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Photoinduced valence instability in the organic molecular compound tetrathiafulvalene-p-chloranil (TTF-CA)

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It was found that a local charge-transfer excitation on the donor(D)-acceptor(A) pair leads to a semimacroscopic valence change from the quasi-ionic (D^+A^-) to quasineutral (D^0A^0) states in organic molecular-compound TTF-chloranil with mixed DA stacks. Photogenerated neutral-ionic domain walls, which are responsible for anomalous photoconductivity, show the temporal annihilation due to the one-dimensional recombination.

Various phenomena associated with the valence instability in solids have been of great interest with respect to electronic phase transitions. One of the prototypical examples is the neutral-ionic transition (NIT) observed in organic charge-transfer compounds.[1-4] Several compounds with mixed stacks of donor (D) and acceptor (A) molecules are known to show the thermally or pressure-induced NIT from the quasineutral (D^0A^0) to the quasi-ionic (D^+A^-) state.[1,2] The NIT has been attributed to the competition of the cost of energy for ionizing D^0A^0 stacks with the gain of Madelung energy in the ionic D^+A^- lattice.[1,3] Upon the NIT, the degree of charge transfer (CT) on the molecules shows a finite jump and the DA stacks in the ionic phase undergo the dimeric lattice distortion. Since the spin state in the ionic phase is approximately described as the $S=\frac{1}{2}$ Heisenberg chain, the lattice transition is quite analogous to the spin-Peierls transition.[4] Such an electron (spin) -lattice interaction obviously plays an important role in promoting the NIT in real systems in addition to the above-mentioned electrostatic mechanism. In this paper, we report the observation that the valence instability in the DA compounds can be also caused by photoexcitation. The photogenerated CT excitations (D^0A^0) or resultant charged species (D^0 and A^0) in the ionic DA lattice locally modify the Coulombic interaction and switch off a channel of the collective spin-lattice interaction. What we have observed in this study is the phenomenon that those local photoexcitations serve as nuclei which evolve into the neutral molecular domains over a semimacroscopic region.

Among a number of CT compounds located near the neutral-ionic interface, tetrathiafulvalene (TTF)-chloranil (CA) was investigated here, since this is the most prototypical compound which shows the NIT not only by applying hydrostatic pressure above P_c (equal to 11 kbar) but by lowering temperature below T_c.[1,2,5-12] At ambient pressure, the first-order NIT is observed at 81 K in the cooling run (and at 84 K in the heating run) accompanying the stack dimerization in the ionic phase. To detect a change in molecular ionicity, optical spectra for local electronic excitations have been known to be very useful.[5,6]

In Fig. 1(a) reflectance spectra are plotted for the neutral and ionic phases taken on the (001) surface at 90 and 77 K, respectively, with the light polarization normal to the stack axis (a axis) ($E\perp a$). The reflectance bands B and C are attributed to intramolecular transitions due to TTF$^+$ molecules, while the band D is due to TTF^0 molecules. As investigated in detail previously,[4-6] spectral intensities and energy positions of these molecular excitation bands sensitively reflect the macroscopic degree of CT ($D^{+\rho}A^{-\rho}$; $\rho=0.3$ in the neutral phase and 0.7 in the ionic phase) which is equal to the *time-averaged* ionicity of molecules.

Keeping this in mind, we discuss the result of the photoinduced effect on these molecular excitation spectra. In Fig. 1(b), photoreflectance (PR) spectra are plotted in the neutral and ionic phases, which are measured at 90 and 77 K, respectively. PR spectra were recorded as a relative difference ($\Delta R/R$) between the spectra with and without photoirradiation. Photoirradiation was made at energies above the CT gap (at 2.0–2.5 eV) utilizing a pulse dye laser (10 ns) or a chopped light (400 Hz) from a cw Ar laser. Solid and open circles in the PR spectra [Fig. 1(b)] were the results for pulse excitation, measured with a gated integrator (delay time, 100 μs; gatewidth, 150 μs). Both PR spectra with cw (solid and broken lines) and pulse laser light show good agreement. In the case of pulse excitation (1.8×10^{13} photons/cm^2, 10 ns), anomalously large PR signals exceeding 4% were observed in the ionic phase, whereas in the neutral phase no detectable signal was observed under the same photoexcitation condi-

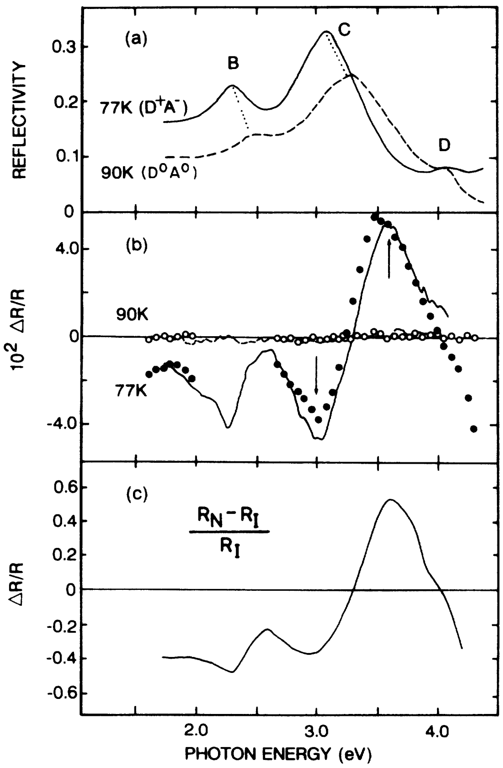

FIG. 1. (a) Reflectance spectra and (b) photoreflectance (PR) spectra for molecular excitations ($E \perp a$) at 77 K (ionic phase) and at 90 K (neutral phase) in TTF-CA crystal. Ordinate scale for $\Delta R/R$ (b) is for the results for pulse excitation shown by open (90 K) and solid (77 K) circles. Solid and broken lines represet the result by cw laser excitation. The spectrum (c) is the calculated differential spectra using the respective ionic phase (R_I) and neutral phase (R_N) spectra shown in (a).

tion.

It is to be noted that the shape of the PR spectrum in the ionic phase can be well reproduced by the calculated differential spectrum $[R(N)-R(I)]/R(I)$, which is plotted in Fig. 1(c). Here, $R(N)$ and $R(I)$ are the typical reflectance spectra in the neutral and ionic phase, respectively, as shown in Fig. 1(a). Therefore, the result indicates that the photoexcitation in the ionic phase causes (semi)macroscopic ionic-to-neutral phase conversion. In the present condition of the pulse laser excitation, a fraction of the photoconverted D^0A^0-type molecular domains is estimated to amount to 11% of the sample surface at 70 K as seen by comparing the ordinate scales of Figs. 1(b) and 1(c). Since the exciting and probing lights in the visible region have the comparable attenuation depth (~ 100 nm), we assume here for a very crude estimation that the total photon flux (1.8×10^{13} photons/cm^2) are absorbed uniformly within the surface region of the depth of ~ 100 nm from the surface and that the PR signal also probes the same region. Then, the photoexcitation density is $\sim 1.8 \times 10^{18}$/cm^3. The density of DA pairs in crystal[13] is 2.46×10^{21}/cm^3, 11% of which is subject to the photoinduced ionic-to-neutral change in the surface region. This means that one absorbed photon can convert as many as 160 DA pairs from the quasi-ionic to quasineutral state.

It might be suspected that the observed photoinduced change would be triggered by a laser-induced heating process across T_c. However, we can exclude the possibility of such a deceptive effect as discussed below. Temperature variation of the PR signal intensity measured at 3.0 eV [the position indicated by a downward arrow in Fig. 1(b)] is plotted in Fig. 2(a). The stack dimerization, which was probed by x-ray measurements[7] and by infrared spectra of molecular vibrations,[5,8] sets in abruptly below T_c because of the spin-Peierls mechanism and simultaneously the molecular ionicity (ρ) jumps from ~ 0.3 to ~ 0.6. In accord with this NIT, PR signals are observed due to the photoinduced ionic-to-neutral conversion, but rather slowly decrease in magnitude with a decrease in temperature from T_c. Even at 15 K, 40% of the maximum magnitude of the PR signal was observed. If this were due to the thermal ionic-to-neutral transition via the heating above T_c (equal to 81 K) by a laser-irradiation, one would have to assume that the increase in the sample temperature is more than 70 K. In that case, the similar heating would be expected in the neutral phase and would cause a comparatively large PR signal above T_c even if the temperature variation in specific heat[9] is taken into account. As far as a simple heating-induced NIT is assumed, it would always result in a distinct and sharp anomaly of the PR signals in a narrow temperature region close to T_c. Apparently, these are not the case. The observed temperature dependence of PR signals indicates that the valence

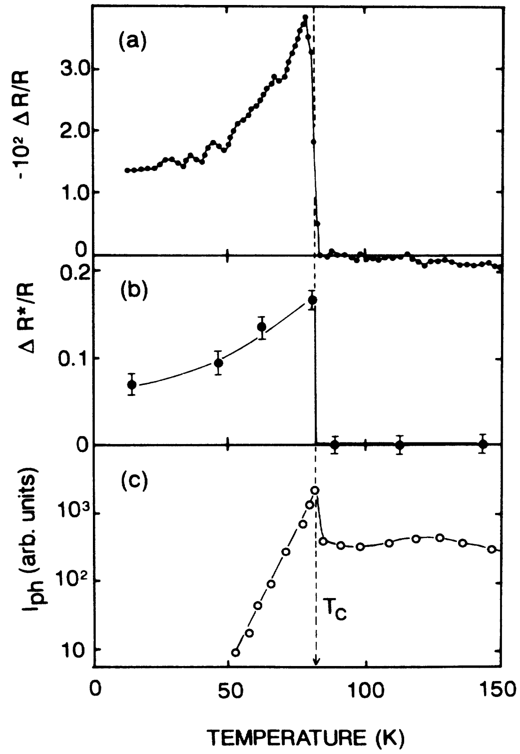

FIG. 2. Temperature dependences of the ionic-to-neutral conversion induced by (a) photoirradiation and (b) by impurity (QCl_3) doping, and of (c) photocurrent (for the definition of the symbol, see text).

conversion over the semimacroscopic molecular region is evolved primarily via photoexcitations in the dimerized stacks of the ionic phase, but not in the uniform stacks of the neutral phase.

Such a stimulated coexistence of the neutral regions with the host ionic regions has also been observed for TTF-CA crystals doped with trichloro-*p*-benzoquinones (QCl_3) as site-substitutional impurities.[7] The QCl_3 molecule, in which one chlorine in the CA moiety (i.e., QCl_4) is hydrogenated, has a lower electron affinity than CA by ~0.1 eV and hence the QCl_3 impurity substituted for CA remains neutral even below T_c. The important feature is that the influence of neutral QCl_3 molecules doped in TTF-CA crystal does not remain local, but several TTF and CA molecules nearby the impurity QCl_3 are neutralized in a temperature-dependent manner. We show in Fig. 2(b) typical temperature variation of the impurity-induced ionic-to-neutral conversion, that is the quantity defined by the differential reflectivity, $\Delta R^*/R = (R' - R)/R$, as in the photoinduced case. Here, R' and R represent the reflectivities in the 7% QCl_3-doped (R') and undoped TTF-CA (R) samples, which were measured at the photon energy (2.5 eV) corresponding to the B band at the same temperature. In the ionic phase of the doped crystal, the B band shows two reflectance peaks at the energy positions 2.3 and 2.5 eV, corresponding to the ionic and neutral regions, respectively.[7] Therefore, the reflectivity change $\Delta R^*/R$ monitored at 2.5 eV can be a measure for the portion of the remaining neutral region at temperatures below T_c. The result shows quite a parallel behavior with the photoinduced case, although the ionic-to-neutral conversion in the former case is static in nature. Such a CT instability induced by the local impurity molecules as observed may also rationalize the present observation that a similar CT instability can be caused by the photoinjection of neutral DA pairs (i.e., CT exciton), or perhaps, of $D^0(A^0)$-type charged species.

The mechanism of the stack dimerization in the ionic phase is likely attributed to the spin-lattice interaction in the radical D^+A^- stack as an $S=\frac{1}{2}$ Heisenberg spin chain.[4,10] Generally, the introduction of the excess charge (of D^0 or A^0 type) into the dimerized (Peierls-distorted) ionic (D^+A^-) lattice would result in the formation of kink-type domain walls or solitons.[10,11] Near the neutral-ionic phase boundary, however, the D^0- or A^0-type charge generates the macroscopic neutral region around itself, as is evidenced by the case of A^0-type impurity doping, and this is also likely the case for photogenerated D^0 and/or A^0 species. In such a circumstance, the concept of neutral-ionic domain wall (NIDW), i.e., a microscopic interface separating a neutral domain from an ionic domain, is useful to describe the photoelectronic process originating from the CT instability. The existence of NIDW was first conjectured by Nagaosa,[12] and subsequently a number of experimental results consistent with the concept of NIDWs have been found in TTF-CA and other DA solids near the neutral-ionic phase boundary.[10,14] In this sense, the presently observed photoinduced CT instability may be interpreted in terms of the photodoping of NIDWs. A pair of NIDW is quite analogous to the bipolaron state postulated in organic conducting polymers with two nondegenerate (stable and metastable) ground states.[15]

A part of the photoinjected NIDWs, which have escaped from the germinate recombination, can carry a fractional charge[11,12,14] and it should be reflected in the photoconduction process in the ionic phase. In Fig. 2(c) we plot the temperature dependence of photoconductivity in a TTF-CA single crystal. The photocurrent was measured by illuminating uniformly the gap between silver painted electrodes. A constant voltage (200 V) was applied across the electrodes of ~1 mm width along the DA stack axis. Remarkably, the photoconductivity shows anomalous increase at T_c and then decreases with a well-defined activation energy (≈ 0.09 eV) at temperatures below T_c.[12] The behavior cannot be explained by the laser-induced bolometric effect, since the dark conductivity *decreases* by 1 order of magnitude on the thermally induced ionic-to-neutral transition.[10] It is possible that such an anomalous increase in photocurrent is attributed to the photogeneration of the NIDW-type excitations. The activation energy of the photocurrent (0.09 eV) coincides with that for the dc dark conductivity, suggesting that the charge-transport phenomena both in the dark and photoexcited states are governed by the activated motion of NIDW-type excitations.[11]

In the ionic phase, most of the photogenerated neutral clusters, or equivalently pairs of NIDWs, may eventually diminish or annihilate by recombination, although a part of the NIDWs escape from the pair recombination contributing the macroscopic charge transport as mentioned above. Typical results of temporal decay of a number of photogenerated NIDWs probed by the transient response of PR signals are shown in Fig. 3. The PR signals were measured at photo energies of 3.0 and 3.6 eV [indicated by arrows in Fig. 1(a)], which monitor the photoinduced reduction of the ionic region and generation of the neutral domain, respectively. In accord with the expectation, the PR signals remain either negative (at 3.0 eV) or positive (at 3.6 eV), respectively, over the whole time domain. Within the time resolution (~1 μs) of the detection sys-

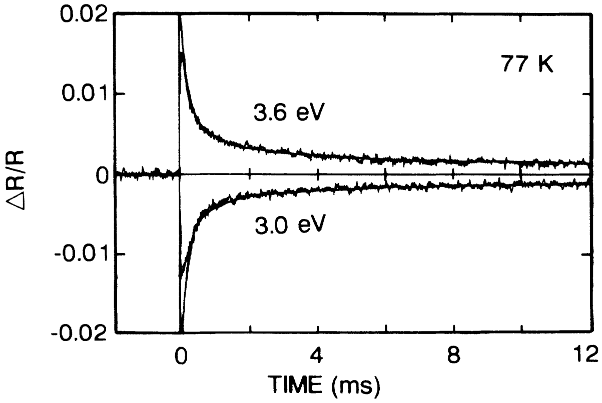

FIG. 3. Transient behavior of the photoreflectance signals monitored at 3.0 eV (for ionic molecules) and 3.5 eV (neutral molecules) in the case of pulse laser (10 ns) excitation. A smooth line represents the $t^{-1/2}$ behavior expected for the one-dimensional recombination process (see text).

tem, the magnitude of PR signals rises instantaneously after the photoexcitation, and decays rather slowly over the time region (traceably up to 10 msec). Such a temporal decay can be excellently fitted by using the function, $R(t)/R = \text{const} \times t^{-1/2}$, over the whole time region after 20 μs, as shown in Fig. 3. An identical time-dependent behavior of PR signals is observed at other temperatures (15-70 K) in the ionic phase. Such a $t^{-1/2}$ behavior is known to be characteristic of the one-dimensional (1D) recombination of excited species which are randomly walking on a chain structure.[16] Thus, the temporal decay of PR signals reflects the 1D motion of the photogenerated NIDWs toward the recombination. The initial rise of the PR signal, which could not be resolved in the present study, should reflect temporal evolution of the neutral domains into the ionic phase and will be of great interest in light of the dynamics of the first-order phase transition.

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