# Observation of the Kohn Anomaly and the Peierls Transition in TTF-TCNQ by X-Ray Scattering

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Evidences of the Kohn anomaly and the Peierls transition in TTF-TCNQ were found by X-ray scattering experiments. The Kohn anomalies observed at $T=293$ K and 63 K give the Fermi wave number, $k_F$, of the one-dimensional electron system as $2k_F=b^*/(3.7\pm0.2)$, where $b^*$ is the reciprocal lattice vector. At 54 K, the one-dimensional ordering of the lattice deformation due to the Peierls transition was found along the $b$-axis with the period of $b'=(3.7\pm0.2)b$. At 27 K, the three-dimensional ordering was observed giving the new unit cell as $a'=4a$, $b'=3.7b$ and $c'=c$.

It is well known that the organic conductor, TTF-TCNQ, behaves as a one-dimensional metal down to 58 K, where it shows the maximum conductivity and undergoes a transition to an insulator.[1] In the one-dimensional metal, the giant Kohn anomaly and the Peierls transition are expected to be observed in the phonon dispersion curve of the metallic state and in the lattice structure at the metal-nonmetal transition, respectively.[2,3] In this letter, we report a direct observation of both the Kohn anomaly and the Peierls transition in TTF-TCNQ by X-ray scattering.

Samples used are single crystals grown by the diffusion method.[4] Typical sizes of crystals are 8 mm along the $b$-axis, 1.5 mm along the $a$-axis and 0.5 mm nearly along the $c$-axis. It was confirmed by dc-conductivity measurements that the metal-nonmetal transition occurs at 58 K. X-ray measurements were made by using a $CuK_\alpha$ source (40 kV, 20 mA), a curved crystal monochromator of graphite and a scintillation detector. The observed reciprocal lattice space was a parallelepiped defined with a set of reciprocal lattice points of (0, 2, 1), (0, 2, $\bar{1}$), (1, 2, $\bar{1}$), (1, 2, 1), (0, 2.5, 1), (0, 2.5, $\bar{1}$), (1, 2.5, $\bar{1}$) and (1, 2.5, 1) as shown in Fig. 1. Resolution of measurements was $0.2a^*$ along $a^*$-axis, $0.04b^*$ along $b^*$-axis and $0.1c^*$ along $c^*$-axis. Measurements were performed at 293 K, 63 K, 54 K and 27 K. The accuracies of the temperature were $\pm2$ K in absolute value and the stability of the temperature was $\pm0.1$ K.

Let us explain the obtained results with the aid of Fig. 1. At the temperatures of 293 K and 63 K, anomalies in diffuse scattering were found on the plane *ABCD* of Fig. 1. This is the so-called diffuse sheet,[5] and corresponds to the Kohn anomaly. At 54 K, the anomaly is enhanced a little. This fact seems to show the occurence of the Peierls transition at 58 K associated with the metal-nonmetal transition. The anomaly on the diffuse sheet was rather indistinct near the center of the sheet. At 27 K, strong diffuse scatterings were found at six points of $P$, $Q$, $P'$, $Q'$, $R$ and $S$ denoted in Fig. 1. These points are on the positions corresponding

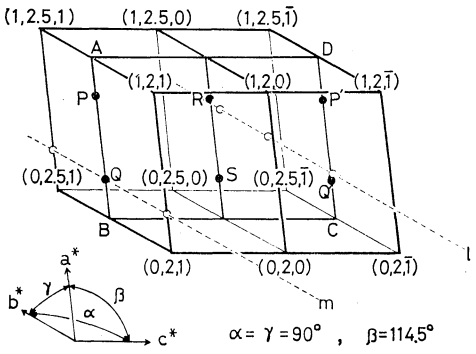


Fig. 1. Schematic representation of the observed reciprocal lattice space. The plane *ABCD* represents the diffuse sheet found at 293 K, 63 K and 54 K. $P$, $Q$, $P'$, $Q'$, $R$, and $S$ denote the points where pronounced anomalies were found at 27 K. Though, lines $l$ and $m$ pass the origin of the reciprocal lattice space in actual scanning, they are drawn as parallel lines to the $b^*$-axis for simplicity.

to ($a^*/4$, $b^*/3.7$, $c^*$). The anomalies on these points are pronounced. The intensity of the anomalous scattering on $Q$ and $Q'$ were very large but relatively small on $S$. Figure 2 shows typical data obtained by scanning along two lines of $l$ and $m$ in Fig. 1.

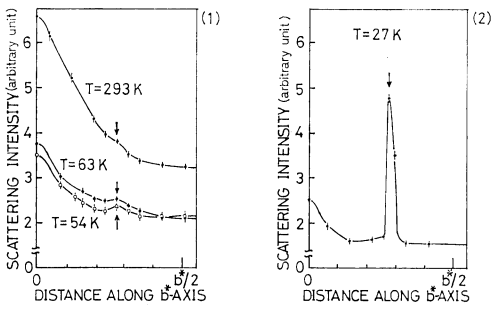


Fig. 2. Typical scattering intensity vs distance along $b^*$-axis. The origins of abscissas are on the plane defined by points, $(0, 2, 1)$, $(0, 2, \bar{1})$, $(1, 2, \bar{1})$ and $(1, 2, 1)$. (1) Scattering intensities measured along the line $l$ in Fig. 1. Arrows indicate the anomaly at $b^*/3.7$. (2) Scattering intensity measured along the line $m$ in Fig. 1. The arrow indicates the anomaly on the point $Q$ in Fig. 1.

All of the anomalies in diffuse scattering are observed at a position of $b^*/(3.7\pm0.2)$ along $b^*$-axis as shown above. This result tells us that the Fermi wave number, $k_F$, of the one-dimensional electron system is given as $2k_F=b^*/3.7$, and hence, indicates that the conduction electron band is filled up to 1/3.7. It is the so-called incommensulate case.[6] When we assume that the Peierls transition occurs at 58 K and the static lattice deformation takes place, the diffuse sheet observed at 54 K indicates that the lattice deformation is one-dimensionally ordered only along the $b$-axis. The strong diffuse scatterings at six *points* observed at 27 K indicatethat the lattice deformation is three-dimension ally ordered. Periods of the new unit cell are given as $a'=4a$, $b'=3.7b$ and $c'=c$. We consider that the distribution in the scattering intensity associated with the anomalies on the diffuse sheet and the relative scattering intensity at six points of $P$, $Q$, $P'$, $Q'$, $R$ and $S$ are to be explained by taking account of the structure factor of the crystal.

On completing this work, we received a preprint on the observation of structural evidence of a low temperature phase transition to the low temperature $3D$ superlattice ($2a\times3.7b\times xc$) at 38 K.[7] In our results the $3D$ superlattice should be read as ($4a\times3.7b\times c$). We cannot give decisive comments on the difference found in the period along the $a$-axis at the present stage, but in general, the counter method adopted by us gives more detailed information than the photographic method adopted by Denoyer *et al.* Further investigations are now in progress.

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