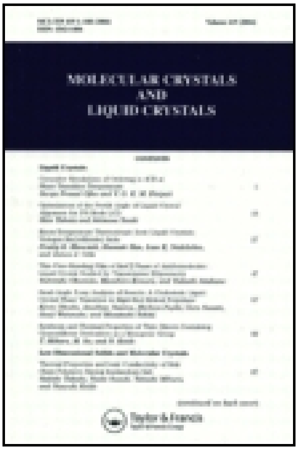

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# Spectroscopic Study Of The Neutral-To-Ionic Phase Transition In Ttf-Chloranil

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# SPECTROSCOPIC STUDY OF THE NEUTRAL-TO-IONIC PHASE TRANSITION IN TTF-CHLORANIL

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Abstract Infrared reflectance spectra have been investigated on TTF-chloranil single crystals near the neutral-to-ionic phase transition temperature $T_c$. It was confirmed that abrupt changes in the ionicity and the stack dimerization take place simultaneously at $T_c$. The effect of an external electric field and light irradiation upon the dimerized lattice below $T_c$ has been investigated by reflectance measurements.

## INTRODUCTION

Tetrathiafulvalene(TTF)-p-chloranil(CA) is a unique organic crystal in exhibiting thermally-induced phase transition from the quasi-neutral state (with the average ionicity $\rho \simeq 0.3$) to the quasi-ionic state ($\rho \simeq 0.7$) at the critical temperature $T_c \simeq 80K$[1]. This neutral-to-ionic (NI) transition in TTF-CA crystal is associated with the dimerization of donor(TTF) and acceptor(CA) molecules along the stack-axis, as evidenced by the infrared vibrational spectra[2] and the X-ray diffuse scattering measurement[3]. Furthermore, a recent ESR study[4] has revealed an exsistence of the mobile soliton-like (and antisoliton-like) paramagnetic defects in the dimerized ionic lattice. But, as for the critical lattice-dynamical behaviours of the NI transition, there still remain considerable ambiguities because of the rather unusual dependence on the sample quality. We have reported before that the visible reflectance spectra of high-quality single crystals show a first-order-like change at $T_c$.[5] This paper reports the infrared reflectance spectra near $T_c$ to get information on the ionicity and the lattice dimerization at the NI transition in well-qualified single crystal samples. The effects of an external electric field and pulse light irradiation upon the dimerized lattice have been also investigated by modulated-reflectivity measurements.

## INFRARED REFLECTANCE SPECTRA

Single crystals of TTF-CA were grown by co-sublimation method.[4,5] The samples were typically $2\text{x}2\text{x}1\text{mm}^3$ in size, having well-developed (001) faces. Infrared reflectance measurements were made by using a polarized monochromatic light through a 1 m monochromator. Temperature of samples was controlled within ±1K throughout the measurements.

FIGURE 1 shows the temperature-dependence of polarized reflectance spectra for E//b (E⊥stack-axis) in the two spectral regions; (a) the TTF $b_{1u}$ and CA $b_{1u}$ bands around 1100 $\text{cm}^{-1}$, and (b) the CA $b_{1u}$ C=O stretch band around $1600\text{cm}^{-1}$. Note that there occur rather abrupt peak shifts, when temperature is increased from 78K to 89K through $T_c \simeq 81\text{K}$[6]. These shifts are supposed to be associated with the change in the charge distribution within the constituent molecules. For an example, the $1120\text{cm}^{-1}$ CA $b_{1u}$ vibration is known to be located at 1110cm$^{-1}$ in a neutral ($\rho$=0) molecule and at 1147cm$^{-1}$ in a fully ionic ($\rho$=1) molecule[7]. It should be noted that there is no indication of coexisting two vibrational bands associated with the quasi-neutral and quasi-ionic molecules near $T_c$. A distinct spectral change is also observed in the CA C=O stretch band as shown in Fig.1(b). A larger frequency shift (ca.160cm$^{-1}$) has been reported for this particular band upon the ionization of CA molecule[7]. When temperature is raised above 78K, the C=O band observed in the I-phase (marked I) is suddenly replaced by much weaker structures $N_{1,2}$ at ca.81K. These observations are in good agreement with the critical behaviour of the visible reflectance spectra at the NI transition[5]. The coexistence

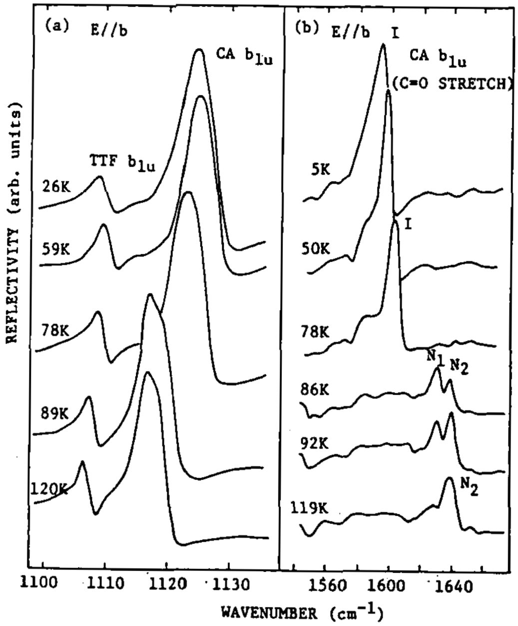

FIGURE 1 Temperature-dependence of infrared reflectance spectra of TTF-CA single crystal for E//a (E⊥ stack-axis).

of the ionic and neutral bands observed on sublimed films in the temperature range of about 30K around $T_c$[1,2] seems to arise from the effect of the structural imperfections in samples. Such a large sensitivity of the charge-transfer process to physical as well as chemical perturbative effects is one of the most important features in the NI transition in TTF-CA crystal.

It is interesting to note here that the C=O band in the N-phase is split into two bands (marked $N_1$ and $N_2$ in Fig.1(b)). The relative intensites of these two bands are gradually changed by temperature in favor of the $N_2$ band at higher temperatures. Such a behaviour was observed in all crystals presently investigated and hence is considered to be of intrinsic nature. There may be a possibility that two different kinds of quasi-neutral molecules having slightly different (presumably by ca.0.1) ionicity exist in the temperature range $T_c \lesssim T \lesssim 120K$.

In Fig.2 we show the reflectance spectra for E//a (stack-axis) at 78K and 88K. The structures in the spectra below $T_c$ are attributable to the $a_g$ vibrational modes of

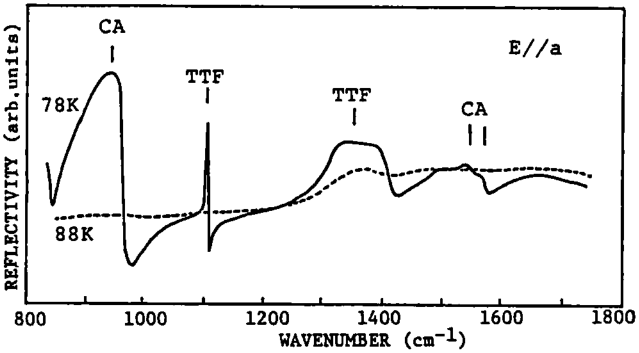

FIGURE 2 E//a(stack-axis) infrared reflectance spectra at temperatures (78K,88K) below and above $T_C$.

TTF and CA molecules, as indicated in the figure. They are activated by the symmetry breaking effect of the lattice dimerization along the stack-axis[2]. These structures were found to suddenly disappear upon the I-to-N conversion, indicating a first-order-like change of the dimerized D-A pairs into equidistant D-A stacks in the N-phase. In FIGURE 3, the peak reflectivities of the CA $a_g$ 945cm$^{-1}$ band are plotted against temperature near $T_c$ (open circles). The reflectivities at the peak of the C=O stretch band (I band in Fig.1(b)) are also poltted (filled circles) for comparison. Both reflectivities are simultaneously decreased at around 81K, clearly indicating that the lattice dimerization (evidenced by the appearance of the $a_g$ band) and the change of ionicity (probed by the C=O band) occur simultaneously at the critical temperature $T_c$=81K[6].

The intensities of the $a_g$ bands in the E//a spectra are dominated by the product of two factors; the strength of electron-molecular vibration coupling[2] and the difference in the charge-transfer (CT) interaction toward the right- and left-hand molecules. As the latter effect is

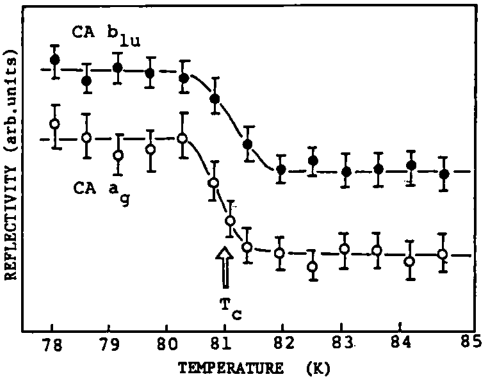

FIGURE 3 Reflectivity change of CA $b_{1u}$ 1596cm$^{-1}$ mode and $a_g$ 945cm$^{-1}$ mode against temperature around $T_c$.

critically dependent on the degree of dimerization along the stack, the infrared active $a_g$ modes can be utilized as a microscopic probe for the lattice distortion in this crystal. The strengths and widths of the $a_g$ bands have been carefully measured over the temperature range from 5K to 80K. As a result, it has been comfirmed that these spectral features are almost unchanged, indicating that the degree of the lattice dimerization is essentially unchanged below $T_c$. We may conclude therefore that the NI transition and the associated lattice transition is almost of the first-order, in accord with the recent diffuse X-ray scattering study[3].

## ELECTRO-REFLECTANCE SPECTRA

The dimerized stacks in TTF-CA crystal below $T_c$ should possess electric dipole moments within a single dimerized domain. These polar domains are presumably separated by the domain walls. A recent ESR measurement[4] has revealed the existence of mobile paramagnetic defects which have been attributed to these soliton(antisoliton)-like domain walls.

The measurements of electro-reflectance (ER) spectra were undertaken to investigate the effect of an electric field (F) upon such polar domains through the field-modulated reflectivities (ΔR) at the CT band. The results are shown in FIGURE 4 for F//stack-axis (400Hz). The ordinary reflectance (R) spectra (broken curves) are also shown for comparison. Fairly large field-induced ΔR signals were observed in the I-phase (at 78K), whereas no detectable signals were observed in the N-phase (at 90K), in accord with the expectation for the absence of centrosymmetry in the dimerized stack below $T_c$. The strong peak of ΔR observed at ca.1.2eV in the I-phase fits fairly well with the energy-derivative curve -dR/dE (a dotted curve) derived from the unmodulated spectra, indicating a positive energy shift of the CT band as a whole under the external field F. Hence the polarity of the excited CT state ($\mu_e$) should be smaller than that of the ground state ($\mu_g$). This is in accord with a simple D-A dimer model where $\mu_e=(1-\rho)ed\simeq0.3ed$ and $\mu_g=\rho ed\simeq0.7ed$ (d; the D-A separation).

The observed ΔR signals were found to be approximately proportional to $F^{1.4}$ in the range of $2\text{KVcm}^{-1}\lesssim F\lesssim6\text{KVcm}^{-1}$. The electro-optic response of the dimerized lattice is expected to be proportional to $\Delta R_0(N_+-N_-)/N$. Here $N_+(N_-)$ is the number of sites within the polar domains polarized parallel (perpendicular) to the field F and $\Delta R_0$ is the response of a single dimerized domain. Since $\Delta R_0$ is expected to be linear to F, the present result indicates that the quantity $(N_+-N_-)/N \propto F^{0.4}$. This implies that the external field not only changes the local polarity within the respective domains, but also gives rise to a field-induced movement of the domain walls such that $N_+ > N_-$. This effect is reversible for $F\lesssim6\text{KVcm}^{-1}$, but when F exceeds a certain critical

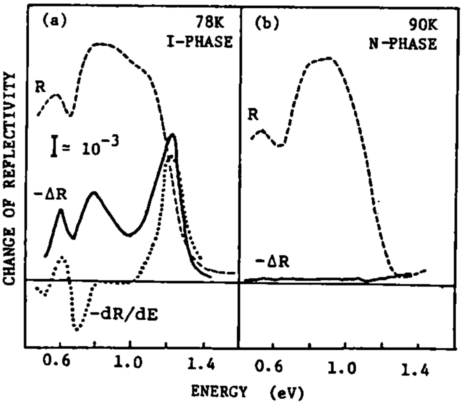

FIGURE 4
Electro-reflectance (ΔR) spectra of the CT excitations in the I- and N-phase. The external electric field F(//a) is $2.5\text{KVcm}^{-1}$.

value (usually near 10KVcm$^{-1}$, depending on samples), a sudden electric discharge takes place through the crystal to break it in pieces. Such an unusual instability of the ionic dimerized lattice under a strong electric field is related with the unpinned motion of solitons (domain walls) when the field strength exceeds a threshold (ca.10KVcm$^{-1}$).

## PHOTO-INDUCED CHANGE OF REFLECTIVITY

Another notable feature of the dimerized lattice of TTF-CA crystal is a large photo-induced change in the reflectivities in the I-phase. This phenomenon is obviously associated with the lattice-relaxation of the photo-excited states in the dimerized chains.

For an example, a transient change in the reflectivity after an irradiation by a laser (580nm) pulse is shown in FIGURE 5. The reflectivity change was monitored at ca.3.1eV corresponding to the strong intramolecular transition in TTF$^+$ in the I-phase[5]. The light pulse (10nsec,0.2mJ) was irradiated on the 3x2mm$^2$ sample surface at ca.80K, just below $T_c$. The signal completely disappears, as shown in the lower part of Fig.5, at ca.90K just above $T_c$, under the same irradiation. The observed reflectivity change ΔR/R

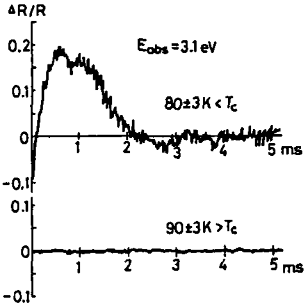

FIGURE 5
Time-dependence of photo-induced reflectivity change at temperatures below and above $T_c$.

is at first negative within the resolution time (ca.30nsec), then changes to positive after about 0.5msec, which is followed by a gradual decay within 1-2msec. The instantaneous response of $\Delta R/R$ after the pulse irradiation depends on the photon energy where $\Delta R/R$ is monitored. For example, it is positive at ca.3.6eV, corresponding to the $TTF^+$ excitation band in the N-phase[5]. These results seem to imply that the lattice ionicity is reduced immediately after the irradiation, but subsequently becomes more ionic in a temporal period of 1-2msec. The initial response is interpreted as a local I-to-N conversion by the photo-induced back CT process ($D^+A^- \rightarrow D^0A^0$). Similar local back CT (I-to-N) transition can also take place below $T_c$ by chemical doping[8]. The quasi-neutral domains produced within the I-phase lattice by the "photo-doping" process have a finite life time ($\lesssim$0.1msec), in contrast with the permanent neutral clusters produced by the chemical doping. The subsequent "shake-back" effect observed as the positive $\Delta R/R$ signal may be attributed to the dynamical behaviours of the soliton-like domain walls in the perturbed lattice. Thus, the photo-induced reflectivity change and the electric-field-induced reflectivity change as presently observed may be used as a powerful tool for the investigation of the lattice-dynamical properties of TTF-CA crystal at the NI transition.

## REFERENCES

1. J.B.Torrance, A.Girlando, J.J.Mayerle, J.C.Crowley, V.Y.Lee, and P.Batail, Phys. Rev. Lett. 47, 1747(1981).
2. A.Girlando, F.Marazola, C.Pecile, and J.B.Torrance, J. Chem. Phys. 79, 1075 (1983).

3. K.Kanai, M.Tani, S.Kagoshima, Y.Tokura, and T.Koda, Synth. Metals, 10, 157 (1984).

4. T.Mitani, G.Saito, Y.Tokura, and T.Koda, Phys. Rev. Lett. 53, 842 (1984).

5. Y.Tokura, T.Koda, T.Mitani, and G.Saito, Solid State Commun. 43, 757 (1982).

6. This temperature is a little lower than $T_c$=84.4±0.5K reported before[5]. The difference is supposedly due to the surface enviromental effect. The sample once immersed in liquid nitrogen seems to exhibit a little higher (by ca. 2-3K) $T_c$ than that placed in vacuum.

7. A.Girlando, L.Morelli, and C.Pecile, Chem. Phys. Lett. 22, 553 (1973).

8. Y.Tokura, T.Koda, G.Saito, and T.Mitani, J. Phys. Soc. Jpn. 53, 4445 (1984).