Successive phase transitions in the organic conductor (TMTSF)₂PF₂O₂

S. Ravy, Jean Pouget, R. Moret, F. Wudl

► To cite this version:

S. Ravy, Jean Pouget, R. Moret, F. Wudl. Successive phase transitions in the organic conductor (TMTSF)₂PF₂O₂. Journal de Physique I, 1991, 1 (5), pp.703-720. 10.1051/jp1:1991164. jpa-00246365

HAL Id: jpa-00246365

<https://hal.science/jpa-00246365>

Submitted on 1 Jan 1991

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

61.50K — 74.70K — 64.70

Successive phase transitions in the organic conductor (TMTSF)₂PF₆O₂

S. Ravy ⁽¹⁾, J. P. Pouget ⁽¹⁾, R. Moret ⁽¹⁾ and F. Wudl ⁽²⁾⁽¹⁾ Laboratoire de Physique des Solides (*), Bât. 510, Université Paris-Sud, 91405 Orsay Cedex, France⁽²⁾ Institute for Polymers and Organic Solids and Department of Physics, University of California, Santa Barbara, CA 93106, U.S.A.*(Received 20 December 1990, accepted 5 February 1991)*

Abstract. — We present an X-ray study of the organic conductor (TMTSF)₂PF₆O₂. At ambient pressure this compound undergoes a metal-insulator transition at about 137 K but, at variance with similar materials, a metallic state is not restored in the whole temperature range under pressure lower than 14.5 kbar. We show that (TMTSF)₂PF₆O₂ undergoes two successive structural phase transitions at $T_{c1/4} = 136.3$ K and $T_{c1/2} = 135.3$ K. Between $T_{c1/2}$ and $T_{c1/4}$ we observe a phase characterized by the presence in the diffraction pattern of superstructure reflections of reduced wave vector $\mathbf{q}_{1/4} = (1/2, \pm 1/4, 0)$. At $T_{c1/2}$ a first order phase transition suppresses this phase and a superstructure with $\mathbf{q}_{1/2} = (1/2, 1/2, 1/2)$ is stabilized as for most (TMTSF)₂X salts built with tetrahedral anions. We have studied the behaviors of the associated thermodynamical quantities (order parameters, susceptibilities) that a Landau model with two biquadratically coupled order parameters qualitatively explains. We discuss the nature and the competition of these two phases.

1. Introduction.

Since the discovery of organic superconductivity [1] in radical cation salts based on the tetramethyltetraselenafulvalene (TMTSF) molecule, numerous studies have been devoted to the so-called Bechgaard salts [2] (TMTSF)₂X, where X is a monovalent anion. In addition to the superconducting properties, these materials exhibit an unusual variety of competitions between metallic, antiferromagnetic or dielectric insulating phases. Salts containing centrosymmetrical octahedral anions like PF₆ have an antiferromagnetic ground state at ambient pressure [3, 4] and become superconducting with the restoration of the metallic state under modest pressures [1]. With the exception of (TMTSF)₂ClO₄, which presents a superconducting state at 1 bar [5], salts containing non-centrosymmetrical tetrahedral anions like ReO₄, have a dielectric insulating ground state at ambient pressure [6]. This insulating state disappears under pressure and the superconductivity is observed [7].

(*) CNRS URA 2.

Crystals of $(\text{TMTSF})_2\text{X}$ consist of chains of molecules forming a « quasi-one-dimensional » (quasi-1D) conductor in the **a** direction. The anions X and the TMTSF molecules form sheets in the (**a**, **b**) plane and these sheets alternate in the **c** direction. If superconductivity and magnetism, which are present in salts with centrosymmetrical and some non-centrosymmetrical anions, arise from instabilities on the TMTSF stacks, the dielectric insulating state, observed only with non-centrosymmetrical tetrahedral anions is due to the interaction between the anions and the molecules. Actually, the metal-insulator phase transition (arising at T_{ao}) is connected with a structural phase transition [8]. The superstructure stabilized below T_{ao} and characterized by the reduced wave vector $\mathbf{q}_{1/2} = 1/2 \mathbf{a}^* + 1/2 \mathbf{b}^* + 1/2 \mathbf{c}^*$ (hereafter noted $(1/2, 1/2, 1/2)$), consists both in an orientational ordering of the anions (disordered at ambient temperature) and in a displacive modulation of the organic chains [9, 21] at precisely twice the Fermi wave vector $2 \mathbf{k}_f (= 1/2 \mathbf{a}^*)$ of the quasi-1D electron gas. However, although $2 \mathbf{k}_f$ charge density waves (CDW) are formed on the organic chains below T_{ao} , the close link between the anion ordering (AO) and these CDW rules out the existence of a conventional Peierls instability, driven through the electron-phonon coupling by the divergence of the electron-hole response function (although a vanishing $2 \mathbf{k}_f$ CDW instability is observed in centrosymmetrical anion salts like $(\text{TMTSF})_2\text{PF}_6$ [10]). The $\mathbf{q}_{1/2}$ instability is most likely driven by the $2 \mathbf{k}_f$ CDW response function [11] through strong anion-electron [12] and anion-cavity distortion coupling. However the $\mathbf{q}_{1/2}$ ordering does not minimize the Coulomb interactions between adjacent tetrahedra [6, 8], which would rather favor an uniform ordering along the chains. The balance between the direct Coulomb interactions and the electron-mediated $2 \mathbf{k}_f$ ones is reversed in $(\text{TMTSF})_2\text{ReO}_4$ under pressure, probably because of an increase of the former interactions and of a further decrease of the $2 \mathbf{k}_f$ CDW response function. The $\mathbf{q}_{1/2}$ ordering is then replaced by the $\mathbf{q}_3 = (0, 1/2, 1/2)$ one [13], leading to a metallic and superconducting electronic ground state [7]. This competition between alternate and uniform ordering along the chains has a drastic influence on the electronic properties of the Bechgaard salts with tetrahedral anions. Here we want to illustrate with $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ a new kind of structural competition involving different interchain periodicities at ambient pressure.

2. Physical properties of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$.

After the observation, from electrical measurements, of an onset of a superconducting transition at about 2 K under 6 kbar in $(\text{TMTSF})_2\text{FSO}_3$ [14], the influence of dipolar anions on the superconducting state has been questioned [15]. In that purpose, the Bechgaard salt with the dipolar anion PF_2O_2 was synthesized.

$(\text{TMTSF})_2\text{PF}_2\text{O}_2$ undergoes a metal-insulator phase transition at about 137 K at ambient pressure [16], temperature which decreases under pressure. But even at 14.5 kbar, the highest pressure reached, the metallic state is not restored in the whole temperature range, contrary to what is observed at these pressures for other Bechgaard salts. Moreover, a very intriguing temperature dependence of the sound velocity was reported at ambient pressure [17]. Unlike $(\text{TMTSF})_2\text{FSO}_3$, which shows a sudden increase of the sound velocity at the $\mathbf{q}_{1/2}$ AO phase transition, $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ exhibits an unusual dip of sound velocity between 137 K and 139 K. In addition, a structural study performed at 125 K failed to detect the expected superlattice reflections at the $\mathbf{q}_{1/2}$ wave vector [18]. For these reasons we decided to perform a new structural investigation of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ at ambient pressure.

The above quoted structural study [18] shows that, at room temperature, crystals of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ belong to the space group $\text{P}\bar{1}$, with lattice parameters quite close to those of $(\text{TMTSF})_2\text{FSO}_3$ and $(\text{TMTSF})_2\text{ClO}_4$. The anion PF_2O_2 , which has the geometry of a distorted tetrahedron, is orientationally disordered at this temperature.

3. Experimental.

Several crystals, with a needle shape and a few mm long were used for the structural study. They were from the same preparation as those used in reference [17]. The crystals were all found to be twinned, as is common in (TMTSF)₂X salts, with two different types of domains which share the same *a* axis and correspond through a 180° rotation about this axis. The relative fraction of the domains ranged from 20/80 to 40/60. This was deduced by comparing the intensities of reflections from the two types of domains. Most crystals were found to have a relatively broad mosaic. The best one was used for the diffractometric study.

This study was performed with the CuK_α (1.5418 Å) radiation obtained after (002) reflection of the X-ray beam on a doubly bent graphite monochromator. A qualitative survey between 10 K and 300 K was done first, using the fixed-film fixed-crystal photographic method. The quantitative study of the phase transitions was performed on a normal beam-lifting-detector type diffractometer installed on a Rigaku 12-kW generator. The crystal was mounted in an helium-filled container where the temperature was controlled within 0.1 K. The experimental resolution measured by the half-width at half-maximum (HWHM) of several Bragg reflections, was : $\Delta Q_{a^*} = 0.018 \text{ \AA}^{-1}$, $\Delta Q_{b^*} = 0.014 \text{ \AA}^{-1}$ and $\Delta Q_{c^*} = 0.014 \text{ \AA}^{-1}$.

4. Results.

4.1 PHOTOGRAPHIC SURVEY. — The results of the photographic survey are summarized in figure 1. They clearly show the existence of two very close phase transitions at $T_{c1/2}$ (~ 135 K) and $T_{c1/4}$ (~ 136 K) :

— Above $T_{c1/4}$ (high temperature phase) broad diffuse scattering spots are observed on the reciprocal lattice planes of index $h = n + 1/2$ (n is an integer).

— Between $T_{c1/2}$ and $T_{c1/4}$ (intermediate phase) sharp satellite reflections appear at the reduced wave vector $\mathbf{q}_{1/4} = (1/2, \pm 1/4, 0)$ (the corresponding phase will be named « 1/4 » thereafter).

— Below $T_{c1/2}$ (low temperature superstructure) these spots disappear and new sharp superlattice reflections are observed at the reduced wave vector $\mathbf{q}_{1/2} = (1/2, 1/2, 1/2)$ (phase named « 1/2 »).

The close vicinity of $T_{c1/2}$ and $T_{c1/4}$ lead us to perform a quantitative study of the competition between the two superstructures.

4.2 STUDY OF THE PHASE TRANSITIONS AT $T_{c1/2}$ AND $T_{c1/4}$. — This study was performed on a crystal different from that used in 4.1. The transition temperatures were determined with a better accuracy and found to be : $T_{c1/4} = 136.3 \pm 0.1 \text{ K}$ and $T_{c1/2} = 135.3 \pm 0.1 \text{ K}$. Above $T_{c1/4}$, $\mathbf{q}_{1/2}$ quasi-isotropic fluctuations were observed until about 160 K and $\mathbf{q}_{1/4}$ ones until about 200 K. Between $T_{c1/4}$ and $T_{c1/2}$ $\mathbf{q}_{1/4}$ -superlattice reflections were found with an average intensity of 10^3 counts/s, 100 times less intense than the fundamental Bragg reflections. Reflections with wave vector $2\mathbf{q}_{1/4}$ were also observed with a maximum intensity of about 10 counts/s. The position of the $\mathbf{q}_{1/4}$ superstructure spots was refined and $\mathbf{q}_{1/4}$ was found to be $(0.5 \pm 0.01, 0.25 \pm 0.01, 0 \pm 0.02)$. Below $T_{c1/2}$, $\mathbf{q}_{1/2}$ superlattice reflections were observed with an average intensity of about 10^4 counts/s, 10 times less intense than the fundamental Bragg reflections. Figure 2 gives the temperature dependence of the intensity of superlattice reflections associated with each superstructure, as measured on cooling.

4.2.1 Order parameter behavior. — From the data shown in figure 2, the $T_{c1/4}$ transition appears to be continuous. The second order character of this transition is also supported by

 $-T_{c1/4}$

 $-T_{c1/2}$

Fig. 1. — X-ray patterns from $(\text{TMTSF})_2\text{PF}_2\text{O}_2$, above $T_{c1/4}$, between $T_{c1/4}$ and $T_{c1/2}$ and below $T_{c1/2}$. The superlattice reflections at the reduced wave vector $q_{1/4}$ and $q_{1/2}$ are indicated by arrows. The chain axis a is vertical.

the divergence of the pretransitional fluctuations : susceptibility and correlation lengths (see Sect. 4.2.2). $T_{c1/4} = 136.3 \pm 0.1$ K is defined by the temperature at which the fluctuations diverge. Within experimental errors there is no hysteresis.

The $T_{c1/2}$ phase transition is clearly first order. Figure 2 shows that the intensity of the $q_{1/2}$ superlattice reflections jumps at $T_{c1/2}$. In addition there is an hysteresis of about 0.8 K at this transition, which masks nearly completely the « 1/4 » phase upon heating. In addition some of the lattice parameters (see Sect. 4.2.3) present anomalies at $T_{c1/2}$.

Fig. 2. — a) Temperature dependence of the $(0.5, 2.25, 7)$ and $(0.3, 1.5, 0.5)$ superlattice reflections in the vicinity of $T_{cl/2}$ and $T_{cl/4}$. b) Temperature dependence of the $(0.3, 1.5, 0.5)$ superlattice reflection. The insert shows the peculiar behavior of the intensity just below $T_{cl/2}$ with an inflexion of the $I(T)$ curve.

The intensity of the superlattice reflections is proportional to the square of the order parameter. However, in the vicinity of $T_{cl/4}$, the measurement of the superlattice intensity is perturbed by critical fluctuations. This leads to a rounding in the temperature dependence of the intensity around $T_{cl/4}$ as observed in figure 2a. In addition figure 2 shows that the order parameters of both phases, $\eta_{q_{1/4}}$ and $\eta_{q_{1/2}}$ have an anomalous temperature dependence which consists in :

- a saturation of $\eta_{q_{1/4}}$ only 0.6 K below $T_{cl/4}$
- a change of curvature of $\eta_{q_{1/2}}(T)$ between 134 K and $T_{cl/2}$.

These anomalous features occur in the temperature range where the other phase, « $1/2$ » and « $1/4$ » respectively, shows sizeable pretransitional fluctuations. This inhibition in the growth of one of the order parameter due to fluctuations of the other order parameter implies that there is a repulsive coupling between $\eta_{q_{1/4}}$ and $\eta_{q_{1/2}}$. This will be discussed in section 5.

4.2.2 Pretransitional fluctuations. — From the temperature dependence of the peak intensity of the diffuse scattering $I(\mathbf{q})$ measured above the background, the generalized susceptibility $\chi(\mathbf{q})$ can be obtained from the classical limit of the fluctuation dissipation theorem [19]:

$$I(\mathbf{q}) \sim k_B T \chi(\mathbf{q}). \quad (1)$$

In practice $\chi(\mathbf{q}_{1/4})$ has been obtained from $I(\mathbf{G} + \mathbf{q}_{1/4})$ and $\chi(\mathbf{q}_{1/2})$ from $I(\mathbf{G} + \mathbf{q}_{1/2})$, where $\mathbf{G}$ is a vector of the reciprocal lattice. $\chi(\mathbf{q})$ has generally a Lorentzian $\mathbf{q}$ -dependence around its maximum at $\mathbf{q}_c$:

$$\chi(\mathbf{q}) = \chi(\mathbf{q}_c) / (1 + (\mathbf{q} - \mathbf{q}_c) \bar{\xi}^2 (\mathbf{q} - \mathbf{q}_c)). \quad (2)$$

The half width at half maximum of the diffuse scattering in the $\mathbf{q}$ direction gives, after a resolution correction, the inverse correlation length ξ^{-1} in this direction [19]. We have measured the correlation lengths of the pretransitional fluctuations of the « 1/4 » and « 1/2 » phases along the $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ reciprocal axis directions.

4.2.2.1 $\mathbf{q}_{1/4}$ fluctuations. — The temperature dependence of $\chi(\mathbf{q}_{1/4})^{-1}$ is given figure 3. It shows a Curie-Weiss behavior between $T_{c1/4}$ and 137 K and, at this temperature, a sudden decrease of the slope. The slope above 137 K strongly depends on the experimental run. In particular, there is some indication of kinetic effects which have not been studied in detail. The 137 K anomaly in the temperature dependence of the $\mathbf{q}_{1/4}$ -pretransitional fluctuations is also observed on the correlation lengths measured in the three directions $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$. It is clearly illustrated by figure 4 showing the temperature dependence of the HWHM of the $\mathbf{q}_{1/4}$ -diffuse scattering along $\mathbf{b}^*$. The correlation lengths were found to be isotropic along the $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ directions.

$\mathbf{q}_{1/4}$ fluctuations under the form of broad diffuse spots were also observed below $T_{c1/2}$ when the $\mathbf{q}_{1/4}$ long range order is replaced by the $\mathbf{q}_{1/2}$ one.

4.2.2.2 $\mathbf{q}_{1/2}$ fluctuations. — $\mathbf{q}_{1/2}$ fluctuations are clearly observed above $T_{c1/2}$ in the « 1/4 » phase and they extend above $T_{c1/4}$. Figure 5 gives the temperature dependence of $\chi(\mathbf{q}_{1/2})^{-1}$. This quantity shows also a well defined Curie-Weiss like behavior above $T_{c1/4}$ followed by a large decrease of the slope in the « 1/4 » phase. No detectable anomaly can be noticed at 137 K. The correlation lengths were also measured above $T_{c1/2}$. A typical temperature dependence is shown by figure 6 from the measurement performed along $\mathbf{a}^*$. This measurement was done at the end of the experiment when the « 1/4 » phase had almost

Fig. 3. — Temperature dependence of T/I proportional to $(\chi_{1/4})^{-1}$, where I is the peak intensity in (0.5, 2.25, 7) for the $\mathbf{q}_{1/4}$ fluctuations above $T_{c1/4}$ and below $T_{c1/2}$. Note the break at 137 K in the slope.

Fig. 4. — a) Temperature dependence of the half-width at half-maximum (HWHM) along $\mathbf{b}^*$ for the $\mathbf{q}_{1/4}$ pretransitional fluctuations $(\bar{0.5}, 0.25, 4)$. b) Magnification of the region near $T_{c1/4}$ which shows more clearly the break at 137 K.

Fig. 5. — Temperature dependence of T/I , proportional to $(\chi_{1/2})^{-1}$, where I is the peak intensity at $(\bar{0.5}, 1.5, 0.5)$, for the $\mathbf{q}_{1/2}$ fluctuations above $T_{c1/2}$. Note the change of regime of fluctuations near $T_{c1/4}$.

disappeared. This could be due to the numerous thermal cycling or to irradiation defects [34]. Therefore figure 6 cannot be used to analyze the competition between the $\mathbf{q}_{1/2}$ and $\mathbf{q}_{1/4}$ order parameters.

Fig. 6. — Temperature dependence of the HWHM. along a^* for the $q_{1/2}$ pretransitional fluctuations at $(\bar{0}, \bar{1}, \bar{0})$ (upper curve) and of the inverse correlation length after correction using a Gaussian resolution function (lower curve).

4.2.3 Lattice parameters. — The lattice parameters of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ have been measured previously at room temperature [18]. At $T_{c1/2}$ a large variation of the angular position of the main Bragg reflections incited us to determine which lattice parameters are mainly affected by this transition. The six triclinic parameters a , b , c , α , β , γ were determined using a least-square refinement of the angular position of a set of Bragg reflections. Their temperature dependence between 90 K and 300 K is given in figure 7. The angles α and β show the strongest anomalies at $T_{c1/2}$. Weaker anomalies are observed for γ and c . A change of slope in the temperature dependence of b can be also detected. Within the accuracy of our measurement (5 %), a does not present any anomaly at $T_{c1/2}$. The temperature dependence of the lattice parameters and the nature of the anomalies (with the exception of β) are similar to those previously reported for the $q_{1/2}$ first order transition of $(\text{TMTSF})_2\text{ReO}_4$ [20]. The magnitude of the anomalies is however quite different for most of the lattice parameters. Within experimental uncertainties, no lattice parameters anomaly is observed at the $q_{1/4}$ phase transition.

5. Discussion.

5.1 NATURE OF THE PHASES.

In analogy with the other Bechgaard salts $(\text{TMTSF})_2\text{X}$ with tetrahedral anions which present the $q_{1/2}$ low temperature superstructure and for which structural refinements have been performed (case of ReO_4 [9, 21], BF_4 [22]), the « $1/2$ » phase of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ certainly consists in an alternate orientational ordering of the PF_2O_2 tetrahedra along the three directions a , b and c as schematically shown in figure 8 in the (a, b) plane. Furthermore and like in the latter cases, the ordering of the anions inside the TMTSF lattice cavities is most likely accompanied by a displacement of the anions and by a $2k_f$ distortion wave of the organic stacks. This wave distorts also the cavities which however remain all equivalent by symmetry.

Fig. 7. — Dependence upon temperature of the triclinic lattice parameters and volume of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ between 90 K and 300 K.

Fig. 8. — Models for the $(1/2, 1/2)$ and $(1/2, 1/4)$ orientational orders of the PF_2O_2 anions in the (a, b) plane. The symbols $+$ and $-$ symbolize the values of the Ising-like order parameter.

We have tried to perform a structural refinement of the « $1/4$ » phase of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ from the collection at 136 K of the intensity of 200 $q_{1/4}$ superlattice reflections. We have only succeeded to show (although with a poor reliability factor of 25.5 %), that the TMTSF stacks are distorted, with an amplitude of distortion and a polarization similar to those found in the structural refinement of $(\text{TMTSF})_2\text{ReO}_4$ [9]. Unfortunately, introducing the ordering of the PF_2O_2 anions as well as their displacements did not improve the fit. This can be explained by the poor quality of our data (a variation of temperature of 0.1 K near 136 K changes the superlattice intensity by 10 %) and the relatively small scattering factor of PF_2O_2 (9 times less electrons than in a TMTSF molecule). However the cooling rate dependence of the behavior of $\chi(q_{1/4})$ see (Sect. 4.2.2), suggests by analogy with kinetic effects previously observed in $(\text{TMTSF})_2\text{ClO}_4$ [23, 24], that the anions are also involved in the nature of the « $1/4$ » superstructure. Figure 8 shows a possible anion ordering pattern compatible with the

doubling of the lattice periodicity along **a**, its quadrupling along **b** and the quasi-absence of $2\mathbf{q}_{1/4}$ superlattice reflections.

Within the above models for the nature of the « $1/4$ » and « $1/2$ » phases, the associated transitions involve an ordering of the anions and displacements of the anions and of the molecules. A description of such phase transitions would then in principle take into account the three associated order parameters: Ising-like variable for the orientational degrees of freedom and amplitude of modulation for the two types of displacements. In the following, we shall assume that, for each ordered state, two of these order parameters have been eliminated and we shall describe each phase by a single order parameter. We present now a simple phenomenological model of this sequence of phase transitions.

5.2 PHENOMENOLOGICAL MODEL. — In this model we shall neglect the fluctuations and consider only the order parameter at the critical wave vectors $\mathbf{q}_{1/2}$ and $\mathbf{q}_{1/4}$.

— the order parameter $\eta_{\mathbf{q}_{1/2}}$ has one component that we shall name $\eta_{1/2}$

— the order parameter $\eta_{\mathbf{q}_{1/4}}$ has two components (the wave vectors $\mathbf{q}_{1/4}$ and $-\mathbf{q}_{1/4}$ are not equivalent) and can be put under the form $\eta_{1/4} \exp(i\theta)$.

The free energy can be expanded as a function of these two order parameters in the vicinity of $T_{c1/2}$ and $T_{c1/4}$. This expansion is justified by the small difference (~ 1 K) between the two critical temperatures. Up to fourth order, we can write:

$$\begin{aligned} F(\eta_{1/2}, \eta_{1/4} \exp(i\theta), T) &= a_{1/2} \eta_{1/2}^2 + (b_{1/2}/2) \eta_{1/2}^4 & \text{a)} \\ &+ a_{1/4} \eta_{1/4}^2 + (b'_{1/4}/2) \eta_{1/4}^4 + (b''_{1/4}/2) \eta_{1/4}^4 \cos(4\theta) & \text{b)} \\ &+ \lambda \eta_{1/2}^2 \eta_{1/4}^2 & \text{c)} \end{aligned} \quad (3)$$

The terms in (3a) are straightforward for a one dimensional order parameter. In (3b) we have included the $b''_{1/4}$ umklapp term ($\eta_{\mathbf{q}_{1/4}}^4 + \eta_{-\mathbf{q}_{1/4}}^4 = 2 \eta_{1/4}^4 \cos(4\theta)$) because $4\mathbf{q}_{1/4}$ is a reciprocal lattice wave vector. The lowest order coupling term between the two order parameters is biquadratic and given by (3c). For a triclinic Bravais lattice the only symmetry to consider in the free energy expansion is the translational invariance.

Choosing $b'_{1/4} > 0$, a first minimization with respect to θ gives $\theta = n\pi/4$ (with $n = 1, 3, 5, 7$), corresponding to the four possible phases between the lattice and the $\mathbf{q}_{1/4}$ modulation. With these conventions and defining $b_{1/4} = b'_{1/4} - b''_{1/4}$ the free energy becomes:

$$F(\eta_{1/2}, \eta_{1/4}, T) = a_{1/2} \eta_{1/2}^2 + (b_{1/2}/2) \eta_{1/2}^4 + a_{1/4} \eta_{1/4}^2 + (b_{1/4}/2) \eta_{1/4}^4 + \lambda \eta_{1/2}^2 \eta_{1/4}^2.$$

As usual for such a Landau expansion, we shall assume that $b_{1/2}$, $b_{1/4}$ and λ are slowly varying functions of the temperature and that $b_{1/2} > 0$, $b_{1/4} > 0$ and $\lambda > -\lambda_c = -(b_{1/2} b_{1/4})^{1/2}$, which insures the existence of a minimum of the free energy. We define also two temperatures $T_{1/2}$ and $T_{1/4}$ from the temperature dependence of $a_{1/2}$ and $a_{1/4}$.

$$\alpha_{1/2}(T - T_{1/2}) = a_{1/2} \quad \text{and} \quad \alpha_{1/4}(T - T_{1/4}) = a_{1/4},$$

that we shall relate later to $T_{c1/2}$ and $T_{c1/4}$. With these conventions, our free energy is exactly of the same form as that already studied by Imry [25].

We shall briefly recall Imry's results. In addition to the trivial $\eta_{1/2} = \eta_{1/4} = 0$ (O phase) high temperature minimum of F , three distinct solutions can be obtained:

$$\text{phase } 1/2: \quad \eta_{1/2} \neq 0, \quad \eta_{1/4} = 0 \quad \text{corresponding to a « } \eta_{1/2}\text{-ordering »},$$

phase 1/4 : $\eta_{1/2} = 0$, $\eta_{1/4} \neq 0$ corresponding to a « $\eta_{1/4}$ -ordering » ,
 phase 1/2 + 1/4 : $\eta_{1/2} \neq 0$, $\eta_{1/4} \neq 0$ corresponding to a « mixed $\eta_{1/2}$ - $\eta_{1/4}$ ordering ».

The domains of stability of these phases are determined by three parameters :

- The ratio of the temperature $t = T_{1/2}/T_{1/4}$, which determines the first ordering to occur when the temperature is lowered.
- The strength of the reduced coupling $\mu = \lambda/\lambda_c$, which controls the existence of a mixed $\eta_{1/2}$ - $\eta_{1/4}$ ordering.
- The ratio of the free energy of the separate 1/2 and 1/4 phases at $T = 0$:

$$f = F(\eta_{1/2}, \eta_{1/4} = 0, T = 0) / F(\eta_{1/2} = 0, \eta_{1/4}, T = 0) \\
= (-a_{1/2}^2/2 b_{1/2}) / (-a_{1/4}^2/2 b_{1/4}) = (\alpha_{1/2}/\alpha_{1/4})^2 t^2 (b_{1/4}/b_{1/2}),$$

which characterizes the most stable low temperature ordering.

Figure 9a shows the domains of existence of the various solutions in the $\mu - T$ plane. We shall restrict our discussion to the case $f > 1$ and $t < 1$. The succession of phase transitions encountered in (TMTSF)₂PF₂O₂ is well accounted for by the case of « strong repulsive coupling » (i.e. $\mu > 1$) as shown by the vertical solid line. In that case, the values of the order parameters (calculated by minimizing F) and of the associated susceptibilities (defined by $\chi_{1/2}^{-1} = (\partial^2 F / \partial \eta_{1/2}^2)$ and $\chi_{1/4}^{-1} = (\partial^2 F / \partial \eta_{1/4}^2)$) in the different phases are given in table I.

Table I.

phase	$\eta_{1/2}$	$\chi_{1/2}^{-1}$	$\eta_{1/4}$	$\chi_{1/4}^{-1}$
O	0	$2 a_{1/2}$	0	$2 a_{1/4}$
1/4	0	$2 a_{1/2} - 2 \lambda a_{1/4}/b_{1/4}$	$(-a_{1/4}/b_{1/4})^{1/2}$	$-4 a_{1/4}$
1/2	$(-a_{1/2}/b_{1/2})^{1/2}$	$-4 a_{1/2}$	0	$2 a_{1/4} - 2 \lambda a_{1/2}/b_{1/2}$

Fig. 9. — a) (μ, T) phase diagram. The vertical solid line corresponds to the case of (TMTSF)₂PF₂O₂. b) Temperature variation of the separate free energies in the case of (TMTSF)₂PF₂O₂.

In the O phase, the two order parameters $\eta_{1/2}$ and $\eta_{1/4}$ are equal to zero and the associated inverse susceptibilities tend to vanish linearly at $T_{1/2}$ and $T_{1/4}$ respectively. The first phase to be stabilized at $T_{c1/4} = T_{1/4}$ is the $1/4$ one ($t < 1$ condition). In that phase $\eta_{1/2} = 0$ and $\eta_{1/4}$ grows as $(T_{1/4} - T)^{1/2}$ when T decreases. Below $T_{1/4}$, $\chi_{1/2}^{-1}$ varies as $(T - T_{1/4}^*)$, where $T_{1/4}^* < T_{1/4}$ is the lowest limit of stability of the « $1/4$ » phase. On further cooling, because the mixed $\eta_{1/2} - \eta_{1/4}$ phase cannot exist (the repulsive coupling is too strong, $\mu > 1$) and since the phase « $1/2$ » is more stable at lower temperature ($f > 1$), a first order phase transition takes place at T_E towards a separate $\eta_{1/2}$ ordering. T_E is the temperature of equality of the separate free energies, which it is assumed to occur only once in the whole temperature range (see Fig. 9b). At T_E , $\eta_{1/2}$ jumps to a non zero value and increases as $(T_{1/2} - T)^{1/2}$ when T decreases, $\eta_{1/4}$ goes abruptly to zero and fluctuates again. $\chi_{1/4}^{-1}$ tends to vanish at $T_{1/2}^*$ (upper limit of stability of the « $1/2$ » phase) with a negative slope. The $T_{1/4}^*$, $T_{1/2}^*$ and T_E temperatures can be derived by the following formulas :

$$\mu^2 t^2 (T_{1/4}^* - T_{1/4})^2 = f (T_{1/4}^* - T_{1/2})^2$$

$$\mu^2 f (T_{1/2}^* - T_{1/2})^2 = t^2 (T_{1/2}^* - T_{1/4}^*)^2$$

$$t^2 (T_E - T_{1/4})^2 = f (T_E - T_{1/2})^2$$

and

$$t T_{1/4} = T_{1/2}.$$

Figure 10 summarizes the variations of $\eta_{1/2}^2$, $\eta_{1/4}^2$, $\chi_{1/2}^{-1}$, $\chi_{1/4}^{-1}$ together with the experimental temperature dependences. For reasons which will appear in the following, we have not tried to fit our data with the results of this crude model, but a good agreement is obtained between calculated and experimental quantities especially from the behavior of the susceptibilities (from the experimental values of $T_{1/4} = 136.3$ K, $T_{1/2} = 135.9$ K, $T_{1/2}^* = 135.6$ K and $T_{1/4}^* = 135$ K, we can obtain the values $T_E = 135.4$ K, $t = 0.997$, $f = 3.365$ and $\mu = 1.268$, used in Fig. 9). However there are several features which cannot be accounted for by such a simple model :

i) The break observed at 137 K in the behavior of the susceptibility and of the correlations lengths of the $\mathbf{q}_{1/4}$ fluctuations (Figs. 3 and 4). This effect could be more likely due to a crossover between two different regimes of fluctuation than to the crossing of a disorder line, where only the correlation lengths are affected [26, 27]. It could be tentatively ascribed to a crossover from a normal short range Ising critical behavior to a dipolar critical behavior [31], the dipolar coupling occurring between the PF_2O_2 anions. Nevertheless kinetic effects remain to be understood.

ii) The anomaly in the temperature dependence of $\eta_{1/2}$ and the saturation of $\eta_{1/4}$ near $T_{c1/2}$ (Fig. 2) require to go beyond the mean field description and to consider the mutual effects of the fluctuations of the order parameters through the coupling term (3c). At the lowest order its effect is to change :

— In the phase « $1/4$ » :

$$a_{1/4} \text{ in } a_{1/4} + \lambda \sum_{\delta \mathbf{q}} \langle \eta_{1/2}^2(\delta \mathbf{q}) \rangle .$$

— In the phase « $1/2$ » :

$$a_{1/2} \text{ in } a_{1/2} + \lambda \sum_{\delta \mathbf{q}} \langle \eta_{1/4}(\delta \mathbf{q}) \eta_{-1/4}(\delta \mathbf{q}) \rangle .$$

In these expressions $\delta \mathbf{q}$ are the wave vector fluctuations around $\mathbf{q}_{1/2}$ and $\mathbf{q}_{1/4}$ respectively. The thermal average $\langle \dots \rangle$ is proportional to the q dependent diffuse intensity given by (1) and (2). The correction is given by an integration of $\chi(\mathbf{q} + \delta \mathbf{q})$ which has been performed for a displacive-type transition, in the mean-field approximation, in reference [28]. Its critical behavior scales with the energy density [29]. It does not diverge at T_c , temperature at which

Fig. 10. — Calculated temperature dependences of the inverse susceptibilities $\chi^{-1}(q_{1/4})$ (high), $\chi^{-1}(q_{1/2})$ (middle) and of the square of the order parameters $\eta_{1/2}$ and $\eta_{1/4}$ (bottom).

$\chi(q_c)$ diverges, but shows a cusped-like behavior. As the coupling is repulsive ($\lambda > 0$), the correction has a sign opposite to that of $a_{1/2}$ and $a_{1/4}$ below $T_{c1/2}$ and $T_{c1/4}$ respectively. Thus it is subtracted to the mean field behavior of $\eta_{1/2}^2$ and $\eta_{1/4}^2$ given in figure 10, in agreement with the experimental observation of figure 2. This reduction of satellite intensity can be alternatively analyzed in term of Debye-Waller factor. Instead of $\eta_{1/4}$ one can introduce in the structure factor of the « 1/4 » superlattice reflections $\eta_{1/4} \exp(-W_{1/2})$, where the Debye-Waller factor :

$$W_{1/2} \sim \langle u_{1/2}^2 \rangle \sim \sum_{\delta q} \langle \eta_{1/2}^2(\delta q) \rangle$$

takes into account the lattice fluctuations of the « 1/2 » phase. The subscripts must be reversed for the structure factor of the « 1/2 » phase.

iii) The coupling to the elastic degrees of freedom. It will be considered in the next section.

5.3. RELATIONSHIP WITH THE ELECTRONIC AND ELASTIC PROPERTIES. — As in the others Bechgaard salts, the $q_{1/2}$ anion ordering corresponds to an insulating electronic ground state [16]. However, in the case of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$, it is not known whether the metal-insulator transition occurs at $T_{c1/2}$ or $T_{c1/4}$ because these two temperatures are too close to each other. However these two phase transitions can be clearly distinguished in the sound velocity measurements of reference [17] but with a shift of about 2 K between these data and our results.

For a triclinic symmetry the coupling between an orientational order parameter « η » and a lattice deformation « e », is at the lowest order, of the form

$$F_{\eta-e}^{(1)} = C_1 \eta^2 e. \quad (4)$$

Terms of this type must be added to the free energy F considered in (3) and to an elastic energy of the form :

$$F_e = 1/2 K e^2 \quad (5)$$

The minimization of $F_{\eta-e}^{(1)} + F_e$ with respect to e gives

$$e = - (C_1/K) \eta^2 \quad (6)$$

The lattice deformation (or more precisely its additional deformation with respect to the normal thermal lattice contraction) behaves like the square of the order parameter (i.e. like the superstructure peak intensity). This is qualitatively the case below $T_{c1/2}$ for the triclinic angles α and β (Fig. 7). This behavior has also been observed for the extra contraction of the parameter a below the $(0,1/2,0)$ anion ordering transition of $(\text{TMTSF})_2\text{ClO}_4$ [30].

The linear-quadratic coupling given by (4) has further consequences [31] :

i) It decreases the coefficient b of η^4 by $-C_1^2/2K$ in the free energy when the variable e has been eliminated. The value of the free energy obtained after all the minimisations, $-a^2/2b$, thus decreases more rapidly with temperature than in absence of coupling. In the case of a strong value of C_1 , this coupling can even change the sign of the η^4 -coefficient which for a negative sign leads to a 1st order phase transition. This effect could be important for the understanding of the first order nature of the $q_{1/2}$ -anion ordering phase transition in $(\text{TMTSF})_2\text{ReO}_4$ and $(\text{TMTSF})_2\text{FSO}_3$.

ii) It leads to a sudden-drop of the elastic constant « K » by C_1^2/b at the critical temperature of a second order phase transition, which could account for the sudden softening of the sound velocity observed below $T_{c1/4}$ in $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ [17].

The next order elastic coupling term :

$$F_{\eta-e}^{(2)} = C_2 \eta^2 e^2 \quad (7)$$

must be considered for deformation in chains direction when the anion ordering transition is accompanied by a metal insulator transition because the opening of an electrical gap (proportional to η) in the 1D electron gas, decreases the electronic screening contribution at the in chain elastic constant K' . This term is essential to understand the sound velocity stiffening observed at the $q_{1/2}$ -transition of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ and of $(\text{TMTSF})_2\text{FSO}_3$ [17].

Finally it is interesting to compare the elastic deformations observed at the $q_{1/2}$ anion ordering transitions of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ (Fig. 7) and of $(\text{TMTSF})_2\text{ReO}_4$ [20]. In $(\text{TMTSF})_2\text{ReO}_4$ the (a, b) plane of ReO_4 anions is mostly distorted by the ordering : b decreases and γ increases sizeably at 180 K. In contrast, for $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ the relative arrangement of two neighboring anion layers is mostly perturbed at $T_{c1/2}$. α increases and β

decreases sizeably and c decreases too. In this salt, the elastic deformations within the (a, b) plane of PF_2O_2 anions are much weaker than between neighboring planes.

5.4 ANALYSIS OF THE RELEVANT STRUCTURAL PARAMETERS. — Even though it is beyond the scope of this section to propose a detailed mechanism for the anion ordering transitions in this series of compounds, we would like to use the $(\text{TMTSF})_2\text{PF}_2\text{O}_2$ study to point out some characteristic features which could help clarify such a mechanism.

— *Longitudinal component of the wave vector :*

It was very soon realized [8] that the alternate ordering of anions along a does not minimize the direct Coulomb interactions between anions of tetrahedral symmetry. A quantitative calculation was performed [6] in the case of $(\text{TMTSF})_2\text{ReO}_4$ although the alternate shift of the ReO_4 inside the organic cavities was omitted. Therefore the alternate ordering corresponding to the $2k_f$ periodicity in stack direction is clearly stabilized by the gain of electronic energy due to the opening of an energy gap in the band spectrum of the 1D electron gas. The metal insulator transition is however not driven by the divergence of the $2k_f$ CDW response function of the conventional Peierls transition, as suggested by the observation of a vanishing $2k_f$ CDW response function $\chi_\rho(2k_f)$ in $(\text{TMTSF})_2\text{PF}_6$ and AsF_6 [10]. The alternate ordering more likely involves a mediated interaction between anions through the CDW response function of the organic stack showing only a weak anomaly at $2k_f$ [10]. Since the anion ordering transition occurs in the temperature range where $\chi_\rho(2k_f)$ is small, it requires strong electron-anion [12] and/or anion-cavity deformation [11] couplings.

— *Transverse component along b^* :*

As shown by the observation of incipient $2k_f$ diffuse sheets in $(\text{TMTSF})_2\text{PF}_6$ and AsF_6 [10], the electron gas is one-dimensional in the temperature range where the anion ordering occurs. This rules out mechanisms where the transverse wave vector component $1/2b^*$ or $1/4b^*$ is stabilized by Fermi surface nesting effects. Thus, this component is due to direct transverse interactions between the anions such as the Coulomb forces.

Within the (a, b) layer of anions, these interactions are difficult to calculate, especially for directions different from a because of the coupling with molecular displacements. Nevertheless, their effect on the ordering can be phenomenologically analyzed using an Ising model with J_i coupling constants. The ordering in the (a, b) layers depends on the relative sign and magnitude of these constants. As $a \sim b$ and $\gamma \sim 70^\circ$, there are three nearest-neighbour interactions along a (J_1), b (J_2) and $a - b$ (J_3) as defined in figure 11a. Moreover, the presence of a $1/4b^*$ component for the $q_{1/4}$ wave vector leads to take into account second neighbours interactions. As we shall see, the simplest way to account for a $(1/2, 1/4)$ order in the (a, b) plane is to consider the interactions along $a - 2b$, i.e. J_4 . In the case of dominant antiferroelectric interactions along a ($J_1 > 0$), figure 11b shows the influence of the J_4 and $J_2 - J_3$ constants on the values of the ordering wave vector [32]. In this figure $(1/2, 1/2)$ and $(1/2, 1/4)$ are the first two components of the critical wave vectors $q_{1/2}$ and $q_{1/4}$ of $(\text{TMTSF})_2\text{PF}_2\text{O}_2$. The $(1/2, 1/4)$ order is stabilized by the J_4 ferroelectric interaction when there is nearly compensation between J_2 and J_3 . This J_4 coupling could originate from the long range dipole-dipole interaction. However, the accuracy of the atomic coordinates given in [18] is not sufficient to evaluate the sign of this interaction and to test this hypothesis.

The good agreement between our results and the phenomenological model of section 5.2 allow us to discuss more physically the parameters t , μ and f .

As emphasized above, the transition temperature of such systems is mainly determined by

Fig. 11. — a) Definition of the coupling constants J_i in the (a, b) plane of anions. b) Superstructures stabilized as a function of J_4 and $J_3 - J_2$ for a dominant antiferroelectric coupling along a ($J_1 > 0$).

the strength of the anion-mediated coupling through the $2\mathbf{k}_f$ response function, this latter one being the same for the two instabilities. The hypothesis that the weak dipole-dipole interactions are relevant in the stabilization of the « 1/4 » phase could explain that this one appears at a slightly higher temperature than the « 1/2 » phase. This is consistent with $t < 1$ ($T_{1/2} < T_{1/4}$).

Due to the absence of a relation between the $\mathbf{q}_{1/2}$ and $\mathbf{q}_{1/4}$ wave vectors, the lowest coupling term between the two order parameters is biquadratic. Moreover it is impossible to order the anions with these two wave vectors simultaneously. This makes an important distinction with the case of pure displacive modulations. We suggest that this is responsible for the strong repulsive coupling between the two order parameters. Although the exact calculations have not been performed in this special case, it bears some analogy with the problem of the competition between the incompatible uniform and alternated ordering of pseudo-spins in β -(BEDTTTF) $_2\text{I}_3$ [33], where the exact entropy derivation yields $\mu = 6$.

Finally, we have seen that the $\mathbf{q}_{1/2}$ order parameter is strongly coupled to the elastic degrees of freedom. This coupling stabilizes more rapidly the « 1/2 » phase by decreasing the corresponding free energy. This could explain why the separate free energies cross at a temperature close to $T_{c1/4}$, as shown figure 9b, and hence why the phenomenological parameter f is greater than 1. These interpretations are consistent with our X-ray data and with previous results on (TMTSF) $_2\text{ReO}_4$ [20] and (TMTSF) $_2\text{ClO}_4$ [30] showing coupling between the orientational and elastic degrees of freedom.

6. Conclusion.

In agreement with an earlier report of sound velocity measurements, we have observed two structural transitions at $T_{c1/2} \sim 135.3$ K and $T_{c1/4} \sim 136.3$ K in (TMTSF) $_2\text{PF}_2\text{O}_2$ that we have tentatively assigned to different competing orders of the dipolar anion PF_2O_2^- . The superstructure stabilized between $T_{c1/2}$ and $T_{c1/4}$ has the $\mathbf{q}_{1/4} = (1/2, 1/4, 0)$ wave vector and that stabilized below $T_{c1/2}$ the $\mathbf{q}_{1/2} = (1/2, 1/2, 1/2)$ one. These transitions were also characterized by the measurement of the pretransitional fluctuations and of the superstructure intensity. The phase diagram is well accounted for by a Landau model with a repulsive biquadratic coupling between the two order parameters. Additional improvements of this model taking into account the fluctuations of the order parameters and the coupling to elastic degrees of freedom were also considered.

In the light of the previous results, the physical origin of these transitions was also discussed in the anion ordering hypothesis. The wave vector component $1/2 \mathbf{a}^* = 2 \mathbf{k}_F$, common to both transitions, is the result of a coupling between the organic stack and the anionic array. This induces $2 \mathbf{k}_F$ CDW on the organic stack and then a gap in the electronic spectrum. It has been proposed that the $\mathbf{q}_{1/4}$ ordering is the result of dipolar coupling between the anions. This coupling could be responsible for the crossover observed at 137 K, just above $T_{cl/4}$ in the temperature dependence of the $\mathbf{q}_{1/4}$ fluctuations. The low temperature stabilization energy of the usual $\mathbf{q}_{1/2}$ ordering is proposed to be enhanced by the coupling of the AO order parameter with the elastic degrees of freedom.

These interpretations emphasize the subtle influence played by the nature of the anions and their coupling with the molecular array on the physical properties of this series of compounds.

Acknowledgments.

We have benefited from useful discussions with T. Garel, R. C. Lacoé and M. Vallade.

References

- [1] JEROME D., MAZAUD A., RIBAUT M. and BECHGAARD K., *J. Phys. Lett. France* **41** (1980) L95.
- [2] BECHGAARD K., JACOBSEN C. S., MORTENSEN K., PEDERSEN H. J. and THORUP N., *Solid State Commun.* **33** (1980) 1119.
- [3] MORTENSEN K., TOMKIEWICZ Y., SCHULTZ T. D. and ENGLER E. M., *Phys. Rev. Lett.* **46** (1981) 1236.
- [4] TORRANCE J. B., PEDERSEN H. J. and BECHGAARD K., *Mol. Cryst. Liq. Cryst.* **86** (1982) 255.
- [5] BECHGAARD K., CARNEIRO K., OLSEN M., RASMUSSEN F. B. and JACOBSEN C. S., *Phys. Rev. Lett.* **46** (1981) 852.
- [6] JACOBSEN C. S., PEDERSEN H. J., MORTENSEN K., RINDORF G., THORUP N., TORRANCE J. B. and BECHGAARD K., *J. Phys. C* **15** (1982) 2651.
- [7] PARKIN S. S. P., JEROME D. and BECHGAARD K., *Mol. Cryst. Liq. Cryst.* **79** (1981) 213.
- [8] POUGET J. P., MORET R., COMES R. and BECHGAARD K., *J. Phys. Lett.* **42** (1981) L543.
- [9] MORET R., POUGET J. P., COMES R. and BECHGAARD K., *Phys. Rev. Lett.* **49** (1982) 1008.
- [10] POUGET J. P., MORET R., COMES R. and BECHGAARD K., FABRE J. M. and GIRAL L., *Mol. Cryst. Liq. Cryst.* **79** (1982) 129.
- [11] POUGET J. P., Organic and Inorganic Low Dimensional Crystalline Materials, P. Delhaes and M. Drillon Eds. *NATO ASI B 168* (Plenum Press, 1987) p. 185.
- [12] BRUINSMA R. and EMERY V., *J. Phys. Colloq. France* **44** (1983) C3-1115
- [13] MORET R., RAVY S., POUGET J. P., COMES R. and BECHGAARD K., *Phys. Rev. Lett.* **57** (1986) 1915.
- [14] LACOE R. C., WOLF S. A., CHAIKIN P. M., WUDL F. and AHARON-SHALOM E., *Phys. Rev. B* **27** (1983) 1947.
- [15] TOMIC S., JEROME D. and BECHGAARD K., *J. Phys. C: Solid State Phys.* **17** (1984) L655.
- [16] COX S., BOYSEL R. M., WUDL F., CHEN J., OCHSENBEIN S. and HEEGER, A. J., *Solid State Commun.* **49** (1984) 259.
- [17] LACOE R. C., CHAIKIN P. M., WUDL F., COX S. and BRENNAN J., *Mol. Cryst. Liq. Cryst.* **119** (1985) 155.
- [18] ERIKS K., WANG H. H., REED P. E., BENO M. A., APPELMAN E. H. and WILLIAMS J., *Acta Cryst.* **C41** (1985) 257.
- [19] See for example MORET R. and POUGET J. P., Crystal Chemistry and Properties of Materials with Quasi One Dimensional Structures, J. Rouxel Ed. (Reidel) (1986) p. 87.
- [20] GUY D. P. R., BOEBINGER G. S., MARSEGRIA E. A., FRIEND R. H. and BECHGAARD K., *J. Phys. C: Solid State Phys.* **16** (1983) 691.

- [21] RINDORF G., SOLING H. and THORUP N., *Acta Cryst. C* **40** (1984) 1137.
- [22] EMGE T. J., WANG H. H., BENO M. A., WILLIAMS J. M., WHANGBO M. H. and EVAIN M., *J. Am. Chem. Soc.* **108** (1986) 8215.
- [23] KAGOSHIMA S., YASUMAGA T., ISHIGURO T., ANZAI H. and SAITO G., *Solid State Commun.* **46** (1983) 867.
- [24] MORET R., POUGET J. P., COMES R. and BECHGAARD K., *J. Phys. France* **46** (1985) 1521.
- [25] IMRY Y., *J. Phys. C: Solid State Phys.* **8** (1975) 567.
- [26] STEPHENSON J., *J. Math. Phys.* **11** (1970) 420.
- [27] GAREL T. and GAILLARD J. M., *J. Phys. C: Solid State Phys.* **19** (1986) L505.
- [28] BORSA F. and RIGAMONTI A., *Phys. Lett. A* **40** (1972) 399.
- [29] BRUCE A. D., *Adv. Phys.* **29** (1980) 111.
- [30] GAONACH C., CREUZET G. and NOGUERA C., *J. Phys. France* **48** (1987) 107.
- [31] COWLEY R. A., *Adv. Phys.* **29** (1980) 1.
- [32] POUGET J. P., Low-Dimensional Conductors and Superconductors, D. Jerome and L. G. Caron Eds., *NATO ASI B 155* (Plenum Press, 1987) p. 17.
- [33] RAVY S., MORET R. and POUGET J. P., *Phys. Rev. B* **38** (1988) 4469.
- [34] X-ray irradiation defects are known to affect significantly the anion ordering transitions, see reference [24].