OPTICAL PROPERTIES OF N-PROPYLQUINOLINIUM(TCNQ)$_2$ THROUGH THE PHASE TRANSITION

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ABSTRACT

We have investigated the infrared and optical reflectivity of a single crystal of N-propylquinolinium(TCNQ)$_2$, a salt containing TCNQ tetramers. For light polarized along the chain axis, the spectra show a change below the 220 K phase transition: the vibrational lines split into doublets. These findings are in contradiction with the crystal structure, where tetramers become more uniform upon cooling and no intermolecular charge redistribution is found.

1. INTRODUCTION

N-propylquinolinium(TCNQ)$_2$, a salt containing chains of TCNQ tetramers, undergoes a second-order metal-semiconductor phase transition at 220 K.[1,2] The origin of the phase transition has not been unambiguously determined.[3,4] In order to examine electron-electron and electron-phonon coupling parameters in both phases, we have performed a temperature-dependent investigation of optical reflectivity of a single crystal in polarized light.

The crystals were grown by reacting N-(n-propyl)-quinolinium (NPrQn) iodide with TCNQ in hot acetonitrile[5] and slowly cooling to room temperature. Spectra were taken by a Bruker 113v Fourier-transform infrared spectrometer from 80 cm^{-1} to 5000 cm^{-1} at nine temperatures between 100 and 300 K and by a grating spectrometer from 4000 to 25000 cm^{-1} at room temperature. The latter was used as high-frequency extrapolation of all infrared spectra when performing Kramers-Kronig analysis to obtain the optical conductivity.
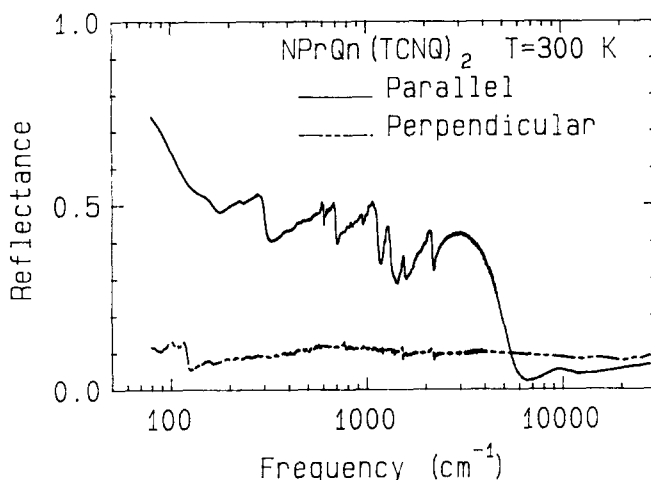
Fig. 1. Reflectivity of NPrQn(TCNQ)₂ at 300 K for light polarized parallel and perpendicular to the TCNQ chains. Note the logarithmic frequency scale.

2. RESULTS

Room temperature spectra. In Fig. 1, the reflectivity over the whole spectral range is shown for two polarizations, indicating the anisotropy typical of this class of compounds: low and flat reflectivity with weak phonon structure in the perpendicular direction, and broad infrared electronic excitations with anomalously strong phonon lines parallel to the chains.

We have attempted numerical simulations of the chain-axis conductivity by several models elaborated by Yartsev[6] which take into account both electron-electron and electron-phonon interactions. The calculated conductivity from a dimer model is presented in Fig. 2; that from a tetramer model is shown in Fig. 3.

The best agreement is found for a tetramer model with the following parameters. For the electronic excitation, $\omega_{CT} = 2200 \text{cm}^{-1}$, $g = 1800 \text{ cm}^{-1}$, $t = 1000 \text{ cm}^{-1}$, $t' = 0.8t$, $U = 6t$, $V = 0.4U$, and $\Delta = 0.25t$. For the phonons, frequencies and (in parentheses) coupling constants[6] g, all in cm^{-1}, are: 115 (110), 307 (225), 606 (120), 701 (200), 959 (126), 1165 (291), 1349 (450), 1570 (480), 2189 (381), 3048 (40).

Temperature dependence. We observe no significant temperature variation perpendicular to the chains, but the chain-axis polarized infrared spectrum shows a gradual change between 150 and 250 K, reflecting the second-order character of the transition. The reflectivity and optical conductivity at the two extreme temperatures are shown in Fig. 4. The most striking difference is the splitting of vibrational lines at low temperature. This indicates a less uniform charge distribution (TCNQ molecular ions of different charge giving a different vibrational pattern), in agreement with the behavior of other physical properties[1,2] but in apparent contradiction with crystallographic results.[7,8] The phase transition does not affect the P$\bar{1}$ space group and intramolecular bond lengths are essentially invariant between 300 K and 100 K; however, the
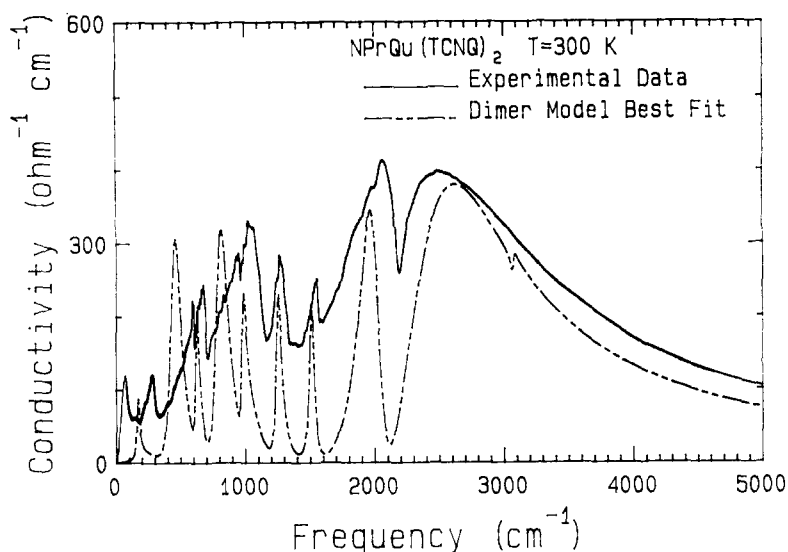
Fig. 2. Solid line: optical conductivity at 300 K. Dash-dotted line: conductivity calculated by the dimer model of Ref. 6.
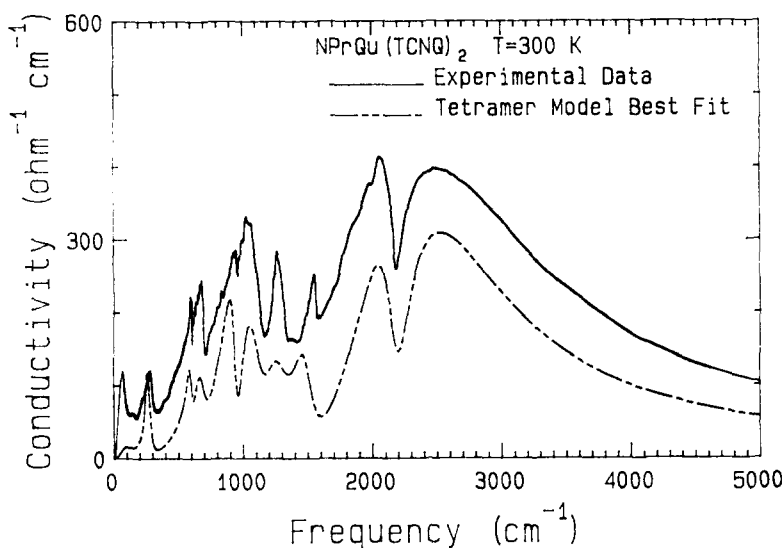

Fig. 3. Solid line: optical conductivity at 300 K. Dash-dotted line: conductivity calculated by the tetramer model of Ref. 6 with parameters given in the text.

intratetramer TCNQ–TCNQ distances grow more uniform upon cooling. Thus, from the structure, one would expect a more uniform charge distribution at 100 K. (We note that at room temperature, estimation of molecular charges from bond lengths[9] gives ambiguous results for this compound.) For a unified picture a more sophisticated model, probably taking into account magnetic interactions, is needed.
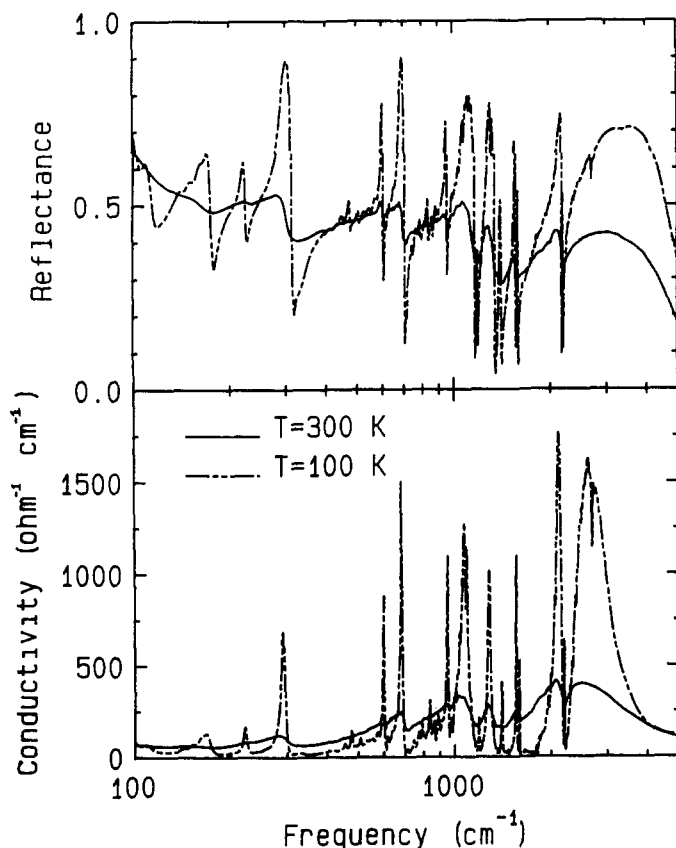
Acknowledgement

Fig. 4. Reflectivity (upper panel) and optical conductivity (lower panel) of NPrQn(TCNQ)$_2$ in light polarized along the chains, at 100 K and 300 K.

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