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Neutron and X-Ray Diffuse Scattering Study of Tetrathiofulvalene Tetracyanoquinodimethane (TTF - TCNQ)

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DISCLAIMER

Series of extensive X-Ray and Neutron scattering experiments[1-11] have been carried out in the last year on TTF-TCNQ and substantial agreement has now emerged. We can summarize the main results as follows :

A/ - Below the Peierls transition taking place at 54 K, two additionnal structural phase transitions are observed at 49 K and 38 K (figure 1). These 3 transitions correspond to a sequence of 3 different low temperature modulated phases which are thought to arise from the successive ordering of the charge density waves on the two different molecular species of TTF-TCNQ[12-17] leading to the successive modulations

$2a \times 3{,}40\,b \times c \quad (49 < T < 54\ K)$

$x(T) \times 3{,}40\,b \times c \quad (38 < T < 49\ K)$

$4a \times 3{,}40\,b \times c \quad (T < 38\ K)$

B/ - Above the Peierls transition two different precursor 1-d fluctuations have been observed, as shown in the X-Ray pattern of figure 2.

1 - At the wave vector $0.295\ b^*$ (attributed to $2k_F$) strongly temperature dependent X-Ray scattering was observed below 150 K. From the distribution of the intensity in the reciprocal space ($2k_F$ planes), the polarization of this modulation is found to have two components : a longitudinal component in chain direction and a transverse component in c^* direction which corresponds to the direction of tilt of the molecules. Inelastic neutron measurements reveal, in the same temperature range, an anomaly in the transverse mode with main polarization along c^* (figure 3). It is this fluctuation which diverges at the Peierls transition at 54 K.

The occurence of both polarizations (b^* and c^*) can be understood in terms of charge density waves as both of these components modify the intermolecular spacing in chain direction because of the tilt angle of the molecules in the stacks.

2 - Additional 1-d X-Ray scattering is observed at the wave vector 0.59 b^* (or 0.41 b^* in the reduced zone) which corresponds to twice the former 0.295 b^* wave vector or 4 k_F. This scattering has a very different temperature dependence : it persists to much higher tem-erature as shown in figure 4 and probably condenses below 49 K.

Several theoretical models have already been proposed in order to explain the simultaneous occurence of both $2k_F$ and $4k_F$ charge density wave anomalies and their different temperature dependence[18-21]. These models all assume important coulomb repulsion between electrons on at least one type of molecular stack.

C/ - The present study, combined with the independent X-Ray investigation of Kagoshima et al[9], rules out the presence of a giant Kohn anomaly at room temperature earlier reported by Mook and Watson[5]. As first suggested by Torrance, $2k_F$ spin density waves are now considered to be a possible origin of these extra cross sections at room temperature[11].

D/ - Future X-Ray and Neutron scattering studies should include :

1. the determination of the atomic motions involved in the charge density waves,
2. phonon studies at $4k_F$ wave vector,
3. further characterization of spin density waves.

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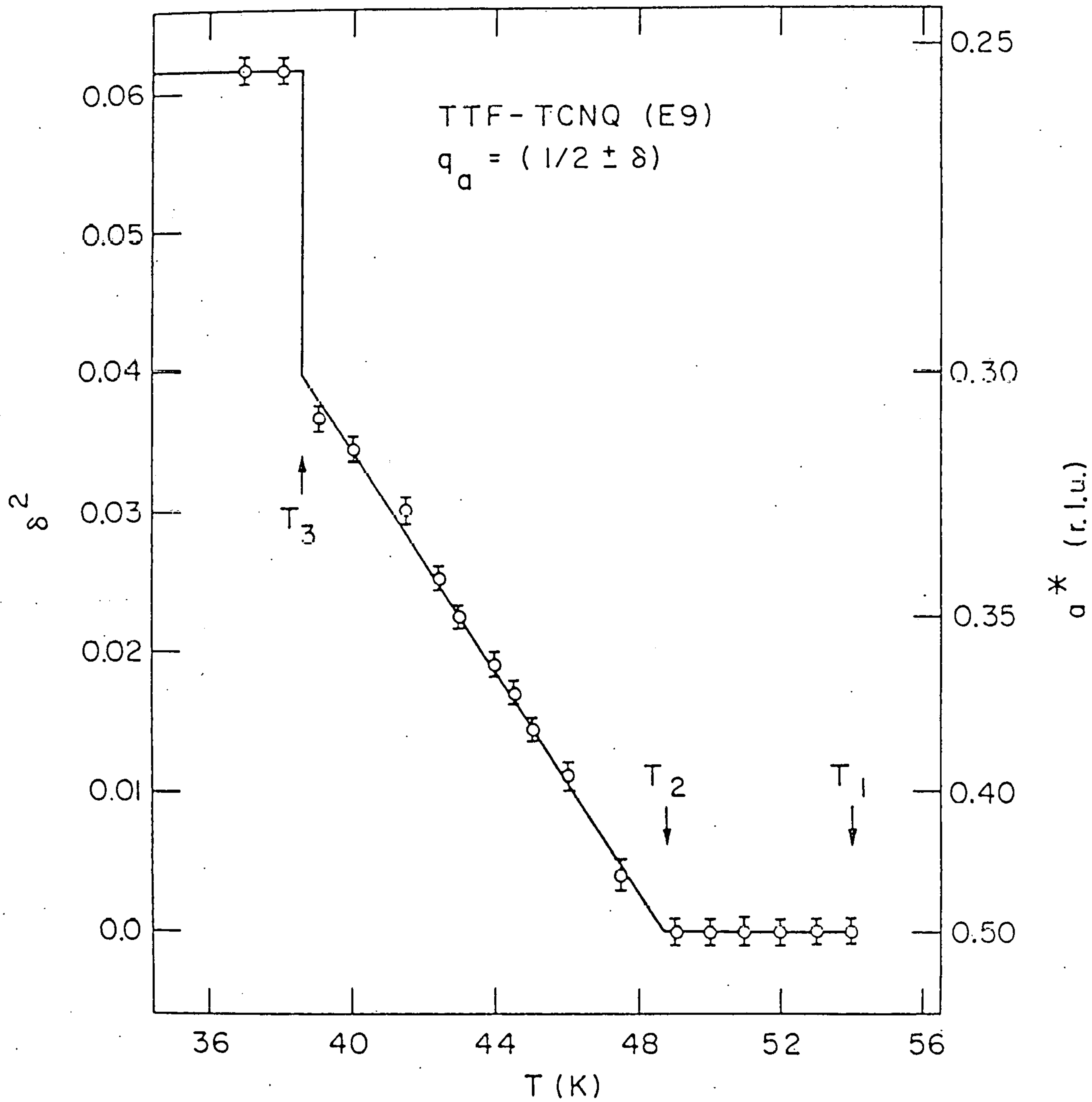

FIGURE 1 (from ELLENSON et al [7])

The occurence of 3 phase transitions in TTF-TCNQ is best visualized from the temperature dependence of the satellite Bragg peak position in reciprocal space when plotted as a function of $\delta^2 = (\frac{1}{2} - q_a)^2$, where q_a is the satellite wave vector component along a*. This was first suggested by BAK and EMERY[12] who discovered the 49 K phase transition.

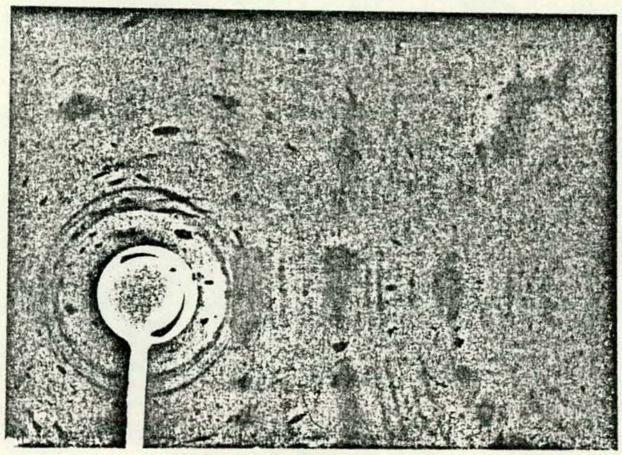

FIGURE 2 (from POUGET et al[8])

Diffuse X-Ray pattern of TTF-TCNQ at 60°K. Satellite reciprocal planes (1-d scattering) are clearly observed at the wave vectors 0.295 b^* ($2k_F$) and 0.59 b^* ($4k_F$). The comparable intensity of these two types of 1-d precursor at 60 K and their different temperature dependence (see figure 4) rules out that the $4k_F$ scattering might arise from a second order diffraction from $2k_F$.

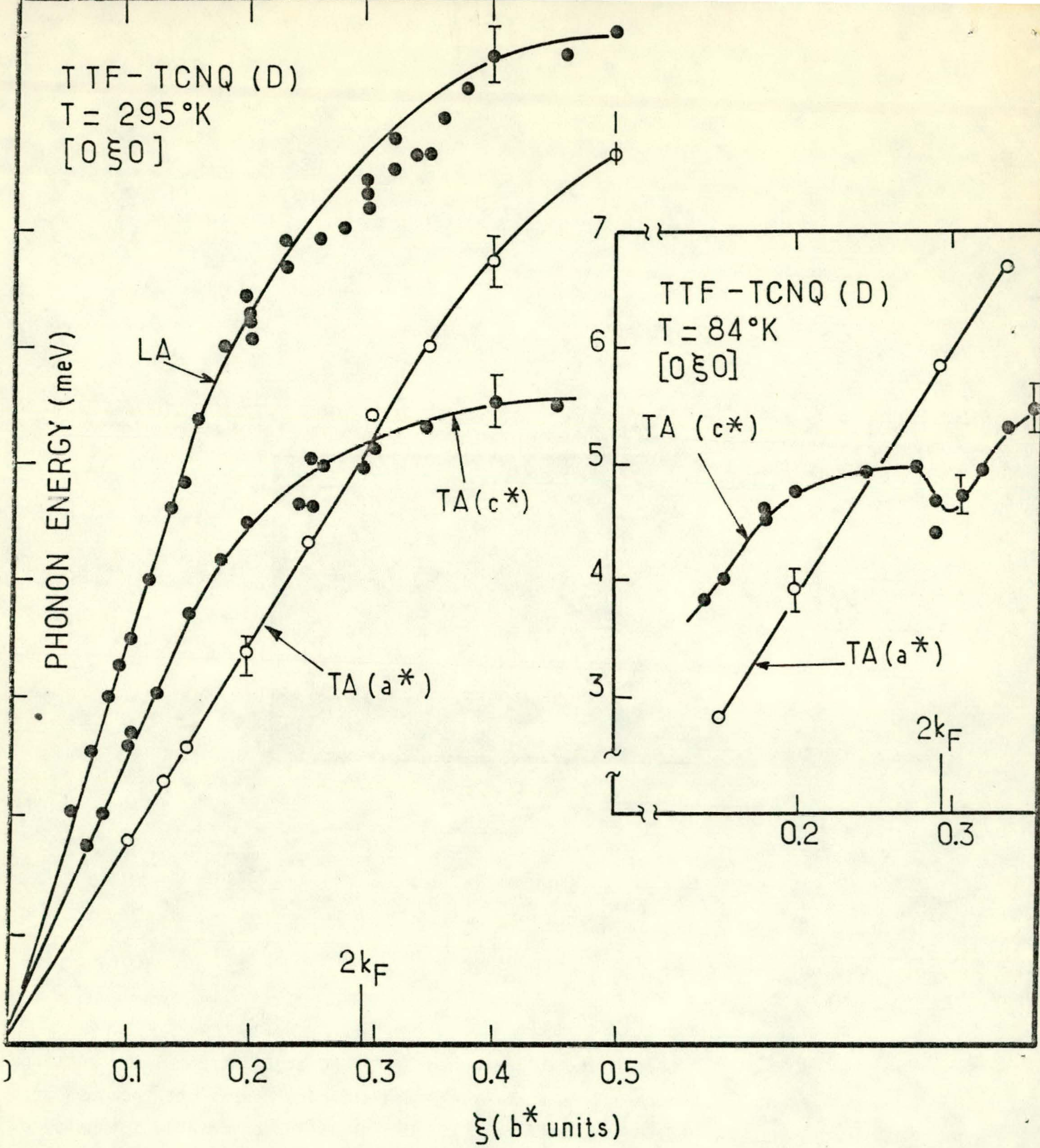

FIGURE 3 (from SHAPIRO et al)

Dispersion curves from TTF-TCNQ for modes propagating along [010], the chain direction, at 295°K.

The insert shows the transverse branches around $2k_F$ at 84°K. Note that the Kohn anomaly occurs in the branch mainly polarized along c*.

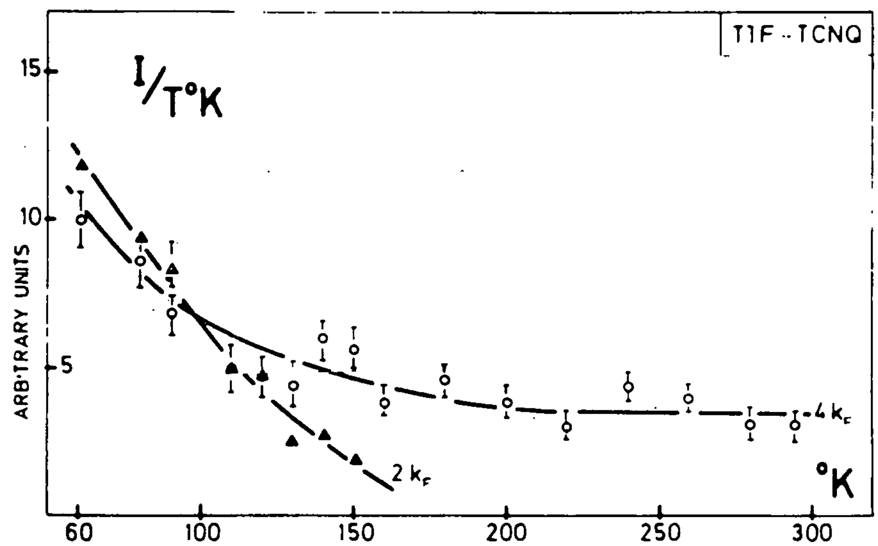

FIGURE 4 (from KHANNA et al)

Temperature dependence of the X-Ray diffuse intensity for the $2k_F$ and $4k_F$ scattering as estimated from microdensitometer readings of photographic patterns. This data is only semi-quantitative, but gives the general trend, it shows in particular that the $2k_F$ scattering only developps below 150°K as observed by SHIRANE et al[6]. The plot corresponds to I/T in order to eliminate the temperature dependence of the phonon population factor which is proportional to kT for such low frequency phonons in this temperature range.