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X-ray diffuse scattering study of $2 k_F$ and $4 k_F$ anomalies in strongly irradiated TTF-TCNQ

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Résumé. — Nous présentons une étude par diffusion diffuse des rayons X des ondes de densité de charges dans TTF-TCNQ fortement irradié. Les ondes de densité de charges à $2 k_F$ et $4 k_F$ deviennent unidimensionnelles jusqu'aux plus basses températures mesurées (28 K), pour des échantillons avec 5 % de défauts moléculaires. Avec 15 % de défauts moléculaires l'anomalie à $2 k_F$ disparaît, tandis qu'une distorsion au vecteur d'onde $4 k_F$, indépendante de la température, est stabilisée. Ce comportement est comparé à celui de l'alliage TTF_{0,97}TSF_{0,03}TCNQ et de TMTSF-DMTCNQ irradié.

Abstract. — We report an X-ray diffuse scattering study of the CDW fluctuations in strongly irradiated TTF-TCNQ. The $2 k_F$ and $4 k_F$ CDW become onedimensional for 5.0 mol % of introduced defects, even at the lowest temperature (28 K). At the concentration level of 15 mol % the $2 k_F$ anomaly disappears, while a temperature independent $4 k_F$ distortion is stabilized. These results are compared with those for the alloy TTF_{0,97}TSF_{0,03}TCNQ and for TMTSF-DMTCNQ.

1. Introduction.

The X-ray diffuse scattering technique has proved to be a very powerful tool for the study of structural instabilities of quasi-one-dimensional conductors like TTF-TCNQ. The observation of a Peierls distortion with $2 k_F$ periodicity, the determination of the Fermi wave vector (k_F) and the values of the correlation lengths of the charge density waves (CDW) have considerably improved the understanding of the exceptional properties of TTF-TCNQ [1-3]. In addition to the observation of $2 k_F$ structural fluctuations, an unexpected result of the X-ray studies was the discovery of a $4 k_F$ instability [3]. Although it reflects at a structural level, the effect of interactions between electrons, its precise understanding is still subject to discussion.

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Introduction of defects in CDW systems has often been used to extract the intrinsic properties of these compounds, and to define more clearly the effects of disorder which is always present in these materials [4, 5]. Recently an X-ray diffuse scattering study was performed on TMTSF-DMTCNQ disordered by irradiation [6]. The pure material exhibits both $2 k_F$ and $4 k_F$ CDW. The former orders three-dimensionally (3D) below 42 K, while the latter remains in the form of 1D fluctuations between 300 K and 60 K. With increasing irradiation dose the correlation length of the $2 k_F$ distortion decreases rapidly. For defect concentrations above 0.3 mol %, the Peierls transition is suppressed even at the lowest temperatures, and defects of the order of 1 mol % completely decouple the CDW on neighbouring chains. A simple analysis of these results shows that irradiation induced defects strongly pin the CDW in a volume of about 30 molecules. Furthermore it turned out that defects first suppress the temperature dependent $4 k_F$ anomaly, then stabilize a new « static » $4 k_F$ distortion.

The purpose of this study was to investigate the behaviour of $2 k_F$ and $4 k_F$ instabilities at higher defect concentrations than those used in the previous study of TMTSF-DMTCNQ. In particular we wanted to study the broadening of the $2 k_F$ anomaly and the effect of stabilization of a $4 k_F$ « static » distortion at defect levels of ~ 10 mol %. Therefore we have chosen for this study TTF-TCNQ for which $2 k_F$ fluctuations grow at lower temperature and $4 k_F$ fluctuations are more divergent than in TMTSF-DMTCNQ [7].

2. Experimental and results.

The experimental set up used for the present X-ray diffuse scattering investigation (fixed film, fixed crystal) is essentially the same as that described in references [6] and [7]. The X-ray photographic patterns were taken between 28 K and 300 K and read with a Joyce Loeble microdensitometer.

In order to introduce pinning centres in a controlled manner, we have created defects by fast electron irradiation (2 MeV) in TTF-TCNQ single crystals. Two crystals of sizes $0.6 \times 5.0 \times 0.2 \text{ mm}^3$ and $0.5 \times 8.0 \times 0.2 \text{ mm}^3$ were irradiated at doses of 40 mC/cm² and 130 mC/cm² respectively. The equivalence between irradiation dose and defect concentration has been obtained from previous electrical conductivity measurements [8]. According to this work the two samples used in this study contain 5 mol % and 15 mol % of radiation induced defects.

The main results of this study are summarized by the X-ray patterns shown in figure 1, all taken at about the same temperature 28 K. Figure 1a (taken from Ref. [7]) recalls that after three successive phase transitions at 54 K, 49 K and 38 K, the $2 k_F$ and $4 k_F$ CDWs of pure TTF-TCNQ are 3D ordered, giving rise to superstructure spots at the wave vectors $q_1 = (0.25, 0.295, 0)$ and $q_2 = (0.5, 0.59, 0)$ for the $2 k_F$ and $4 k_F$ distortions respectively. With 5 mol % of defects (Fig. 1b) these superstructure spots are replaced by diffuse lines at about the same wave vector in the b^* direction, measured from the layers of main Bragg reflections, as that found in pure TTF-TCNQ. This means that the $2 k_F$ and $4 k_F$ CDW distortions are still well established in the chain direction, but are not ordered transversely. Between 5 mol % (Fig. 1b) and 15 mol % (Fig. 1c) defects, the X-ray diffuse pattern of TTF-TCNQ has changed quite a lot. In particular for 15 mol % defects the $2 k_F$ diffuse scattering cannot be clearly detected. The $4 k_F$ scattering can be observed at this high defect concentration, but it is considerably broadened along b^* . In figure 1c the $(2 + 4 k_F) b^*$ and $(3 - 4 k_F) b^*$ diffuse lines form a very broad scattering centred at about $2.5 b^*$. However the microdensitometer reading of this scattering (Fig. 3) shows that the two components of the $4 k_F$ scattering can still be separated.

The $2 k_F$ scattering of TTF-TCNQ with 5 mol % of defects can be detected until about 150 K as in pure samples. The half width at half maximum along the b direction, $\Delta_b(2 k_F)$, is shown in figure 2a as a function of temperature and compared to that of pure TTF-TCNQ [7] and the

TTF TCNQ

Fig. 1. — (a) : X-ray pattern of pure TTF-TCNQ at 28 K showing the $2 k_F$ (black arrows) and $4 k_F$ (white arrows) satellite spots at $0.295 b^*$ and $0.590 b^*$ wave vectors respectively between layers of main Bragg reflections (This pattern is taken from Ref. [7]). (b) and (c) : X-ray patterns of TTF-TCNQ at 28 K for various defect concentrations. The crystal orientation is nearly the same as in pattern a. (b) 5 mol % of defects : black arrows point to $2 k_F$ diffuse lines and white arrows to $4 k_F$ diffuse lines. (c) 15 mol % of defects : white arrows point to the $4 k_F$ scattering. No $2 k_F$ scattering can be clearly detected !

alloy $\text{TTF}_{0.97}\text{TSF}_{0.03}\text{TCNQ}$ [14]. After a Lorentzian correction of $\Delta_b(2 k_F)$ for the resolution of the apparatus, the inverse of the resulting quantity gives the correlation length of the $2 k_F$ CDW. It is found that $\xi_b(2 k_F) \sim 30 \text{ \AA}$ at 28 K and $\xi_b(2 k_F) \sim 5 \text{ \AA}$ at 150 K.

The $4 k_F$ scattering of TTF-TCNQ with 5 mol % and 15 mol % of defects is observed up to room temperature as in pure TTF-TCNQ. The half width at half maximum along the b direction, $\Delta_b(4 k_F)$, is given in figure 2b as a function of temperature and is also compared to that of pure TTF-TCNQ [7] and the alloy $\text{TTF}_{0.97}\text{TSF}_{0.03}\text{TCNQ}$ [14]. The decrease of the onchain correlation length with the amount of defects can be clearly seen at low temperatures. At 28 K, $\xi_b(4 k_F) \sim 22 \text{ \AA}$ for 5 mol % of defects and $\xi_b(4 k_F) \sim 8 \text{ \AA}$ for 15 mol % of defects. For the sample with 5 mol % of defects the $2 k_F$ and $4 k_F$ anomalies have roughly the same width and the same intensity at 28 K. At room temperature the correlation length of the $4 k_F$ anomaly in TTF-TCNQ with 5 mol % of defects coincides with that of the pure sample $\sim 10 \text{ \AA}$. It is slightly larger than that of the sample with 15 mol % of defects $\sim 8 \text{ \AA}$.

Figure 2b shows that within experimental errors the width of the $4 k_F$ scattering of the sample with 15 mol % of defects does not change with temperature, while that of the sample with 5 mol % of defects increases with temperature until about 150 K, then appears to saturate. Figure 2 shows clearly that the $4 k_F$ scattering of the sample with 5 mol % of defects has a different temperature

Fig. 2. — Temperature dependence of the half width at half maximum (HWHM) of the $2k_F$ (a) and $4k_F$ (b) scattering along the b direction for samples of TTF-TCNQ with 5 mol % and 15 mol % of defect concentrations. After the subtraction of the experimental resolution this quantity gives the inverse correlation lengths $\xi_b^{-1}(2k_F)$ and $\xi_b^{-1}(4k_F)$ respectively, in the chain direction. The data of $\text{TTF}_{0.97}\text{TSF}_{0.03}\text{TCNQ}$ are from Ref. [14]. (The dotted curves corresponding to pure TTF-TCNQ are taken from Ref. [7]. They have been shifted by the difference of experimental resolution). For the calculation of the HWHM along b^* , we have used the convention $b^* \cdot b = 2\pi$.

Fig. 3. — Microdensitometer readings along the b^* direction across the $2 + 4k_F$ and $3 - 4k_F$ diffuse lines of X-ray patterns of TTF-TCNQ with 15 mol % of defects for different temperatures. Taking into account the scale factor corresponding to the exposure time, the $4k_F$ scattering shows no appreciable temperature dependence. The arrows point at the positions of $(2 + 4k_F)b^*$ and the $(3 - 4k_F)b^*$ wave vectors.

dependence than the $2k_F$ scattering of the same sample, and it differs from the temperature dependence of the $4k_F$ scattering of the pure TTF-TCNQ and the alloy $\text{TTF}_{0.97}\text{TSF}_{0.03}\text{TCNQ}$ as well.

Microdensitometer readings of the $4k_F$ scattering of TTF-TCNQ with 15 mol % of defects (Fig. 3) show that the $4k_F$ anomaly does not change appreciably in intensity between 295 K and 28 K. Thus in this sample the $4k_F$ scattering appears as a temperature independent static 1D distortion. The peak intensity of the $4k_F$ anomaly of the sample with 5 mol % of defects increases slightly for decreasing temperature, but the integrated intensity does not depend on temperature. Finally, the integrated intensity of the $4k_F$ anomaly is essentially the same for the samples with 5 mol % and 15 mol % of defects.

3. Discussion.

The X-ray study performed on TTF-TCNQ confirms our previous findings on irradiated TMTSF-DMTCNQ. At low temperature the defects strongly pin the CDW on several molecules, fixing their phase which prevents their growth in chain direction, and their lateral coupling. In agreement with the absence of structural phase transition, electrical conductivity [9] and magnetic susceptibility measurements [10] show no sharp electronic transition for these strongly irradiated samples. Disorder breaks the onchain and lateral coherences between CDW necessary for the phase transition, but does not completely inhibit the $2k_F$ and $4k_F$ lattice instabilities.

The temperature dependence of the $2k_F$ scattering of TTF-TCNQ with 5 mol % of defects is similar to that of the corresponding scattering in TMTSF-DMTCNQ. Figure 2a shows a saturation of the width of the scattering toward a finite value at low temperatures, due to the presence of the pinning centres, inhibiting the infinite growth of the CDW in the chain direction and, at high temperatures, a broadening of the width due to the thermally limited correlation length of the CDW, which is comparable to that found in the pure compound.

It is important to notice that 5 mol % of defect in TTF-TCNQ and ~ 1 mol % of defects in TMTSF-DMTCNQ (see Ref. [6]) gives the same value $\sim 30 \text{ \AA}$ for the low temperature saturation of the $2k_F$ CDW onchain correlation length. According to the analysis performed in reference [20], this clearly demonstrates that the volume of the crystal perturbed by an irradiation induced defect is smaller in TTF-TCNQ than in TMTSF-DMTCNQ. In agreement with this observation, calculations based on conductivity measurements [20] show that a defect influences a volume 6 times larger in TMTSF-DMTCNQ than in TTF-TCNQ. In addition the $2k_F$ scattering of irradiated TTF-TCNQ does not have an asymmetrical profile as found in TMTSF-DMTCNQ with ~ 1 mol % of defects. This, and the absence of detectable $2k_F$ scattering for TTF-TCNQ with 15 mol % of defects suggest that the $2k_F$ scattering observed in irradiated TTF-TCNQ comes from the unperturbed part of the crystal. This would also indicate that the defects do not induce an appreciable $2k_F$ distortion in the perturbed volumes of TTF-TCNQ. On the contrary, the constancy of the integrated intensity of the $4k_F$ scattering with increasing number of defects suggests that a substantial part of the $4k_F$ distortion takes place in the perturbed volumes. For 15 mol % of defects the observed « static » $4k_F$ scattering comes mostly from the perturbed volumes which strongly overlap and occupy most of the volume of the crystal. Thus the observed $4k_F$ lattice distortion can be viewed as the distortion accompanying charge density oscillations of wave vector $4k_F$ induced by defects. In the case of a strongly correlated electronic gas the usual $2k_F$ wave vector of Friedel oscillations is changed into the wave vector $4k_F$. It is interesting to notice that strongly irradiated TMTSF-DMTCNQ and TTF-TCNQ exhibit opposite behaviours with respect to their $2k_F$ and $4k_F$ scattering. Between 0.7 mol % and 2.8 mol % of defects the $4k_F$ scattering of TMTSF-DMTCNQ vanishes while its $2k_F$ scattering keeps roughly the same integrated intensity. Between 5 mol % and 15 mol % of defects in TTF-TCNQ the $4k_F$ scattering keeps roughly the same integrated intensity while the $2k_F$ scattering is lost. In the case of TMTSF-DMTCNQ it is believed that the electronic gas (on the donor stack at least)

is less correlated than in TTF-TCNQ. Thus, for the former compound, defects more likely induce Friedel oscillations with $2 k_F$ wave vector.

Finally it is also interesting to compare the structural properties of irradiated TTF-TCNQ with those of the substitutional alloy $\text{TTF}_{1-x}\text{TSF}_x\text{TCNQ}$. Although TTF and TCNQ molecules may have different sensitivity to electron irradiation [11], strong pinning centres are formed on both type of stacks. In the alloys $\text{TTF}_{1-x}\text{TSF}_x\text{TCNQ}$ the random substitution [12] affects the donor stacks, and can be viewed as creating weaker pinning centres for the CDW. This difference is clearly illustrated by the rapid suppression of the Peierls transition of TTF-TCNQ under irradiation and its existence in $\text{TTF}_{1-x}\text{TSF}_x\text{TCNQ}$ [13], whatever is x . More precisely the alloy $\text{TTF}_{0.97}\text{TSF}_{0.03}\text{TCNQ}$ still presents the 3 phase transitions of TTF-TCNQ, but slightly shifted to 50 K, 45 K and 30 K respectively, while in TTF-TCNQ about 0.3 mol % of defects created by irradiation suppresses the structural phase transitions [19].

It is also instructive to compare the onchain correlation length of $2 k_F$ and $4 k_F$ CDW of pure TTF-TCNQ, the alloy $\text{TTF}_{0.97}\text{TSF}_{0.03}\text{TCNQ}$ and TTF-TCNQ with 5 mol % of defects as done in figure 2. The substitution of 3 mol % of molecules on the donor-stack does not appreciably change the temperature dependence of the $2 k_F$ fluctuations, while it has a strong influence on the $4 k_F$ fluctuations. At 28 K one gets for the alloy $\xi_b(2 k_F) \geq 200 \text{ \AA}$ while $\xi_b(4 k_F) \sim 50\text{-}100 \text{ \AA}$ [14]. Of course only the $2 k_F$ scattering condenses in superstructure at low temperatures, while the $4 k_F$ scattering remains in the form of diffuse sheets, as remarked earlier by Kagoshima *et al.* [15]. Between the 3 phase transitions of $\text{TTF}_{0.97}\text{TSF}_{0.03}\text{TCNQ}$ only the wave vector component q_a of the $2 k_F$ satellite reflections varies : being $q_a = 1/2 a^*$ between 50 K and 45 K, $q_a = 1/4 a^*$ below 30 K and changing continuously between these two values between 45 K and 30 K [14, 15]. This means that the formation of $4 k_F$ satellite reflections is not necessary to describe the sequence of the 3 structural phase transitions of TTF-TCNQ. Thus the suppression of the Peierls transition of TTF-TCNQ by irradiation comes mostly from the pinning of $2 k_F$ CDW, which prevents their inchain growth and their lateral coupling. Figure 2 also shows that the substitution of 3 % of TSF in TTF-TCNQ does not appreciably change the inchain linewidth of the $2 k_F$ scattering, but substantially increases that of the $4 k_F$ scattering. This clearly indicates that TCNQ is the driving stack for the $2 k_F$ instability [16], while TTF is the driving stack for the $4 k_F$ instability [17]. However, this does not imply that the $2 k_F$ and $4 k_F$ distortions are only situated on the above mentioned stacks [18]. In TTF-TCNQ the observation of a similar broadening of the $2 k_F$ and $4 k_F$ scattering at low temperatures is in agreement with a comparable perturbation of the two kinds of stacks for 5 mol % defect concentration, affecting more particularly the $2 k_F$ fluctuations on the TCNQ stacks (and the structural phase transitions) and the $4 k_F$ fluctuations on the TTF stacks.

In conclusion, we have shown that 1 D CDW are still present in TTF-TCNQ strongly disordered by irradiation. In contrast to the alloy $\text{TTF}_{0.97}\text{TSF}_{0.03}\text{TCNQ}$, the strong perturbation introduced by irradiation defects suppresses the phase transition and limits the coherence length of both $2 k_F$ and $4 k_F$ CDW fluctuations. Under high doses of irradiation the $2 k_F$ anomaly disappears, while a temperature independent $4 k_F$ distortion is stabilized. This behaviour is the opposite of that found in strongly irradiated TMTSF-DMTCNQ.

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