RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 1 1 JULY 1991-I

Inverse Peierls transition induced by photoexcitation in potassium tetracyanoquinodimethane crystals

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(Received 10 January 1991; revised manuscript received 25 February 1991)

Photoinduced absorption spectra for vibrational and electronic excitations have been investigated in a prototypical one-dimensional Peierls-Hubbard system, potassium tetracyanoquinodimethane crystals. Strong photoinduced-absorption signals and their temperature- and time-dependent characteristics are discussed in terms of dynamics of photoconverted molecular domains with no Peierls distortion in the background Peierls-distorted tetracyanoquinodimethane stacks. A close correlation between domain excitations and photoconductivity has also been confirmed.

The dynamical relaxation process of photoexcitations and the resultant lattice deformations in strongly electron-lattice coupled systems have been of considerable interest in recent decades. Notable among a number of relevant phenomena is the recent advance in the understanding of nonlinear excitations (e.g., solitons and polarons) in organic conducting polymers.[1] As another prototype of the quasi-one-dimensional electron-lattice coupled system, one can consider organic charge-transfer (CT) crystals, which are composed of stacking columns of π molecules. Such a CT compound is susceptible to lattice distortion arising from the electron (spin) -lattice interaction characteristic of one-dimensional (1D) systems. In fact, many CT solids undergo the thermally induced phase transition associated with a Peierls distortion of the lattice.[2,3] The purpose of this paper is to report a photoinduced phenomenon observed in a typical CT compound, potassium tetracyanoquinodimethane (K-TCNQ) crystals. What we have found is that lattice-relaxed photoexcitations convert the Peierls-distorted (dimerized) molecular stacks to the nearly regular ones over a semimacroscopic region.

K-TCNQ crystals are composed of 1D columns of TCNQ molecules which stand face to face along the *a* axis.[3,4] Complete charge transfer takes place between the TCNQ molecule and the cation (K) and electrons are nearly localized on TCNQ molecules due to the large on-site Coulomb energy ($U \approx 1.5$ eV) which overwhelms the transfer integral ($t \approx 0.2$ eV).[5] Crystals of K-TCNQ undergo a first-order phase transition accompanying the stack dimerization or Peierls distortion at $T_c = 395$ K like other crystals of the alkali-metal TCNQ family.[3,4,6,7] The dimerization of molecular sites alternatively modulates the electron-transfer energy t and hence causes a sort of bond-ordered wave (BOW). When $U \gg t$, the regular $(\mathrm{TCNQ})^-$ stacks can be considered to be an $s=\frac{1}{2}$ Heisenberg chain with antiferromagnetic exchange interaction J ($\approx 4\,t^2/U$). In this sense, the observed phase transition is analogous to the spin-Peierls transition,[8] although the energy scale of J is considerably large (≈ 0.1 eV) in K-TCNQ as compared with the case of the well-established prototypical spin-Peierls systems.[3]

Such a BOW-type distortion and its change upon the phase transition manifest themselves not only in x-ray-diffraction patterns,[7] but in optical spectra for molecular vibrations and CT excitations.[5,9-11] In Fig. 1(a), we show the optical-absorption spectra for the low-temperature phase (measured at 293 K) and for the high-temperature phase (at 409 K). The vibrational spectra were measured on the polycrystalline samples dispersed in KBr pellets,

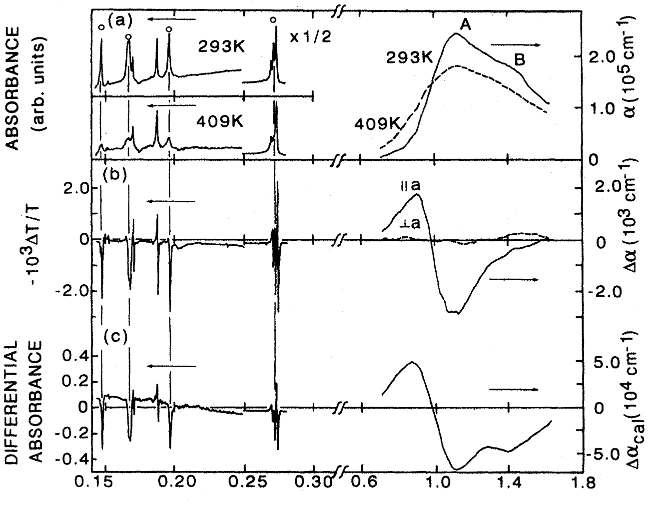

FIG. 1. Spectra of (a) absorption, (b) photoabsorption, and (c) simulated differential absorption for molecular vibrations (left-hand side) and charge-transfer excitations (right-hand side) of K-TCNQ. The absorption and photoabsorption bands of a_g vibrations are indicated by open circles. Solid and dashed lines in the right-hand side of (b) represent the polarized photoabsorption spectra for E∥*a* (stack axis) and for E⊥*a*, respectively.

while the absorption spectra for the CT excitation,

$$(\mathrm{TCNQ})^{1-} + (\mathrm{TCNQ})^{1-} \rightarrow (\mathrm{TCNQ})^{0} + (\mathrm{TCNQ})^{2-} ,$$

were obtained by a Kramers-Kronig analysis of the polarized ($\mathbf{E} \parallel a$) reflectance spectra of a single crystal. The CT band in the low-temperature phase shows a maximum (A) around 1.0 eV and a sideband (B) around 1.4 eV, as shown on the right-hand side of Fig. 1(a). Most simply, the splitting of the band has been ascribed to the coexistence of intradimer and interdimer CT excitations in the low-temperature BOW phase,[11] although other possible origins of the doublet structures have been proposed in the literature.[5,10,12] Across the phase transition, the magnitude of the CT gap changes little since the CT gap energy is mostly governed by the electron correlation U; nevertheless, an abrupt and appreciable broadening of the absorption profile and the disappearance of the sideband B are observed around T_c.

More distinct changes upon such a spin-Peierls-like transition are observed in infrared (IR) absorption spectra for molecular vibrations, as shown on the left-hand side of Fig. 1(a). In the low-temperature phase associated with stack dimerization, a_g molecular vibrations [indicated by open circles in Fig. 1(a)] are strongly activated via mixing with the electronic CT excitation.[12,13] These a_g modes are optically inactive for the regular molecular stack, and hence their intensities can be a sensitive microscopic probe for the BOW-type lattice distortion. The intensities of the a_g modes are observed to abruptly decrease above T_c, as shown in Fig. 1(a), although their residues are barely observed, perhaps due to the 1D fluctuation effect.[11]

Keeping the above in mind, we proceed to consider the experimental results of photoinduced changes in the vibrational and CT excitation spectra shown in Fig. 1(b). What we have observed here is that pulse- or cw-laser irradiation of a K-TCNQ crystal with dimerized stacks (BOW) produces mesoscopic-size molecular domains with nearly regular (non-BOW) stacks.

Photoinduced change for IR vibrational spectra were measured on polycrystalline samples dispersed in KBr pellets, which are irradiated by 514.5-nm light from a cw Ar laser. The differential spectra with and without laser irradiation were recorded by use of a Fourier-transform-type spectrometer. Typical laser intensity was 300 mW/cm^2 on the sample surface of KBr pellets and the absorbed light power was estimated to be ~ 100 W/cm^3. Differential spectrum at 293 K ($< T_c$) clearly shows a decrease in the intensity of each a_g band, as shown on the left-hand side of Fig. 1(b). This means that the photoexcitation produces molecular domains which are free from the BOW distortion. In fact, the observed photoinduced absorption (PA) spectrum shown in Fig. 1(b) can be reproduced by the calculated differential spectrum [Fig. 1(c)], which is obtained by subtracting the spectrum taken at 409 K (non-BOW phase) from that at 293 K (BOW phase).

A considerable photoinduced change in the optical spectra was observed also for the CT excitation region as shown on the right-hand side of Fig. 1(b). The photoinduced change in the absorption spectra was obtained by performing a Kramers-Kronig analysis of the photoinduced reflectance (PR) change ($\Delta R/R$) in the sample. The photoexcitation was done by an excimer-laser-driven dye laser (2.1 eV) with a pulse width of ~ 10 ns. The PR spectra were recorded by a boxcar integrator with a delay time of 3 μs and a gate width of 5 μs. For light polarization parallel to the stack axis (a axis), a fairly large change in reflectance or absorbance is observed, while the $\mathbf{E} \perp a$ spectrum shows no prominent signal. It is noted that the $\mathbf{E} \parallel a$ PA spectrum shown in Fig. 1(b) is well reproduced by the calculated differential-absorbance spectra shown in Fig. 1(c). The behavior is consistent with the above-mentioned observation about the photoinduced change in the IR vibrational spectra: Both results indicate that photoexcitation in the BOW phase of K-TCNQ generates molecular states analogous to those of the high-temperature phase. These photoinduced changes are not due to simple irradiation-induced heating, which is evidenced by their temperature-dependent behaviors, as described later.

As an advantage of the pulse-excitation experiment, we can estimate the size of a photoconverted molecular domain and observe its change with time. Plotted in Fig. 2 are the photoinduced reflectivity changes ($\Delta R/R$) detected at 1.1 eV against the photon density at the crystal surface. The right-hand ordinate indicates the fraction of the photoconverted non-BOW molecular domains to the background BOW lattice. The converted fraction could be estimated by assuming that the exciting and probing light penetrate the same depth ~ 140 nm from the surface and that the observed spectrum is well approx-

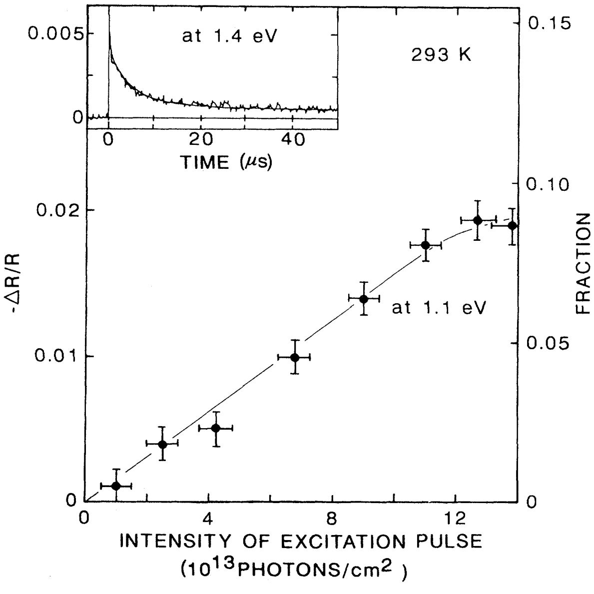

FIG. 2. Dependence of photoreflectance (PR) signals (monitored at 1.1 eV) on the intensity of exciting light ($\mathbf{E} \parallel a$, 2.1 eV, and 10 ns duration) at 290 K. The scale of the right-hand side ordinate indicates the fraction of the photoconverted molecular region (see text). Shown in the inset is the time dependence of a PR signal at 1.4 eV. A thin smooth line in the inset represents the $t^{-0.5}$ behavior expected for the one-dimensional recombination process.

imated by the differential spectrum between the high-temperature non-BOW phase and the low-temperature BOW phase. [See Figs. 1(b) and 1(c).] The magnitude of $\Delta R/R$, or equivalently the converted fraction of the non-BOW region, is approximately proportional with the exciting light intensity I_e, provided that I_e does not exceed 1×10^{14} photons/cm^2. Using the density of (TCNQ)$^-$ molecules (3.6×10^{21}/cm^3) in a K-TCNQ crystal,[4] we can estimate that one absorbed photon generates a non-BOW molecular domain consisting of as many as 40 (TCNQ)$^-$ molecules. This is a conservative estimate, since we have assumed that *all* the photoexcited species can take part in causing the inverse-Peierls-like transition with *100%* efficiency.

In the inset of Fig. 2, we show a typical trace of temporal decay of a photoinduced signal, which should represent the temporal disappearance of photoconverted non-BOW domains. The time dependence of the signal is excellently fitted by a $t^{-1/2}$ curve shown as a thin smooth line. This indicates that the photoconverted molecular domains extinguish by recombination of a pair of domain walls (DW's) which walk randomly on the 1D stack.[14]

It might be suspected that the observed semimacroscopic change in the lattice structure induced by photoexcitation was simply due to an increase in the temperature of the sample surface region across T_c. However, we can exclude the possibility of such a supposition by making the following experimental observations. Plotted in Fig. 3(a) is the temperature variation of the photoinduced signal ($\Delta R/R$) shown by a solid line. Solid squares represent the result for the bleaching degree of the 1570 cm^{-1} a_g molecular vibration by cw-laser excitation [see the left-hand side of Fig. 1(b)]. In spite of a large difference in absorbed light power per unit volume between the two cases (100 W/cm^3 for cw excitation and 5 W/cm^3 for pulse excitation operated at 5 Hz), both results show an essentially identical temperature dependence: The photoconversion efficiency increases with temperature up to 330 K, but then begins to decrease as temperature goes towards T_c. Around T_c, the photoinduced signals are observed to disappear. Such a temperature dependence cannot be explained by laser-induced heating of the sample surface. If it were the case, the photoinduced change would be strongly enhanced around T_c due to the first-order character of the phase transition. To demonstrate this, the temperature dependence of the PR signal was simulated assuming laser-induced heating with a temperature increase of 10 K. (For this calculation, the observed temperature dependence of reflectivity at 1.2 eV was used.) The result, which is shown by a dashed line in Fig. 3(a), is entirely different from the observed temperature variation of the PR.

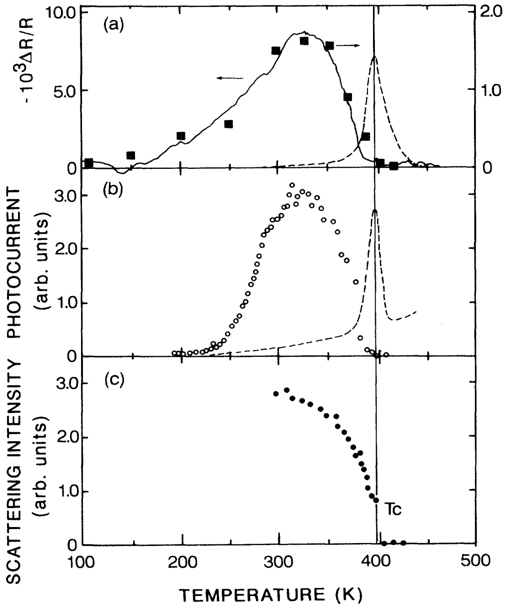

FIG. 3. Temperature dependences of (a) a photoreflectance signal at 1.2 eV (solid line) and an absorbance change of the 0.195 eV (1570 cm^{-1}) a_g mode (solid squares), (b) a photocurrent (solid line), and (c) the x-ray diffuse diffraction intensity due to the dimeric lattice distortion by Terauchi (Ref. 7). Dashed lines in (a) and (b) represent the simulated results, assuming irradiation-induced heating of the sample (see text).

In Fig. 3(c), we reproduce, for comparison, the temperature dependence of the x-ray diffuse scattering intensity due to the BOW-type lattice distortion which was previously reported by Terauchi.[7] The lattice distortion was observed to show a finite jump at T_c due to the first-order nature of this transition, and an increase with decreasing temperature below T_c down to ~300 K. Since the observed PR intensity similarly increases from the zero level with decreasing temperature below T_c, the temperature dependence of the size of photoinjected non-BOW domain seems to be closely correlated with the background BOW amplitude. This implies that the initial process of the lattice relaxation of photoexcited states may depend critically on the BOW distortion of the ground state. A possible scenario is as follows: The photoexcitation around 2.1 eV may rapidly (probably within a picosecond) relax to the local CT exciton, such as a (TCNQ)^0-(TCNQ)$^{2-}$ pair. This state may be further subject to decomposition into a distant electron-hole-like pair and this process is likely to be sensitive to the BOW distortion. Such lattice-relaxed charged excitation, or polaron, may serve as nuclei of the non-BOW domain.

In this context, it is worth noting that the temperature dependence of the photocurrent shown in Fig. 3(b) exhibits quite a parallel behavior with that of the PR signal, except for the low-temperature region below 250 K. The photocurrent was measured for the 2.1-eV pulse-laser excitation (as in the PR measurement) with application of a dc electric field (200 V/cm) along the *a* axis (stack axis). The signal is not due to a simple heating effect, such as a photovoltaic effect. Also in this case, the simulated curve [a dashed line in Fig. 3(b)], which was calculated with dc conductivity data assuming the irradiation-induced temperature increase of 10 K, is entirely different from the observed one. Nearly identical thermal variation of the PR and photoconduction data suggests that the photoconverted non-BOW domains or their domain walls can carry an electric charge. A steeper decrease of the photocurrent below 300 K may be ascribed to the fact that photoconduction is a macroscopic transport phenomenon which should be more susceptible to undergoing some carrier-trapping process at lower temperatures. The gradual decrease of the PR signal itself below 300 K should be explained by another microscopic deactivation process, since below 300 K the BOW amplitude is considered to be nearly constant [see Fig. 3(c)].

In conclusion, we have found the photoinduced inverse-Peierls-like transition in a K-TCNQ crystal over a mesoscopic-size molecular domain (at least 40 molecules per absorbed photon). The photoconverted domains or their domain walls between the BOW and non-BOW regions can likely carry an electric charge, which is observed as a photocurrent. The precursory excitation for such a phase conversion is not clear at present, but is presumably the lattice-relaxed CT excitons or dissociated polarons which can switch off the collective channel of electron (spin) -lattice interactions characteristic of this 1D system.

We would like to acknowledge helpful discussions with Dr. H. Okamoto and Professor T. Mitani. This work was supported in part by a Grant-In-Aid from the Ministry of Education, Science and Culture of Japan, and also by the International Joint Research Project from the New Energy and Industrial Technology Development Organization.

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