Ionic-to-neutral phase transformation induced by photoexcitation of the charge-transfer band in tetrathiafulvalene-*p*-chloranil crystals

T. Suzuki, T. Sakamaki, and K. Tanimura

Department of Physics, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8602, Japan

S. Koshihara

Department of Applied Physics, Tokyo Institute of Technology, Tokyo 152, Japan

Y. Tokura

Department of Physical Engineering, University of Tokyo, Tokyo 113, Japan

The transformation from ionic to neutral phases in tetrathiafulvalene-*p*-chloranil crystals is induced by exciting the charge-transfer absorption band below the transition temperature. The transformation takes place only above a threshold intensity of excitation, and the efficiency of generating neutral-phase domains is lower than the case induced by the excitation in intramolecular optical transitions of tetrathiafulvalene molecules. The mechanism of the photoinduced phase transition in this crystal is discussed based on these results.
[S0163-1829(99)15133-6]

Among several phenomena associated with the valence instability in solids, the structural phase transition in low-dimensional systems is of great current interest.[1] A typical example is the neutral-to-ionic (NI) phase transition observed in a class of mixed-stack organic charge-transfer (CT) complexes.[2,3] These crystals have electron donor (D) and acceptor (A) molecules, alternating along the same stack, and are classified into two categories according to the degree of CT (ρ): quasineutral for $\rho < 0.5$ and quasi-ionic for $\rho > 0.5$. Some of the crystals undergo the transition between neutral to ionic phases under applying hydrostatic pressure. The NI transition in tetrathiafulvalene-*p*-chloranil (TTF-CA) takes place also with changing temperature; below 81 K TTF-CA takes ionic phase with ρ of 0.7, while it takes neutral phase with ρ of 0.3 above 84 K.[4–6]

Koshihara *et al.* have shown that the transition from ionic to neutral phases is induced by exciting the crystal with light in visible region (2.0–2.5 eV).[7] Based on the careful examination of the characteristics of the reflectance-spectral changes, they have concluded that the transition is not associated with any temperature increase by the excitation, but is induced by purely electronic stimulation. Based on the fact that the site-substitutional impurities with a lower electron affinity than CA can induce a macroscopic neutral domain in ionic phase below 81 K,[5] the photoinduced *I* to *N* transformation has been proposed to be due to photoinjection of neutral *DA* pairs, or $D^0(A^0)$-type charged species.[7] The photon energies of laser light used in their study correspond to the intra-molecular excitations of TTF molecules. Accordingly, the effective relaxation of photoexcited TTF-molecular state (Frenkel-exciton state) into the charge-transfer excitons has naturally been assumed, although the relaxation processes has not been clarified yet. Therefore, it is of great importance to study the direct consequence of photoexcitation of CT transitions in TTF-CA in order to understand the mechanism of this photoinduced structural phase transition.

In this paper, we report the experimental results of the NI transition in TTF-CA induced by the direct photoexcitation of CT absorption band. It is shown that the CT-band excitation indeed induces the NI transition, but that the features of the photoinduced NI transition show some significant differences from those by the intramolecular excitation. Mechanism of the photoinduced NI transition is discussed based on the results.

Single crystals of TTF-CA were grown by a cosublimation of the powder materials of TTF and CA, which were carefully purified by repeated recrystallization and sublimation processes. A typical size of crystals used was $3 \times 3 \times 0.5$ mm^3, with well-developed (001) surfaces. Specimens were attached to a cold finger of a conventional cryostat capable to be cooled down to 78 K. For measuring transient optical reflectance spectra, a multichannel spectrometer consisting of a monochromator (Jobin-Yvon CP200) and a charge-coupled device detector (Princeton Instruments TE/CCD-1100PFUV) was used with a Xe-flash lamp which generated 0.9-μs light pulse. Specimens were excited with 1064-nm laser pulses from a *Q*-switched Nd:YAG laser (Coherent Infinity 400). In order to excite specimens uniformly and to determine the photon fluence on the sample surface with least ambiguity, relay imaging technique was used for the top-hut spatial beam profile. Specimens were also excited with second harmonics (532 nm) of the fundamental laser pulses. Laser intensities were simultaneously monitored with a calibrated photodiode detectors.

In Fig. 1, we show the relative difference ($\Delta R/R$) between the reflectance spectra with and without photoexcitation induced by exciting specimen with 532-nm and 1064-nm laser pulses. The curves are the results measured at time delay of 3 μs after excitation. It is clear in the figure that the feature of the reflectance changes are essentially the same for both wavelengths of excitation, and is characteristic of the injection of neutral-phase domains in ionic lattice.[7] The change in the reflectance spectrum induced by a
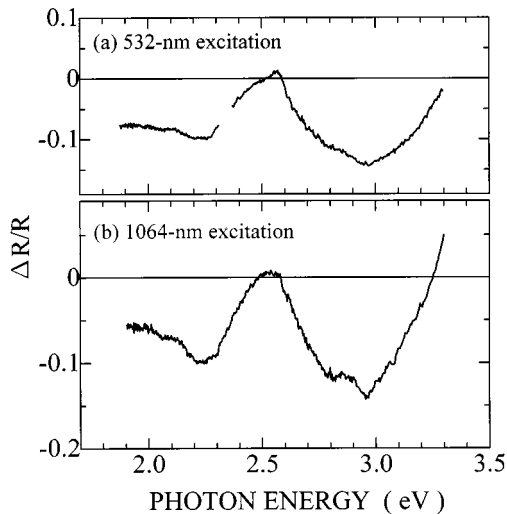
FIG. 1. Changes in reflectance spectra induced by a 532-nm laser pulse (a) and by an 1064-nm laser pulse (b) measured at time delay of 3 μs with respect to the incidence of the excitation pulse. The relative difference ($\Delta R/R$) between the spectra with and without photoirradiation is shown.

1064-nm light mostly decays within 10 ms, similarly to the case of intramolecular excitation at 532 nm. Therefore, it is evident that the 1064-nm light can induce the NI transition as well.

Since $\Delta R/R$ of 0.38 at 3.0 eV corresponds to the complete conversion of I phase into N phase,[7] the $\Delta R/R$ of 0.13 in Fig. 1 means that about 34% of the I-phase sites are converted into N phase after excitation. We hereafter use the magnitude of $\Delta R/R$ at 3.0 eV as a measure of the yield of fraction of the N phase photogenerated in the I phase.

The photon energy of 1.165 eV at 1064 nm falls in the energy range of the CT-exciton transition in TTF-CA.[2,4,8] In order to confirm this nature of the optical transition, we measured $\Delta R/R$ as a function of the angle Θ between the electric vector of the exciting light and the stack axis (a axis). The magnitude of 3.0-eV peak in $\Delta R/R$ spectrum is plotted as a function of Θ in Fig. 2, where $\Theta = 0$ corresponds to the case where polarization is parallel to the stack axis. It is evident in the figure that $\Delta R/R$ shows the highest value at $\Theta = 0$. This
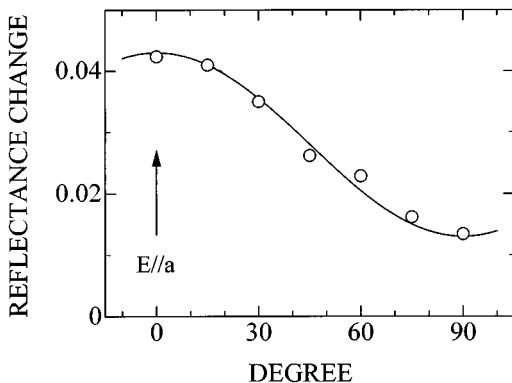

FIG. 2. Magnitudes of the reflectance changes at 3.0 eV as a function of the angle Θ between the electric vector of the laser light and the a axis of the crystal. $\Theta = 0$ corresponds to the parallel configuration of the electric vector and a axis.

result confirms that the optical transition induced by 1064-nm light is certainly the CT transition to generate CT excitons; any intramolecular transitions show opposite polarization characteristics with respect to the stack axis.[4] Therefore, we can conclude that CT-band excitation induces the NI transition in TTF-CA crystal.

In Fig. 3, we show the magnitude of $\Delta R/R$ at 3.0 eV as a function of excitation intensity scaled by the photon fluence. The result for the CT-exciton excitation is compared with that for the intramolecular excitation at 2.33 eV. In the case of 2.33-eV photon excitation, the yield of the N phase appears to be in proportion to the excitation intensity. On the other hand, we can definitely define the threshold excitation intensity in the case of CT-exciton excitation; the signal of the NI transition increases only beyond the fluence of 1.7×10^{15} photons/cm^2 in this case. Also, when we compare the yields for both cases, the yield for the CT-exciton excitation is much smaller than the intramolecular excitation for the same photon fluence. These differences imply some important feature in the mechanism of photoinduced NI transition in the TTF-CA crystal.

In the dimerized radical D^+A^- stack in the ionic phase, the excess charge in the form of A^0 does not remain local, but generates the macroscopic neutral region, as is shown by the spectroscopic studies of the TTF-CA doped with site-substitutional impurities.[5] Although the formation of CT excitons in the ionic phase may be regarded as photoinjection of similar excess charges when they are localized, the present result shows that a single CT exciton cannot generate such a macroscopic neutral-phase domain, as evidenced by the presence of the threshold excitation intensity. Rather, it suggests strongly that a superlinear interaction of CT excitons plays an essential role in inducing the structural phase transformation. Below we discuss the origin of this superlinear interaction in terms of energetics during the transformation from photogenerated CT excitons on an ionic stack chain to the N-phase domain on the chain.

As pointed out by Toyozawa, CT excitons in the ionic phase are associated with the formation of electric dipole, and CT excitons are attracted with each other through the dipolar interaction.[9] Therefore, we may introduce a string consisting of n CT excitons in the ionic-phase lattice as the state after optical transition and electronic relaxation; the process of forming the string from randomly distributed n CT excitons is clearly exothermic. In a simple one-dimensional scheme, the dipolar-interaction energy Δ_e of the CT-exciton string is given by

$$\Delta_e = \sum_{m=1}^{n-1} (n-m) \frac{V_{01}}{m^3}, \qquad (1)$$

where n is the total number of DA-pair sites at which a string is formed, m the distance among the sites in a unit of lattice constant, and V_{01} the dipolar interaction energy at the nearest-neighbor site.[9] In the transformation from the string into the neutral-phase domain, lattice relaxation must be involved, which includes the change in DA-pair distance and also the three-dimensional distortion corresponding to the changes in the lattice constants of b and c axes.[10,11] When the DA-pair distance is enlarged by q from the magnitude at I-phase configuration, V_{01} is enhanced.

Therefore, the dipolar interaction among CT-exciton string may provide energy gain upon lattice relaxation of releasing dimerization of *DA* pairs. On the other hand, the relaxation costs the elastic energy δ, which may be given by

$$\delta = \frac{M_r \omega_N^2}{2} q^2 \qquad (2)$$

per *DA* pair, where M_r and ω_N are the reduced mass of *DA* pair and angular frequency of the *LO*-phonon mode, respectively.[12] For neutral-phase domain with n *DA* pairs, the energy cost may be given by δ times n. Similar elastic-energy cost may be added for including three-dimensional structural changes.

We think that the photoinduced phase transformation is favored when the energy gain exceeds the energy cost upon the lattice relaxation. The energy gain in the dipolar interaction is a superlinear function with respect to the size of the string, or the number of the CT excitons which forms a string, whereas the energy cost in the elastic energy is a linear function of the number of the sites involved. Then, we expect a critical size of the string upon which the structural transformation into the neutral phase becomes possible energetically. The numerical evaluation of Δ_e and δ with using typical values available in literatures shows, in fact, the crossover between these two quantities around n of 4; Δ_e is smaller than δn for $n < 4$, whereas Δ_e is larger than δn for $n > 4$. Therefore, the threshold excitation intensity observed in this study can be tentatively interpreted to be the excitation density to form the string with a critical size.

In contrast to the case of CT-exciton excitation, generation of the intramolecular excited states, or Frenkel excitons, appears to show structural transformation without a threshold excitation density (the present result indicates that the threshold, if any, is much smaller than the case of CT-exciton excitation, as seen in Fig. 3). Although relaxation pathways from the intramolecular excited states into the neutral-phase domain in the ionic phase have not yet been clarified completely, a model has been proposed that the intramolecular excited state is relaxed into a group of CT excitons to induce
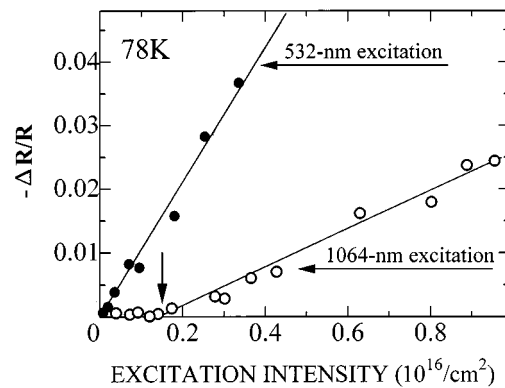

FIG. 3. Magnitudes of the reflectance changes at 3.0 eV induced by 1064-nm laser pulse, open circles, and by 532-nm laser pulses, solid circles, as a function of excitation intensity of the laser pulses scaled in terms of fluence.

the phase transformation.[7] In this relaxation process, substantial amount of excess energy may be released to induce violent lattice vibration around the sites where intramolecular excited states are converted into a group of CT excitons. This feature, which is certainly a different aspect from those in direct photoexcitation of CT excitons, may be a reason why the NI transformation is induced without threshold excitation density.

In conclusion, we have demonstrated that the direct photoexcitation of the CT-absorption band in TTF-CA induces the structural transformation from ionic to neutral phases. In this photoinduced phase transition, there exists a threshold excitation intensity which is not observed in the similar process induced by the intramolecular excitation. We have tentatively interpreted the threshold intensity in terms of superlinear interaction of CT excitons. Further studies on this threshold excitation intensity as a function of temperature and of the excitation wavelength, together with ultrafast time-resolved studies, will be of great interest in light of the dynamics of the photoinduced phase transition.

[1] *Relaxations of Excited States and Photo-induced Structural Phase Transitions*, edited by K. Nasu, Vol. 124 of Springer Series in Solid State Sciences (Springer, Berlin, 1997).

[2] J. B. Torrance, J. E. Vazquez, J. J. Mayerls, and V. Y. Lee, Phys. Rev. Lett. **46**, 253 (1981).

[3] J. B. Torrance, in *Low Dimensional Conductors and Superconductors*, edited by D. Jerome and L. G. Caron, Vol. 155 of *NATO Advanced Study Institute, Series B: Physics* (Plenum, New York, 1987).

[4] Y. Tokura, T. Koda, T. Mitani, and G. Saito, Solid State Commun. **43**, 757 (1982).

[5] Y. Tokura, T. Koda, G. Saito, and T. Mitani, J. Phys. Soc. Jpn. **53**, 4445 (1984).

[6] Y. Kanai, M. Tani, S. Kogoshihara, Y. Tokura, and T. Koda, Synth. Met. **10**, 157 (1984).

[7] S. Koshihara, Y. Tokura, T. Mitani, G. Saito, and T. Koda, Phys. Rev. B **42**, 6853 (1990).

[8] C. S. Jacobsen and J. B. Torrance, J. Chem. Phys. **78**, 112 (1983).

[9] Y. Toyozawa, Solid State Commun. **84**, 255 (1992).

[10] N. Nagaosa, Solid State Commun. **57**, 179 (1986).

[11] M. Le Cointe, M. H. Lemee-Cailleau, H. Cailleau, B. Toudic, L. Toupet, G. Heger, F. Moussa, P. Schweiss, K. H. Kraft, and N. Karl, Phys. Rev. B **51**, 3374 (1995).

[12] T. Iizuka-Sakano and Y. Toyozawa, J. Phys. Soc. Jpn. **65**, 671 (1996).