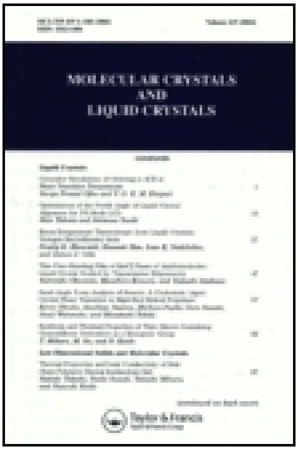

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STRUCTURAL STUDIES OF PHASE TRANSITION IN ONE DIMENSIONAL CONDUCTORS AND SUPERCONDUCTORS

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Abstract Competing effects in real one dimensional conductors have considerably enriched the original structural picture of the instability of a single metallic chain. Such effects include transverse as well as longitudinal polarizations of the Peierls distortion, instabilities on different molecular chains, 2 and $4k_F$ instabilities, and commensurability effects. With the more recent class of organic superconductors $(TMTSF)_2X$, superconductivity is not only in competition with the Peierls instability but also with order-disorder phase transitions involving the non-centrosymmetric counter ions. In $(TMTSF)_2ClO_4$ which is the only superconductor at atmospheric pressure, further complication arises from quenching effects and X-ray radiation induced modifications.

It is now well known that a typical structural feature of one dimensional conductors is a particular lattice distorsion predicted long ago by theories of an ideal one dimensional metal (1). In these early models, this distorsion takes place at 0°K with precursor fluctuations in a wide temperature range and a giant anomaly in the phonon dispersion at twice the Fermi wave vector ($2k_F$) (2).

Real systems retain these main 1-D features (3,4,5) of the precursor effects as illustrated in figures 1 and 2, but weak coupling between conducting chains raises to a finite value the temperature at which the lattice distorsion takes place and results in a real phase transition (6,7,8).

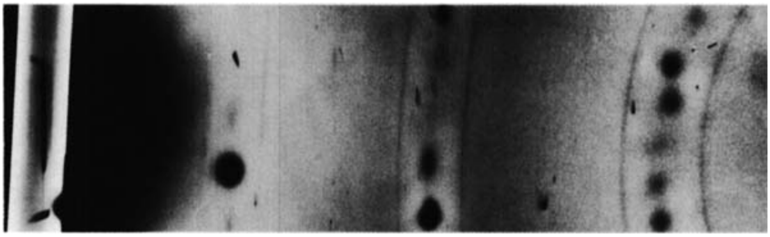


Figure 1 : X-Ray diffuse scattering pattern from $K_2Pt(CN)_4Br_{0.30}$ - x H_2O at room temperature. The enhanced amplitude of the precursor 1-D distorsion waves corresponding to the giant kohn anomaly in the metallic state appear as diffuse lines at the wave vector ± $2k_F$ from the layers of Bragg spots. The scattering of X-Rays comes predominently from the single rows of platinum chains. It is the absence of extension of such chains perpendicular to the chain axis together with the uncoupled phases of the distorsions on parallel chains which are responsible for the continuous aspect of the diffuse lines. This is typical of a strictly one-dimensional diffraction phenomenon.

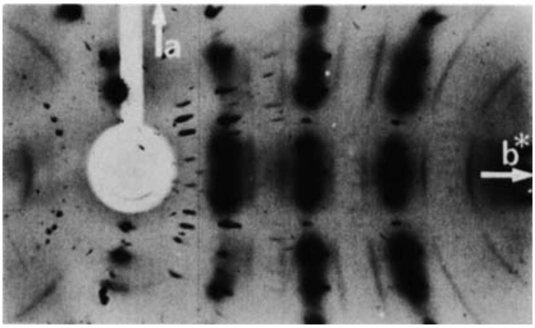


Figure 2 : X-Ray diffuse scattering pattern from TseF-TCNQ above the metal-insulator phase transition. The 1-D precursor distorsion waves give here rise to diffuse lines with a variable intensity. The distorsion is still quasi 1-D on the organic stacks of molecules, but the extension of the molecules in the transverse direction give rise to interference phenomena between atoms within each molecule. The variable intensity along each $2k_F$ diffuse line corresponds to the form factor of each molecule. In the present case of TSeF-TCNQ, there is again one heavier atom (Se) which is responsible for most of the intensity, and the distance between two maxima on the diffuse lines relates precisely to the distance between 2 Selenium atoms.

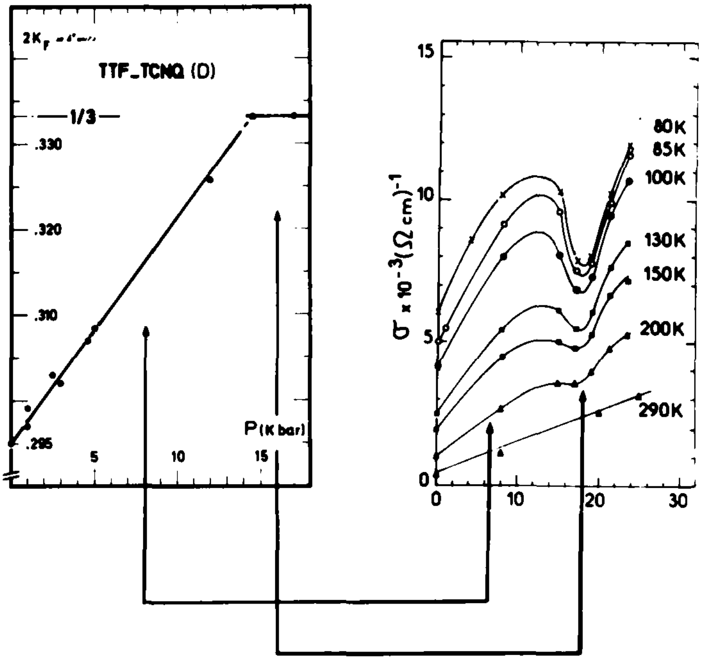


Figure 3 : Pressure modifies the energy of the conduction bands of the TTF and TCNQ stacks relative to one another, and consequently the filling of each band, the charge transfer and the $2k_F$ wave vector. In TTF-TCNQ with increasing pressure, the $2k_F$ wave vector increases from its incommensurate value of 0,295b* at atmospheric pressure until it reaches the commensurate value 1/3 b*(superstructure 3b) where it remains locked in a certain pressure range above 15 Kbar (left-hand side figure after 14). The phase of commensurate-distorsion waves is locked on the lattice, inducing a drop of conductivity which is most pronounced just above the metal-insulation Peierls transition where a substantial fraction of the conductivity comes from the sliding charge density waves, (righ hand side figure after 12)

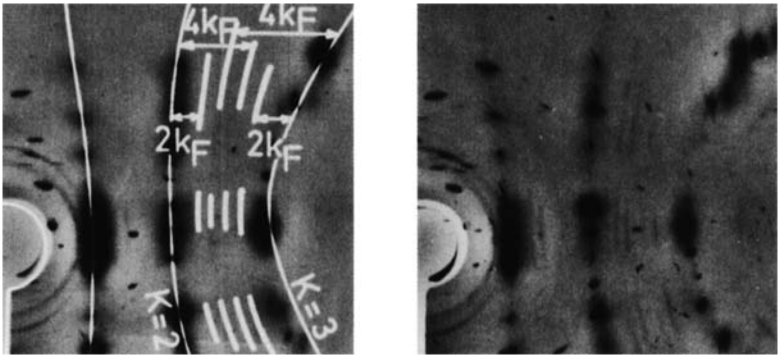


Figure 4 : X-ray diffuse scattering pattern from TTF-TCNQ above the metal insulator phase transition. Two sets of diffuse lines are in this case observable respectively at the $2k_F$ and $4k_F$ wave vectors. From the different temperature dependence of both the intensity and the intensity profile of the two sets of diffuse lines, one can conclude that they arise from two different physical instabilities (after 15).

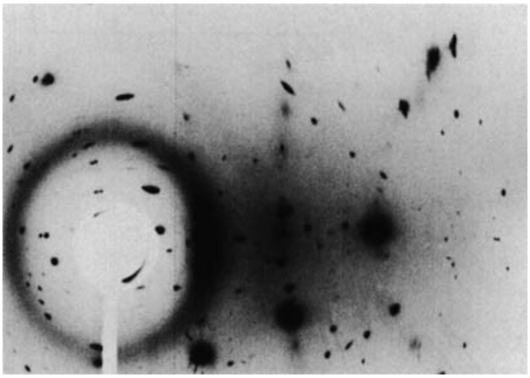


Figure 5 : X-ray pattern from TTF-TCNQ below 38K. Note the presence of both $2k_F$ and $4k_F$ Bragg spots corresponding to the incommensurate long range ordered superstructure of the Peierls insulating state (after 15).

Competing effects, particularly in the molecular organic 1-D conductors have further enriched the original picture. Such features include transverse, as well as longitudinal polarizations of the distortion (9), instabilities taking place at different temperatures on different molecular chains (10,11), and even spectacular commensurability effects (see figure 3) (12,13), altogether giving rise to several phase transitions and very complex phase diagrams under applied pressure (14).

Another competing phenomenon was the observation of the $4k_F$ instability (15,16), which is illustrated on X-Ray patterns figures 4 and 5 for TTF-TCNQ. The interplay between the $2k_F$ and $4k_F$ instabilities is probably best illustrated with $(NMP)_{1-x}(PHEN)_xTCNQ$ where the alloying leads to cross over phenomena from one type of instability to the other (18).

With the discovery of the $(TMTSF)_2X^-$ family and superconductivity in many of its members (19,20) yet some other new structural effects entered in this already complex game. As shown in the X-Ray patterns of figure 6, and from subsequent

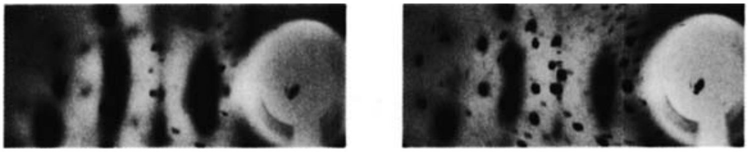


Figure 6 : X-ray diffuse scattering pattern from $(TMTSF)_2ReO_4^-$ above (200K, left-hand side) and below (49K, right-hand side) the 182K metal insulator phase transition. Precursor effects appear here (200K) as isotropic broad diffuse spots which are typical of 3-D short range correlations. The phase transition is in this case driven by the ordering of the non-centrosymmetric ReO_4^- ions which induce a $2k_F$ distorsion on the organic conducting stacks accounting for the metal insulator transition.

structure analysis (21,23), the ordering of non-centrosymmetric X^- anions can also lead to metal insulator transitions and more generally to a large variety of superstructures (summarized in Table 1). Among these superstructures there

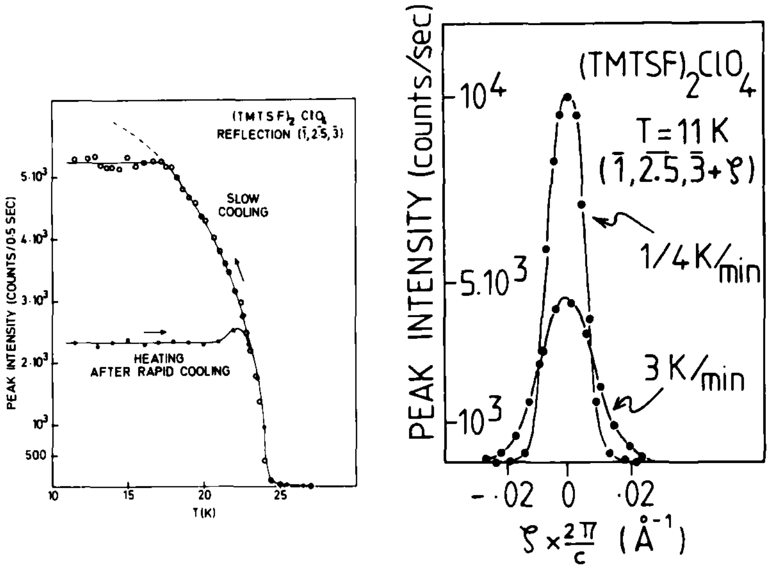
NON-CENTROSYMMETRIC IONS

$(TMTSF)_2X$			$(TMTTF)_2X$		
X	T_c	Q	X	T_c	Q
ClO_4	24	0 1/2 0	ClO_4	70	1/2 1/2 1/2
ReO_4	177	1/2 1/2 1/2	ReO_4	160	1/2 1/2 1/2(24)
BF_4	39	1/2 1/2 1/2	BF_4	40	1/2 1/2 $1/2^+$
BrO_4	250	1/2 ? ?			
FSO_3	87.5	1/2 1/2 1/2			
NO_3	41	1/2 0 0	NO_3	50	1/2 0 0
SCN	85	.48, .65, .10	SCN	160	0 1/2 1/2
H_2F_3	63	∿1/2 1/2 1/2 (25)			

TABLE 1

Table 1 : To date Summary of observed superstructures in $(TMTSF)_2X$ and $(TMTTF)_2X$ compounds due to non-centrosymmetric anions ordering effects. Remind that the conduction direction is always along a corresponding to the wave vector component along a* with : $\frac{1}{2}a^* = 2k_F$.

is one (0, $\frac{1}{2}$, 0) corresponding in real space to a superstructure a × 2b × c, which is observed in (TMTSF)$_2$ClO$_4^-$, that is to say in the case of atmospheric pressure superconductivity (20), which seems to be intimely related to the superconducting properties. Very low concentrations of alloying (26), quenching (27), and very small concentrations



(a) (b)

<u>Figure 7</u> : Quenching effects on (TMTSF)$_2$ClO$_4^-$
a) Temperature dependence of a superstructure reflexion for a slowly cooled sample (1/4K/Min) and a rapidly cooled sample (3K/Min);
b) Intensity profile at 11K of a superstructure reflexion for the same two cooling rates. Rapid cooling quenches the anion disorder. From the difference in intensities, and width of the superstructure reflexions respectively, one can conclude that for a crystal cooled at 3K/Min, less than half of the anion order in regions of about 200 Å (from figure 7a).
Note that even at the slow cooling rate of 1/4 K/Min. the intensity of the superstructure reflexion saturates at a value below the expected one (doted line in figure 7a).

of X-Ray irradiation induced effects (28) destroy superconductivity, but also strongly affects the anion ordering (22,29,31), as illustrated here on figures 7 and 8. Centrosymmetric anions (PF_6^-, AsF_6^-, etc...) seem to have a much simpler behaviour, only weak signs of a $2k_F$ instability (32), and a puzzling anions disorder (33), but no real phase transition.

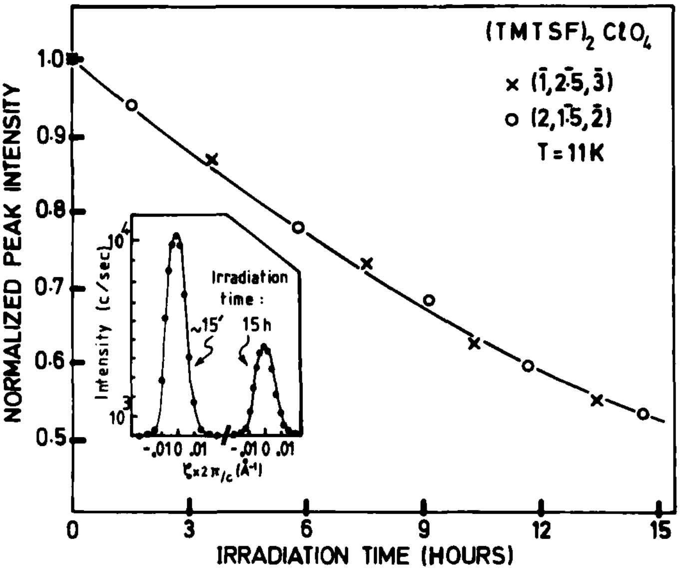


Figure 8 : irradiation effects in $(TMTSF)_2ClO_4^-$.
Intensity of a low temperature superstructure reflexion as a function of irradiation time at 11K; In this range, the main reflexions as well as the superstructure reflexion width are unchanged. The main effect of 15 hours irradiation is to disorder about half of the anions with little effect on the average structure and on the size of the ordered regions. This leads to a picture of large disordered regions around each defect within an overal ordered matrix, which is exactly the inverse situation of the quenched case of several ordered regions within an overal disorder matrix.

Now, as a last example to date, we have to mention $(BEDT\text{-}TTF)_4(ReO_4^-)_2$ which was the first sulphur based organic molecular superconductor to be discovered (34). This compound displays ordered anions (34,35) already at room temperature (wave vector $(0, \frac{1}{2}, \frac{1}{2})$ and superstructure (a x 2b x -b+c); in spite of that, it undergoes yet a metal insulator transition at 80K which corresponds to an additional modulation of this superstructure (36) with the wave vector $(\frac{1}{2}, 0, \frac{1}{2})$. The fact that again the wave vector component along a of the new low temperature phase coincides with $2k_F$ can probably again explain the metal insulator character of the phase transition.

This summarizes very briefly the situation at atmospheric pressure which looks already very complex.

Structural studies of phase transitions in these compounds under applied pressure is a challenging goal.

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