**X-ray investigation of the
tetramethyldithiadiselenafulvalene (TMDTDSF)2X
series of organic conductors. I. Study of the
orientational disorder of the TMDTDSF molecule**

Q. Liu, S. Ravy, Jean Pouget, I. Johannsen, K. Bechgaard

► **To cite this version:**

Q. Liu, S. Ravy, Jean Pouget, I. Johannsen, K. Bechgaard. X-ray investigation of the tetramethyldithiadiselenafulvalene (TMDTDSF)2X series of organic conductors. I. Study of the orientational disorder of the TMDTDSF molecule. Journal de Physique I, 1993, 3 (3), pp.803-819. 10.1051/jp1:1993164 . jpa-00246759

HAL Id: jpa-00246759

<https://hal.science/jpa-00246759>

Submitted on 1 Jan 1993

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
74.70K — 61.65

X-ray investigation of the tetramethyldithiadiselenafulvalene (TMDTDSF)₂X series of organic conductors. I. Study of the orientational disorder of the TMDTDSF molecule

Q. Liu ⁽¹⁾, S. Ravy ⁽¹⁾, J. P. Pouget ⁽¹⁾, I. Johannsen ⁽²⁾ and K. Bechgaard ⁽²⁾

⁽¹⁾ Laboratoire de Physique des Solides (*), Université Paris-Sud, Bâtiment 510, 91405 Orsay Cedex, France

⁽²⁾ H. C. Oersted Institute, Universitetsparken 5, DK 2100 Copenhagen, Denmark

(Received 29 July 1992, accepted in final form 4 November 1992)

Résumé. — Nous présentons l'étude des composés de formule (TMDTDSF)₂X où la molécule TMDTDSF (Tétraméthyl-dithiadisélenafulvalène) est une molécule hybride des molécules TMTSF et TMTTF et X (PF₆, AsF₆, SbF₆, ReO₄, BF₄ et ClO₄) est un anion monovalent. Cet article traite de l'étude par diffusion des rayons X du désordre statique de l'orientation des molécules non-centrosymétriques TMDTDSF. Nous présentons un calcul de l'intensité diffusée par un modèle de désordre tenant compte des corrélations entre les orientations des molécules premières voisines et des déplacements associés (effet de taille). Des simulations de l'intensité diffuse permettent de reproduire les résultats expérimentaux. Nous trouvons que dans tous les systèmes les deux orientations des molécules ne sont pas corrélées de site à site et sont équiprobables en accord avec les affinements de structure. L'interprétation de la diffusion diffuse de (TMDTDSF)₂PF₆ donne un effet de taille entre molécules première et deuxième voisines de l'ordre de 0,1 Å et 0,03 Å respectivement. Comme le désordre orientationnel des molécules est aléatoire, ces systèmes sont de bons candidats pour une étude de l'influence d'un désordre aléatoire sur les transitions structurales caractéristiques de ces matériaux, comme les transitions de mise en ordre des anions non-centrosymétriques et l'instabilité de type Spin-Peierls.

Abstract. — We present a study of the (TMDTDSF)₂X materials, where TMDTDSF (Tetramethyldithiadiselenafulvalene) is a hybrid of the TMTSF and TMTTF molecules and X (PF₆, AsF₆, SbF₆, ReO₄, BF₄ and ClO₄) a monovalent anion. This paper deals with an X-ray diffuse scattering study of the static disorder of the orientation of non-centrosymmetrical TMDTDSF molecules. We present a calculation of the diffuse scattering by a model of disorder which takes into account the intrachain correlations between first neighbor molecules and the associated displacements (size effect). Computer simulations of the diffuse scattering intensity allows us to account for the experimental results. We find that in all the compounds investigated the two orientations of the molecules are not correlated and have equal probability in agreement with structural refinements. The interpretation of the diffuse scattering of (TMDTDSF)₂PF₆ gives a size effect between first- and second-neighbor molecules of about 0.1 Å and 0.03 Å respectively.

(*) URA 2 CNRS.

As the orientational disorder is random, these systems are good candidates for the study of the influence of a random disorder on the structural transitions of these materials such as the anion ordering and the Spin-Peierls instability.

1. Introduction.

In the past, experimental and theoretical studies devoted to the disorder in metals have shown the efficiency of X-ray diffuse scattering techniques to characterize the disorder [1, 2]. Disorder has been however less studied in molecular materials. In these crystals, molecular disorder can result either from two different molecules being able to occupy the same site in solid solutions, or from the same molecule being able to take different orientations on the same site. In the latter case, the probability of orientation of a molecule plays the role of the concentration in alloys and the earlier calculations of diffuse scattering can be directly generalized to the orientational disorder. A complete orientational disorder will give the analogue of the Laue monotonic diffuse scattering observed in alloys, while the existence of correlation of orientation from site to site (short range order (S.R.O.)) will periodically modulate the Laue diffuse scattering intensity in the reciprocal space. Similarly, an analogue of the « size effect » can be expected in molecular crystals if slight displacements of the molecules, correlated to their orientation, occur. These effects are well known in metals [2] and in orientational glasses [19] but have been less studied in molecular crystals although significant works have been performed in this field [3]. As pointed out by Welberry [4] the difficulties of such studies come from the usually low degree of symmetry of molecular crystals which multiplies the numbers of parameters to be considered, as well as the complex shape of the molecules, the structure factors of which vary rapidly as a function of the scattering wave vector. More information on the reciprocal space dependence of the diffuse scattering is then needed when one is dealing with such disorder effects. This information can be obtained either by Weissenberg or precession films down to about 80 K or by the so-called fixed-film fixed-crystal method at lower temperatures. The former method was used by Welberry *et al.* [3a, c] with the help of optical transform methods and the latter method was earlier used by Amoros [5] to study the thermal diffuse scattering of molecular crystals and more recently by Doucet *et al.* [6] to study the difference of conformation of DNA in single crystals. The fixed-film fixed-crystal method allows one to detect the diffuse scattering intensity in extreme sample environments at the expense of a difficult indexation of the films. In our study, one purpose of the computer simulations was to overcome the indexation difficulties.

In this paper, we present an X-ray study of the molecular disorder in the series of organic conductors (TMDTDSF)₂X where TMDTDSF is the tetramethyldithiadiselenafulvalene molecule and X represents an inorganic anion. As shown in figure 1, as a hybrid of the TMTTF and TMTSF molecules, the unsymmetrical TMDTDSF molecule can take two orientations on the same site. In this first article, we characterize the disorder of the unsymmetrical molecule TMDTDSF by means of the X-ray diffuse scattering technique. Experimental results are presented in part 2. Part 3 will be devoted to the modelling of the disorder and the presentation of computer simulations. Some conclusions will be drawn in part 4.

2. Experimental results.

The (TMDTDSF)₂X compounds (X = PF₆, AsF₆, SbF₆, ReO₄, BF₄ and ClO₄) were prepared at Orsay and Copenhagen according to the procedure described in reference [7]. For each kind of anion, several crystals with a needle shape and a few mm long in the chain direction were used. They were chosen from the same preparations as those used in magnetic and transport

Fig. 1. — a) TMTTF molecule ; b) TMTSF molecule ; c) and d) the two possible orientations of the hybrid molecule TMDTDSF.

measurements [7, 8, 9]. These crystals have the same average structure as their analogues (TMTSF)₂X and (TMTTF)₂X [10]. The space group is $P\bar{1}$. For the PF₆, SbF₆ and ReO₄ materials the lattice parameters (for the PF₆ salt, $a = 7.206 \text{ \AA}$, $b = 7.632 \text{ \AA}$, $c = 13.374 \text{ \AA}$, $\alpha = 83.23^\circ$, $\beta = 85.59^\circ$, $\gamma = 108.39^\circ$ [7]) were found to be intermediate between those of (TMTSF)₂X and (TMTTF)₂X [10].

Because of the non centro-symmetry of the molecule, disorder due to the orientations of the TMDTDSF is expected, as shown in figure 3. The orientation taken by a molecule is defined by the nature (sulfur or selenium) of the atom closest to the anion. Structural refinements of the average structure [10] were performed by assuming a mixture of sulfur and selenium atoms on the chalcogen molecular sites and by refining a c^+ parameter which represents the fraction of molecules with a selenium close to the anion. The refinements gave $c^+ \approx 0.5$ for (TMDTDSF)₂X with X = PF₆, SbF₆ and ReO₄. In order to complete this information, X-ray diffuse scattering experiments were performed.

In these investigations, we used the CuK α (1.542 $\text{\AA}$) radiation after a (002) reflection on a doubly bent graphite monochromator. We first record room temperature long exposure time Weissenberg photographs. It appeared that all the crystals investigated were twinned as the (TMTSF)₂X ones, the two elements of the twin being related by a 180° rotation around the chain axis **a**. Only the photographs of the (0 k l) reciprocal plane, for which each twin contributes in the same way, were easily interpretable. These patterns revealed also, in addition to the Laue scattering, additional diffuse scattering, with comparable intensity, due to thermal diffuse scattering (TDS). In order to eliminate this TDS contribution, low temperature (10 K) photographs were taken by the so-called fixed-crystal fixed-film method. Another advantage of this method is the possibility to record long exposure X-ray diffuse scattering patterns which could reveal the presence of weak intensity modulations of the monotonic Laue scattering.

In these experiments, the crystals were mounted with the **a** axis approximately horizontal and rotated by about 60° with respect to the incident X-ray beam direction. Because of their needle shape, we cannot orient the crystals around the **a** axis with accurate reproducibility. The crystals were fixed at the center of a vertical cylindrical camera on which the X-ray films are placed. For all the crystals investigated, large diffuse stripes directed in the **a** direction were observed at 10 K as shown in figure 2a for the PF₆ salt.

In the ReO₄ and the SbF₆ compounds, the Laue diffuse scattering intensity was weaker than that observed for the PF₆ salt. For the SbF₆ salt strong contaminations due to fluorescence of

Fig. 2. — a) X-ray pattern from $(\text{TMDTDSF})_2\text{PF}_6$ at 10 K. The crystal is mounted with the *a* axis approximately horizontal and rotated by about 60° with respect to the incident X-ray beam direction. b) Simulation of the experimental pattern shown in a). White (Black) arrows indicate the 1st (2nd) neighbor size effect in which the intrachain correlations of the displacement of the molecules modulate the Laue diffuse scattering intensity.

antimony render the interpretation difficult, even after filtration with a thin aluminium foil. The diffuse scattering of the other compounds was almost of the same intensity as that observed for the PF_6 salt. However, for the BF_4 and especially for the ClO_4 salts, an additional diffuse scattering due to a local ordering of the non centro-symmetric anions at low temperatures prevents a clear analysis of the shape and of the distribution of the Laue diffuse scattering intensity. These supplementary effects have also been studied (see the following paper II).

Among the six salts studied, the diffuse scattering of the PF_6 and the AsF_6 compounds were quantitatively analyzed. Their main features will be accounted for by a Laue scattering due to randomly oriented TMDTDSF molecules. In addition, the X-ray pattern, shown in figure 2a, exhibits some slight variations of intensity in the *a* direction (white and black arrows). These variations suggest that some intrachain correlations in the orientations or in the displacement of the molecules certainly occur. In order to account for all these effects, we have calculated the diffuse scattering with a one-dimensional model of disorder with intrachain correlations. This model is the object of the next part.

3. Calculation and simulation of the diffuse scattering.

It is well known that in the kinematic approximation, the coherent diffracted intensity $I(\mathbf{s})$, as a function of the scattering vector $\mathbf{s} = s_1 \mathbf{a}^* + s_2 \mathbf{b}^* + s_3 \mathbf{c}^*$, is written [1] :

$$I(\mathbf{s}) = \sum_{\mathbf{m}} \langle F_{\mathbf{n}} F_{\mathbf{n}+\mathbf{m}}^* \rangle_{\mathbf{n}} \exp(2 i \pi \mathbf{s} \cdot \mathbf{r}_{\mathbf{m}}), \quad (1)$$

where $F_{\mathbf{n}}$ is the structure factor of the n^{th} cell located at $\mathbf{r}_{\mathbf{n}} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$, and $\langle \rangle_{\mathbf{n}}$ means a spatial average over the crystal. The sum over $\mathbf{m}$ is performed over all the cells of the crystal, which is defined by three indices (m_1, m_2, m_3) . The quantity $I(\mathbf{s})$ is usually decomposed into two terms as

$$\begin{aligned} I(\mathbf{s}) &= \sum_{\mathbf{m}} |\langle F \rangle|^2 \exp(2 i \pi \mathbf{s} \cdot \mathbf{r}_{\mathbf{m}}) + \sum_{\mathbf{m}} [\langle F_{\mathbf{n}} F_{\mathbf{n}+\mathbf{m}}^* \rangle_{\mathbf{n}} - |\langle F \rangle|^2] \exp(2 i \pi \mathbf{s} \cdot \mathbf{r}_{\mathbf{m}}) \\ &= I_{\text{Bragg}}(\mathbf{s}) + I_{\text{Diff}}(\mathbf{s}), \end{aligned} \quad (2)$$

where $\langle F \rangle$ represents the average structure factor of the unit cell. The first term of (2) gives the Bragg reflection intensity and the latter one the diffuse scattering intensity.

If there is only one-dimensional correlations along the chain direction $\mathbf{a}$, the triple sum can be reduced to a sum over the chain index. The diffuse scattering intensity is thus written as (Appendix 1) :

$$I_{\text{Diff}}(\mathbf{s}) = \sum_m \langle F_n F_{n+m}^* \rangle_n \exp(2i\pi s_1 m) - |\langle F \rangle|^2 \delta(h - s_1) \quad (3)$$

where δ is the Dirac function. In formule (3) we have dropped the subscript 1 for n_1 or m_1 .

3.1 DESCRIPTION OF THE MODEL. — In (TMDTDSF)₂X crystal, the TMDTDSF molecules occupy two sites per unit cell, related by an inversion center. On the same site, one molecule can take two orientations, indexed by « + » or by « - », depending on which atom (selenium or sulfur) is closer to the anion (Fig. 3). We use F_n^σ to represent the structure factor of the TMDTDSF molecule, where $\sigma = \text{« + »}$ or « - » is the orientation index previously defined. With these definitions, expression (3) becomes (Appendix 2)

$$I_{\text{Diff}}(\mathbf{s}) = \sum_m \langle F_n^\sigma F_{n+m}^{\sigma'*} \rangle_n \exp(i\pi s_1 m) - |\langle F \rangle|^2 \delta(h - s_1), \quad (4)$$

where, here and below, m and n now denote the position of the molecule. Furthermore we can show (Appendix 2) that

$$\langle F_n^\sigma F_{n+m}^{\sigma'*} \rangle_n = \langle F^\sigma F_{1+m}^{\sigma'*} \rangle + \text{c.c.}, \quad (5)$$

where $F^\sigma \equiv F_1^\sigma$ and c.c. indicates the complex conjugate. The relationship (5) shows that the spatial average over the index n has been reduced to an orientational average over the index σ .

In order to calculate this average, we introduce a model of disorder which takes explicitly into account the correlations of orientation between the nearest neighbor molecules in the chain

Fig. 3. — Stacking of the (TMDTDSF)₂X salts, and definition of the orientational index $\sigma = +$ or $-$, and of the position of center of the molecule with respect to the origin of the unit cell, x_0 .

direction. Such a one-dimensional (1D) model allows us to perform an exact calculation of the diffuse scattering by using the transfer matrix method [2]. We construct a simple Markov chain by adding one by one the molecules. The probability of the orientation of a new molecule depends only on the orientation of the previous molecule. It is shown in appendix 3 that for such a Markov chain the conditional probabilities $p_m^{\sigma\sigma'}$ to have a σ' molecule at the position $(n+m)a/2$ given a σ molecule at position $na/2$ can be put under a matrix form

$$\begin{pmatrix} p_m^{++} & p_m^{+-} \\ p_m^{-+} & p_m^{--} \end{pmatrix} = \begin{pmatrix} c^+ + c^- \alpha^{|m|} & c^- - c^+ \alpha^{|m|} \\ c^+ - c^- \alpha^{|m|} & c^- + c^+ \alpha^{|m|} \end{pmatrix}, \quad (6)$$

where c^+ is the probability to have a selenium atom close to the anion, $c^- = 1 - c^+$ and α is the Warren-Cowley short range order parameter defined by

$$\alpha = 1 - p^{-+}/c^+$$

3.2 CALCULATION OF THE SHORT-RANGE ORDER (S.R.O.) DIFFUSE SCATTERING INTENSITY. — Using the previous definitions, expression (5) can be written as

$$\begin{aligned} \langle F^\sigma F_{1+m}^{\sigma'*} \rangle &= \\ &= c^+ p_m^{++} F^+ F_{1+m}^{+*} + c^+ p_m^{+-} F^+ F_{1+m}^{-*} + c^- p_m^{-+} F^- F_{1+m}^{+*} + c^- p_m^{--} F^- F_{1+m}^{-*}. \end{aligned}$$

Applying (A1), (A4) and (6) to this expression, we obtain

$$\begin{aligned} \langle F^\sigma F_{1+m}^{\sigma'*} \rangle + \text{c.c.} &= \\ &= c^+ p_m^{++} F^+ F^{+*} + c^+ p_m^{+-} F^+ F^{-*} + c^- p_m^{-+} F^- F^{+*} + c^- p_m^{--} F^- F^{-*} + \text{c.c.} \\ &\quad m \text{ even} \\ &= (c^+ p_m^{++} F^+ F^+ + c^+ p_m^{+-} F^+ F^- + c^- p_m^{-+} F^- F^+ + c^- p_m^{--} F^- F^-) e^{-i\pi s_1} + \text{c.c.} \\ &\quad m \text{ odd} \end{aligned}$$

$$= \begin{cases} |c^+ F^+ + c^- F^-|^2 + c^+ c^- \alpha^{|m|} |F^+ - F^-|^2 + \text{c.c.} & m \text{ even} \\ [(c^+ F^+ + c^- F^-)^2 + c^+ c^- \alpha^{|m|} (F^+ - F^-)^2] e^{-i\pi s_1} + \text{c.c.} & m \text{ odd} \end{cases} \quad (7)$$

In expression (7), the summation of the term independent of m compensates the last term of expression (4) :

$$\begin{aligned} &\sum_{m \text{ even}} 2 |c^+ F^+ + c^- F^-|^2 e^{i\pi m s_1} + \sum_{m \text{ odd}} [(c^+ F^+ + c^- F^-)^2 e^{-i\pi s_1} + \text{c.c.}] e^{i\pi m s_1} \\ &= |c^+ F^+ + c^- F^- + c^+ F^{+*} + c^- F^{-*}| \sum_{m \text{ even}} e^{i\pi m s_1} \\ &= |\langle F \rangle|^2 \delta(h - s_1). \end{aligned}$$

Next we consider the m dependent term of expression (7). By putting these two terms into expression (4), we obtain the diffuse scattering intensity :

$$\begin{aligned} I_{\text{Diff}}(\mathbf{s}) &= \\ &= c^+ c^- \left[2 |F^+ - F^-|^2 \sum_{m \text{ even}} \alpha^{|m|} e^{i\pi m s_1} + [(F^+ - F^-)^2 e^{-i\pi s_1} + \text{c.c.}] \sum_{m \text{ odd}} \alpha^{|m|} e^{i\pi m s_1} \right], \end{aligned}$$

which gives

$$I_{\text{Diff}}(s) = c^+ c^- \frac{2|F^+ - F^-|^2 (1 + \alpha^2) + 2[(F^+ - F^-)^2 e^{-i\pi s_1} + \text{c.c.}] \alpha \cos(\pi s_1)}{1 + \alpha^4 - 2\alpha^2 \cos(2\pi s_1)} (1 - \alpha^2), \quad (8)$$

where we have used the summation

$$\sum_{m=-\infty}^{+\infty} \alpha^{|m|} e^{imx} = \frac{1 - \alpha^2}{1 - 2\alpha \cos x + \alpha^2}.$$

If $\mathbf{x}_0$ denotes the position of the center of the molecule with respect to the origin of the unit cell, as shown in figure 3, and if we assume that the skeleton of the molecule is centrosymmetric, the two following relations are obtained :

$$F^+ = F^-^* e^{-4i\pi s \cdot \mathbf{x}_0} \quad \text{and} \quad F^- = F^+^* e^{-4i\pi s \cdot \mathbf{x}_0}$$

This approximation assumes that the distances S-C and Se-C are equal. Actually they are not the same, however this difference (0.14 Å) is much smaller than $\lambda = 1.542$ Å and cannot be appreciated with our experimental conditions.

By defining $\varphi(s) = 4\pi s \cdot \mathbf{x}_0 + \pi s_1$ and noting that

$$I_{\text{Laue}} = 2 c^+ c^- |F^+ - F^-|^2 \quad (9)$$

corresponds to the Laue monotonic diffuse scattering intensity from a crystal without correlation of orientation ($\alpha = 0$), expression (8) can thus be written as

$$I_{\text{Diff}}(s) = I_{\text{Laue}} \frac{1 + \alpha^2 - 2\alpha \cos \varphi(s) \cos(\pi s_1)}{1 + \alpha^4 - 2\alpha^2 \cos(2\pi s_1)} (1 - \alpha^2). \quad (10)$$

The Warren-Cowley parameter α leads to a modulation of the s_1 dependence of $I_{\text{Diff}}(s)$. When $\alpha \rightarrow \pm 1$ (maximum correlation), expression (10) becomes

$$I_{\text{Diff}}(s) \rightarrow \frac{1}{2} I_{\text{Laue}} [(1 - \cos \varphi) \delta(s_1 - 2h) + (1 + \cos \varphi) \delta(s_1 - 2h + 1)].$$

We thus see that the correlations of orientation give rise to a concentration of the diffuse scattering intensity near the $h = \text{integer}$ layers. In addition, as I_{Laue} has a complex s dependence, computer simulations are needed to obtain $I_{\text{Diff}}(s)$. Simulations of expression (10), with the wave vector s situated on the X-ray pattern shown in figure 2a, are displayed in figure 4 for the cases $\alpha = 0$ and $\alpha = 0.4$. In this figure only the diffuse scattering and the locus of the $h = \text{integer}$ Bragg layers have been indicated. As the intensity of the light transmitted through a film of thickness L is proportional to $\exp(-\mathcal{D}L)$ where $\mathcal{D}$ is the optical density, a quantity proportional to the diffuse scattering intensity, a logarithmic correction is needed to compare our simulation with the experimental X-ray pattern. The white arrows in figure 4b show the intensity modulations due to the correlations of orientation. A comparison with experimental X-ray patterns clearly shows that the modulations of the diffuse intensity are not due to correlations of the orientation of the molecules. A more precise comparison with the experimental X-ray pattern shown in figure 2a gives $|\alpha| < 0.1$. We shall furthermore improve our model in section 3.3 by introducing one-dimensional size effects.

From expression (10), it appears that the diffuse scattering intensity is proportional to $c^+ c^-$. Thus, the exact value of c^+ could be only obtained by an absolute measurement of

Fig. 4. — Simulations of the diffuse scattering a) without S.R.O. ($\alpha = 0.0$) and b) with S.R.O. ($\alpha = 0.4$) in the orientation of the molecules, and for the crystal orientation leading to the experimental X-ray pattern of figure 2a. In (b) white arrows indicate the reinforcement of the Laue intensity near the $h = \text{integer}$ layers (solid lines) due to the intrachain correlations of the orientation of the molecules.

intensity that we have not performed. We will show below that c^+ can be estimated by comparing the Laue intensity with the TDS intensity. If we assume that all molecules vibrate independently (Einstein oscillators without intermolecular correlations) with the same amplitude of displacement on average, then the TDS intensity is given by [5]

$$I_{\text{TDS}} = 2(1 - D^2) |c^+ F^+ + c^- F^-|^2,$$

where D is a Debye-Waller factor taken from structural refinements [10]. Comparison of simulations of this expression with the room temperature (RT) Weissenberg photographs taken for $(\text{TMTTF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{PF}_6$ indicates that the Einstein model allows us to reproduce nicely the s dependence of the TDS except in the vicinity of the Bragg reflections where the acoustic vibrations dominate the TDS. The RT Weissenberg photographs show that I_{TDS} and I_{Laue} have the same order of magnitude in all the $(\text{TMDTDSF})_2\text{X}$ salts investigated. Simulations of the RT Weissenberg photographs show that comparable values of I_{TDS} and I_{Laue} are only obtained if $c^+ \approx 0.5$ [16]. This finding is consistent with the results of structural refinements performed for the PF_6 , SbF_6 , and ReO_4 salts [10] and of ^{77}Se NMR study of the PF_6 and ReO_4 salts [9]. In the following, we shall thus assume $c^+ = c^- = 0.5$.

3.3 THE SIZE EFFECT. — As the selenium atoms are larger than the sulfur ones, static displacements of the molecules correlated with their orientations are expected (Fig. 5). This effect, called size effect, is well documented in metallic alloys [2], but, to our knowledge, only one study [12] mentions the existence of similar effects in organic molecular materials. In order to take into account such static displacements, we used the simplest model first described by Warren [2]. In this model, the variation of distance between two atoms only depends on the nature of these atoms. It is known that this model neglects the effect of the other atoms and that more precise calculations must include multi-site correlations [13]. Nevertheless, this approximation is a good one if there are no clustering effects [4] as in our case where $\alpha \approx 0$. We shall assume moreover that the molecules can only translate and do not rotate by size effect. The displacements of the molecules are also assumed to be in the $\mathbf{a}$ direction so that the average distance between the m -th neighboring molecules $\mathbf{r}_m$ is given by $m \mathbf{a}/2$. We thus

Fig. 5. — Static displacements of the TMDTDSF molecules due to their relative orientations. The signs of the β 's are those obtained from the computer simulation of the diffuse scattering of (TMDTDSF)₂PF₆, however for clarity the amplitude of the β 's is amplified.

write the distance between a first (σ) and a $(m+1)^{\text{th}}$ (σ') molecules as

$$\mathbf{r}_m^{\sigma\sigma'} = \mathbf{r}_m(1 + \beta_m^{\sigma\sigma'}).$$

It should be noted that the parameters $\beta_m^{\sigma\sigma'}$ have the symmetry properties of the crystal i.e. $\beta_m^{+-} = \beta_m^{-+}$ and verify the relation

$$c^+ p_m^{++} \beta_m^{++} + c^+ p_m^{+-} \beta_m^{+-} + c^- p_m^{-+} \beta_m^{-+} + c^- p_m^{--} \beta_m^{--} = 0. \quad (11)$$

which comes from the existence of an average lattice.

To include size effects we have to replace $\langle F_n^\sigma F_{n+m}^{\sigma'*} \rangle_n$ in expression (4) by $\langle F_n^\sigma F_{n+m}^{\sigma'*} e^{i\pi s_1 m \beta_m^{\sigma\sigma'}} \rangle_n$. This last quantity can be expressed as

$$\langle F_n^\sigma F_{n+m}^{\sigma'*} e^{i\pi s_1 m \beta_m^{\sigma\sigma'}} \rangle_n = \langle F_n^\sigma F_{n+m}^{\sigma'*} \rangle_n + i\pi s_1 m \langle F_n^\sigma F_{n+m}^{\sigma'*} \beta_m^{\sigma\sigma'} \rangle_n \quad (12)$$

by using the usual approximation $\pi s_1 m \beta_m^{\sigma\sigma'} \ll 1$. The first term of (12) gives the S.R.O. diffuse scattering intensity calculated in section b, and the second term gives the size effect. As for expression (5), this term can be written as :

$$\langle F_n^\sigma F_{n+m}^{\sigma'*} \beta_m^{\sigma\sigma'} \rangle_n = \langle F^\sigma F_{1+m}^{\sigma'*} \beta_m^{\sigma\sigma'} \rangle + \text{c.c.}$$

As in expression (7) we have thus, using (11) and (A4)

$$\begin{aligned} & \langle F^\sigma F_{1+m}^{\sigma'*} \beta_m^{\sigma\sigma'} \rangle + \text{c.c.} = \\ & = c^+ p_m^{++} \beta_m^{++} F^+ F^{+*} + c^+ p_m^{+-} \beta_m^{+-} (F^+ F^{-*} + F^- F^{+*}) + \\ & \quad + c^- p_m^{-+} \beta_m^{-+} F^- F^{-*} + \text{c.c.} \quad m \text{ even} \\ & [c^+ p_m^{++} \beta_m^{++} F^+ F^+ + c^+ p_m^{+-} \beta_m^{+-} (F^+ F^- + F^- F^+) + \\ & \quad + c^- p_m^{--} \beta_m^{--} F^- F^-] e^{-i\pi s_1} + \text{c.c.} \quad m \text{ odd} \\ & = \begin{cases} -\frac{1}{c^-} p_m^{+-} \beta_m^{+-} I_{\text{Laue}} & m \text{ even} \\ \frac{1}{c^-} p_m^{+-} \beta_m^{+-} I_{\text{Laue}} \cos \varphi(s) + (c^+ p_m^{++} \beta_m^{++} + c^+ p_m^{+-} \beta_m^{+-}) I_1 & m \text{ odd} \end{cases} \end{aligned}$$

with

$$I_1 = [(F^+)^2 - (F^-)^2] e^{-i\pi s_1} + \text{c.c.} \\ = i 2 \sin \varphi (F^+ - F^-) (F^+ + F^-)^*$$

This expression thus shows that the size effect leads simply to a modulation of the Laue diffuse scattering, since $I_1 = 0$ when $I_{\text{Laue}} = 0$, without adding new diffuse scattering features.

In agreement with the results of the last section we shall consider in the following that the molecular orientations are not correlated ($\alpha = 0$). In this case, the diffuse intensity, given generally by (4), becomes :

$$I_{\text{Diff}}(\mathbf{s}) = I_{\text{Laue}} - 2 \pi s_1 \sum_{m \text{ odd}} m [\beta_m^{+-} I_{\text{Laue}} \cos \varphi(\mathbf{s}) + c^+ (c^+ \beta_m^{++} + c^- \beta_m^{+-}) I_1] \sin(m\pi s_1) \\ + 2 \pi s_1 \sum_{m \text{ even}} m \beta_m^{+-} I_{\text{Laue}} \sin(m\pi s_1). \quad (13)$$

It is clear from expression (13) that the 1st(2nd) neighbor size effect modulates the laue monotonic diffuse scattering intensity by a sine function $\sin(\pi s_1)(\sin(2\pi s_1))$ which has the $2a^*$ (a^*) reciprocal lattice periodicity. These variations are displayed by the X-ray pattern shown in figure 2a (white (black) arrows). Figures 6 and 7 show computer simulations of the diffuse scattering intensity given by expression (13) for the 1st and 2nd neighbor size effects ($m = 1$ and $m = 2$) respectively and for the crystal orientation previously considered. In these figures the white arrows indicate the weak periodic modulation of the Laue scattering intensity expected from expression (13).

Fig. 6. — Simulations of the diffuse scattering due to the first neighbor size effect (white arrows) in the case of $\alpha = 0.0$, $\beta_1^{++} = -\beta_1^{+-}$ for a) $\beta_1^{+-} = 0.03$ and b) $\beta_1^{+-} = 0.05$ and for the crystal orientation leading to the experimental X-ray pattern of figure 2a. Note the $2a^*$ sinusoidal modulation of the Laue diffuse scattering intensity.

By comparison of the simulations with the experimental pattern of the PF_6 salt, some parameters can be extracted : the coefficient $(c^+ \beta_1^{++} + c^- \beta_1^{+-})$ is found to be small, which means that $\beta_1^{++} \approx -\beta_1^{+-}$ in the case of $c^+ = c^-$, and $\beta_1^{+-} > 0$. These results mean that the intrachain distances are imposed by the pair of the largest chalcogen atoms along the 1-4 or 2-

Fig. 7. — Simulations of the diffuse scattering due to the second neighbor size effect (white arrows) in the case of $\alpha = 0.0$ for a) $\beta_2^{+-} = 0.004$ and b) $\beta_2^{+-} = 0.008$ and for the crystal orientation leading to the experimental X-ray pattern of figure 2a. Note the a^* sinusoidal modulation of the Laue diffuse scattering intensity.

3 directions (see Fig. 5). The presence of Se-Se pairs in the $(+ -)$ and $(- +)$ configurations and only of S-Se pairs in the $(+ +)$ and $(- -)$ configurations accounts for the positive value of β_1^{+-} and lead, with the use of (11), to $\beta_1^{++} \approx \beta_1^{--} = -\beta_1^{+-}$. It should be remarked that in the opposite situation, where the intrachain distances are imposed by pairs of chalcogen atoms along the 1-3 direction, one should get (for $c^+ = c^-$) $\beta_1^{++} \approx -\beta_1^{--}$ and $-\beta_1^{+-} \approx 0$ and thus a maximum contribution of the $(c^+ \beta_1^{++} + c^- \beta_1^{+-})$ term in (13). This situation is ruled out by our simulation. The finding of an intrachain distance imposed by the 1-4 and 2-3 pairs of chalcogen atoms is that expected from the (TMTSF)₂PF₆ [17] and (TMTSF)₂PF₆ [18] structural refinements which give an average intrastack chalcogen-chalcogen distance shorter along 1-4 and 2-3 than along 1-3 by 0.14 Å and 0.11 Å respectively. The best agreement with the experimental results of (TMDTDSF)₂PF₆ is obtained for $\beta_1^{+-} = 0.03$ and $\beta_2^{+-} = 0.004$. The corresponding simulation is shown in figure 2b. These β parameters correspond to displacements of 0.10(5) Å and 0.03(1) Å for the first and second neighbors respectively. The first neighbor displacement is close to 0.08 Å, the difference of the $a/2$ parameters of (TMTTF)PF₆ (3.57 Å) and (TMTSF)PF₆ (3.65 Å). It leads to a relative variation of intermolecular distance of about 3 %, which has the same order of magnitude as those measured in metallic alloys (≈ 6 %) [2b].

4. Conclusion.

In this study we have characterized the structural disorder existing in the (TMDTDSF)₂X series. This disorder, which is not due to alloying, has an important influence on the electric and structural properties of these series of organic conductors, as we shall show in paper II. Our study was complicated by additional effects such as the twinning of the crystals, the thermal diffuse scattering and the diffuse scattering announcing structural instabilities. Nevertheless, three kinds of information were obtained: the degree of disorder of the molecules (c^+ , the probability to have a selenium atom near the anion), the correlations between the orientations of neighboring molecules (α) and the static displacements of the molecules due to their environment (β).

In all the crystals investigated we have never observed a significant modulation of intensity due to correlations of molecular orientations in the *a* direction (an upper limit of $|\alpha|$ is 0.1). We emphasize here that transverse correlations should have led to intensity modulations in the transverse directions. Such effects are not observed, except perhaps in the ClO_4 salt, although in this salt we have been unable to discriminate between such variations of diffuse scattering and those due to the local ordering of the anions.

We have not obtained an accurate value of c^+ because an absolute measurement of the diffuse scattering intensity is required for that. However, a comparison between the diffuse scattering intensities due to the orientational disorder and to the RT thermal agitation suggests that $c^+ \approx 0.5$ for all the crystals investigated. Such an estimate is consistent with the value obtained by structural refinements [10].

All the $(\text{TMDTDSF})_2\text{X}$ crystals exhibit an intrachain size effect. As expected from the difference of size of the selenium and sulfur atoms, the molecules, in PF_6 salt for example, slightly move in the *a* direction in order to accommodate the difference of size of atoms in close contact. The displacements are estimated at about 0.10(5) Å and 0.03(1) Å for first- and second-neighbor molecules respectively. The 1st neighbor size effect amounts to the dimerization amplitude of the organic stacks in the $(\text{TMTTF})_2\text{X}$ series, but is larger than that of the $(\text{TMTSF})_2\text{X}$ series. Moreover, the TMDTDSF disorder is random and thus the associated size effect is not correlated spatially. The induced disorder of dimerization does not seem to have a drastic influence on the charge localization process which occurs in $(\text{TMDTDSF})_2\text{PF}_6$ at a $T_p \approx 100$ K [9], intermediate between those of the $(\text{TMTTF})_2\text{PF}_6$ ($T_p \approx 230$ K) and $(\text{TMTSF})_2\text{PF}_6$ (no T_p), and which vanishes under pressure with about the same rate of decrease as in the $(\text{TMTTF})_2\text{X}$ series [8]. A simple explanation of the weak effect of this disorder could be that the charge localization is mainly caused by the $4 k_F$ electronic response of the organic stack to the coherent anionic potential. However this disorder could lead to a weak localization of the electrons at low temperatures and under pressure when the metallic state is restored. This could prevent the onset of a superconductor ground state.

This series of materials exhibits a strong random orientational disorder of the molecules. As the diffuse scattering does not evolve with time and temperature, the disorder is quenched. This means that the molecular orientations do not change. The molecules thus keep the orientations adopted during the growth of the crystal. This behavior contrasts with that of some molecular crystals, where a segregation of two chiral species has been observed [15].

Finally let us conclude this study by a remark concerning the environment of the anions. As indicated in figure 8, the anions are in close contact with two molecules and can thus experience three distinct kinds of environment depending on the S-S, S-Se or Se-Se pairs of chalcogen neighbors. The unsymmetric S-Se environment breaks locally the inversion symmetry of the cavity whose effect on the position and orientation of the anion can be modelled by the action of a local field. Due to the absence of correlation between TMDTDSF molecular orientations this field is random. Its influence on the anion ordering mechanism will be considered in the following paper II.

Acknowledgments.

Useful exchanges of information with N. Thorup and discussions with J. Lajzerowicz are acknowledged. This work has been partly supported by the ESPRIT-Basic Research Action MOLCOM 3121.

Fig. 8. — The three types of environment (Se-S, Se-Se and S-S) of the anion in a (TMDTDSF)₂X crystal.

Appendix 1.

The sum over $\mathbf{m}$ in formula (2) involves three indices (m_1, m_2, m_3) in the case of a 3D crystal. In the 1D case where there is no correlation between the chains directed along $\mathbf{a}$, we thus distinguish two cases :

- a) If $m_2 = m_3 = 0$, the $\mathbf{n}$ and $\mathbf{n} + \mathbf{m}$ unit cells are situated on the same chain, then :

$$\langle F_{\mathbf{n}} F_{\mathbf{n}+\mathbf{m}}^* \rangle_{\mathbf{n}} = \langle F_{n_1} F_{n_1+m_1}^* \rangle_{n_1}$$

where the spatial average is only made over the index n_1 .

- b) If $m_2 \neq 0$ or $m_3 \neq 0$, the $\mathbf{n}$ and $\mathbf{n} + \mathbf{m}$ unit cells belong to two different chains, then :

$$\begin{aligned} \langle F_{\mathbf{n}} F_{\mathbf{n}+\mathbf{m}}^* \rangle_{\mathbf{n}} &= \langle F_{\mathbf{n}} \rangle \langle F_{\mathbf{n}+\mathbf{m}}^* \rangle \\ &= |\langle F \rangle|^2 \end{aligned}$$

where we have neglected the index $\mathbf{n}$ for the average of $F_{\mathbf{n}}$. In this case expression (2) becomes

$$\begin{aligned} I(\mathbf{s}) &= \sum_{m_1} \langle F_{n_1} F_{n_1+m_1}^* \rangle_{n_1} \exp(2 i \pi s_1 m_1) + \sum_{m(m_2, m_3 \neq 0)} |\langle F \rangle|^2 \exp(2 i \pi \mathbf{s} \cdot \mathbf{r}_{\mathbf{m}}) \\ &= \sum_{\mathbf{m}} |\langle F \rangle|^2 \exp(2 i \pi \mathbf{s} \cdot \mathbf{r}_{\mathbf{m}}) + \sum_{m_1} [\langle F_{n_1} F_{n_1+m_1}^* \rangle_{n_1} - |\langle F \rangle|^2] \exp(2 i \pi s_1 m_1). \end{aligned}$$

If we drop the subscript 1 for the index m_1 or n_1 , then the diffuse scattered intensity I_{Diff} is given in the 1D case by

$$\begin{aligned} I_{\text{Diff}}(\mathbf{s}) &= \sum_{\mathbf{m}} [\langle F_{\mathbf{n}} F_{\mathbf{n}+\mathbf{m}}^* \rangle_{\mathbf{n}} - |\langle F \rangle|^2] \exp(2 i \pi s_1 m) \\ &= \sum_{\mathbf{m}} \langle F_{\mathbf{n}} F_{\mathbf{n}+\mathbf{m}}^* \rangle_{\mathbf{n}} \exp(2 i \pi s_1 m) - |\langle F \rangle|^2 \delta(h - s_1) \end{aligned}$$

where δ is the Dirac function. One must note that the last term does not give rise to Bragg reflections as the condition integral h is only required by one of three Miller indices (h, k, ℓ) . Such a result is expected when the diffuse scattering intensity is the sum of the intensities scattered independently by each chain.

Appendix 2.

If each structure factor of the molecule F_n^σ is calculated with respect to the origin $na/2$, the structure factor of the cell F_n can be expressed, with the help of figure 3, as

$$F_n = F_{2n-1}^\sigma + \exp(i\pi s_1) F_{2n}^{\sigma'}.$$

We thus obtain the following relation

$$F_{n+1}^\sigma = \begin{cases} F_n^\sigma & \text{if } m \text{ is even} \\ \exp(i\pi s_1) F_n^{\sigma*} & \text{if } m \text{ is odd} \end{cases} \quad (\text{A1})$$

where $F^\sigma \equiv F_1^\sigma$. The sum entering in expression (3) thus becomes

$$\begin{aligned} \sum_m \langle F_n F_{n+m}^* \rangle_n e^{2i\pi s_1 m} &= \\ &= \sum_m \langle (F_{2n-1}^\sigma + \exp(i\pi s_1) F_{2n}^{\sigma'}) (F_{2(n+m)-1}^{\rho*} + \exp(i\pi s_1) F_{2(n+m)}^{\rho'*}) \rangle_n e^{2i\pi s_1 m} \\ &= \sum_m \langle (F_{n-1}^\sigma + \exp(i\pi s_1) F_n^{\sigma'}) (F_{n+m-1}^{\rho*} + \exp(i\pi s_1) F_{n+m}^{\rho'*}) \rangle_n \exp(i\pi s_1 m). \end{aligned}$$

Since

$$\begin{aligned} \langle (F_{n-1}^\sigma + \exp(-i\pi s_1) F_n^{\sigma'}) (F_{n+m-1}^{\rho*} + \exp(i\pi s_1) F_{n+m}^{\rho'*}) \rangle_n &= \\ &= \langle (F_{n-1}^\sigma F_{n+m-1}^{\rho*}) \rangle_n + \langle (F_n^\sigma F_{n+m}^{\rho*}) \rangle_n + \langle (F_{n-1}^\sigma F_{n+m}^{\rho*}) \rangle_n \exp(i\pi s_1) + \\ &+ \langle (F_n^\sigma F_{n+m-1}^{\rho*}) \rangle_n \exp(-i\pi s_1) \\ &= 2 \langle (F_n^\sigma F_{n+m}^{\rho*}) \rangle_n + \langle (F_{n-1}^\sigma F_{n+m}^{\rho*}) \rangle_n \exp(i\pi s_1) + \langle (F_n^\sigma F_{n+m-1}^{\rho*}) \rangle_n \exp(-i\pi s_1), \end{aligned}$$

we get

$$\begin{aligned} \sum_m \langle F_n F_{n+m}^* \rangle_n \exp(2i\pi s_1 m) &= \\ &= \sum_m [2 \langle (F_n^\sigma F_{n+m}^{\rho*}) \rangle_n + \langle (F_{n-1}^\sigma F_{n+m}^{\rho*}) \rangle_n \exp(i\pi s_1) + \\ &+ \langle (F_n^\sigma F_{n+m-1}^{\rho*}) \rangle_n \exp(-i\pi s_1)] \exp(i\pi s_1 m) \\ &= \sum_m [2 \langle (F_n^\sigma F_{n+m}^{\rho*}) \rangle_n + \langle (F_{n-1}^\sigma F_{n-1+m}^{\rho*}) \rangle_n \exp(i\pi s_1) + \\ &+ \langle (F_n^\sigma F_{n+m-1}^{\rho*}) \rangle_n \exp(-i\pi s_1)] \exp(i\pi s_1 m) \\ &= \sum_m 4 \langle (F_n^\sigma F_{n+m}^{\rho*}) \rangle_n \exp(i\pi s_1 m). \end{aligned}$$

If m and n now indicate the position of the molecule, the factor 4 is included in $\sum_m$ and formula (4) is obtained. Furthermore using (A1) we have

$$\begin{aligned} \langle F_n^\sigma F_{n+m}^{\rho*} \rangle_n &= \begin{cases} \langle F_n^\sigma F_{n+1}^{\rho*} \rangle & \text{if } m \text{ is odd} \\ \langle F_n^{\sigma*} F_{n+1}^\rho \rangle & \text{if } m \text{ is even} \end{cases} \\ &= \langle F_n^\sigma F_{n+1}^{\rho*} \rangle + \text{c.c.} \end{aligned} \quad (\text{A2})$$

where c.c. indicates the complex conjugate. The spatial average over the index n has been reduced to an orientational average over the index σ .

Appendix 3.

In a Markovian process [14], pair correlation terms can be calculated from the knowledge of the four nearest neighbor conditional probabilities p_1^{++} , p_1^{+-} , p_1^{-+} and p_1^{--} ($p_1^{\sigma\sigma}$ defined as the probability to find a molecule with the orientation « σ' » when the last one has the orientation « σ »). We neglect here a possible dependence of this probability with the site index (1 or 2) of the previously placed molecule, i.e. we neglect any correlation with an eventual dimerization of the molecular chain. The conditional probabilities p_m^{++} , p_m^{+-} , p_m^{-+} and p_m^{--} of pairs of molecules separated by $ma/2$ are simply obtained by an iterating process usually written in a matrix form as

$$\begin{aligned} \begin{pmatrix} p_m^{++} & p_m^{+-} \\ p_m^{-+} & p_m^{--} \end{pmatrix} &= \begin{pmatrix} p_1^{++} & p_1^{+-} \\ p_1^{-+} & p_1^{--} \end{pmatrix} \begin{pmatrix} p_{m-1}^{++} & p_{m-1}^{+-} \\ p_{m-1}^{-+} & p_{m-1}^{--} \end{pmatrix} \\ &= \begin{pmatrix} p_1^{++} & p_1^{+-} \\ p_1^{-+} & p_1^{--} \end{pmatrix}^m \\ &\equiv P^m, \end{aligned} \quad (\text{A3})$$

where the P matrix is called the transfer matrix or stochastic matrix.

As a molecular orientation is either « + » or « - », we have the following relations for any m

$$\begin{cases} p_m^{++} + p_m^{+-} = 1 \\ p_m^{-+} + p_m^{--} = 1 \end{cases}$$

which allow us to define two independent probabilities which completely characterize our Markovian process

$$p = p_1^{+-} \quad \text{and} \quad q = p_1^{-+}$$

It is yet useful to introduce the limit $m \rightarrow \infty$ of this stationary process as

$$\begin{aligned} \lim p_m^{++} &= \lim p_m^{-+} \\ &= c^+ \\ &= 1 - c^- \end{aligned}$$

which, in our case, represents the probability to have a selenium atom close to the anion. The equality of the numbers of + - and - + pairs at a distance $ma/2$ gives the additional relation

$$c^+ p_m^{+-} = c^- p_m^{-+} \quad (\text{A4})$$

It is known that correlations of occupation are well described by the so-called Warren-Cowley short range order parameter α_m defined as

$$\alpha_m = 1 - p_m^{-+}/c^+$$

The two independent parameters of the Markov process are now $\alpha_1 \equiv \alpha$ and c^+ . Relation (A3) becomes

$$\begin{aligned} p^m &= \begin{pmatrix} c^+ + c^- \alpha_m & c^- - c^- \alpha_m \\ c^+ - c^+ \alpha_m & c^- + c^+ \alpha_m \end{pmatrix} \\ &= \begin{pmatrix} c^+ + c^- \alpha & c^- - c^- \alpha \\ c^+ - c^+ \alpha & c^- + c^+ \alpha \end{pmatrix}^m \end{aligned}$$

It is easy to find the eigenvalues and eigenfunctions of the matrix P that we diagonalize according to :

$$P = \begin{pmatrix} 1 & 1 \\ 1 & -c^+/c^- \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -c^+/c^- \end{pmatrix}^{-1}$$

This shows that $\alpha_m = \alpha^{|m|}$, since our process is also defined for $m < 0$. The high order coefficients are finally found to be

$$\begin{pmatrix} p_m^{++} & p_m^{+-} \\ p_m^{-+} & p_m^{--} \end{pmatrix} = \begin{pmatrix} c^+ + c^- \alpha^{|m|} & c^- - c^- \alpha^{|m|} \\ c^+ - c^+ \alpha^{|m|} & c^- + c^+ \alpha^{|m|} \end{pmatrix}.$$

References

- [1] GUINIER A., « X-ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies » (San Francisco, W. H. Freeman and Company, 1963).
- [2] a) WARREN B. E., « X-ray Diffraction » (Addison-Wesley Publishing Company, 1975).
b) WARREN B. E., AVERBACH B. L. and ROBERT B. W., *J. Appl. Phys.* **27** (1951) 1493.
- [3] a) WELBERRY T. R. and JONES R. D. G., *J. Appl. Cryst.* **13** (1980) 244.
b) LAJZEROWICZ J., CHIRON B. and LAJZEROWICZ J., *J. Chem. Phys.* **74** (1981) 3500.
c) WELBERRY T. R., JONES R. D. G. and EPSTEIN J., *Acta Cryst.* **B 32** (1982) 1518.
- [4] WELBERRY T. R., *Rep. Prog. Phys.* **48** (1985) 1543.
- [5] AMOROS J. L. and AMOROS M., « Molecular Crystals » (New-York, Wiley, 1968).
- [6] a) DOUCET J., BENOIT J.-P., CRUSE W. B. T., PRANGE T. and KENNARD O., *Nature* **337** (1989) 190.
b) DOUCET J., BENOIT J. P., FAURE P. and DURAND D., *J. Phys. I France* **2** (1992) 981.
- [7] AUBAN P., JÉROME D., LESTRUP K., JOHANNSEN I., JORGENSEN M. and BECHGAARD K., *J. Phys. France* **50** (1989) 2727.
- [8] AUBAN P., JÉROME D., JOHANNSEN I. and BECHGAARD K., *Synth. Met.* **41-43** (1991) 2285.
- [9] GOTSCHY B., AUBAN-SENZIER P., FARALL A., BOURBONNAIS C., JÉROME D., CANADELL E., HENRIQUES R. T., JOHANNSEN I. and BECHGAARD K., *J. Phys. I France* **2** (1992) 677.
- [10] THORUP N., Private communication.
- [11] LIU Q., RAVY S., SENHAJI A., POUGET J. P., JOHANNSEN I. and BECHGAARD K., *Synth. Met.* **41-43** (1991) 1711.
- [12] WELBERRY T. R., JONES R. D. G. and PUZA M., *Acta Cryst.* **C 39** (1983) 1123.
- [13] COWLEY J. M., *Acta Cryst.* **A 24** (1968) 557.

- [14] See reference [4] for a clear and complete review of models of disorder and their use in X-ray diffuse scattering calculations.
- [15] LAJZEROWICZ-BONNETEAU J., LAJZEROWICZ J. and BORDEAUX D., *Phys. Rev. B* **34** (1986) 6453.
- [16] In the case of the ReO₄ salt, this finding contradicts the conclusion of a preliminary report (Ref. [11]) where it was suggested that c^+ was sizeably different from 0.5.
- [17] THORUP N., RINDORF G., SOLING H. and BECHGAARD K., *Acta Cryst. B* **37** (1981) 1236.
- [18] GALLOIS B., Thesis, Université Bordeaux I (1987).
- [19] MICHEL K. H. and ROWE J. M., *Phys. Rev. B* **22** (1980) 1417.