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To cite this version:
K. Yamaji, S. Megtert, R. Comes. 2D displacement pattern in TSeF-TCNQ model analysis of the 2k F diffuse lines. Journal de Physique, 1981, 42 (9), pp.1327-1343. 10.1051/jphys:019810042090132700. jpa-00209325
2D displacement pattern in TSeF-TCNQ model analysis of the 2k_F diffuse lines

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(Reçu le 9 avril 1981, accepté le 4 mai 1981)

Abstract. — The observed intensity distribution of the X-ray 2 k_F diffuse lines of TSeF-TCNQ has been reproduced by a detailed model of rigid molecular translations with components along the b- and c-axes, including weak correlations between translations on the neighbouring chains in the c-direction. Due to overwhelmingly larger molecular scattering factor, only TSeF was taken into account. Good semiquantitative agreement, including detailed substructures over broad maxima, was obtained between the calculated curves and observed data from photographs for three different crystal orientations. In the movement of the 2 k_F soft mode, the two-dimensional (2D) displacement pattern in each TSeF sheet is close to that in which each molecule moves nearly parallel to its molecular plane. The c-components are in phase and the b-components are antiphase on the nearest neighbour chains, following the alternate change of the tilt direction of the molecular planes from chain to chain. A small difference from this simple picture is featured by a phase progression of about 65° per unit cell in the c-direction. No features were discernible as coming from libration modes.

1. Introduction. — It is very important to study the structural aspect of the metal-insulator transition in quasi-one-dimensional (1D) conductors, since it can afford direct microscopic information on the lattice modulation accompanying the transition, which allows to specify the form of electron-lattice interaction and to determine the microscopic nature of the transition. Actually, X-ray diffuse scattering provided definite structural evidence for the phase transitions of many quasi-1D conductors in the form of 2 k_F diffuse precursor lines in the metallic phase and satellites in the insulator phase, which tell the lattice modulation with wavenumber 2 k_F [1]. But it is very difficult to obtain further detailed knowledge on the 2 k_F « soft mode » at T > T_c and the lattice modulation at T < T_c from such data, since they are mostly at the border of detectability and neither strong enough nor abundant enough in order to make a detailed analysis. Such is the situation in particular for TTF-TCNQ.

Taking advantage of the much larger atomic scattering factor of selenium in the isomorphous compound TSeF-TCNQ earlier studied by Weyl et al. [2], Megert et al. [3] succeeded to get 2 k_F diffuse lines strong enough to allow a preliminary analysis of the intensity distribution. They found that the main
intensity maxima within the $2k_F$ diffuse sheets can be well understood as due to the scattering from a 1D lattice modulation of pure translation of TSeF molecules on the TSeF columns; the contribution to the diffuse scattering from the TCNQ columns is almost two orders of magnitude smaller than that from the TSeF molecules due to the overwhelmingly larger scattering factor of selenium and therefore negligible from an experimental point of view. They further pointed out qualitatively that additional intensity variations within the broad intensity maxima provided evidence of weak correlation between the translational waves on the neighbouring TSeF columns which are arranged in the $bc$-plane.

Pushing forward this analysis, i.e., carrying out model fitting to the above mentioned data, we have determined with high plausibility the type of translation of the TSeF molecules in each column, and also the type of correlation between the translations on the neighbouring columns, which reproduce acceptably well the intensity distribution data including its smallest features.

According to the results of our analysis we find:

(i) Firstly, that in each column consisting of planar TSeF molecules, the modulation is accomplished by a rigid translation of each molecule nearly parallel to the molecular surface and along its longest axis. This is in accordance with an intuitive picture that TSeF forms a rigid bulky body defined by the Van der Waals radius of each composing atom and that the easiest movement is to slide along its surface.

(ii) Secondly, that the translations of the TSeF molecules on the neighbouring columns are weakly correlated and nearly in phase concerning their $c$-components; this means nearly antiphase concerning their $b$-components, since the tilt of the molecular plane changes its direction between the nearest neighbour columns in the $c$-direction, so that the molecules are arranged in a herringbone (HB) pattern. Therefore our displacement pattern makes also a HB pattern.

Our paper is organized in the following way: in section 2, we first describe our model of the lattice displacement and calculate the X-ray scattering intensity. The model is a very generalized one considered at the final stage of this study and gives all the special models studied here by putting constraints to the parameter values. In section 3, we briefly present the preliminaries which we need in order to compare the calculated intensity distribution to the observed one. In section 4, the procedure of analysis is presented with the above results. Detailed analysis shows the necessity of slight modification of the above simplified pattern of lattice modulation and brings in the phase progression of about 65° as one goes one unit cell in the $c$-direction. Related questions are discussed in section 5.

### 2. Model and scattering intensity.

We consider the translational displacements of the TSeF molecules only for the reasons already stated further above. They have the $b$- and $c$-components according to the experimental observations [3]. They make a periodic modulation with wavenumber $2k_F$ on the uniform stack of TSeF molecules along the $b$-axis. We take account of the correlation between the displacements on TSeF columns neighbouring in the $c$-direction only and do not allow the possibility of correlations in the $a$-direction which are ruled out from the experimental observations [3]. Thus we consider essentially one sheet of TSeF molecules in the $bc$-plane as schematically drawn in figure 1. The short bars denote the TSeF molecules, which are planar but have rigid thickness due to the Van der Waals radii of the composing atoms. They are tightly stacked along the $b$-axis but columns of TSeF are relatively loosely arranged in the $c$-direction, since it is the larger TCNQ molecules that determine the repeat distance in this direction.

![Fig. 1. — Schematic figure of one sheet composed of TSeF molecules parallel to the $bc$-plane in TSeF-TCNQ. The short bars represent the planar molecules of TSeF. They are labelled by symbol $p$ for each TSeF column and $n$ for each molecule in the column. The direction of the tilt of the molecular plane changes alternately from column to column. The centre of mass of the molecule in odd-numbered columns is shifted by $b/2$ in the $b$-direction.](image)

Following the usual way [3], we assume that the translation of the $n$-th molecule in the $p$-th column situated at site $R_{np}$ is given by

$$U_{np} = \frac{b}{2} \sin (q_0 \cdot R_{np} + \Phi_p) + \alpha \sin (q_0 \cdot R_{np} + \Theta_p),$$

with

$$q_0 = 2 \pi b^* k_F,$$

where $k_F = 2 k_F = 0.315$, $b^*$ is the reciprocal lattice vector corresponding to $b$ ($b \cdot b^* = 1$); $\nu_p$, $\Phi_p$ and $\Theta_p$ are considered as thermally agitated random variables, which are only weakly correlated with those in the neighbouring chains; their properties will be defined later. $\alpha$ determines the amplitude of the $c$-component in relation to the $b$-component. We neglect the finiteness of the correlation length along each chain, since it is long enough to be approximated by infinity for the present purpose.
The scattering intensity \( I(Q) \) for scattering vector \( Q \) by the above sheet is given by

\[
I(Q) = \left( \sum_{n,p,v} f_v \exp[iQ \cdot (p_{nv} + \rho_{pv} + u_{np})] \right),
\]

where \( \langle \cdots \rangle \) means the thermal average; \( \rho_{pv} \) is the position of the \( v \)-th atom measured from the centre of the molecule and depends on the chain which is labelled by \( p \); \( f_v \) is the atomic scattering factor of the \( v \)-th atom. This is rewritten as :

\[
I(Q) = \sum_{n,p} \sum_{p'} \mathcal{S}_p(Q) \mathcal{S}_{p'}(Q) \times \exp[iQ \cdot (u_{np} - u_{n'p'})] \langle \exp[iQ \cdot (p_{nv} - p_{nv'})] \rangle,
\]

where \( \mathcal{S}_p(Q) = \sum_v f_v \exp(Q \cdot p_v) \) is the molecular form factor for the molecules of the \( p \)-th chain; there are two kinds of \( \mathcal{S}_p(Q) \), i.e., \( \mathcal{S}_{p=even}(Q) = \mathcal{S}_p(Q) \) and \( \mathcal{S}_{p=odd}(Q) = \mathcal{S}_p(Q) \) due to the different directions of the tilt of the molecular plane. Since the molecule has the inversion symmetry these factors are real. In the harmonic approximation we have

\[
I_B(Q) = \pi^2 \sum_p \mathcal{S}_p \mathcal{S}_{p'} \exp\{ i\pi [k \text{ mod } (p) + l \text{ mod } (p') - (k' \text{ mod } (p) - l') \}, \times
\]

\[
\times \left\{ \frac{\sin \pi (k' + k_0) N_y}{\sin \pi (k' + k_0)} \right\}^{2} (k, l) \cdot \mathcal{P}(p, p') \cdot \left\{ \frac{\sin \pi (k' - k_0) N_y}{\sin \pi (k' - k_0)} \right\}^{2} (k, l) \cdot \mathcal{P}^*(p, p') \left( k', l' \right),
\]

where \( N_y \) is the number of molecules along the \( b \)-axis and \( \mathcal{P}(p, p') \) is a \( 2 \times 2 \) matrix giving the correlation functions between the displacements on the \( p \)-th and \( p' \)-th columns and is defined by

\[
\mathcal{P}(p, p') = \left\langle \left( \frac{v_p \exp(i\Phi_p)}{\alpha_p \exp(i\Theta_p)} \right) \left( \frac{v_{p'} \exp(-i\Phi_{p'})}{\alpha_{p'} \exp(-i\Theta_{p'})} \right) \right\rangle.
\]

Since the correlation is considered to be small, the absolute magnitude of each component of \( \mathcal{P}(p, p') \) is as usual assumed to diminish exponentially with the distance between two columns, i.e., in proportion to

\[
e^{-\kappa |p-p'|} \equiv \psi |p-p'|
\]

where \( \psi = \exp(-\kappa) \) gives the strength of the correlation between the displacements on the neighbouring chains. Both the amplitude and phase fluctuations contribute to diminish the correlation.

Concerning its phase we preserve the possibility that it is neither equal to zero nor to \( \pi \), since we have no evidence showing that the soft mode giving the biggest contribution to the above correlation function has vanishing \( c \)-component of its wave vector in the metallic phase. For simplicity let us imagine that the main contribution comes only from one soft mode (the phonon mode corresponding to the minimum energy of the \( 2k_F \) anomaly) with the phase relations between the components of the translations of two TSeF molecules composing a unit cell as shown in figure 2:

\[
\begin{align*}
& \text{(i) the } b \text{-component of the translation of the chain at } p = 2\mu (\mu \text{ being an integer}) \text{ is in advance of the } c \text{-component by } \theta_0; \\
& \text{(ii) the } c \text{-component at } p = 2\mu + 1 \text{ is in advance of that at } p = 2\mu \text{ by } \theta_1 \text{ and the } b \text{-component of the same chain is in advance by } \theta_0 + \phi; \\
& \text{(iii) when we go ahead by } 2 \text{ chains, i.e., by one unit cell, in the } c \text{-direction both phases advance by } \theta_2.
\end{align*}
\]

![Fig. 2. — Figure defining the phase relations of the components of the translational displacement in the lattice vibration corresponding to the soft mode. The phase of the } b \text{-component on column } p = 2\mu (\mu \text{ being an integer}) \text{ in the sense in equation (1) is in advance by } \theta_0 \text{ in reference to that of the } c \text{-component on the same column } (p = 2\mu). \text{ The phase of the } c \text{-component on column } p = 2\mu + 1 \text{ is in advance by } \theta_1 \text{ and that of the } b \text{-component is in advance by } \theta_0 + \phi, \text{ in the same reference. When we pass two columns, i.e., one unit cell in the } c \text{-direction, the phases of both components advance by } \theta_2.]
In general the amplitudes of the two components on the second molecule can be different from those on the first. Here we choose the same amplitudes since it is the phases that characterize principally the nature of the correlations.

If we consider that the molecular translations and the correlations between their components, which are responsible for the intensity variation within the $2k_F$ diffuse sheets, are mainly due to the modes around the minimum energy of the $2k_F$ phonon dispersion anomaly, we can naturally assume that the above phase relations are also held in the correlation functions $\Psi(p, p')$ in the following way:

$$
\begin{align*}
\Psi(2\mu, 0) &= v^2 e^{-2\kappa|\mu|+i\theta_0\mu} \left( \alpha e^{i\theta_0}, \frac{\alpha e^{i\theta_0}}{\alpha^2} \right), \\
\Psi(2\mu + 1, 1) &= v^2 e^{-2\kappa|\mu|+i\theta_1\mu} \left( \alpha e^{i(\theta_0+\varphi_1-\theta_1)}, \frac{\alpha e^{i(\theta_0+\varphi_1-\theta_1)}}{\alpha^2} \right), \\
\Psi(2\mu, 1) &= v^2 e^{-\kappa(2\mu-1)+i\theta_2(2\mu-1)/2} \left( \alpha e^{i(\theta_2/2-\varphi_1)}, \frac{\alpha e^{i(\theta_2/2-\varphi_1)}}{\alpha^2} \right), \\
\Psi(2\mu + 1, 0) &= v^2 e^{-\kappa(2\mu+1)+i\theta_2(2\mu+1)/2} \left( \alpha e^{i(-\theta_2/2+\varphi_1)}, \frac{\alpha e^{i(-\theta_2/2+\varphi_1)}}{\alpha^2} \right).
\end{align*}
\tag{11}
$$

Here $\nu$ is the root mean square average of the longitudinal component. The correlation matrix has the following property:

$$
\Psi(p + 2, p' + 2) = \Psi(p, p').
\tag{12}
$$

Putting the above expressions into equation (8), we obtain

$$
I_D(Q) = \frac{2^{-1}}{2^{-1}} \left[ \frac{\sin \pi(k + k_0) N_y}{\sin \pi(k + k_0)} \right]^2 \frac{1 - \psi^2}{1 - 2 \psi^2 \cos \theta_0} \times \left[ (1+\psi^2) \{ (\mathcal{F}_0^2 + \mathcal{F}_1^2) (k^2 + \alpha^2 l^2) + 2 \alpha k l \mathcal{F}_0 \mathcal{F}_1 \cos \theta_2 \cos (\theta_0 + \varphi_1 - \theta_1) \} \right. \\
+ 4 \psi (-1)^{k+k_0} \cdot \frac{y}{2} \cdot \mathcal{F}_0 \mathcal{F}_1 \left[ k^2 \cos \left( \frac{1}{2} \varphi_1 - \frac{\theta_2 - \theta_1}{2} \right) + \alpha^2 l^2 \cos \left( \frac{1}{2} \theta_2 - \theta_1 \right) \right] \\
\left. + 2 \alpha k l \cos \left( \frac{\theta_0 - \varphi_1}{2} \right) \cdot \cos \left( \frac{\theta_2 - \theta_1 - \varphi_1}{2} \right) \right] + (\text{same except for changing } k_0 \rightarrow -k_0 \text{ and } y \rightarrow y'),
\tag{13}
$$

where $y = 2\pi l + \theta_2$, $y' = 2\pi l - \theta_2$ and the second term means that it is given from the first one by replacing $k_0$ and $y$ by $-k_0$ and $y'$, respectively.

Since $N_y$ is very large, this expression gives diffuse planes in the reciprocal space at $k = \text{integer} \pm k_0$ with $\delta$-function type sharpness along the $k$-direction. The linear term in the correlation strength $\psi$ in the large square bracket gives the leading contribution coming from the correlation between neighbouring chains and modulates the intensity through the factor 

$$
\cos \left( y/2 \right) = \cos \left( \pi l \pm \theta_2/2 \right).
$$

For short range correlations as is the case here, this factor gives an additional fine structure to the slowly varying scattering intensity from the molecular form factor which determines the general feature of the intensity distribution. Modulation of higher order in $\psi$ arises from the common factor $[1 - 2 \psi^2 \cos (2\pi l + \theta_2) + \psi^4]^{-1}$. Since the above model has many parameters due to possible phase differences, we call it phase difference (PD) model.

If we put in the following constraint:

$$
\theta_0 = 0, \quad \varphi_1 = \theta_2/2,
\tag{14}
$$

we have the case of the simplest plane wave of translation whose polarization is parallel to $b + \alpha c$.

If we put in another constraint:

$$
\theta_0 = 0, \quad \theta_2 = 2 \theta_1, \quad \varphi_1 = \theta_1 + \pi,
\tag{15}
$$

we have a phonon mode in which the $b$-component of polarization on the odd-number column has the opposite sign to that of the $c$-component, although both components have the same sign on the even-number column. Therefore, apart from the uniformly advancing part of the phases, the translation pattern
Herringbone (HB) pattern of the translational displacements of TSeF molecules. Each arrow shows schematically the translational displacement of a molecule when we put off the part of phase advancing with wavenumber \(2 k_F\) along each column.

is given by figure 3. We call it herringbone (HB) pattern. If

\[
\alpha = b \cot \theta_{\text{tilt}}/c \approx 0.43 ,
\]

where \(\theta_{\text{tilt}}\) is the angle between the molecular plane and the ac-plane, the molecular translations are completely parallel to the molecular surfaces both on the even-number and odd-number columns.

If we put \(\alpha = 0\) in equation (13), we get the scattering intensity given by the purely longitudinal mode. If we keep only the terms of order \(a^2\), we get that given by the purely transverse mode.

We found first that if we put \(\alpha \approx 0.25\) and \(\theta_\parallel = 0\) with equations (15), a relatively good agreement to the observed data is obtained and then we expected that only slight modifications to the above constraint would improve the agreement and eliminate small discrepancies. For further work of fitting, it appeared convenient to introduce another combination of variables as is described in Appendix A.

3. Preliminaries for fitting. — Our purpose is to fit the calculated scattering intensity in equations (13) and (A.2) to the observed intensity distribution by choosing appropriate values for the parameters appearing in the calculation and to extract the information on the displacement pattern in TSeF-TCNQ.

This section describes preliminaries to relate the calculated intensity with the observed X-ray photographs.

The experimental technique used for obtaining the X-ray diffuse scattering photographs was the same as in the previous work [3], the fixed-film, fixed-crystal monochromatic method described with more details in reference [1]. Figure 4 illustrates schematically the experimental setup and figures 5a and 5b show typical photographs of the patterns used in the present analysis (patterns D' 9 and D' 3).

3.1 VALUES OF h, k and l. — First we need the relation between the position on the photograph and the corresponding values of \(h, k\) and \(l\) which determine the scattering vector, \(Q\) or \(S = Q/2\pi\), for the fixed-crystal, fixed-film recording technique.

In figure 6, we see the relation between the crystal axes \(a, b\) and \(c\), the incident X-ray wave vector \(K\), the out-going one \(K'\) and the scattering vector \(S\):

\[
S = K' - K .
\]

The sample is situated at the centre \(O\), and the directions of the axes \(a, b\) and \(c\) are associated to it. For our analysis the incident X-ray beam is desirable to be parallel to the ac-plane. The small orientational error in setting the sample is specified by angle \(\delta\) as is shown in figure 5; \(\delta\) is defined as the angle between the incident wave vector and the ac-plane. The most important parameter of the sample orientation is the angle \(\epsilon\) which is defined by the angle spanned between \(K\) and the ab-plane as in figure 6. The photographic film is set upon a cylinder, which is similar in the
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Fig. 6. — Figure illustrating the angular relation among the incident and scattered X-ray wave vectors, K and K', and the crystal lattice vectors, a, b and c. The orientational angles, \(\varepsilon\) and \(\delta\), and the horizontal component \(\gamma\) of the scattering angle are defined in the text in reference to this figure. \(\beta\) is the angle between the a- and c-axes. \(S = K' - K\) is the scattering vector and can be expressed in units of the reciprocal vectors, \(a^*\), \(b^*\) and \(c^*\), which are defined with respect to the lattice vectors fixed to the sample crystal. The sphere is the Ewald sphere. The photographic film is set upon a cylinder, which is similar to the cylinder touching to the Ewald sphere at the dotted line on the sphere.

generical sense to the cylinder touching to the Ewald sphere at the dotted circle in figure 6.

The intensity of the X-ray scattered in the direction of wave vector K' is proportional to \(I_0(Q)\) obtained in section 2 with \(Q = 2\pi S = 2\pi(K' - K)\) illustrated in figure 6 [4]. \(h, k\) and \(l\) are defined from \(Q\) by equation (6). According to the calculation, the lattice modulation with reduced wavenumber \(k_0\) gives diffuse scattering lines corresponding to the intersections of the Ewald sphere with planes defined by

\[
k = \text{integer} \pm k_0.
\]

The value of \(k\) for each diffuse line can be easily identified from its relation to the incident beam and the crystal orientation.

Each point on a diffuse line is specified by the horizontal component \(\gamma\) of the scattering angle, which is defined as the angle between the two planes formed by \(K'\) and \(b\) and by \(K\) and \(b\), respectively. On the film \(\gamma\) is obtained from the distance \(x\) between the point considered on the diffuse line and the intersection of this line with the vertical plane containing the incident X-ray beam. If the experimental setup is well oriented, \(\gamma\) is proportional to \(x\).

The values of \(h\) and \(l\) for \(S\) corresponding to the point on the film are given as follows:

\[
h = \frac{\lambda}{2\pi} \left[ \sqrt{1 - (\zeta - \sin \delta)^2} \cos (\gamma - \varepsilon) - \cos \delta \cos \varepsilon \right], \tag{19a}
\]

\[
l = \frac{\lambda}{2\pi} \left[ \sqrt{1 - (\zeta - \sin \delta)^2} \cos (\beta + \varepsilon - \delta) - \cos \delta \cos (\beta + \varepsilon) \right], \tag{19b}
\]

with

\[
z = \frac{\lambda}{2\pi} k, \tag{19c}
\]

where \(\lambda\) is the wavelength of the X-ray and in our case we put \(\lambda = 1.542\ \text{Å}\), since we used the Cu-K\(\alpha\) line which is composed of two components with wavelength 1.540 Å and 1.544 Å. For the value of \(k_0\) we take \(k_0 = 0.315\).

Although using only Se atoms seems to give a good approximation, we took account of all atoms in the TSeF molecules. We used the values of lattice parameters

\[
a = 12.504 \text{ Å}, \quad b = 3.872 \text{ Å}, \quad c = 18.504 \text{ Å}
\]

and also the atomic positions, both given by Laplaca [5] for TSeF-TCNQ at room temperature.

3.2 TWIN. — Unhappily, all available crystals were twin crystals, which made our work more complicated. The twin crystal is composed of two kinds of domains of single crystals; in each domain the directions of the crystal axes are well defined. If we denote the two systems of crystal axes by \((a, b, c)\) and \((a', b', c')\), they have the relation defined by \(a' = -a\) and \(b' = -b\). The corresponding relation between \((h, k, l)\) and \((h', k', l')\) are given by

\[
h' = -h, \quad k' = -k, \quad l' = l - 2c.\cos \beta/a.h. \tag{21}
\]

The two kinds of domains share the same diffuse scattering sheets in the reciprocal lattice space, although the value of \(k\) for each plane is different by sign in each coordinate system. At each point on the diffuse line, both systems give different values of \(h\) and \(l\). In the calculation of the scattering intensity at this point, we have to add two contributions from both kinds of domains multiplying the weight of each twin component. In most cases the ratio of both components is found to be 50-50. We define the parameter \(C\) as the ratio of the twin component having the system \((a, b, c)\) to the whole crystal.

3.3 ATOMIC SCATTERING FACTOR. — We used the atomic scattering factors as approximated by Moore [6]. For the Se atom, for example, it is given by

\[
f_{\text{Se}} = 18.662 \exp \left[ -2.849 \left( \frac{\sin \theta}{\lambda} \right)^2 \right] + 6.835 \exp \left[ -33.858 \left( \frac{\sin \theta}{\lambda} \right)^2 \right] + 8.465, \tag{22}
\]

where \(\theta\) is the half of the scattering angle and related with scattering wave vector \(S\) as

\[
S^2 = 4(\sin \theta/\lambda)^2. \tag{23}
\]
3.4 Anisotropic thermal factor. — The exponent of this factor was estimated for room temperature according to the structure reported by Laplaca [5]. It was found to reduce the intensity by less than 10% at 40 K and was therefore neglected.

3.5 Polarization correction. — Due to the process of monochromatization, the incident beam is polarized. For this reason we bring in the following correction factor [4] to the scattering intensity:

$$f_{pol} = \frac{1 + \cos^2 2 \bar{\alpha} \cos^2 2 \bar{\beta}}{1 + \cos^2 2 \bar{\alpha}}.$$  (24)

In our case $\cos^2 2 \bar{\alpha} \approx 0.8$.

3.6 Integrated scattering intensity. — We can show that the coefficient of $\delta$-function-like factor $[\sin(nk + k_0)/\sin(nk + k_0)]^2$ in the expression of $I_d(Q)$, e.g., equation (13), multiplied by the above mentioned correction factors, is proportional to the integrated scattering intensity, which is defined as the integration over the scattering intensity profile of the diffuse line at a fixed value of $\gamma$ in the perpendicular direction to the diffuse line.

3.7 Correction for the background. — The ordinary microdensitometer reading, by scanning along a $2_kF$ diffuse line of an X-ray pattern as shown in figure 6 of reference [3a], only gives a qualitative outline of the intensity distribution. The main reason is that besides the $2_kF$ phonons, of interest, such readings always include the background scattering from the other phonons, and what is worse is that with a given aperture setting of the microdensitometer this background is weighted differently for the successive $2_kF$ lines ($k = 2_kF, 1 - 2_kF, 1 + 2_kF, 2 - 2_kF$, etc.). In order to get the appropriate data we made the correction for the background in the way described in Appendix C.

3.8 Photographs. — Three different photographs corresponding to three different crystal orientations ($\varepsilon = 48^\circ$ (pattern D' 9), $\varepsilon = 54^\circ$ (pattern D' 3) and $\varepsilon = 65^\circ$ (pattern RIV)) as defined above were analysed in the present work. Twinning could be directly estimated to correspond to almost 50% of each of the two monoclinic components ($C = 0.5$) for the two first cases, and to almost 30% ($C = 0.2$) for the last case (different crystal). The temperature of cooling gas was 40 K but the actual temperature of the sample was estimated to be about 55 K. Comparison with patterns obtained for the similar orientations but at higher temperatures around 100 K revealed little temperature dependence of the distribution of the scattered intensity. Besides an overall intensity increase which can be attributed to the increased Boltzmann phonon population factor, one only notes a very small smearing of the fine substructures of the intensity distribution which is related to decrease of the correlation between chains is the $c$-direction; but the effect is too small to be estimated quantitatively.

4. Process and results of fitting. — 4.1 Previous work. — As shown in the patterns of figures 5a and 5b, the intensity distribution along the diffuse lines show two remarkably distinct features: rapid and small intensity variations within broader slowly varying primary maxima. Most often this results in the observation of double peaked maxima (arrows on the X-ray pattern of figure 5a).

The primary broad maxima were assigned [3] as due to translations of TSeF molecules in 1D uncoupled modulation waves along the stacks (purely 1D phonon anomaly), with two independent translation components along $b$ and $c$ of comparable amplitudes. The smaller variations (referred below as substructures of the intensity distribution) were suggested to arise from weak correlations between the modulation waves on neighbouring TSeF stacks, i.e., in the $c$-direction.

4.2 Herringbone (HB) model. — Rather than two independent translations implying two independent phonon modes, it is more natural to assume only one important mode contributing to the $2_kF$ diffuse scattering. We tried to find a mode which has both $b$- and $c$-components of translation and reproduces the features of the X-ray photographs.

4.2.1 Displacement components in the purely 1D approximation. — As in reference [3], in the first step of our analysis, we neglect the weak coupling between neighbouring stacks in the $c$-direction, with the aim to reproduce only the primary broad intensity maxima with their relative intensities.

The simplest type is the model in which the $b$- and $c$-components are everywhere in phase or antiphase relative to one another so that the TSeF molecules...
move along one common direction regardless of the direction of the tilt of the molecular plane on the stack. This gives very different calculated features. Clear resemblance with the experimental data is observed only when we take account of the possibility that the direction of the molecular translation changes from stack to stack in accord with the alternate change of the direction of the molecular tilt. In this situation the extreme cases are those in which the TSeF molecules move parallel to their molecular plane or on the contrary perpendicular to it as shown in figure 7.

If we choose the relation between the phase $\Phi_p$ for the longitudinal component and that $\Theta_p$ for the transverse component defined in equation (1) as follows:

$$\Phi_p - \Theta_p = \begin{cases} 2\pi v & \text{if } p = \text{even}, \\ \pi(2v + 1) & \text{if } p = \text{odd}, \end{cases} \quad (25)$$

where $v$ is an integer, the above two cases are specified by the sign of $\alpha$, i.e., $\alpha > 0$ in the case of the nearly parallel movement and $\alpha < 0$ in the nearly perpendicular case. The phases on the different chains have no correlation, i.e., $\psi = 0$. Computing the scattering intensity in both cases we found that the case $\alpha > 0$ reproduces at good positions the primary big peaks in the pattern D'9 with reasonable relative magnitudes. The results are better than those of the independent two modes model. The case $\alpha < 0$ did not work. So we carried out extensive efforts for fitting by a model based on the type of translation in the case of $\alpha > 0$. From the feature of the displacement pattern we call it herringbone (HB) model.

4.2.2 Correlation between TSeF stack — the HB description. — Next we bring into this model a weak correlation between the translations defined by equation (1) on neighbouring stacks. The correlation functions and the expression of the scattering intensity are given by putting into the expressions for the phase difference (PD) model in section 2 a special set of parameter values satisfying equation (15). Then the scattering intensity is given by

$$I_0(Q) = \frac{1}{2} N_z \pi^2 v^2 \left[ \frac{\sin \pi(k+k_0)Ny}{\sin \pi(k+k_0)} \right]^2 \frac{1-\psi^2}{1-2\psi^2 \cos(\pi l + \theta_2) + \psi^4} \times$$

$$\times \left\{ (1+\psi^2) \left[ (k+u,l)^2 \bar{S}_0^0 + (k-u,l)^2 \bar{S}_1^0 \right] + 4\psi(1+\psi^2) \cos \left( \pi l + \theta_2 \right) \cos \frac{1}{2} \theta_2, \langle x^2 l^2 - k^2 \rangle \bar{S}_0 \bar{S}_1 \right\}$$

$$+ \left( \begin{array}{c} \kappa_0 - \kappa_0' \\ \kappa_2 - \kappa_2' \end{array} \right) \cdot \right. \quad (26)$$

We keep here the possibility that the phase progresses by $\theta_2$ when we proceed by a unit cell along the $c$-axis.

Adding both contributions of the equally weighted twin components we tried to find agreement with the data for the patterns D'9 (Fig. 5a) and D'3 (Fig. 5b). The best fitting was obtained with the following set of parameter values:

| Pattern D'9 | $\varepsilon = 48^0$, $\delta = 1^0$ |
| Pattern D'3 | $\varepsilon = 54^0$, $\delta = 1^0$ |

$$\alpha = 0.25, \quad \psi = 0.30, \quad \theta_2 = 0. \quad (27)$$

The results for the HB model are given in figures 8a through 8e. The black circles represent the observed integrated scattering intensities as explained in section 3. The dotted curve corresponds to our first approximation without correlations. The continuous curve is the calculated one taking into account the correlation between stacks. The vertical dash-dot line shows the position $\gamma = \varepsilon$ around which the data is deformed due to heavy absorption of the scattered X-ray by the sample edge. For each 2 $k_F$ diffuse lines ($k = \text{integer} \pm 2 k_F$), the horizontal scales give the correspondence between the horizontal component $\gamma$ of the scattering angle, and the respective indices $h$, $l$ on one hand and $h'$, $l'$ on the other for the two monoclinic twins.

Since the direct estimate of the sample orientation is somewhat imprecise, in the fitting procedure we have allowed small variations of the value of the angle $\varepsilon$ in the horizontal plane, and small deviations from zero for the angle $\delta$ in the vertical plane (angles defined in section 3 and in figures 4 and 6).

Results yield an upper limit of $\pm 0.5^0$ for the error on $\varepsilon$. Outside this range the calculation cannot reproduce the fine substructures of the intensity distribution. In order to reproduce in the calculations the small differences observed between corresponding 2 $k_F$ lines from the upper and lower part of the patterns (i.e., between $+2 k_F$ and $-2 k_F$, or $+1 - 2 k_F$ and $-(1 - 2 k_F)$), the angle $\delta$ had to be fixed to $1^0$ for both patterns D'9 (Fig. 5a) and D'3 (Fig. 5b). Similar variations around the estimated $50\%$ twinning (value of parameter $C$) gave no significant changes for the calculated intensities.

If one excludes the region of the patterns corresponding to a horizontal component $\gamma$ of the scattering angle around $48^0$ for D'9 and $54^0$ for D'3 where the
Fig. 8. — Results of fitting to patterns D' 9 (a ~ d) and D' 3 (e) by the HB model whose parameter values are chosen as in equation (27): \( \alpha = 0.25, \theta = 0.30, \delta_2 = \delta_3 = \delta_4 = 0 \) for D' 9 with \( \varepsilon = 48^\circ, \delta = 1^\circ \) and for D' 3 with \( \varepsilon = 54^\circ, \delta = 1^\circ \). The black circles represent the observed integrated scattering intensity of the 2 \( k_F \) diffuse lines in arbitrary units at scattering angle \( \gamma \). The error in the difference between the successive points is believed to be smaller than 30 units, although the absolute error bound for each point is slightly larger. The continuous curve is the calculated one taking account of the correlation between chains and the dotted curve is that taking no account of correlation. The vertical dash-dot line shows the position \( \gamma = \varepsilon \) around which the data is deformed due to the strong absorption of the scattered X-ray by the sample edge so that proper recording of the scattered beam intensity has not been possible in this region. The scales below give the values of \( l \) and \( h \) and their counterparts, \( l' \) and \( h' \), in the twin component. The 2 \( k_F \) line treated in figure 8b is the same as in figure 6 in reference [3a].
scattering is shadowed by the sample maximum absorption, the two main features characterize the curves shown in figures 8a through 8e:

(i) a broad primary maximum around \( \gamma = 90^\circ \) appearing in all the cases studied here, which corresponds to very large values of the index \( l(\gamma') \) and for which the largest contribution therefore comes from the transverse component along \( c \) \((a l \times \text{molecular form factor})^2\), see equation (26), and

(ii) another broad primary maximum around \( \gamma = 10^\circ \) appearing in the cases of \( k = 1 + 2 k_F \) and \( k = 2 - 2 k_F \), which corresponds to smaller values of \( l(\gamma') \) and where therefore the longitudinal displacement component contributes most substantially \((k \times \text{molecular form factor})^2\).

The ratio of these main peaks along each diffuse \( 2k_F \) line is therefore controlled by the relative contributions from the two displacement components along \( c \) and \( b \), respectively. A least square fit to the relative magnitudes of the six broad peaks of pattern D'9 yields \( \alpha = 0.25 \); taking into account the difference in the lattice constants \( b \) and \( c \) the ratio of the longitudinal to the transverse component is found to be \( b/2c = 0.8 \) in close agreement with the ratio derived by Megtert et al. [3].

On the top of the main features considered above, one observes a substructure of the intensity distribution. This substructure is produced in equation (26) by the denominator and more strongly in the case of small \( \psi \) by the second term in the big square bracket.

The position of the secondary maxima are determined by the conditions \( \cos(\pi l \pm \theta_2/2) = + 1 \) or \(-1 \), where \( \theta_2 \) is the phase progression from one unit cell to the next in the \( c \)-direction. In the simple case of the herringbone model or \( \theta_2 = 0 \), these maxima are calculated to occur at integer values of \( l \); this corresponds to the position of the satellites of the 3D ordered low temperature modulated phase below 29 K.

The sharpness of the secondary peaks is controlled by the parameter \( \psi \) which is related to the extension of the correlation in the \( c \)-direction. The best fit is obtained for \( \psi = 0.3 \) and corresponds to very weak correlations extending at most to 2 or 3 successive stacks.

The calculated curves are in good agreement with the observed ones; they reproduce not only the primary broad peaks at good positions with appropriate relative magnitudes but also most substructures fairly well. Especially good agreement is found in the range of big \( \gamma \) where the main contribution comes from the transverse component of translation. For example, they reproduce two double peaks similar to the observed ones around \( \gamma = 10^\circ \) and \( \gamma = 80^\circ \) in the case of \( k = 1 + 2 k_F \), a double peak around \( \gamma = 80^\circ \) in the case of \( k = 2 - 2 k_F \), and also good double peaks around \( \gamma = 90^\circ \) in the cases of \( k = 1 - 2 k_F \) and \( k = 2 k_F \). With nonzero \( \delta \) the difference of the substructures between the cases of \( k = \pm (1 - 2 k_F) \) are well reproduced.

But the results of the HB model leaves two small discrepancies; the subpeak at \( \gamma \approx 2^\circ \) in the case of \( k = 1 + 2 k_F \) is a little too small; we cannot eliminate the substructure around \( \gamma \approx 20^\circ \) in the case of \( k = 2 - 2 k_F \) and the peak around \( \gamma \approx 15^\circ \) is a little shifted from the observed position.

We tried similar calculations with a model in which the longitudinal (L) and transverse (T, in the \( c \)-direction) displacement components were independent. This model was found to give similar results for D'9 with both good and bad features except that the peak around \( \gamma \approx 80^\circ \) in the case of \( k = 2 - 2 k_F \) is unacceptable much smaller. This suggests that for this angle the scattering amplitudes from both the longitudinal and transverse components of the lattice modulation have to be added in phase to generate a bigger peak. This supports the HB model and its coherence of the two displacement components which indeed increases this particular peak intensity.

We made much effort to improve the agreement with the data in the framework of the HB model. For example, we examined the effects of thermal contractions of the lattice parameters, decrease of the tilt angle of the molecule, rotation and contraction of the molecule and the change of the value of \( 2k_F \). Such changes proved to have little effect on the calculated intensity distribution. We examined also the effects of an eventual \( a \)-component in the translation. With a reasonable small magnitude, such an additional component introduces only negligible changes.

4.3 Phase Difference (PD) Model. — As stated above, the HB model is obtained by fixing the parameters which introduce arbitrary phase differences in the more general PD model described above. Improvements can be expected by relaxing this constraint and examining the situation where these parameters are allowed to vary around the values of the HB model.

The first aim was to enhance the subpeak around \( \gamma = 2^\circ \) in the calculated curve for \( k = 1 + 2 k_F \). This was first tried by using the expression of the intensity for the generalized model and trying nonzero values of \( \theta_2 \), the phase progression along the \( c \)-axis, defined in figure 2. The adjustment of the sign and magnitude of the correlation term (or 2D term) by varying the other phase difference parameters remarkably improved the agreement between calculated and observed results, not only around \( \gamma = 2^\circ (k=1+2 k_F) \) but also around \( \gamma \approx 10^\circ \) in the case of \( k = 2 - 2 k_F \) for the same choice of parameters. But it also introduced difficulties for other scattering angles. For further improvements, we found that we had to take into account, with the same weight, all symmetry related equivalent modes of one TSeF bc-plane as discussed in Appendix B.

To calculate the scattering intensity for given values of \( k \) and \( \gamma \), we have to sum up four contributions, since for each twin component of the sample, we have two types of contributions coming from the equivalent modes, each given by equation (A.2) but with
the different values of the phase parameters related by equation (B.1) or (B.2). For each type of contribution we have two sets of values of \( h, k \) and \( l \) related to one another by equation (21) for the twins. Apparently this situation makes the adjustment of the parameters hopelessly complicated but it proved feasible.

When the value of the correlation strength \( \psi \) is small, the secondary peaks in the intensity distribution arise from the second term with the 2D coefficient \( f_{2D}(a, \theta, \delta_2, \delta_1) \) in the big square bracket of equation (A.2). Analysing each of the four contributions mentioned above for each substructure, we found the desirable sign and magnitude of the 2D coefficient for the contributions which happened to be important. Then, we looked for the parameter space spanned by \( \theta \), \( \delta_2 \) and \( \delta_1 \) in which the requirements for the 2D coefficients are fulfilled, and reproduced the features adjusting the other parameter values. Through such a procedure for all substructures in the patterns D'9 and D'3 the set of parameters converged to the following values:

\[
\begin{align*}
\alpha &= 0.25 \pm 0.10, \\
\psi &= 0.36 \pm 0.07, \\
\theta &= 40^\circ \pm 15^\circ, \\
\delta_2 &= -30^\circ \pm 10^\circ, \\
\delta_1 &= -46^\circ \pm 8^\circ, \\
\theta_2 &= 65^\circ \pm 15^\circ, \\
\end{align*}
\]

with the orientation parameters:

\[
\begin{align*}
\varepsilon &= 48^\circ \pm 0.5^\circ \text{ and } \delta = 0.7^\circ \pm 0.5^\circ \text{ for D'9}, \\
\varepsilon &= 54^\circ \pm 0.5^\circ \text{ and } \delta = 0.7^\circ \pm 0.5^\circ \text{ for D'3}.
\end{align*}
\]

The values in the parentheses give the magnitude of variation which changes the features of the intensity curves unacceptably, with the other parameters being unchanged. A strong correlation was observed between the values of \( \delta_2 \) and \( \delta_1 \); there is a very wide range where the results are comparably good if we optimize one parameter after changing the other.

A remarkable result is the nonzero value of \( \theta_2 \), in contrast with \( \theta_2 = 0 \) observed in the low temperature insulating phase \([7, 2]\). A value of \( \theta_2 \) of the order of \( 90^\circ \) was required for the improvement of the features of the medium-sized peaks around \( \gamma \sim 10^\circ \) on the lines \( k = 1 + 2k_F \) and \( k = 2 - 2k_F \), especially to obtain the adequate peak position. On the other hand the line \( k = 1 - 2k_F \) of D'9 required \( \theta_2 \leq 80^\circ \) in order to keep its sharp-structured double peak. The value \( \theta_2 = 65^\circ \) appeared to give the best compromise. Allowing small variation of the angels \( \varepsilon \) and \( \delta \) defining the sample orientation yielded no change for \( \varepsilon \), and only negligible changes for \( \delta \) compared to those obtained for the simpler HB model. We observe a tendency for improved features around \( \gamma \sim 10^\circ \) with bigger values of \( \alpha \) (defining the relative magnitude of the longitudinal and transverse components) but we kept to the previous value of \( \alpha = 0.25 \) which was obtained from the relative intensities of the primary broad peaks. The present model also required somewhat larger values of \( \psi \) (correlation strength), since the substructures from all four contributions mentioned above have a tendency to smear the resulting features.

The calculated intensity obtained with this elaborate model is compared to the experimental data in figures 9a through 9h. We can note that the features around \( \gamma \sim 10^\circ \) for the pattern D'9 show appreciably better agreement; we have now a distinct double peak around \( \gamma \sim 10^\circ \) at least qualitatively similar to the observed one; the more pronounced dip in the experimental curve can be a consequence of an overestimated background as mentioned in Appendix C. In the case of \( k = 2 - 2k_F \) the peak position around \( \gamma \sim 10^\circ \) is well improved. The features in the range around \( \gamma \sim 80^\circ \) are also somewhat closer. For other parts of the pattern both models work as well.

Concerning the results for the pattern D'3, qualitatively similar improvements are found for the peaks in the range around \( \gamma \sim 10^\circ \) on the lines with \( k = 1 + 2k_F \) and \( 2 - 2k_F \), which remain almost the same as in D'9. The results in the range of larger \( \gamma \) are very good for both models except for the case of \( k = 2 - 2k_F \), where the PD model is only a little better than the HB model. Even though the features are drastically changed when going from pattern D'9 to pattern D'3, the calculated curves reproduce well the experimental results, i.e., the appropriate relative magnitudes of the primary broad peaks and their substructures at the correct positions.

A further checking of our models was also performed for a third pattern R1v corresponding to a very different orientation (\( \varepsilon = 65^\circ \)), but also to a different crystal. Smaller sample size and different experimental conditions resulted, however, in this case in weaker \( 2k_F \) diffuse scattering; as a consequence the absolute evaluation of the integrated intensity (as described in Appendix C) used for patterns D'9 and D'3 could not be performed with pattern R1v, and we had to rely on the more usual microdensitometer reading obtained by scanning along each diffuse line. This allows only a very qualitative comparison between calculated and observed intensity distributions. Good agreement was obtained both for the PD model and for the simpler HB model if the ratio between the two twins was set to 20-80 (\( C = 0.2 \)); this is reasonable in view of an apparent better crystal quality. Again, and in
spite of the qualitative nature of the comparison between calculated and observed intensity distributions concerning pattern R_{1V}, this good agreement is very satisfactory since not only the features from pattern R_{1V} are very different from those of patterns D'_{9} and D'_{3}, but also because in pattern R_{1V} the absence of absorption shadowing (imagine a photograph like figures 5a and 5b for $\gamma = 65^\circ$) makes a much wider scattering range observable without disturbance on the single X-ray pattern.

5. Discussion. — The elaborate phase difference (PD) model with the fitted parameter values (Eqs. (28) and (29)) is found to reproduce very well the overall features of the X-ray scattering intensity distribution within the 2kF sheets. The agreement between calculation and experimental observation remains however semiquantitative. The broad maxima (which are a direct consequence of the type of molecular movement) are well reproduced with the adequate positions and relative intensities. The detailed features within the broad maxima (which are due to the weak coupling of the TSeF modulation waves in the bc-plane) leave appreciable differences; the agreement is excellent in the range of large scattering angles ($\gamma \sim 10^\circ$), which concerns more directly the correlation between the longitudinal translation components, further improvements seem possible.

At the stage of agreement reached with our PD model, other factors than those considered so far, may become meaningful. One can think for instance of an additional independent longitudinal mode which would only contribute in the small $\gamma$ region as already mentioned above where some small discrepancies remain; this would recall the independent longitudinal mode observed in the insulating phase of TTF-TCNQ stable below 49 K [8]. Such an addition, however, did not bring a meaningful improvement and it was felt that with the precision of the presently available experimental data it would make little sense to introduce such minor refinements.

Since several authors [9] have insistently claimed that the 2k modulation waves of TTF-TCNQ and related compounds could consists of molecular librations, we have also examined the possible contributions from such modes to the 2kF intensity distribution. Neither of the librations, around the three main axes of the TSeF molecules, produces an intensity distribution with the slightest resemblance to the observed scattering. Our analysis thus denies that such modes could appreciably contribute to the 2kF scattering.

Recently Eldridge et al. [10] found abundant features coming from the TSeF torsion mode around its longest axis besides many features from intramolecular vibrations in the bolometric spectrum of TSeF-TCNQ. Since our analysis is limited to the rigid molecular displacements, we do not know if weak contributions from such a torsion mode could eliminate the small remaining discrepancies in the region of $\gamma \sim 10^\circ$ or not. The other intramolecular vibrations are unlikely to be of importance in our problem because of their modest coupling constants and high vibration frequencies.

According to the results obtained in the previous section, the displacement pattern in the soft mode is not so far from the herringbone (HB) pattern. The phase differences defined in figure 2 are given in the present results as follows:

$$\theta_1 = -13.5^\circ, \quad \theta_2 = 65^\circ, \quad \theta_0 = 55^\circ,$$

$$\theta_0 + \varphi_1 = 191.5^\circ \quad \text{and} \quad \theta_2 + \theta_0 = 120^\circ.$$ (30)

The value of $\alpha = 0.25$ is smaller than

$$b. \cot \theta_{\text{ubl}}/c = 0.43$$

expected from the naive HB picture, but not so far. We can understand that the TSeF molecules slide preferably along their planar surface which consists of hard sphere atoms with the Van der Waals radii.

This displacement pattern calculated by equation (1) with the above parameter values are shown schema-
Fig. 10. — 2D displacement pattern calculated by equation (1) with the best fit parameter values for the PD model, given by equation (28) or (30). The continuous line denotes the translated TSeF molecules and the dashed line is the averaged position of the molecule. The amplitude of the longitudinal component is chosen to be 0.2 \( \mu \text{m} \), which is at least ten times larger than the realistic value, so that we can see the features easily.

tically in figure 10, where continuous thick lines denote the translated TSeF molecules and the dashed lines are for the average positions of molecules.

One of the surprising results provided by our final model is the nonzero value of \( \theta_2 \), phase progression per unit cell in the \( c \)-direction; \( \theta_2 = 0 \) is indeed obtained for the low temperature satellite peak positions (\( l = \) integer) in the insulating phase below 29 K [7, 2]. Horowitz and Mukamel [11] have in fact worked out a model for TTF-TCNQ which predicts a nonzero value of \( \theta_2 \), but for the stable state in the insulating phase where it is not observed; it might however bring some insight to our results. In their model the nonzero value of \( \theta_2 \) is due to the interaction between neighbouring columns, including the neighbours in the \( a \)-direction, and to the lack of mirror symmetry with respect to the \( bc \)-plane.

X-ray diffuse scattering counter measurements in more limited range of the 2\( k_F \) diffuse sheets have also been reported by Kagoshima et al. [12]. Their results concerning the building up of correlations in the \( a \)-direction (between TSeF and TCNQ molecules) when the 29 K transition is approached from above concerns the temperature region below 55 K, while for our measurements we considered mainly higher temperatures precisely to avoid the critical region. Kagoshima's investigation also revealed 2D type correlations in the \( bc \)-plane extending well above 55 K and still visible at 100 K, which are consistent with the experimental data obtained here from photographic patterns.

The main result from the present work is the nature of the molecular translation of the TSeF molecules, that is to say, nearly parallel to their molecular plane. By analogy with the movements observed in \( K_2\text{Pt(CN)}_4\cdot0.3\text{Br-xH}_2\text{O} \) (translations perpendicular to the \( \text{Pt(CN)}_4 \) planar units), it was usually assumed [1] that the two translation components of the 2\( k_F \) charge density waves of TTF-TCNQ were due to a translation of the molecules perpendicular to their molecular plane. Such movements indeed modulate the intermolecular distances, recalling the modulation of the interatomic distances of the ideal linear single atom chain used for many theories.

With the translational movement nearly parallel to the tilted molecular plane unambiguously revealed by the present work, it is clear that the intermolecular energy is also well modulated since the molecular \( \pi \)-orbitals extend in the direction perpendicular to the molecular plane and is relatively well localized in the parallel direction (Fig. 11). Unfortunately there seems to be no proper analysis available for this type of electron-phonon coupling.

The present work deals only with TSeF-TCNQ, and more precisely even with the TSeF molecule alone. It clearly needs to be extended to other compounds of the same family in order first to check the generality of the translational movement along the molecular plane, which can be done with other selenium compounds. Further work should of course include the sulfur compounds, and in particular TTF-TCNQ not only to try to get information on the movements of both molecular species in the 2\( k_F \) modulation waves, but also in order to try to characterize the movements in the 4\( k_F \) modulation.

After this type of analysis on the one-dimensional scattering is completed, it could provide an excellent starting point in order to investigate the low temperature insulating phases.

Fig. 11. — Varying overlap of the \( \pi \)-orbitals in the case of the translations parallel to the molecular surfaces which are represented by the thick lines.
APPENDIX A

Another combination of variables. — For the reason stated at the end of section 2, we introduce the following combination of variables:

\[ \delta_1 = \theta_1 - \theta_2/2, \quad \delta_2 = \varphi_1 - \pi - \theta_1 \quad \text{and} \quad \theta = \theta_0 + \delta_2/2 \]  

(A.1)

and rewrite equation (13) for the scattering intensity as follows:

\[
I_0(Q) = \frac{\pi^2}{2} v^2 N_l \left[ \frac{\sin(\pi(k + k_0)Ny)}{\sin(\pi(k + k_0))} \right]^2 \frac{1 - \psi^2}{1 - 2\psi^2 \cos(2\pi l + \theta_2) + \psi^2} \times \\
\times \left[ (1 + \psi^2) \left( F_2^2 + F_1^2 \right) \left( k^2 + \alpha^2 \lambda^2 \right) + 2\psi k \left[ F_2^2 \cos\left( \theta - \frac{1}{2} \delta_2 \right) + F_1^2 \cos\left( \theta + \frac{1}{2} \delta_2 \right) \right] \right] \\
+ 4\psi \cdot (-1)^{\delta_2} \cdot \cos\left( \pi l + \frac{1}{2} \theta_2 \right) \cdot F_0 \cdot F_1 \cdot f_{2D}(x_1, \theta_1, \delta_2, \delta_1) \\
+ \text{(same except for changing } k_0 \rightarrow -k_0 \text{ and } \theta_2 \rightarrow -\theta_2),
\]  

(A.2)

where \( f_{2D}(x, \theta, \delta_2, \delta_1) \), named « 2D coefficient », is defined by

\[
f_{2D}(x, \theta, \delta_2, \delta_1) = -k^2 \cos(\delta_1 + \delta_2) + \alpha^2 \lambda^2 \cos \delta_1 + 2\psi k \sin \theta \sin(\delta_1 + \frac{1}{2} \delta_2).
\]  

(A.3)

In principle, we have to look for the best fit parameter values as a point in the parameter space given below:

\[ \alpha \geq 0, \quad \psi \geq 0, \quad \theta \leq \pi, \quad \delta_2 \leq \pi, \quad \delta_1 \leq \pi, \quad \theta_2 \leq 2 \pi. \]  

(A.4)

Since equation (A.2) holds the relation

\[
I_0(Q) \bigg|_{\theta = \pi - \theta_0} = I_0(Q) \bigg|_{\theta = \pi + \theta_0}
\]  

(A.5)

we can safely neglect the space \( \alpha < 0 \). Concerning the 2D coefficient, we have the following properties:

\[
\begin{align*}
&f_{2D}(\alpha, \theta, \delta_2, \delta_1) = f_{2D}(\alpha, \theta + \pi, \delta_2, \delta_1), \\
f_{2D}(\alpha, -\theta, -\delta_2, -\delta_1) = f_{2D}(\alpha, \theta, \delta_2, \delta_1), \\
f_{2D}(\alpha, \theta, \delta_2, \delta_1 + \pi) = -f_{2D}(\alpha, \theta, \delta_2, \delta_1).
\end{align*}
\]  

(A.6)

Thanks to the last relation, equation (A.2) is not changed when we replace simultaneously \( \delta_1 \) and \( \theta_2 \) by \( \delta_1 + \pi \) and \( \theta_2 + 2 \pi \), respectively. From these properties the space to be examined is narrowed to

\[ \alpha \geq 0, \quad \psi \geq 0, \quad 0 \leq \theta \leq \pi, \quad \delta_2 \leq \pi, \quad \delta_1 \leq \frac{\pi}{2}, \quad \theta_2 \leq 2 \pi. \]  

(A.7)

APPENDIX B

Equivalent modes. — As in the original 3D system, one sheet of TSeF molecules, besides identity, has three symmetry elements:

- inversion with respect to the molecular centre: \( I \),
- twofold screw axis around \( b \):
  \[ C_2^\beta = \{ 1/2.b + 1/2.c \mid C_2 \}, \]
- glide plane parallel to the \( ac \)-plane:
  \[ \sigma^* = C_2^\beta I = \{ 1/2.b + 1/2.c \mid \sigma \}. \]

If we operate any one of the three symmetry operations to the original system, the correlation function \( \Psi(p, p') \) changes its form from the point of view of the fixed coordinate system. Such a correlation function comes from an equivalent soft modes related by symmetry to one another and must contribute to the scattering with the same weight.

Each contribution to the diffuse scattering is obtained from the previous equation (13), if we replace in it \( \theta_0, \theta_1, \theta_2 \) and \( \varphi_1 \) by a new set \( \theta'_0, \theta'_1, \theta'_2 \) and \( \varphi'_1 \), which is defined as follows in each case:

\[
\begin{align*}
&\text{for } I: \quad \theta'_0 = -\theta_0, \quad \theta'_1 = -\theta_2 - \theta_1, \quad \theta'_2 = \theta_2, \quad \varphi'_1 = \theta_2 - \varphi_1, \\
&\text{for } C_2^\beta: \quad \theta'_0 = \theta_0 - \theta_1 + \varphi_1 + \pi, \quad \theta'_1 = -\theta_1, \quad \theta'_2 = -\theta_2, \quad \varphi'_1 = -\varphi_1, \\
&\text{for } \sigma^*: \quad \theta'_0 = -\theta_0 + \theta_1 - \varphi_1 + \pi, \quad \theta'_1 = \theta_1 - \theta_2, \quad \theta'_2 = -\theta_2, \quad \varphi'_1 = \varphi_1 - \theta_2.
\end{align*}
\]  

(B.1)
or by replacing in equation (A. 2) the arguments $\theta, \delta_1, \delta_2$ and $\theta_2$ by $\theta', \delta_1', \delta_2'$ and $\theta_2'$ defined in each case as follows:

for $I$ : 
$$\theta' = - \theta, \quad \delta_1' = - \delta_1, \quad \delta_2' = - \delta_2, \quad \theta_2' = \theta_2,$$

for $C^*_2$ : 
$$\theta' = \theta, \quad \delta_1' = - \delta_1, \quad \delta_2' = - \delta_2, \quad \theta_2' = - \theta_2,$$

for $\sigma^*$ : 
$$\theta' = - \theta, \quad \delta_1' = \delta_1, \quad \delta_2' = \delta_2, \quad \theta_2' = - \theta_2.$$

The expression of the scattering intensity $I_D(Q)$ remains the same for $I$ but for $C^*_2$ and $\sigma^*$ it takes another form common for both. We add these two different types of contributions with equal weight.

Incidentally, $I_D(Q)$ for the HB pattern with $\theta_2 = 0$ suffers no change from the above three transformations.

**APPENDIX C**

**Background correction.** — In order to make the correction for the background, the diffuse scattering must be scanned in the direction perpendicular to the $2 k_F$ diffuse lines which allows a proper subtraction of the varying background and the integration of the obtained profile. For this purpose we have used an automatic microdensitometer recording directly the 2D intensity distribution over the entire X-ray pattern with 50 $\mu$m meshes.

In these conditions the scattered X-ray intensity is given by

$$I = \log \left( \frac{I_o}{I_t} \right) \quad (C.1)$$

where $I_o$ is the intensity of the incident light flux and $I_t$ is that of the transmitted beam through the pattern. Figures 5a and 5b represent patterns D'9 and D'3, respectively. An example of a scan perpendicular to the $2 k_F$ diffuse lines is illustrated in figure 12 and shows typical profiles of the $2 k_F$ scattering for $k = 1 + 2 k_F$ and $k = 2 - 2 k_F$; in this case the curve was smoothed by taking the weighted average among the values of neighbouring meshes. The integrated intensity was estimated through such scans from the area remaining after subtraction of the background as evaluated by interpolation of its value from both sides of the diffuse line.

Repeating this procedure every 0.5 mm along each diffuse $2 k_F$ line from an X-ray pattern, the variation of the measured intensity distribution can be reconstructed as shown by the full circles in figures 8 and 9 for the $2 k_F$ scattering lines from patterns D'9 (Fig. 5a) and D'3 (Fig. 5b), respectively. In these figures the abscissa is proportional to the distance $x$ as defined in subsection 3.1, from which the horizontal component $\gamma$ of the scattering angle can be deduced; further below in the fitting procedure the proportionality factor between $x$ and $\gamma$ will be varied slightly around the measured value of the cylindrical camera radius, in order to allow to take into account the deviation of the camera window from ideal cylindrical form, the film thickness, etc.

As shown in the trace profile of figure 12, fluctuations of the background are appreciable, which makes the estimation of the background very delicate. We have chosen throughout this work to restrict the contribution range of the $2 k_F$ profile by subtracting an upper limit of the plausible background. While this allows to reduce the data scattering, it underestimates almost certainly the tailing around $2 k_F$ scattering and introduces a systematic error, especially in the case of larger $k$ values whose $2 k_F$ diffuse lines have a broader line width. Although the error in the differences between the estimates of successive profiles along a diffuse line is estimated to be smaller than 30 units in figures 8 and 9, the absolute error bound due to the fluctuations is slightly larger. The minima around $\gamma = 10^\circ$ for the data points (full circles) in the cases of $k = 1 + 2 k_F$ (Figs. 8b and 8e) are very likely a consequence of such a systematic error.
Acknowledgments. — One of the authors (K. Y.) heartily thanks his colleagues from Laboratoire de Physique des Solides at Orsay for their hospitality during his stay in France. We would like to express our gratitude to J. P. Pouget for many useful discussions, and to D. Taupin and Service National du Microdensitomètre for efficient help in recording the intensity distribution from the X-ray patterns.

References

   b) MEGETERT, S., thesis presented to Université Paris-Sud, 1978.
[5] LAPLACA, S., private communication. We are grateful to S. KAGOSHIMA and T. D. SCHULZT for passing us the data.