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INFRARED PROPERTIES OF THE MAGNETIC SEMICONDUCTOR DBTTF-TCNQCl$_2$

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Abstract Dibenzo-TTF-dichloro-TCNQ constitutes a particularly clean example of a strongly Coulomb correlated, incommensurate organic conductor. The bands are narrow, and are near quarter-filled. The infrared chain axis excitation spectrum is that of a semiconductor with a sizeable energy gap of 1500-2000 cm^{-1}. In addition the spectrum has strong absorption bands near molecular vibration frequencies. The strength of these indicates that they arise from the electron-molecular vibration coupling. They are apparently activated by $4k_F$-charge density waves. The overall behavior is consistent with a model, where strong Coulomb correlations exclude double occupancy of sites.

INTRODUCTION

Many potential organic metals, i.e. compounds with partially filled one-electron bands, no $2k_F$ Peierls distortion, and no strong disorder, are known to be poor conductors. For some of them it has been suggested that their transport properties are those of semiconductors: The broad maximum in conductivity, $\sigma(T)$, usually observed, is attributed to the combination of an activated carrier density and a strongly temperature dependent mobility[1]. However, the true nature of the semiconductor gap is unclear.

An informative method for characterizing the electronic structure of organic conductors is polarized infrared and optical reflectance spectroscopy, which through Kramers-Kronig analysis yields quantitative excitation spectra of fair reliability. In the ideal metal, the frequency dependent conductivity, $\sigma(\omega)$, simply falls from the dc value in a Lorentzian manner (Drude behavior). In semiconductors, $\sigma(\omega)$ has an onset at photon energies equal to the gap.

We recently compared $\sigma(\omega)$ for some potential organic metals with uniformed stacks[2], and found a clear correlation between, on one hand, position and size of infrared oscillator strength, and on the other, the metallic quality characterized by the temperature dependence of the conductivity and its room temperature value. The best metal has a near Drude-like $\sigma(\omega)$, while in the less good metal

oscillator strength is shifted to the mid infrared. In addition, signs of electron-molecular vibration (emv) coupling appear in the latter systems. These effects may be understood[2] as arising from the combined effect of electron-electron and electron-phonon interaction in creating $4k_F$-charge density waves (CDWs), as also discussed below. Similar ideas have been advanced at this conference in describing the systems $(NMP)_x(Phen)_{1-x}(TCNQ)$[3] and[4] $Qn(TCNQ)_2$.

The case of dibenzo-TTF-dichloro-TCNQ (DBTTF-$TCNQCl_2$) seems to constitute a very clear example of these effects. We shall first review the physical properties in general, and next present and analyse the infrared excitation spectrum.

PHYSICAL PROPERTIES OF DBTTF-$TCNQCl_2$

DBTTF-$TCNQCl_2$ has[5] $\sigma_{\parallel}(300K) = 40\ \Omega^{-1}cm^{-1}$, and is a near quarter-filled double-stack conductor with uniform chains (degree of charge transfer, $\rho=0.56$)[6,7]. Fig. 1 shows schematically some physical properties of the material[5,7].

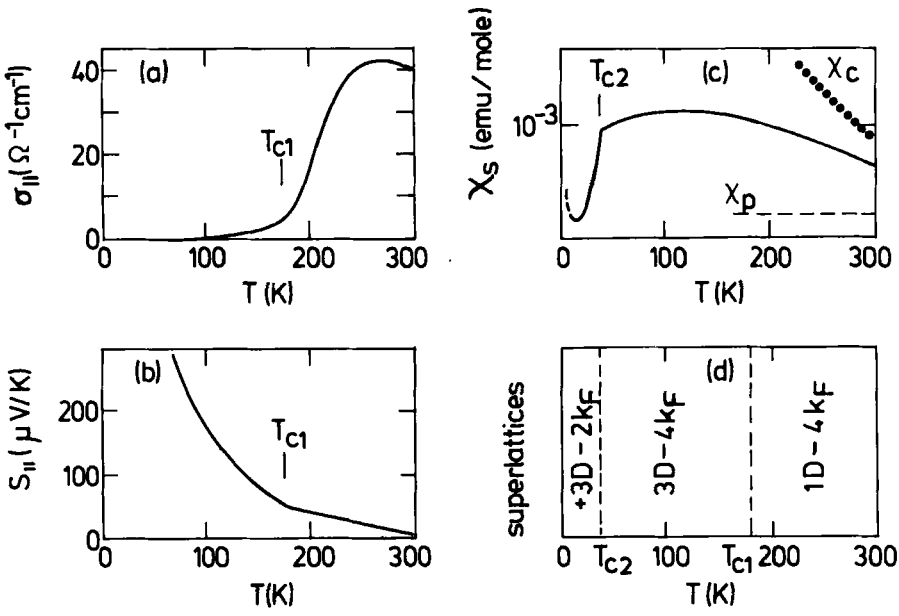

FIGURE 1 Basic physical properties of DBTTF-$TCNQCl_2$ (Ref, 5,7).

The dc conductivity, $\sigma_{\parallel}$, and the thermoelectric power, $S_{\parallel}$, are both

consistent with the existence of a one-electron gap of order 200-250 meV (1500-2000 cm^{-1}). The activated behavior is cleanest below T_{c1} = 180K, where a slight anomaly is found. The spin susceptibility, χ_s, is high, about three times the expected, non-enhanced Pauli value (χ_p) at 300K, and remains high to T_{c2}= 36K, below which temperature it vanishes rapidly. Note that χ_s (300K) is about 2/3 of the Curie value (χ_c) for the appropriate carrier density. Finally, diffuse X-ray scattering[7] have shown the existence of rather large amplitude $4k_F$-CDWs. Down to T_{c1} there are only weak interchain correlations. T_{c1} is found to be a three-dimensional (3D) ordering temperature, while T_{c2} involves the onset of 3D-$2k_F$ scattering.

The implications of these observations are obvious: Enhanced magnetic susceptibility and occurrence of $4k_F$-scattering may both be taken as evidence for important electron-electron correlations[8]. The two transition temperatures also indicate a substantial decoupling of the spin and electronic degrees of freedom. The overall behavior found here is common to a large group of low conductivity materials and the physical picture is the following: The carriers are rather localized, even at high temperature, due to the Coulomb repulsion between them. The $4k_F$-CDWs may most easily be understood either as resulting from Wigner lattice formation[9], or from the Peierls mechanism discussed below. The spins experience a rather weak antiferromagnetic exchange coupling and through interaction with the lattice undergo a spin-Peierls transition at low temperature[10].

With this discussion we have established that DBTTF-TCNQCl$_2$ is a strongly correlated, incommensurate organic conductor.

INFRARED CONDUCTIVITY OF DBTTF-TCNQCl$_2$

In Fig. 2 we show the infrared conductivity of DBTTF-TCNQCl$_2$ at T=300K and T=100K. Both spectra show energy gaps of order 1500-2000 cm^{-1} (consistent with transport properties), and resonant/anti-resonant structure near the molecular vibration frequencies. This structure sharpens on cooling and a few new lines appear. The strength of the modes in the 1000-1300 cm^{-1} range and the antiresonant character of the 2200 cm^{-1} feature proves that the bands arise from the emv coupling[11] involving the fully symmetric Ag-modes.

The IR spectra of Fig. 2 have a striking similarity to that of, for example, TEA-TCNQ$_2$, so successfully analysed by Rice and coworkers[12] in terms of phase oscillations of intramolecularly stabilized $2k_F$-CDWs plus single particle excitations across the CDW-gap. This experimental analogy strongly suggests that the present data must be analysed in a similar way. However, the $4k_F$-CDWs observed would not account for a gap at the Fermi level in the non-interacting band model. Instead we propose that it is appropriate to adopt the picture, where the on-site Coulomb repulsion, U, is high enough to exclude double occupancy of sites ($U\to\infty$). In this case the spin system is completely decoupled from the electronic

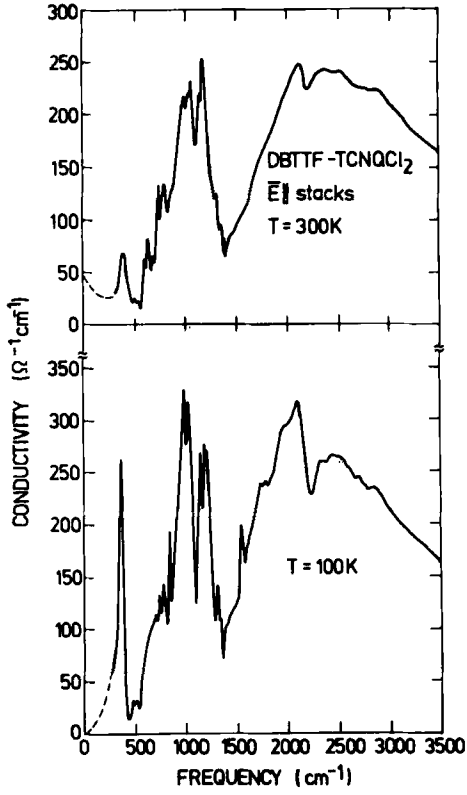

FIGURE 2 Frequency dependent chain axis conductivity of DBTTF-TCNQCl$_2$ as obtained from Kramers-Kronig analysis of reflectance. T=300K and 100K.

degrees of freedom, and a Curie-like susceptibility is expected. The data quoted above show that DBTTF-TCNQCl$_2$ is relatively close to that limit. Theoretically the case has been discussed by Bernasconi et al.[13] The electrons behave like spinless Fermions, and it is found that the usual Fröhlich Hamiltonian governs the electron-phonon system. The main difference from the U=o case is that the density of states is reduced by a factor of 2, thus the band is filled to $2k_F$ instead of k_F. Thus the usual Peierls mechanism now works at $q=4k_F$ and accounts for the $4k_F$-CDWs. The

crucial point is that the dimensionless electron-phonon coupling constants, entering the theory, are given by $\lambda_i = N(o) g_i^2/\hbar\omega_i$, where g_i is the bare coupling constant, ω_i the bare phonon frequency, and N(o) is the density of states at the Fermi level. For a formally quarterfilled band N(o) is reduced by $2\sqrt{2}$ going to $U \to \infty$ | Thus the g_i-values obtained by analysing the data provide an important test on the consistency of the present approach.

The mathematical details of the model are given by Rice[14]. The only modification is the introduction of a modest electronic damping rate, γ_{el} . Also, since we are dealing with a double-stack system, we assume that the total $\sigma(\omega)$ is simply a sum of the individual stack conductivities.

The donor stacks clearly dominate the spectrum. Bare Ag-mode frequencies for DBTTF were taken from studies on the single-stack compound DBTTF$(BF_4)_{0.42}$. The quality of the final fit for the 100K data, as it presently stands, is shown in Fig. 3. The parameters are given in Table I.

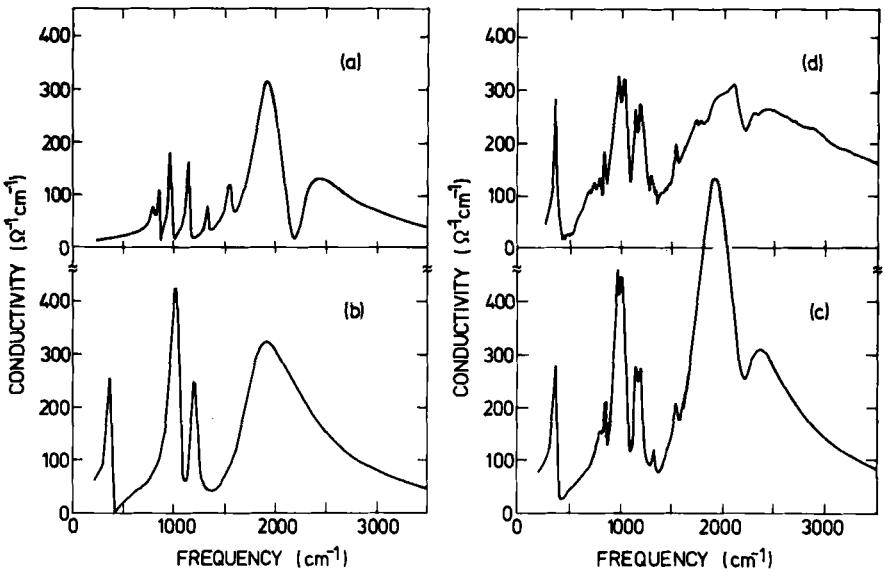

FIGURE 3 $4k_F$-CDW model for $\sigma(\omega)$. (a) $TCNQCl_2$-contribution, (b) DBTTF-contribution, (c) Total $\sigma(\omega)$ in model, (d) experimental data. T=100K.

TABLE I $4k_F$-CDW parameters[a] for DBTTF-$TCNQCl_2$, T=100K.

	DBTTF			$TCNQCl_2$		
$\omega_p(cm^{-1})$	4500			3570		
$4t(eV)$	0.43			0.27		
$2\Delta(cm^{-1})$	1700			1900		
$\gamma_{e\ell}/2\Delta$	0.2			0.2		
λ	0.46			0.60		
b	0.08			0.08		
$\Delta\varepsilon_\infty$	1.0			1.0		
	ω_i (cm^{-1})	λ_i	g_i[b] (cm^{-1})	ω_i (cm^{-1})	λ_i	g_i[c] (cm^{-1})
	1430	.16	1100(940)	2253	.04	550(350)
	1130	.017	320(170)	1573	.01	230(540)
	473	.11	530(630)	1345	.01	210(500)
	(40	.17	190)	1200	.04	400(300)
				1020	.03	340 (85)
				870	.009	160
				820	.012	180
				(40	.45	250)

a: symbols are defined in Ref. 14.
b: values in parenthesis are estimates for TTF (Ref. 15) for corresponding modes.
c: values in parenthesis are estimates for TCNQ (Ref. 16) for corresponding modes.

A number of comments are in order:
(1) The overall quality of the fit is reasonable, especially with respect to distribution of oscillator strength between the phase modes and the single particle contribution. We note that it is possible to introduce only a modest electronic damping in the model, hence the electronic peak in the fit is sharper than in the data.
(2) The derived g_i-values are consistent with previous knowledge. Thus the use of the reduced density of states is justified, and the $U\to\infty$ model appears credible.
(3) As seen by comparing Fig. 3 (b) and (c) the spectrum is indeed dominated by the DBTTF-stacks. Among the three A_g-modes included for this stack, the 1430 cm^{-1} and 1130 cm^{-1} modes display an interesting interference effect. The 1130 cm^{-1} mode digs a hole in the strongly coupled 1430 cm^{-1} mode.
(4) Assuming mean field behavior, the observed gap position corresponds to a scale temperature, $T_{MF} \simeq 600K$. This is consistent with the well-established gap and CDW-structure at 300K and below.
(5) In the fitting procedure the estimated gap-values were used to derive the total electron-phonon coupling constant, λ, for the

two stacks by using the gap equation[17]. Part of λ is assumed to be associated with low frequency (external) modes outside the experimental range (given in the last lines of Table I). However, it is striking that more than 60% of λ for the DBTTF-stack is due to the internal modes. Thus the CDW is predominantly stabilized by the emv coupling[12]. On the acceptor chain this is less pronounced.

CONCLUSIONS

The infrared spectrum of DBTTF-TCNQCl$_2$ has been analysed in terms of the $U\to\infty$ $4k_F$-CDW model. The reduced density of states, which enters the model, has been confirmed quantitatively. We believe that the picture is applicable to a wide class of intermediate conductivity organic crystals, and even qualitatively applicable to highly conducting materials where $4k_F$-CDWs are found[2].

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