Satellite X-Ray Scattering by TCNQ-Phenothiazine Complex and Diffuse Scattering by TCNQ-*N*-Methylphenothiazine Complex

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1:1 complexes formed between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and two electron donors, phenothiazine (PHT) and *N*-methylphenothiazine (*N*-MePHT were investigated by X-ray diffraction method. The black PHT-TCNQ complex crystallizes in the form of needles elongated along the *a* axis It is monoclinic with space group $C2/c$ or Cc and has a super lattice structure with transverse phase modulation. The cell constants of fundamental lattice are: $a=7.04$, $b=25.38$, $c=10.51$ Å and $\beta=92.1°$. Crystals of *N*-MePHT-TCNQ are monoclinic with space group $C2/m$ and $a=10.90$, $b=13.32$, $c=7.09$ Å, $\beta=91.9°$, $Z=2$. General features of intensity distributions of both complexes indicate that the two structures are similar in a broad sense.

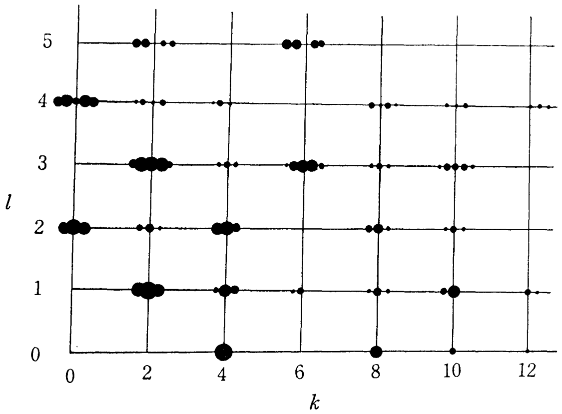

Fig. 1. Distribution of satellite scatterings around $(0,k,l)$ Bragg reflections from PHT-TCNQ. Magnitude of a circle is drawn in proportion to the intensity of X-ray reflection.

In the case of PHT-TCNQ complex, satellite reflections appear in reciprocal space at $(h,\ k\pm m\delta,\ l)$, where h, k, and l are Miller indices, $m=1, 2, 3$, and 4 and $\delta=0.232\pm0.015$ at room temperature. Distribution of satellites around $(0,k,l)$ reflections is schematically shown in Fig. 1. The general features of the satellite reflections are similar to those observed in the crystals of ferroelectric thiourea.[1] The observed diffraction patterns can be explained on the basis of the lattice with transverse phase modulation. That is, the lattice points are sinusoidally distorted. The position of the *n*th lattice point is approximately given by

$$\boldsymbol{r} = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c} + (p\boldsymbol{a}/a + q\boldsymbol{c}/c)\sin(2\pi n_2\delta),$$

where $(n_1\boldsymbol{a},\ n_2\boldsymbol{b},\ n_3\boldsymbol{c})$ is the position of the *n*th lattice point, p and q are 0.85 Å and 0.75 Å, respectively, and $1/\delta$ is the period of modulation and is equal to 4.3. The donor and acceptor molecules seem to be stacked alternately forming columns parallel to the *a* axis. The origin of this sinusoidal structure seems to be particularly interesting, because such a modulation may arise owing to the delicate balance of various interactions in the crystal, such as charge-transfer interaction, repulsion between non-bonding atoms, hydrogen-bonding, dipole-dipole interaction, *etc.* Detailed analysis is now under way.

The structure of *N*-MePHT-TCNQ complex was deduced from packing consideration and refined to an *R*-value of 0.096. The donor and acceptor molecules are alternately stacked face to face forming columns parallel to the *c* axis. Unlike PHT complex, diffuse scattering associated with strong Bragg reflections is observed. In fact, the orientation of *N*-MePHT molecule is disordered and the apparent molecular asymmetry is D_{2h}. The intermolecular spacing between *N*-MePHT and TCNQ is 3.43 Å. The molecular dimension of TCNQ is intermediate between those of TCNQ^0 [2] and $\mathrm{TCNQ}^{-1/2}$ [3,4] where TCNQ^0 and $\mathrm{TCNQ}^{-1/2}$ represent the neutral TCNQ molecule and TCNQ with formal charge of $-\frac{1}{2}$, respectively.

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