PHYSICAL REVIEW B VOLUME 38, NUMBER 3 15 JULY 1988-II

Nonlinear electric transport and switching phenomenon in the mixed-stack charge-transfer crystal tetrathiafulvalene-*p*-chloranil

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(Received 22 October 1987; revised manuscript received 12 May 1988)

A remarkable nonlinearity and a switching effect have been observed for electric transport in a tetrathiafulvalene (TTF)-*p*-chloranil crystal. Experimental evidence indicates that these features are of an intrinsic origin associated with the neutral-ionic transition. A possible mechanism is discussed in terms of field-dependent low-energy excitations, such as solitons and neutral-ionic domain walls, which are inherent to the quasi-one-dimensional donor-acceptor stacks in the TTF-*p*-chloranil crystal.

The mixed-stack organic charge-transfer (CT) crystal tetrathiafulvalene-*p*-chloranil (TTF-CA) has attracted considerable interest because of its characteristic phase transition, namely, the neutral-ionic transition (NIT) discovered first by Torrance and co-workers.[1,2] Extensive studies have been made so far on optical, magnetic, thermal, and structural properties as well as the theoretical aspect of the NIT. The electric properties were also found to exhibit notable features at the NIT,[3,4] such as a sharp increase of the electric conductivity when the temperature is lowered across the critical temperature $T_C = 81$ K and a remarkable increase of the conductivity by pressure from about 10^{-6} S/cm (at ambient pressure) to more than 10^{-2} S/cm (at about 8 kbar).

It has been argued[5-7] that these features of the electric conductivity are closely related to the dynamics of intrinsic low-energy excitations, specifically charged kink solitons in the dimerized ionic state and neutral-ionic domain walls (NIDW's) induced in the neutral-ionic mixed state. Here, kink solitons are schematically represented by either $\ldots, DA, DA, D, AD, AD, \ldots$ or $\ldots, AD, AD, A, DA, DA, \ldots$, where DA or AD represents the dimerized donor-acceptor pairs on a quasi-one-dimensional (1D) stack in the ionic state. Unpaired donor or acceptor molecules located at the kink can bear extra fractional charges[7,8] in the degenerate ground state of the dimerized ionic phase, analogous to charged kink solitons in the degenerate conjugated polymer *trans*-polyacetylene. On the other hand, the NIDW's are depicted as the boundaries between the neutral and ionic domains in a nearly degenerate state near the NIT at low temperatures or high pressures. Either of these excitations is expected to show a nonlinear response to an external electric field, as observed in many quasi-1D Peierls-Hubbard systems.[9] This Rapid Communication reports the first observation of such a nonlinear electric transport and an accompanying switching phenomenon in TTF-CA crystal. Various experimental facts clearly indicate that the observed features are directly associated with the instability of the CT states in TTF-CA crystal. Although a definitive physical model is difficult to derive at present, the unique features reported here will deserve considerable attention in the future study of NIT.

Single crystals of TTF-CA were grown by the cosublimation of purified polycrystalline powders of the TTF and CA molecules. Platelet samples of about 1 mm^2 cross section and 0.2–0.3 mm thickness were sliced from crystal blocks. Electrodes were provided by painting silver paste on the parallel square faces of the platelets. It has been ascertained that there is no harmful electrode effect in the conductivity measurements. The dc conductivity has been measured by the two-point method at various temperatures by cooling the sample in cold N_2 or He-gas flow.

The temperature variation of the electrical conductivity is shown in Fig. 1 in the low-field region, at various applied electric fields E below a certain threshold field E_{th} which will be defined later. The conductivity along the stack axis (the a axis) is about one order of magnitude larger than the perpendicular value shown by a broken curve for $E = 4$ V/cm. At low field ($E < 10$ V/cm), the response is almost Ohmic, and shows an exponential dependence upon T^{-1} (except near T_C) with the activation energy $\Delta (\cong 0.095$ eV) in both neutral ($T > T_C$) and ionic ($T < T_C$) regions. This energy is much smaller than the CT excitation energy (about 0.8 eV), indicating that lower-energy excitations are responsible for the conductivity. As the field is increased, the conductivity becomes appreciably dependent on field, as seen in curves a–c in Fig. 1, in both neutral and ionic regions. In the neutral region above T_C, the slope of $\log_{10}\sigma$-T^{-1} curves decreases

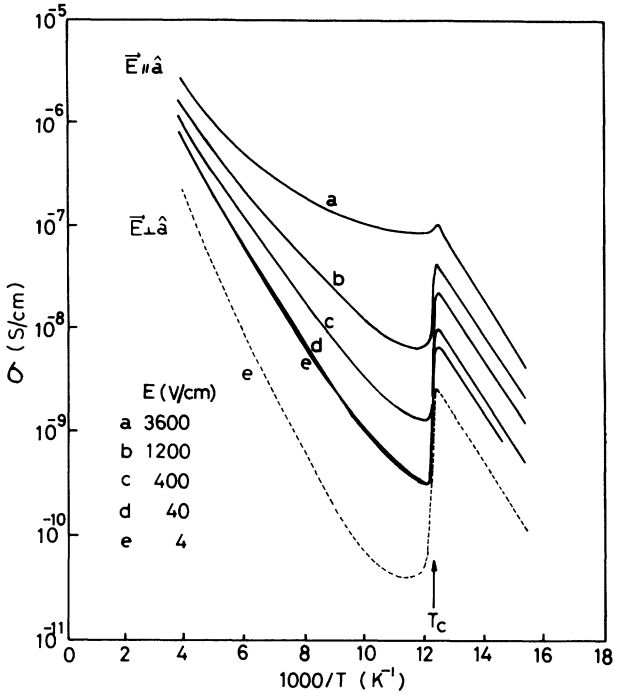

FIG. 1. Temperature and electric field dependences of electric conductivity of TTF-CA crystal in the positive resistance region ($E < 4\times10^4$ V/cm). The solid lines represent the parallel conductivities (E∥â) and a broken line the perpendicular conductivity (E⊥â). The arrow indicates the critical temperature $T_c = 81$ K for the neutral-ionic transition.

gradually with increasing field, while the slope of curves in the ionic region ($T < T_C$) is almost independent of field strength.

One of remarkable features of nonlinear electric response in TTF-CA crystal is a current switching phenomenon observed at low temperatures near T_C. Typical examples are shown in Fig. 2(a). In the measurements, a sample crystal was connected to a variable voltage supply V_0 through a 1-MΩ load resistor R_L in series, as shown in the inset of Fig. 2(a). When the temperature is sufficiently above T_C, the current I is a continuous function of V_0. However, as the temperature is lowered, the I-V_0 curve begins to show a discontinuous jump at a certain threshold field E_{th}(∥â), which is almost independent of samples if corrected for its thickness along the â axis. The current above E_{th} is predominantly determined by R_L. When a small load resister is used ($R_L \ll 1$ MΩ), then the sample crystal shatters at E_{th}. In order to protect the sample from damage at E_{th}, R_L must be sufficiently large. The high-conductivity state (HCS) can be switched back to the original low-conductivity state (LCS) by reducing V_0 below a certain critical value. This switching-on and switching-off cycle is reversible, following a hysteresis loop as shown in Fig. 2(a). The switching behavior is observed only for the E∥â (the stack-axis) configuration and not for E⊥â. The I-V_0 curve shown in Fig. 2(b) is a calculated one based on a phenomenological model discussed below.

The results shown in Fig. 2(a) are replotted in Fig. 3(a) as the current density J versus the internal electric field E within the crystal. E is obtained by correcting the applied V_0 for the voltage drop across R_L and dividing by the crystal thickness (d), i.e., $E = (V_0 - R_L I)/d$. As seen, there is a negative resistance behavior in the high-J region, which becomes more prominent as the temperature is lowered. Furthermore, at lower temperatures below about 130 K, the J-E curves begin to show discontinuous jumps like those in Fig. 2(a). (To avoid complexity, current jumps are shown here only for the HCS-to-LCS process by dotted downward arrows.) The vertical current jumps in Fig. 2(a) correspond to the slanted dotted lines in Fig. 3(a). This is due to the fact that the field E in the sample jumps to a higher value upon switching from the HCS to the LCS because of the sudden decrease in the voltage drop ($R_L I$) across the load resistor. Note that the J-E curves at temperatures above 86 K seem to merge into a single common curve in the high-J region ($J > 10^{-1}$ A/cm^{-2}). This indicates that the negative resistance effect in the neutral state is not sensitive to temperature. On the other hand, the curves below 77 K are

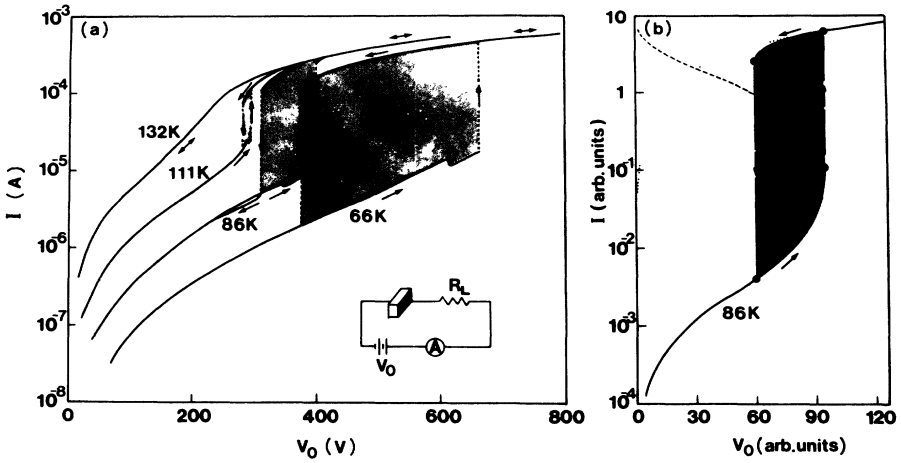

FIG. 2. (a) Experimental and (b) calculated I-V_0 characteristics of a circuit shown in the inset ($R_L = 1$ MΩ). Reversible hysteresis loops for the current-switching process are indicated by arrows encircling shaded regions.

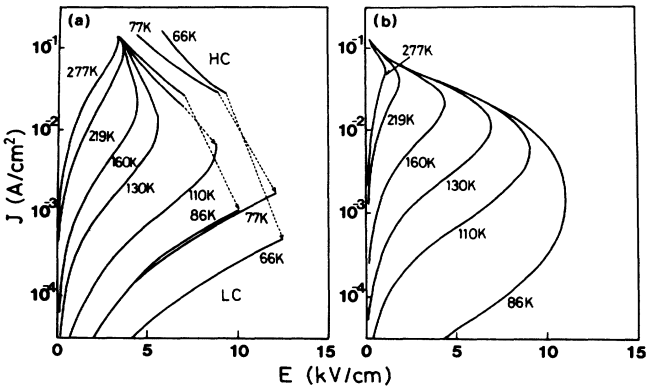

FIG. 3. (a) Experimental and (b) calculated J-E characteristics of TTF-CA crystal at various temperatures. Sudden current jumps between the low-conductive (LC) states and high-conductive (HC) states are shown only for the HC-to-LC switching to avoid confusion.

significantly dependent on temperature in the high-J region. Such a clear difference in the J-E characteristics between 86 and 77 K (that is a region of $T_C \pm 5$ K) provides additional evidence that the nonlinear response is closely related with the NIT at 81 K, and also that the possible heating of samples must be at most a few degrees even in the high-J region.

To understand the basic features of the remarkable nonlinear conductivity presently observed, let us discuss it phenomenologically. The conductivity in the LCS is dominated by a thermally activated process with an activation energy Δ in both neutral and ionic states, while the negative resistance effect in the HCS obviously indicates a contribution of some self-multiplication process of carriers. To take account of these two processes, we propose the following empirical expression for the nonlinear conductivity:

$$\sigma(T,J)=\sigma_1 \exp(-\Delta/k_B T)+\sigma_2 f(J) . \quad (1)$$

The first term represents the thermally activated process, and the second, the unstable carrier multiplication process in terms of a J-dependent function $f(J)$. For $f(J)$, we assumed the heuristic form,

$$f(J)=\exp(\alpha J)-1 . \quad (2)$$

In this phenomenological approach, the electric field E as a function of T and J is determined by the condition $E(T,J)=J/\sigma(T,J)$ in terms of the adjustable parameters, $\sigma_{1,2}$, Δ, and α in Eqs. (1) and (2). The calculated results are shown in Figs. 2(b) and 3(b), with $\sigma_1=1.7\times10^{-3}$ S/cm, $\sigma_2=1.7\times10^{-6}$ S/cm, $\alpha=50$ cm^2/A, and $\Delta=0.095$ eV which have been determined from a semiquantitative comparison with experimental results. The calculations were made only for the neutral state above $T_C=81$ K, where the negative resistance effect (represented by a constant α) shows little dependence on temperature.

Although this phenomenological model is very crude and empirical, the calculated results can give some insight into the nonlinear electric response in TTF-CA crystal: In the calculated I-V_0 curve for 86 K in Fig. 2(b), it is seen that the total voltage V_0 (a solid line) is composed of two parts, the voltage drop across the crystal (a dashed line) and that voltage drop across the load resistor R_L (a dotted line). The resultant I-V_0 curve shows an S shape, which implies a switching behavior around a hysteresis loop indicated by arrows. The calculated T dependence of J-E curves in Fig. 3(b) reproduces fairly well the observed features of the switching effect. The calculated J-E curves do not show the discontinuous jumps seen in Fig. 3(a). This is simply because the field E was calculated as a function of J in Fig. 3(b), while the experiment in Fig. 2(a), which was used to plot Fig. 3(a), was made by varying the voltage V_0 in the circuit shown in Fig. 2(a).

From the experimental results described above, it is evident that the presently observed nonlinearity is closely related to the intrinsic lattice dynamics associated with the NIT in TTF-CA. It was suggested in the beginning that the formation of kink solitons and NIDW's are likely to be responsible for the microscopic mechanism. There are some features which are consistent with the concept of the soliton and NIDW models, as argued in the following.

In the $\log_{10}\sigma$-T^{-1} curves in Fig. 1, the curves exhibit a rather simple behavior in the low E region below T_C, showing a linear T^{-1} dependence and a nearly quadratic E dependence. Such a feature is just what is expected for a 1D Onsager model for geminate carrier recombination,[10] which predicts that the dissociation probability of oppositely charged carriers is proportional to the field and is independent of the temperature. Since soliton-antisoliton pairs are supposed to be generated below T_C,[3] it is quite likely that the field-induced dissociation of these pairs is responsible for the nonlinear conductivity observed at low fields below T_C.

On the other hand, above T_C the $\log_{10}\sigma$ curves are no longer linear with T^{-1} nor quadratic with field, indicating that the mechanism of the nonlinear conductivity substantially differs in the neutral and ionic states. In the neutral state near T_C, where the neutral and ionic states are nearly degenerate, there are several experimental results, such as a sharp increase in the conductivity[11,12] and the dielectric constant[13] with decreasing temperature, which indicate a participation of thermally activated NIDW's, as discussed before.[5,7,11-14] It is suggested that the same NIDW mechanism is also responsible for the nonlinear conductivity observed in the neutral state. A pair of oppositely charged NIDW's, which is analogous to a bipolaron in nondegenerate conjugated polymers like *cis*-polyacetylenes, is expected to have an electric dipole moment along the donor-acceptor stack. Then, the formation energy of the NIDW's will decrease linearly with field, in agreement with the experimental result. If one applies this interpretation to the explanation of the observed E dependence of $\log_{10}\sigma - T^{-1}$ curves above T_C, the averaged dipole moment of an NIDW pair is roughly estimated to be about 6×10^3 D, which corresponds to an average domain size of about 300 nm or 800–900 donor-acceptor unit length.

When the crystal is switched to the HCS, the nonlinear current can no longer be stable due to a negative-resistance effect. To explain this, one has to assume some

carrier multiplication process as discussed before by an phenomenological model. The physical description of this striking effect is a key point in the study of the nonlinear response of the TTF-CA crystal. Although its definitive origin is beyond our comprehension at the present stage, it will be helpful to consider a possible implication of experimental results. An important point to be noted is that the J-E curves above T_C tend to converge to a common curve in the negative-resistance region. This implies that carriers are self-multiplicated in a temperature-independent manner. It should be also noted that the slope of $\log_{10}\sigma - T^{-1}$ curves in the neutral state approaches an asymptote at high fields [see Fig. 1(a)]. A reasonable interpretation of these facts is that in the high-field region the NIDW's can be generated by field more easily than by thermal excitations. In the presence of such a high-density field-induced NIDW's, the carrier transport will become more and more correlated in space, for example between the neighboring donor-acceptor columns, by the Coulombic interaction. Once this kind of correlated motion occurs, it will be automatically expanded in crystal leading to an unstable negative-resistance effect. This interpretation is rather speculative, and needs to be substantiated by more extensive experimental and theoretical studies.

Finally, it will be interesting to investigate possible interrelation between the present switching effect and the current switching phenomena previously observed in some organic materials.[15,16] In particular, the switching effect in copper-tetracyanoquinodimethane (Cu-TCNQ) (and its derivative) CT crystals reported first by Potember, Poehler, and Cowan,[15] has been attributed to the solid-state reaction between the neutral and ionic states, i.e., $Cu^{+}TNCQ^{-} \rightleftarrows Cu^{0} + TCNQ^{0}$. Such a field-induced instability of the CT states, as observed in both crystals of TTF-CA and Cu-TCNQ, may have a common physical origin, which deserves a further comprehensive study. For this purpose, the availability of high-quality single crystals of TTF-CA will provide an further unique opportunity.

Many enlightening discussions with Dr. N. Nagaosa and Dr. Y. Iwasa are greatly appreciated. Thanks are also due to T. Arima and K. Fukagai for their experimental assistance.

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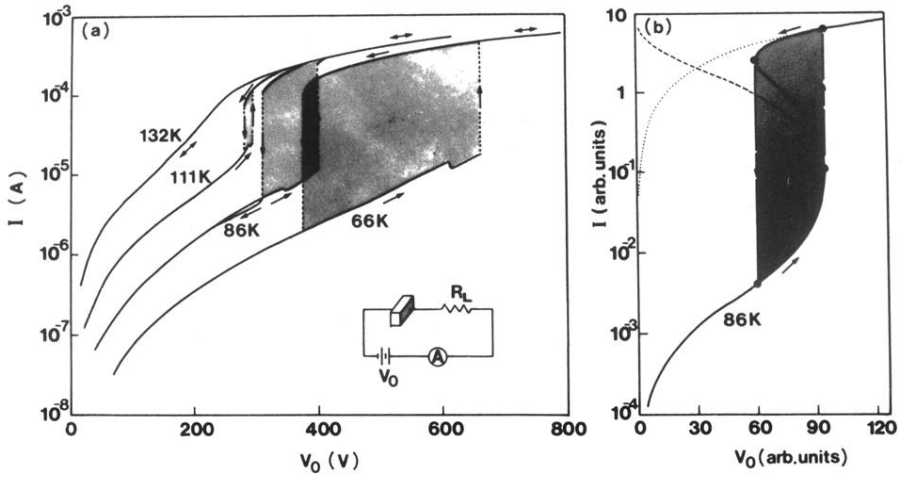

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