | cm$^{-1}$ |

Direction cosines of the TCNQ | $\beta$ | 0.57 | — | — |

Rotation $\chi_Q$ | $\gamma$ | 0.824 | — | — |

(*) Calculated with data from ref. [56].
(**) Calculated with data at 100 K from ref. [22].

charge density of the additional $\pi_-$ electron (or hole) on a given atom (represented by $|c_1|^2$), and the total charge density on a given atom, which also includes the polarization of the cores, and $\sigma$-bonds. For example, in neutral TCNQ, the sum of the orbital charges on all atoms vanishes, however, the CN groups have dipole moments (with the nitrogen negative). In TCNQ$^-$, the orbital charge density on the nitrogens is only $-0.061$ e while the total charge density is $-0.251$ e. If we approximate the net charge of the nitrogen in TCNQ$^{0.6}$ by the linear interpolation between the TCNQ$^+$ and TCNQ$^-$ charges, then $z_N = -0.21$ is obtained. The values of the orbital charge densities $|c_1|^2$ and the atomic total charges densities both for the TTF and TCNQ molecules were calculated with data from ref. [25] and are listed in table II. The $M_{14}$ matrix element was also calculated including the interaction between a TTF molecule and all four nearest TCNQ chains. These results are summarized in table III and IV, and detailed calculations are presented in Appendix I.

The dimensionless electron-libron interaction parameter

$$\lambda_{14} = \frac{[M_{14}(q)]^2 N_1(\epsilon_F)/N}{I_q \omega_q^2(1 - u^2)} = \frac{[M_{14}(q)]^2 N_1(\epsilon_F)/N}{2 A_{44}(1 - u^2)}$$

is found to be equal to 0.02 and 0.13 for the first and the second models, respectively. From eq. (19) $\lambda_{11} \approx 0.2$ so $\lambda_{14}/\lambda_{11} \approx 0.1-0.65$. Note that $A_{14}$ depends on the Fermi Energy $\epsilon_F$ and on the transition temperature $T_1$.

Table II. — The LCAO coefficients $c_i$ of the $\pi$-electron of the TTF and TCNQ molecules and the net charge density $z_i$ of the TTF$^{0.6}$ and TCNQ$^{0.6}$ ions. $|c_1|^2$ are the differences between the charge densities of the neutral and the once ionized molecules (Fig. 13) and $z_i$ the linear interpolation between them as explained in the text.

<table>
<thead>
<tr>
<th></th>
<th>TCNQ</th>
<th>H</th>
<th>C$_1$</th>
<th>C$_2$</th>
<th>C$_3$</th>
<th>C$_4$</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>c_1</td>
<td>^2$</td>
<td>0.025</td>
<td>0.037</td>
<td>0.015</td>
<td>0.159</td>
<td>0</td>
</tr>
<tr>
<td>$z_1$</td>
<td>0.012</td>
<td>-0.033</td>
<td>0.054</td>
<td>-0.078</td>
<td>0.093</td>
<td>-0.211</td>
<td></td>
</tr>
<tr>
<td>TTF</td>
<td>C$_1$</td>
<td>S</td>
<td>C$_2$</td>
<td>C$_3$</td>
<td>H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$</td>
<td>c_1</td>
<td>^2$</td>
<td>0.002</td>
<td>0.178</td>
<td>0.023</td>
<td>0.046</td>
<td></td>
</tr>
<tr>
<td>$z_1$</td>
<td>0.050</td>
<td>0.037</td>
<td>0.021</td>
<td>0.067</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

eq. (23)), and therefore this quantity is not sensitive to the precise values of $\epsilon_F$ and $T_1$.

In the same way we estimate $\alpha_{22}$, $C_{22}$, and $A_{23}$ from eq. (1). The estimate of $A_{12}$ may also be obtained by including a longitudinal phonon in the second chain. This phonon produces change of potential on the conduction electron of the first chain by modulating the $R_{NS}$ and $R_{NC}$ distances. The result of this calculation is analogous to eq. (21) for $A_{14}$ [43]. We obtain

$$|A_{12}| = N_1(q) \omega_2(q) \times$$

$$\left[ \left( \frac{\lambda_{11}^2}{\lambda_{11}} M_1 M_2 \right)^{1/2} + \left( \frac{\lambda_{21}^2}{\lambda_{22}} M_1 M_2 \right)^{1/2} \right]$$

(31)
Table III. — Matrix elements in the nearest neighbours approximation for some chosen pairs of atoms

\[ M_{ij}^{*}(ij) = 4 \sin \left( q_b \right) e^{2} \left| c_i \right|^{2} \frac{\partial R_{ij}^{-1}}{\partial \chi_{F}} \]
\[ M_{ij}^{G}(ij) = 4 \sin \left( q_b \right) e^{2} \left| c_i \right|^{2} \frac{\partial R_{ij}^{G}}{\partial \rho_{F}} \]
\[ M_{ij}^{*}(ij) = 4 \sin \left( q_b \right) e^{2} \left| c_i \right|^{2} \frac{\partial R_{ij}^{1}}{\partial \rho_{Q}} \]
\[ M_{ij}^{E}(ij) = 4 \sin \left( q_b \right) e^{2} \left| c_i \right|^{2} \frac{\partial R_{ij}^{1}}{\partial \rho_{Q}} \]

(*) The first (second) atom in each pair belongs to the TCNQ(TTF) molecule, and the nearest of all the pairs bearing the same symbol is meant.

(**) The values of the CDW-libron matrix elements are given in meV/deg. and the charge densities are those of table II.

(***) The values of the CDW-longitudinal phonon matrix elements are given in meV/(10^{-2} A).

Table IV. — Theoretical estimations of the CDW-libron LFEF parameters.

<table>
<thead>
<tr>
<th>Pair (*)</th>
<th>( M_{ij}^{<em>}(</em>**) )</th>
<th>( M_{ij}^{+}(***) )</th>
<th>( M_{ij}^{<em>}(</em>**) )</th>
<th>( M_{ij}^{<em>}(</em>**) )</th>
<th>( M_{ij}^{<em>}(</em>**) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>2.98</td>
<td>4.87</td>
<td>0.05</td>
<td>0.018</td>
<td>0.025</td>
</tr>
<tr>
<td>NC_{2}</td>
<td>0.53</td>
<td>1.82</td>
<td>-0.13</td>
<td>0.004</td>
<td>-0.010</td>
</tr>
<tr>
<td>NS</td>
<td>0.08</td>
<td>13.34</td>
<td>-3.80</td>
<td>0.044</td>
<td>-0.440</td>
</tr>
<tr>
<td>C_{2}H</td>
<td>0.00</td>
<td>-0.94</td>
<td>-0.01</td>
<td>0.000</td>
<td>0.010</td>
</tr>
<tr>
<td>C_{2}C_{2}</td>
<td>0.00</td>
<td>-0.39</td>
<td>0.02</td>
<td>0.000</td>
<td>0.008</td>
</tr>
<tr>
<td>C_{2}S</td>
<td>0.00</td>
<td>-3.47</td>
<td>0.56</td>
<td>0.000</td>
<td>0.171</td>
</tr>
<tr>
<td>C_{3}H</td>
<td>1.46</td>
<td>0.36</td>
<td>0.00</td>
<td>0.028</td>
<td>-0.009</td>
</tr>
<tr>
<td>C_{3}C_{2}</td>
<td>0.32</td>
<td>0.15</td>
<td>0.00</td>
<td>0.010</td>
<td>-0.005</td>
</tr>
<tr>
<td>C_{3}S</td>
<td>0.24</td>
<td>1.42</td>
<td>0.00</td>
<td>0.040</td>
<td>-0.095</td>
</tr>
</tbody>
</table>

( *) The first (second) atom in each pair belongs to the TCNQ(TTF) molecule and the nearest of all the pairs bearing the same symbol is meant.

(**) The values of the CDW-libron matrix elements are given in meV/deg. and the charge densities are those of table II.

(***) The values of the CDW-longitudinal phonon matrix elements are given in meV/(10^{-2} A).

The explicit expression for \( M_{12}(q) \) in the tight binding approximation follows from eq. (30a) by replacing \((1 - u^{2})^{1/2} \) by \( u \) and \( \chi_{P} \) by \( \rho_{F} \). The numerical estimate of \( A_{12} \) is presented in table IV (\( \lambda_{12} \sim 10^{-3} \)).

All our numerical estimates of the interaction parameters in eq. (1) are based only on monopole-monopole nearest neighbour interactions between TTF and TCNQ molecules. Polarization leads also to monopole-dipole, dipole-dipole interactions [21], etc. It is worthwhile to note that the effective charge \( z_{N} \) (and \( z_{S} \)) is also somewhat modulated by the phonons (librons), (see ref. [21], section 2). The modulation of the effective charge by the phonons also contributes to the Frohlich coupling constant. This effect follows directly from the phonon (libron) modulation of the expansion coefficients of the LCAO wave function of the chain [44]. We do not consider that effect here.

We have also neglected the intramolecular screening of the interaction between the charges localized on atoms which do not lie on the periphery of the molecules. That is why the more simpler first model which uses only the charges on the periphery of the TTF and TCNQ molecules is useful as a kind of
limiting case. We return to this question in section 4. The values of some physical quantities needed for the calculations of the different interaction parameters are listed in table I.

We note that all interaction parameters above estimated are of the interference nature. But the $A_{12}$ parameter has another contribution which follows from the direct CDW-CDW Coulomb interaction of two different stacks. Therefore we can write

$$A_{12} = A'_{12} + A''_{12}$$

where the first is the CDW-CDW contribution and the second is from eq. (31). We estimate the first term in the next section (see also Appendix II). Here we note that these two parts differ in their dependence upon the charge transfer

$$A'_{12} \propto \cos \left( \frac{2\pi}{A} b \right)$$

and

$$A''_{12} \propto \sin \left( \frac{2\pi}{A} b \right).$$

So the $A_{12}$ interaction vanishes not exactly for the 1/4 filled band but for $q_b = 2\pi/4$ which depends upon the ratio $A_{12}'/A_{12}''$. Our estimate (see next section) shows that the interference mechanism (eq. (31)) contributes about 5 to 10% to the $A_{12}$ interaction parameter (see Table IV).

In view of all the approximations used for the estimate of the interaction parameters we believe that they are accurate within a factor of about two.

The parameters $A_{33}$ and $A_{44}$ follow from experiment [22] where the mean square amplitude of the TTF and TCNQ librations were measured. The experimental uncertainties are about 30% and our choice of the $A_{44}$ and $A_{33}$ parameters corresponds to the values of the force constants for a temperature of 100 K. The experimental data [22] for the TCNQ molecule show that the elastic restoring force for the $\eta$-libration is much larger (11 eV/rad.²) than for the $\zeta$-librations (1.4 eV/rad.²). This fact leads to the redefinition of the libron coordinate $x_Q$. Indeed, geometrically the $\eta$-libration is the most important factor in the modulation of the S-N distance [21] but because of the relative small amplitudes of this libration and the large amplitude of the $\zeta$-librations, the last must be included in the electron libron free energy. The straightforward inclusion of the additional order parameter in eq. (1) would complicate the free energy. Therefore, we redefine $x_Q$-librations as rotations around an intermediate axis between the $\eta$ and $\zeta$ ones, and find the direction cosines $\beta$ and $\gamma$ by minimizing the part of the free energy that depends only upon $x_Q$.

This procedure gives $A_{23} = A_{23}^\# \beta + A_{23}^\gamma \gamma$ and

$$A_{33} = A_{33}^\# \beta^2 + A_{33}^\gamma \gamma^2$$

with $\gamma/\beta = (A_{33}^\#/A_{33}^\gamma)/(A_{33}^\#/A_{33}^\gamma)$. Taking $[22] A_{33}^\# = 11$ eV/rad.², $A_{33}^\gamma = 1.4$ eV/rad.² and estimating $A_{33}^\#/A_{33}^\gamma \approx 5.5$ we get $\beta = 0.57$ and $\gamma = 0.824$ which lead to the parameters $A_{23}$ and $A_{33}$ in table IV.

Similarly, $\rho_F$ is a linear combination of a longitudinal phonon and a transverse phonon (polarized in the $c^*$-direction), as found from experiment in TTF-TCNQ [36], but in the present estimates of the LFEF parameters, we took the $\rho_F$ as a pure longitudinal order parameter.

4. Direct Coulomb interaction model. — In this section we calculate the CDW-CDW interaction parameters for the nearest and the next nearest chains, $A_{12}$ and $A_{11}[a]$ ($A_{22}[a]$) respectively. (See also Appendix II.) These parameters were estimated by Bjelis and Barisic [15] but for the continuum model of the CDW (a linear CDW along the $b$-axes). We develop here a method of calculation of these parameters which takes into account the geometry of the molecules. For the nearest chain parameter $A_{12}$ the geometry factors are essential (we obtain an order of magnitude reduction of the $A_{12}$ parameter compared to the results of ref. [15]). To be closer to the papers which treat the phase transitions in TTF-TCNQ [13, 14, 15] we use here instead of the displacement order parameters $x_Q$ and $\rho_F$ the order parameters $x_{Q'}$ and $\rho_{Q'}$ related to them. The latter are the CDW amplitude relative to the average charge transfer $\rho$. To be specific we use in the case of the $\kappa$ order parameters the small letters for labeling the LFEF parameters in eq. (1a) (e.g. $\alpha_{12}, \alpha_{11}[a], \alpha_{11}$ and so on). We first determine the relation between the CDW parameter $\kappa$ and the displacement parameter $\rho$ used in eq. (1).

If we expand the electron density on a chain, $n(y) = \sum_{kq} |\psi_{kq}(y)|^2$, in a Fourier series

$$n(y) = n_0 \left( 1 + \sum_{q \neq 0} \kappa_q \cos(qy + \varphi_q) \right)$$

components $\kappa_q$ with $q \neq n \frac{2\pi}{b}$ (n integer) appear in the case of a non-commensurate CDW. We define the CDW parameter $\kappa$ in the case of the usual Peierls transition by the equality $\kappa = |\kappa_{2}\kappa_{2}|$.

To calculate a one-chain parameter $a_i$ and $c_{ij}$, $i=1,2$, it is sufficient to calculate the ratio $\Gamma = \kappa/\rho$ for a chain. With given $\Gamma$ the one-chain parameters may be obtained by the simple scaling of eq. (23) and eq. (24). In the frame of the one-electron MF-theory [33, 34, 39, 40], it is a simple matter to prove that

$$\kappa = \frac{N(e_g)}{vN} \frac{2 |\Delta|}{\lambda}$$

where $vN$ is the number of electrons in a chain and $\Delta$ is defined by eq. (18) with $g_{14} = 0$. From eq. (22) and eq. (32) we obtain

$$\Gamma = \frac{2}{v} \left( \frac{N(e_g) M_0 \omega^2}{N} \right)^{1/2}$$

where $\omega$ is the longitudinal phonon frequency. For the values of the constants listed in Table I,

$$\Gamma \approx 0.2 \times 10^{-2} \text{ Å}^{-1}.$$
Eq. (32) has a simple meaning. Because
\[
\frac{N(\varepsilon_F)}{N} \propto \varepsilon_F^{-1}
\]
we see that \( \kappa \propto \frac{1}{\lambda} \frac{2 | \Delta | }{\varepsilon_F} \). For free 1d electrons
\[
\kappa = \frac{1}{4 \lambda} \frac{2 | \Delta | }{\varepsilon_F} \quad \text{and if} \quad \lambda \approx 0.2 \quad \kappa = k = \frac{2 | \Delta | }{\varepsilon_F}
\]
and from eq. (32) and table I we obtain \( k = 1.4 \).

Table V presents the LFEF parameters \( a_{ij} \) and \( c_{ij} \) as scaled from the related parameters of table IV of the LFEF of eq. (1).

<table>
<thead>
<tr>
<th>( a_{11} )</th>
<th>( a_{22} )</th>
<th>( c_{11} )</th>
<th>( c_{22} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 meV</td>
<td>1.3 meV</td>
<td>5.6 meV</td>
<td>1.9 meV</td>
</tr>
<tr>
<td>NS only</td>
<td>4.3 meV</td>
<td>4.9 meV</td>
<td>1 meV</td>
</tr>
<tr>
<td>all bridges</td>
<td>2.7 meV</td>
<td>3.8 meV</td>
<td>23 meV</td>
</tr>
</tbody>
</table>

The calculations of the CDW-CDW interaction parameters using the discrete CDW model and taking into account the atomic structure of TTF-TCNQ, are explained in Appendix II. Also in this calculation, we use two models for the charge distribution. The next nearest chains parameters \( a_{11}[a] \) and \( a_{22}[a] \) are not sensitive to the actual charge distribution over the molecules (and the continuum model is not too bad for them) but the \( a_{12} \) parameter increases about 20 times for the second model compared with the first one. This is not an accidental effect. As shown in ref. [21] the \( a_{12} \) interaction in the first (NS) model is weak mainly because the sum of the projection of the nitrogen-nitrogen distance in the TCNQ molecule along the b-axis and the sulphur-sulphur distance in the TTF molecule is approximately equal to half the wavelength of the CDW (\( \lambda = 2 \pi/2 k_F \)).

Because of the effect of the intramolecular screening much of the non-nearest neighbour pair interactions are screened. Thus the true value of the \( a_{12} \) CDW-CDW interaction parameter must lie between these estimates. Because of the large difference between them we took this parameter as a fitting parameter (see next section).

Table V presents the results of the calculations of the DCI parameters. The CDW-libron interaction parameters \( A_{14} \) and \( A_{23} \) are much less sensitive to the charge distribution model than the CDW-CDW \( A_{12} \) interaction parameter (see Table IV). This is due to the fact that the relative tilting of the TTF and TCNQ molecules nearly cancels the NS and NC (end carbons) interactions in \( A_{12} \) while there is no such a cancellation in \( A_{14} \) and \( A_{23} \) (a factor \( \sin \frac{q_0(N_N - y_s)}{y_s} \) appears in the \( A_{14} \) and \( A_{23} \) calculations and \( \cos \frac{q_0(N_N - y_s)}{y_s} \) \( \ll 1 \) in the \( A_{12} \) one).

5. The fitting procedure (which mechanism is responsible for the 3d ordering in TTF-TCNQ ?). — As follows from the previous sections (section 3 and section 4) our estimations of the interaction parameters are not sufficiently precise to expect them to fit the available experimental information exactly. Therefore, we try to find a best set of three interaction parameters (for instance, \( A_{14} \), \( A_{23} \) and \( A_{12} \) or \( a_{11} \), \( a_{22} \) and \( a_{12} \)) to fit some experimental measurements and then we compare this best set (set a in table IV) with our theoretical estimates. Note that we fix the other parameters of the LFEF, (eq. (1)) at their theoretical estimates (see table IV). Along with the best set we also solve the LFEF, eq. (1a), for two other sets of three interaction parameters and compare the results. We first discuss the CDW-libron mechanism and then the DCI model.

The available experimental evidence is scarce; the measured phase transition temperatures [6, 11, 58] (\( T_{p1} \) and \( T_{p2} \)), the temperature dependence of the transverse period \( q_a(T) \) [4, 12, 58], and the specific heat anomaly [3, 38].

The jump of the specific heat \( \Delta C_p(T_{p1}) \) at the high temperature phase transition determines with the help of eq. (15) the unrenormalized phase transition temperature \( T_1 \) and this via eq. (8a) determines the interaction parameter \( A_{14} \). Two other parameters, namely, \( A_{23} \) and \( A_{12} \) were chosen to fit the initial slope and the curvature of the \( q_a(T) \) dependence [58]. Thus, set a (Table VI) is chosen to fit both the \( \Delta C_p(T_{p1}) \) jump (see Table VI) and the \( q_a(T) \) dependence (see Fig. (4)). At first sight the correspondence between the parameters \( A_{23} \) and its theoretical estimate \( A_{23}^0 \) is very poor. But if we pay attention to the large renormalization of the transition temperature (see Table VI, \( T_{p3} - T_2 = 39 \) K) we conclude that the temperature dependence of the \( A_{23} \) parameter between \( T_{p2} \) and \( T_2 \) is not negligible. As was explained in section 3 in this case \( A_{23}(T_{p2}) < A_{23}(T_2) = A_{23}^0 \). We can estimate \( A_{23}^0 \) with the help of eq. (27) for the given value of the \( A_{23} \). For the coupling constant \( \lambda = 0.2 \) and \( \Delta T_2 = 39 \) K we obtain

\[
A_{23}^0 \approx A_{23} \left( 1 - \lambda \frac{T_2}{T_2} \right) = 0.97 \text{ meV} \frac{10^{-2} \text{ Å deg.}}
\]

which is close to our theoretical estimation of \( A_{23}^0 \).

The \( A_{14} \) parameter value from the set a is not very different from the theoretical estimate for the case
Table VI. — Sets of interaction parameters which were used in the numerical calculations. Set a is the best fit, sets b and c are for illustrative purposes. The unrenormalized transition temperatures, order parameter amplitudes and the specific heat jump at 53 K are also listed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{14}(T_{p1})$ (meV)</td>
<td>0.3 (*)</td>
<td>0.5</td>
<td>0.21</td>
</tr>
<tr>
<td>$A_{23}(T_{p2})$ (meV)</td>
<td>0.29 (*)</td>
<td>0.85</td>
<td>0.18</td>
</tr>
<tr>
<td>$A_{12}$ (meV)</td>
<td>0.09</td>
<td>0.46</td>
<td>0.036</td>
</tr>
<tr>
<td>$A_{14}^2/A_{44}$ (meV)</td>
<td>0.06</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td>$T_1$ (K)</td>
<td>25</td>
<td>13</td>
<td>35</td>
</tr>
<tr>
<td>$T_2$ (K)</td>
<td>10</td>
<td>1.5</td>
<td>22</td>
</tr>
<tr>
<td>$\rho_0$ (38 K) (10$^{-2}$ Å)</td>
<td>2.1</td>
<td>3</td>
<td>1.8</td>
</tr>
<tr>
<td>$\rho_f$ (38 K) (10$^{-2}$ Å)</td>
<td>1</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>$\lambda_0$ (38 K) (deg.)</td>
<td>0.17</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>$\lambda_f$ (38 K) (deg.)</td>
<td>0.34</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>$\Delta C_p$ (53 K) ($k_B$) (***)</td>
<td>0.34</td>
<td>1.3</td>
<td>0.19</td>
</tr>
</tbody>
</table>

(*) Corresponding to unrenormalized values $A_{14}^a \approx 0.38$ and $A_{23}^a \approx 0.97$ as explained in the text (see eq. (27)).

(**) To be compared with the experimental value [3] of the chain integration (see Table IV). The renormalization of the $T_{p1}$ temperature is not as large as in the previous case ($\Delta T_{p1} \approx 20$ K) and we obtain for the same $\lambda = 0.2$

$$A_{14}^a \approx 0.38 \frac{\text{meV}}{10^{-2} \text{ Å} \text{ deg.}}.$$  

Thus the libron-CDW parameters from the set a are in good agreement with the theoretical estimate.

As was discussed at the end of the previous section, it is rather difficult to obtain a precise theoretical estimate of the CDW-CDW interaction parameters. In fact, the first (N-S) model and the second (the unscreened all pairs interactions) model give the lower and upper bound, respectively. The value $A_{12}$ appearing in the set a (Table VI) falls in between these two estimates.

The temperature dependence of the order parameters, the transverse $q_a$ wave vector and the specific heat anomaly $\Delta C_p$ are shown in the figures 2a, 3a, 4 and 5a and were discussed in section 2. As was mentioned in section 2 it was not possible to reproduce the maximum of the heat capacity at 46 K, for the parameters of the set a it appears at a certain temperature below 38 K. The smallness of the jump $\Delta C(T_{p2})$ at the second phase transition is due to the proximity of the two transition temperatures as was already explained in section 5. It is important to investigate if it is possible to obtain both the maximum at 46 K, the experimental values of the jumps $\Delta C_p$ and the $q_a(T)$ dependence simultaneously in the frame of the LFEF, eq. (1). Because the $C_p(T)$ behaviour depends upon the renormalization of the phase transition temperatures it is better to postpone this investigation until the interaction in the $c^*$-direction will be included. Of course, additional experimental measurements of the $C_p(T)$ are very desirable.

We have also solved the LFEF for illustrative purposes for another two sets of interaction parameters. These two sets and some results are listed in table VI (column b and c), and the corresponding graphs appear in figures 2b and c, 3b and c, 4 and 5b and c. The set b consists of large interaction parameters while the set c consists of small ones. Both fit the temperature dependence of the transverse period. The set b is characterized by large transition temperature renormalizations which enhance the specific heat jump at 53 K and diminish the $\rho_f^2/\rho_0^2$ ratio (see eqs. (6a and b)). Rather large libronic amplitudes are obtained. The set c shows the effects of smaller interaction parameters.

The LFEF was also solved in terms of the DCI model alone (i.e. the CDW-libron interaction parameters $A_{14}$ and $A_{23}$ were taken equal to zero). Our results showed that if $a_{12}$ were chosen to be half of the estimated value summing over all the possible pairs ($a_{12} = 10$ meV) and the direct interaction between similar chains were the same as calculated (see Table V) then the temperature dependence of the transverse period could be fitted. This set of parameters is equivalent to the above mentioned set b in the sense of the correspondence relations of eq. (5a) and eq. (5b) (i.e. $2 A_{11}[a] = 0.16 \frac{\text{meV}}{10^{-2} \text{ Å}^2}$ plays the same role as $A_{14}^2/A_{44} = 0.17 \frac{\text{meV}}{10^{-2} \text{ Å}^2}$ in the set b and analogously for $2 A_{22}[a] = 0.34 \frac{\text{meV}}{10^{-2} \text{ Å}^2}$).

The difference between the DCI model solution and the CDW-libron solution (set b) appears in the unrenormalized transition temperature $T_1$ which is larger in the former because only $A_{11}[a] = 0.08 \frac{\text{meV}}{10^{-2} \text{ Å}^2}$ enters in the renormalization eq. (5a). Therefore, the specific heat jump in the DCI model ($\Delta C_p \approx 0.5 k_B$) is closer to the experimental value than that obtained in set b.

To complete this discussion we show in figures 6a and 6b the contour lines and the three dimensional view of the CDW-libron LFEF with the best set of
6. The possible phase diagrams for TTF-TCNQ systems. Lifshitz points. — To obtain a theoretical phase diagram from first principles, the $T, P$ dependence of the parameters of the LFEF must be known in detail. At this stage, we discuss qualitatively some possibilities for the phase diagram in the $T$-$P$ plane (or in a $T$-external parameter plane). Somewhat analogous phases (without the libronic order parameter) were already mentioned by Bjelis and Barisic [15]. The complexity of the observed phase diagram [7, 8, 45] is probably a result of the complicated pressure variation of several terms in the LFEF. At this preliminary stage, we discuss an idealized situa-

![Fig. 6. The LFEF of eq. (1) with the parameters of the set $a$ as function of $P_F$ and $u = \cos (qa \alpha_2)$ for $T = 35$ K and $\rho_0 = 2.4 \times 10^{-2}$ Å. a) Contour lines graph. The energy levels are shown in meV. b) Three dimensional view.]

![Fig. 7. Two possible phase diagram of the decoupled $(PQ X F)$ and $(PF XQ)$ subsystems. a) Divergent transition lines. b) Convergent transition lines with quadruple point.]

parameters (Table VIa) at a temperature $T=40$ K. We feel that figure 6a and 6b deserve some detailed considerations. When we go along the line $P_F=0$ the free energy has a minimum at $u=0$ ($q_a=2 \pi/2 a$), i.e., a $2a$ period. Similarly, when we go along the $u=0$ line the free energy has a minimum at $P_F=0$. Therefore, it is frequently argued that this is a theoretical proof that the point $u = P_F = 0$ is a minimum of the free energy and explains the experimental observation of this state in the temperature range 48 K-53 K. Inspection of figures 6a and 6b shows that this proof is fortuitous. The point $u = 0$, $P_F = 0$ is a saddle-point of the free energy and for a diagonal line it is maximum.

From the present numerical estimates it is not possible to decide unambiguously whether the CDW-libron or the DCI mechanism or both are responsible for the 3d ordering. But the screening effects (dielectric constant of the material) diminish the next nearest chain interaction parameters $A_{11}[a]$ and $A_{12}[a]$ significantly.

The nearest chain interaction parameters $A_{14}$, $A_{23}$ and $A_{12}$ are not influenced by the screening very much. Thus when screening effects upon the $A_{A1}[a]$ and $A_{12}[a]$ parameters are significant, only the CDW-libron mechanism can provide the coupling which drives the 3d ordering in TTF-TCNQ.

However, the main difference between the CDW-libron and the DCI model manifests itself in the pressure dependence, since $A_{33}$, $A_{44}$ increase rapidly under pressure, while $A_{i}[a]$, $i = 1,2$ should not be strongly pressure dependent. This point will be elaborated in a subsequent publication.
tion, where only one or two terms in the LFEF are varied arbitrarily.

In the case when $A_{12}/(A_{21}/A_{44}) < 1$ it is natural to start from the decoupled subsystems ($\rho_Q \chi_F$) and ($\rho_F \chi_Q$) (see section 2). If $A_{12} = 0$ we would expect two topological distinct cases. In one case, the $T_{p1}(P)$ and $T_{p2}(P)$ lines are divergent (see Fig. 7a). In the second case (Fig. 7b) there is a crossing point, $T_{p1} = T_{p2}$, where the disordered and three ordered phases coexist. According to the Gibbs phase rule [46] $r + f - 2 = r$ at equilibrium where $r$ is the number of the phases and $f$ is the number of the components. For TTF-TCNQ, $f = 1$, so the quadruple point violates the Gibbs phase rule. For TTF-TCNQ, $f = 1$, so the quadruple point violates the Gibbs phase rule. In reality, a coupling between the two subsystems (through $A_{12} \neq 0$ in our case) splits the quadrupole point into two triple points. Two topologically different possibilities for this splitting are shown in figures 8a and 8b. In figure 8a, the AB line which divides the disordered phase and the completely ordered phase III is a line of second order phase transition points. The $A'B'$ lines in figure 8b dividing the ($\rho_Q \chi_F$) and ($\rho_F \chi_Q$) phases must be a first order transition line because of the different symmetry of these two phases.

$$T_{p2} - T_2 + \Delta T_2 > T_1 + \Delta T_1 + T_1 T_2 W/\Delta T_2 = T_{p1}$$

(35)

where $W$ is given by eq. (8c).

It is clear that the inter-subsystem interaction renormalizes the second transition temperature towards the first as is shown in figure 8a. So we are now in the position to argue, that for our model (eq. (1)), only the phase diagram of the type shown in figure 8a is possible. Indeed, for obtaining the diagram of figure 8b from the diagram of figure 7b one needs a negative inter-subsystem renormalization (for instance, in the $T_{p1} > T_{p2}$ case one needs $T_{p2} = T_2 + \Delta T_2 - |\Delta T_1|$). It is possible to obtain such renormalization if a term like $C_{1122}(u) \rho_2^k \rho_2^k$ with $C_{1122}(u) > 0$ is included in eq. (1). But at the quadrupole point all the order parameters are zero and therefore the renormalization of the transition temperature by the biquadratic term is negligible in the vicinity of the quadrupole point. So a splitting of the quadrupole point into two multi-critical points $A'$ and $B'$ (as in figure 8b) is unlikely.

As was mentioned in section 2 (eq. (9)) a fourth phase is possible for $u = 1$ ($\chi_Q = \chi_F = 0$, $\rho_Q \rho_F \neq 0$). The line dividing regions of phase III and this new phase IV may intercept the AB line of figure 8a at two new multi-critical points C and D (see Fig. 10). Because phase III is a phase with no commensurate transverse period, the four multi-critical points A, B, C and D can be identified as of Lifshitz type which were introduced by Hornreich et al. [24] in connection with magnetic systems. We note that point A (Fig. 8a) is consistent with the group theoretical considerations of E. Abrahams and I. Dzyaloshinskii [17].

It is interesting to note that in the vicinity of the Lifshitz point $A$ the quadratic ($T_{p2} - T_2$) contribution is essential in $\rho_2^k$. This may be seen from eq. (7b) where the renormalization $A\rho_2^k$ of the fourth-order constant in eq. (1) becomes very large near the point $A(\rho_2^k(T_{p2}) \to 0$ when $T_{p2} \to T_{p1}$).

Concerning the first uncoupled case (Fig. 7a), we may expect here several possibilities when the interaction $A_{12}$ is switched on. In the first one, the strong renormalization of the $T_2$ temperature leads to the monotonic increase of $T_{p2}$ with the external parameter (say, pressure) so that the Lifshitz point is reached (Fig. 9a). The other alternative is the fall of the $T_{p2}(P)$ line. In this case, the Lifshitz point also may be reached after the initial divergence of the $T_{p1}$ and $T_{p2}$ lines (see Fig. 9b). Theoretically, the renormalization may be so weak that the topological character of the picture, figure 7a will not change.

To illustrate the general picture we present in figure 10 the numerical calculations of $T_{p1}$ and $T_{p2}$ as function of the difference $(T_2 - T_1)$ for a highly idealized case when $T_i \ (i = 1, 2)$ were changed only in the differences $(T - T_i)$ to which the parameters $A_{ii}$
Fig. 9. — Two possible phase diagrams of the coupled \((\rho_Q x_F)\) and \((\rho_F x_Q)\) subsystems which follow from the divergent case, figure 9a. a) Strong attractive renormalization. b) Crossover from the pronounced divergent regime to the convergent one.

are proportional, and the other parameters were kept fixed. Figure 11 presents another phase diagram in which only the inter-subsystem interaction parameter is changed and the rest of the parameters are the same as those listed in table I. In this graph two Lifshitz points appear.

Returning to the \(P-T\) phase diagram, we note that extensive experimental work on the phase diagram of TTF-TCNQ under pressure has been carried out in Orsay [7, 8, 45]. The phase diagram is found to be rather complicated. The upper transition temperature \(T_{p1}\) (the Peierls transition of the TCNQ stack) increases with pressure from 53 K, at first slowly (0.7 K per kbar), and around 20 kbar there is a sharp maximum of about 70 K, followed by a drop, and then a plateau at about 65 K. The second transition temperature \(T_{p2}\) (the Peierls transition of the TTF stack) seems to fall rapidly at low pressures, as manifested by a rather low resistivity, which is only weakly temperature dependent (see figure 2 of Ref. [45], and figure 1 of Ref. [8] for example). At 15 kbar, and above, there seems to be only one transition, so that \(T_{p2}\) must have risen sharply with \(P\) in this region. There is a first order transition at 38 K [8, 12] which falls rapidly with pressure (about 1 K per kbar [7]).

Since all parameters of the LFEF can be expected to be pressure dependent, this rather complicated behaviour is not surprising. At this stage, we do not attempt a quantitative calculation, mainly since the parameters

\[
C_{34} \left[ \frac{a}{2} \right] \chi_Q \lambda_F \cos q_a a, \quad A_{11} \left[ \frac{e}{2} \right] \rho_Q \cos \frac{q_c c}{2},
\]

\[
A_{22} \left[ \frac{e}{2} \right] \rho_F \cos \frac{q_c c}{2}
\]

have not yet been calculated, and they seem to be essential for a quantitative calculation. However, we can point out at this stage that a particularly strong pressure dependence is expected for \(A_{33}\) and \(A_{44}\) \((- \ln A_{33}/\ln b \approx 21\) for a Lennard Jones potential [47]). The pressure variation of \(A_{44}\) is expected...
to be even stronger, since the TTF $\eta$-libration at 40 cm$^{-1}$ is particularly soft. This frequency is determined from the Debye-Waller factor [22], which shows also that the analogous mode in TCNQ is much harder (\(\sim 60\) cm$^{-1}$). Raman effect measurements by Kuzmany and Stoltz [48] verify the presence of modes at these frequencies in TTF-TCNQ. Measurements of the Bordeaux group show that in the analogous compounds TTTT-TCNQ [49], HMTTF-TCNQ [50] and HMTSF-TCNQ [51], the donor $\eta$-libration is much harder (\(\sim 60\) cm$^{-1}$).

Also, $A_{12}[a/2]$ is expected to increase rapidly with pressure, because of the change in charge transfer [52], and the vanishing of this term for a charge transfer of approximately 0.5. Thus, at 20 kbar, where the charge transfer increases from 0.59 to 0.66 [45], $A_{12}[a/2]$ may increase by a factor of 2 or so, while $A_{12}/A_{44}$, $A_{23}[a]/A_{33}$ may be expected to decrease by a factor of 2 or so. $A_{11}[a]$ and $A_{22}[a]$ should be much less affected, since they do not depend critically upon the charge transfer. Since the 2 $a$ period, and the existence of two separate phase transitions, depend on $A_{44}$ to overwhelm $A_{12}$, this condition no longer exists above 15 kbar, and therefore, only one transition (possible with $q_a = 0$) should be present in agreement with experiment. According to our previous discussion it is plausible that the transition from the $q_a = \pi/a$, separate $T_{p1}$ and $T_{p2}$ state, proceeds via two Lifschitz points. However, a quantitative calculation has yet to be carried out. The commensurability term proposed by Friend et al. [45], increasing $T_{p1}$ and giving rise to a first order transition there, must also be included.

7. Discussion. — We have shown here that because of the large number of parameters in the LFEF, symmetry considerations alone are not sufficient to determine the phase transitions since virtually an infinite range of possibilities exists. Therefore, ab-initio calculations of the parameters of the LFEF are essential for an understanding of the phase transitions of TTF-TCNQ.

We demonstrated that there is ground to believe that Coulomb coupling between CDW's cannot account for the two successive transitions at 48 K and 53 K, while the CDW-libron coupling accounts immediately for the existence of the two separate transitions, and the temperature dependence of the transverse period.

The crucial point in the CDW-libron model is the existence of the libron order parameters $\chi$. Our estimations give for $T \sim 38$ K, $\chi = 0.34$ deg. and $\chi_0 = 0.17$ deg. The question arises about the experimental evidence for such rotations. We note that in the TTF-$\Gamma_7$ salt Johnson and Watson [37] detected rotations with an amplitude of the order of $\chi \sim 5^\circ$. The reason why in the scattering experiments up to date these rotations were not detected lies partially in the smaller value of $\chi$ in TTF-TCNQ in comparison with TTF-$\Gamma_7$, also the measurements on TTF-$\Gamma_7$ involved intensity measurements of a few thousand Bragg spots; no such detailed work has been done on TTF-TCNQ. The careful search for the libron order parameter in TTF-TCNQ is very desirable.

The CDW-libron model predicts various possible phases; one disordered phase, and four ordered phases: $\rho_{Q \neq 0}$, $\rho_{Q \neq 0}$, $\rho_{Q \neq 0}$, $\rho_{Q \neq 0}$, $\rho_{Q \neq 0}$, $\rho_{Q \neq 0} = \rho_{Q \neq 0} = 0$. The realization of these phases depends upon the values of the LFEF parameters. It is interesting to note that it is possible to influence these parameters not only by external pressure but also by chemical substitutions (i.e. replacing S by Se).

The TTF-TCNQ system may be an appropriate system for the realization of the Lifshitz point. This is interesting because the critical behaviour near this point is peculiar.

We note also the interesting behaviour of $C_p$ near the second phase transition (see Fig. 5). The maximum of the $C_p(T)$ curve is due to the $A_{12}$-interaction. Its realization is due to the closeness of the two successive phase transitions. This $C_p(T)$ behaviour exists also in the frame of the CDI model.

We developed here a method for estimating the various interaction parameters. This method may be easily generalized for more realistic wave functions of a TCNQ(TTF) molecule.

The present work is a first step of an ab-initio calculation of the phase transitions in TTF-TCNQ and analogous systems. Further work must include:

1) Calculation of the interaction parameters in the $c^*$-direction, and perhaps the [101] direction [19, 53] (1).

2) Calculation of fourth-order terms; in particular, the term $C_{ts} \chi_0 \chi_0$, which is responsible for the first order transition at 38 K, the locking to the 4 $a$ period, and the peculiar properties of the state below 38 K.

3) Calculations of the interaction parameters in more realistic models to account for various screening effects, polarizability of molecules, etc.

4) The redistribution in charge of the molecules brought about by the translations and rotations. This redistribution changes the electron-phonon coupling constants considerably. Also, non-rigid distortions (intra-molecular phonons) must be considered.

5) The variation of the various parameters with volume, that should account for the rather complicated phase diagram observed.

6) The microscopic theory of the Peierls transi-

(1) Recent calculations show that the interaction between similar chains in the $c^*$ direction is strong ($a_{11}, a_{22}, (c/2) \sim 50$ meV). This interaction should be responsible for the decreasing of the fluctuations and the restoring of the mean field transition temperature.
tion, for the case when several phonons go soft simultaneously.

7) The effect of electron hopping between the chains on the various parameters.
8) The effect of the finite lifetime of the electronic states on the various parameters.

APPENDIX I

Calculation of the $A_{14}$ interaction parameter. —

The one electron tight-binding TCNQ chain wave function

$$
\Psi_n(r) = \frac{1}{\sqrt{N}} \sum_n \varphi(r - R_n) e^{i k \cdot R_n} \quad (A.1)
$$

is built of the molecular wave function which we approximate by the LCAO w.f.

$$
\varphi(r - R_n) = \sum_i c_i \psi_i(r - R_{ni}) \quad (A.2)
$$

where $\psi_i(r - R_{ni})$ is the atomic wave function of atom $i$ belonging to the $n$-th TCNQ molecule.

Substituting eq. (A.1) and (A.2) into eq. (25) we get

$$
M_{14}(q) = \sum_{n} e^{i q \cdot R_n} \left| \sum_i c_i \right|^2 
\times e \int \psi^*_i(r - R_{ni}) \frac{\delta V(r)}{\delta \chi_F} \psi_i(r - R_{ni}) d^3r \quad (A.3)
$$

where $\frac{\delta V(r)}{\delta \chi_F}$ is the potential change due to a libration $\delta \chi_F$ of one TTF$^{+0.6}$ molecule. When the net charge distribution on the TTF$^{+0.6}$ molecule is taken in the form $e \sum_j z_j \delta(r - R_j)$ we obtain

$$
\left. \frac{\delta V_i}{\delta \chi_F} \right|_{\chi_F=0} = \sum_j e z_j \left. \frac{\delta R_{ij}^{-1}(n)}{\delta \chi_F} \right|_{\chi_F=0} \quad (A.4)
$$

where $z_j$ is the net charge (in units of the electron charge $e$) of the $j$-th atom of the TTF$^{+0.6}$ molecule and $R_{ij}$ is the distance between the $i$ and $j$ atoms. If we neglect the spread of the charge around the atoms ($\psi_i(r - R_{ni}) \approx \delta(r - R_{ni})$) then

$$
M_{14}(q) = \sum_{n} e^{i q \cdot R_n} \sum_{ij} c_i^2 c_j \left. \frac{\partial R_{ij}^{-1}(n)}{\partial \chi_F} \right|_{\chi_F=0} \quad (A.5)
$$

The summation over $n$ can be broken into four summations over the four bridges shown in figure 12. For the first bridge (see Fig. 12)

$$
\left. \frac{\partial R_{ij}^{-1}}{\partial \chi_F} \right|_{\chi_F=0} = R_{ij}^{-3} (\Delta x \xi_j^{0} + \Delta y \sin \theta_F \xi_j^{0} + \Delta z \cos \theta_F \xi_j^{0}) \quad (A.6)
$$

where $R_{ij}$ is the distance between the $i$ and $j$ atoms. If we neglect the spread of the charge around the atoms ($\psi_i(r - R_{ni}) \approx \delta(r - R_{ni})$) then

$$
M_{14}(q) = \sum_{n} e^{i q \cdot R_n} \sum_{ij} c_i^2 c_j \left. \frac{\partial R_{ij}^{-1}(n)}{\partial \chi_F} \right|_{\chi_F=0} \quad (A.5)
$$

The summation over $n$ can be broken into four summations over the four bridges shown in figure 12. For the first bridge (see Fig. 12)
The nearest neighbour approximation is obtained when only $p = 1$ is taken (the $p = 0$ contribution is zero because of the symmetry of the configuration as can be seen in eq. (A.9)). To perform the summation in eq. (A.9) we write the derivatives from eq. (A.6) in the form (for simplicity, we omit the indices $i, j$)

$$
\left. \frac{\partial R_{ij}^{-1}}{\partial \chi_F} \right|_{\chi_F = 0} = \frac{A + B(p + \epsilon) b}{d_1^2 + (p + \epsilon)^2 b^2} \quad (A.10)
$$

where

$$
A = \Delta x \zeta_0 + \Delta z \cos \theta \zeta_0 \quad B = \sin \theta \zeta_0^2 \quad d_1^2 = (\Delta x)^2 + (\Delta z)^2
$$

and use the integral representation

$$
\sum_{q = -\infty}^{\infty} \frac{(-bq)^n}{n!} \frac{1}{n!} \int_0^{\infty} \cos [(ub(p + \epsilon)] K_n(ud) u^n du \quad n = 0, 1, 2, \ldots
$$

(A.12)

where $K_n(x)$ is the modified Bessel function of the $n$-th order with the asymptotic behaviour

$$
K_n(x) \approx \sqrt{\frac{\pi}{2x}} e^{-x}.
$$

For $n = 0$ this representation was used by Saub, Barisic and Friedel [54]. After some calculations we obtain from eq. (A.10) and eq. (A.12) that

$$
\sum_{p = -\infty}^{\infty} \frac{\partial R_{ij}^{-1}}{\partial \chi_F} \sin \left( \frac{q}{2} \pi (p + \epsilon)^2 b^2 \right) = \frac{2}{\pi} \frac{1}{(2n - 1)!} \int_0^{\infty} \cos \left[ ub(p + \epsilon) \right] K_n(ud) u^n du \quad n = 0, 1, 2, \ldots
$$

(A.13)

where $q = \frac{2\pi}{\beta} n$ is a reciprocal lattice vector. The substitution of (A.13) into eq. (A.9) gives the final result for the $M_{14}(q)$ matrix element. The series converges very fast, and two terms are sufficient. The geometrical factors, $A, B, d_1$ and $\epsilon$ depends upon the tilting angles and coordinates $\zeta_0, \theta, \zeta_0$ of corresponding atoms.

In the second model where all the pair interactions between atoms of the TTF and TCNQ molecules are taken into account in the summation of eq. (A.5), a total of $20 \times 14$ pair interactions must be calculated. All of these calculations were performed with the help of the computer.

**APPENDIX II**

**A. Calculation of the $A_{12}$-parameter.**

1. The contribution to $A_{12}$ from the interference effect is obtained from eq. (31). The calculation of this contribution is the same as in the previous case of the $A_{14}$-parameter. Instead of $\partial R_{ij}^{-1}/\partial \chi_F$ now appears the derivative $\partial R_{ij}^{-1}/\partial \rho$. The latter has the same form as eq. (A.10), only the parameters $A$ and $B$ of eq. (A.10) will be different. The results of calculation are given in table IV. Some matrix elements calculated in the NN approximation are listed in table III.

2. The CDW-CDW contribution to the $A_{12}$ parameter is the sum of the Coulomb interaction between corresponding pairs of CDW's on the TCNQ and TTF stacks. The charge distribution in a chain is supposed to be

$$
\rho^{0}(r) = \sum_{\text{atom}} e |c_i|^2 \nu \delta(r - R_n) \quad (A.14)
$$

where $c_i$ is the LCAO coefficient of the molecular wave function, $\nu$ is the charge transfer ($\nu \approx 0.6$) and $R_n$ is the position of the $i$-th atom in the $n$-th molecule. In the presence of a CDW this charge distribution is modulated:

$$
\rho(r) = \sum_{\text{atom}} e |c_i|^2 \nu \delta(r - R_n) \left[ 1 + \kappa \cos (q_n nb + \phi) \right].
$$

(A.15)
Eq. (A.15) defines the discrete CDW model with the assumption that the amplitude $x$ and the phase $\phi$ is the same for each atom of the molecule. This equation defines $\kappa$ as the CDW amplitude relative to the average charge transfer. The CDW-CDW interaction energy per cell is equal to

$$E_{12} = \nu^2 e^2 \kappa^2 \kappa_F \sum_{ij} \left| c_i \right|^2 \left| c_j \right|^2 \frac{1}{2N} \sum_{n=-N}^{N} \cos \left( q_n \rho_b + \phi_{12} \right) \cos \left( q_n \rho_b + \phi_2 \right)$$

$$= \nu^2 e^2 \kappa^2 \kappa_F \sum_{ij} \left| c_i \right|^2 \left| c_j \right|^2 \frac{1}{2} \sum_{p=-\infty}^{\infty} \cos \left( q_p \rho_b + \phi_{12} \right) \cos \frac{q_p \rho_b + \phi_2}{p} .$$

Using eq. (A.12) for $n = 0$ we transform eq. (A.16) into a sum over the reciprocal lattice wave numbers [54]. After summation over four interaction bridges, we obtain in full analogy with the above described $A_{14}$ calculation that the CDW-CDW interaction energy per (cell) between neighbouring TCNQ and TTF stacks is equal to:

$$E_{12} = 2 a_{12} \cos \phi_{12} \cos \left( \frac{q \rho_b}{2} \right) \kappa \kappa_F$$

where

$$a_{12} = \frac{2 e^2 \nu^2}{b} \sum_{ij} \left| c_i \right|^2 \left| c_j \right|^2 \sum_{n=-\infty}^{\infty} \cos \left( (q_b + q_a) b c_{ij} \right) K_0 \left( q_b + q_a \mid d_{ij} \right)$$

The first ($q_a = 0$) term in eq. (A.17) according to the minimum conditions for the free energy.

The quasi continuous CDW approximation where the discrete stacks of molecules are replaced by continuous threads passing through each atom of the molecules. Additional terms contribute about 25% of the total value depending on the value of $d_{ij}$. For $d \geq 6$ Å terms other than the first can be neglected.

**B. Calculation of the next nearest neighbour interaction parameters.** The CDW-CDW interaction between similar chains was calculated in the same manner as in the NN CDW-CDW interaction. For example, the TCNQ-TCNQ interaction is

$$a_{11}(a) = \frac{4 e^2 \nu^2}{b} \sum_{ij} \left| c_i \right|^2 \left| c_j \right|^2 \cos \left( q_b b c_{ij} \right) K_0 \left( q_b d_{ij} \right)$$

where $i$ and $j$ refer to atoms in a pair of neighbouring TCNQ stacks. Terms with $q_a$ other than zero were neglected due to the large distances between similar chains. The values of $a_{12}, a_{11}(a)$ and $a_{22}(a)$ are listed in table V.

**References**


