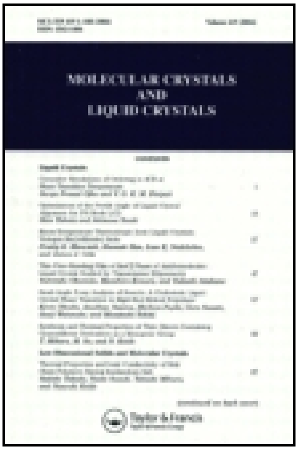

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Low Temperature Raman Spectra of TTF-TCNQ and other Organic Conductors

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LOW TEMPERATURE RAMAN SPECTRA OF TTF-TCNQ AND OTHER ORGANIC CONDUCTORS

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Abstract Polarized Raman spectra of TTF-TCNQ single crystals were measured in the a-b and b-c* surfaces at low temperatures. Temperature dependences of the frequency, intensity, and band profile were studied for TTF ν_3 and TCNQ ν_4.

INTRODUCTION

In the mixed valence organic conductors such as TTF-TCNQ, Raman bands are fairly influenced by the motion of conduction electrons and the frequency, intensity, and band profile are expected to contain useful information on the conduction mechanism. TTF-TCNQ is a suitable material for investigation of the influence, but the Raman spectra has not yet been studied in detail.[1] In this study, polarized Raman spectra of TTF-TCNQ single crystals are measured in the a-b and b-c* surfaces at liquid nitrogen and helium temperatures, and the results are discussed in the connection with the property at low temperatures.

EXPERIMENTAL

TTF-TCNQ single crystals were prepared by the standard diffusion technique in acetonitrile. The sample crystals were fixed on the cold copper block of a glass cryostat by silver paste. Raman spectra were measured in the back scattering geometry excited by 514.5 nm Ar^+ laser light, which was focused by a cylindrical lense to avoid thermal decomposition of the sample. Temperature was measured by a thermocouple fixed on the copper block. Laser power

TABLE I Frequency of TCNQ ν_4 (cm^{-1})

	RT	LHeT
TCNQ	1454	1459
K·TCNQ	1395	1399
$Cs_2(TCNQ)_3$	1435 1386	1443 1394
$Qn(TCNQ)_2$	1425	1431
TTF-TCNQ	1420	1419

Qn; quinolinium

was typically 30 mW at low temperatures and 5 mW at room temperature.

RESULTS AND DISCUSSION

TCNQ ν_4 mode of all the complexes studied and the neutral molecule except TTF-TCNQ shows high frequency shift of 4-8 cm^{-1} at liquid helium temperature (LHeT). (See TABLE I) The shift is probably due to thermal contraction of the crystal lattice. Linear relation of TCNQ ν_4 frequency (ν) and the degree of charge transfer (ρ) is valid even at LHeT as well as RT.[2] Practical invariance of the ν_4 frequency in TTF-TCNQ results in an increase in ρ ($0.58 \rightarrow 0.65$) at LHeT (FIG.1). The tendency agrees with

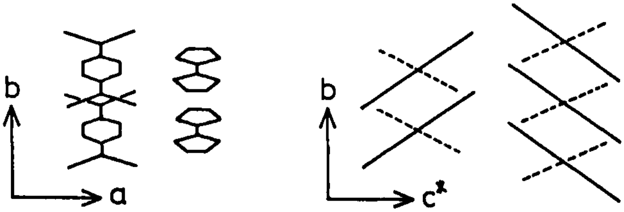

FIGURE 1 Scheme of crystal structure of TTF-TCNQ. Molecular-fixed axes; x is perpendicular to the molecular plane, y and z are parallel to the molecular short and long axes respectively. Crystal-fixed axes; X, Y, and Z are parallel to a, b, and c* respectively.

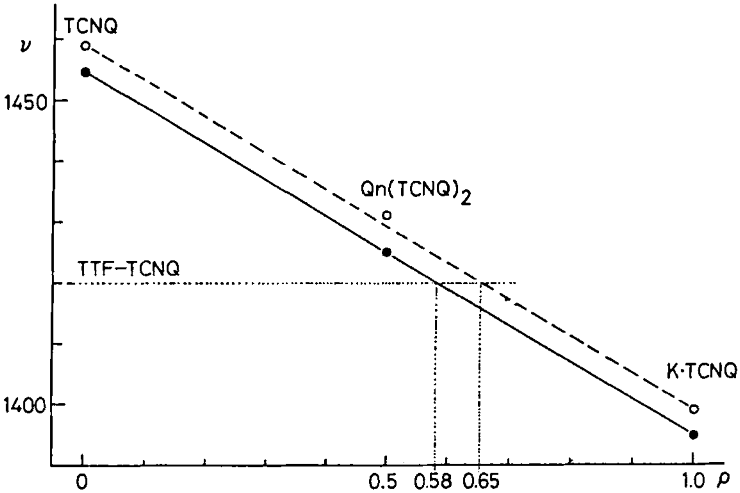

FIGURE 2 Linear relation of TCNQ ν_4 frequency (ν) and degree of charge transfer (ρ) at RT (——) and LHeT (---).

that observed by X-ray scattering (0.55⟶ 0.59). Consequently high frequency shift by the thermal contraction probably cancels out the low frequency shift by the increase in ρ to give the frequency invariance observed.

Both TTF ν_3 and TCNQ ν_4 had intensities only in the YY-component of the a-b spectra. The polarization property shows that the bands are not contributed by the scattering tensor component, α_{yy}, along the molecular short axis (FIG.1). On the other hand, both the two bands appeared in all the components of b-c* spectra. This shows α_{zz} contributes to the intensity of the bands, although the polarization ratios were inconsistent with those calculated by the oriented gas model.

Considerable temperature dependence was observed in the intensity of the YY-component of TTF ν_3. Relative intensity of the band to TCNQ ν_4 slightly decreased at liquid nitrogen temperature (LNT) compared with that at LHeT, and the ν_3 band came to practically disappear at RT (FIG.3). On the other hand, the powdered sample showed the band even at RT. Therefore, the

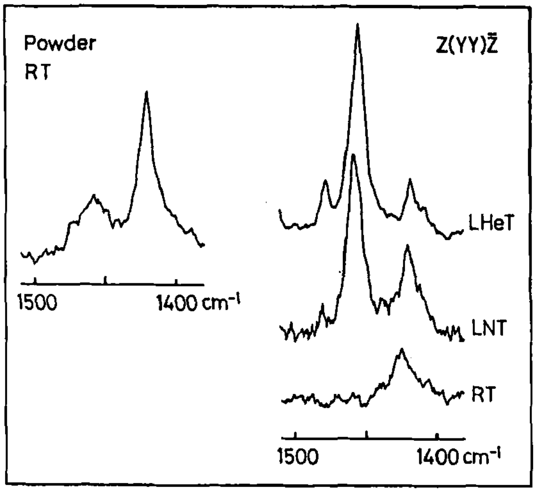

FIGURE 3 Temperature dependence of polarized Raman spectra of TTF-TCNQ.

ZZ-component is expected to have intensity at RT, although no b-c* spectra were obtained at RT because of the very small sample area. Further investigation between RT and LNT are required for elucidating origin of the temperature dependence.

High resolution spectra were obtained for the component, Z(YY)$\bar{Z}$, at LHeT in the region of 1390-1500 cm^{-1} (2 cm^{-1} slit width). The band profile of TTF ν_3 was found to be Lorentzian. In the CDW structure below Peierls transition temperature, there are many TTF sites of various charge densities, which is expected to give inhomogenious broadening to the ν_3 band. Inconsistency between this expectation and the observation may arise from local heating of the sample by laser light.

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