Domain-Wall Dynamics in Organic Charge-Transfer Compounds with One-Dimensional Ferroelectricity

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(Received 26 June 1989)

It has been widely observed in ionic donor-acceptor charge-transfer (CT) compounds that kink-type domain walls between one-dimensional ferroelectric molecular domains show strong dielectric response with a thermally activated relaxation frequency over a wide temperature range. The domain walls can carry spin and electric charge, which produce the anomalous charge-transport phenomena observed in this type of CT dielectric.

PACS numbers: 77.80.−e, 72.20.−i, 72.80.Le, 75.90.+w

Semiconducting or insulating organic charge-transfer (CT) compounds, which are composed of mixed stacks of alternating donor (D) and acceptor (A) molecules, can be classified into two categories, i.e., "neutral" and "ionic" compounds according to the degree of CT (ρ) within the stack ($\cdots D^{+\rho}A^{-\rho}D^{+\rho}A^{-\rho}\cdots$).[1-3] Fully ionic ($\rho=1$) compounds with the mixed stack possess $S=\frac{1}{2}$ spin on each molecule, whereas the neutral ($\rho=0$) DA stacks are diamagnetic in origin. Real compounds have an intermediate ρ value, yet this simplified picture of the spin state remains valid as long as we consider the effective interaction between spins in the quasi-ionic ($\rho>0.5$) compound. The effective exchange interaction between spins on D and A ions is of antiferromagnetic nature: It is given by the relation $J=-t^2/E_{\rm CT}$, when $E_{\rm CT}\gg t$. Here, t and $E_{\rm CT}$ stand for the CT interaction energy (electron transfer energy) and the CT excitation energy for the transition $D^+A^-\rightarrow D^0A^0$, respectively. Such an antiferromagnetic Heisenberg chain with $S=\frac{1}{2}$ is known to be vulnerable to the dimeric or bond-ordered-wave- (BOW-) type lattice distortion, which alternatively modulates the electron transfer t or the exchange energy J. The well-known example is the spin-Peierls transition observed in several segregated-stack CT compounds with rather weak exchange interaction J (<50 K).[4] The dimerization of $S=\frac{1}{2}$ spin sites leads to the formation of localized singlet pairs, which modifies the original spin-liquid states characteristic of the one-dimensional (1D) $S=\frac{1}{2}$ spin system with antiferromagnetic exchange interaction. Recently, Torrance[2] has pointed out that a quite similar magnetic phase transition associated with the BOW distortion is widely observed in a number of ionic CT compounds with DA mixed stacks, although they have a relatively large J ($=100$–1000 K). In this Letter, we report the first demonstration that such a magnetic phase transition spontaneously generates ferroelectric DA molecular domains with mobile spin- and charge-carrying domain walls in the 1D stacks. The domain-wall motion probed by dielectric measurements is of thermal-activation type and highly nonlinear with electric field, which explains anomalous charge-transport phenomena in this type of CT dielectric.

A hypothetically isolated D^+A^- stack, which is dimerized by the spin-lattice interaction, exhibits degenerate ground states, the IA phase and IB phase with opposite polarity of the domains, as shown in Fig. 1(a). As in the case of polyacetylenes $(\mathrm{CH})_x$,[5] the domain walls between the IA and IB phases are expected to behave as mobile kink-type defects or solitons. Extensive theoretical studies[6-8] on the DA-type CT solids as well as on the analogous diatomic polymers have predicted that there

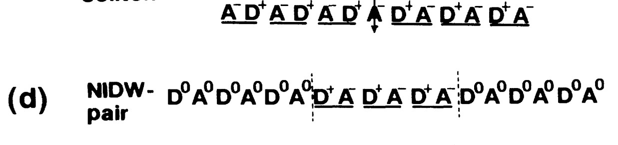

FIG. 1. Schematic structures of donor (D) and acceptor (A) stack: (a) dimerized stacks, (b) spin-0 solitons, (c) spin-$\frac{1}{2}$ solitons, and (d) a pair of neutral-ionic domain walls (NIDW's).

are two kinds of solitons, i.e., spin-0 solitons and spin-$\frac{1}{2}$ solitons, which are schematically illustrated in Figs. 1(b) and 1(c) for the case of the strong dimerization limit. In this simplified case, the spin-0 solitons (D^0- and A^0-type defects in the ionic stack) can carry electric charge. In real compounds, the ionicity of the *DA* stack is not exactly 1.0 and hence the both types of solitons with spin-0 and spin-$\frac{1}{2}$ can bear fractional charge.[6-8] Here, we should note that the dimerized D^+A^- regions sustain the permanent electric dipoles. Therefore, there kink solitons are nothing but the domain walls between the 1D ferroelectric domains and the motion of the charge-carrying solitons is the microscopic origin for the displacement current in this type of dielectrics. It has been pointed out[8-10] that a steady electric current in the ionic *DA* compounds may be carried by successive pairwise passing of spin-0 and spin-$\frac{1}{2}$ kink solitons.

Among several ionic mixed-stack CT compounds investigated, we show results on two prototypical examples. (i) TTF (tetrathiafulvalene)-BA (bromanil) (Ref. 11) and (ii) TTeC$_1$TTF [tetrakis(methyltelluro)tetrathiafulvalene]-TCNQ (tetracyanoquinodimethane).[12] Figure 2 shows the temperature dependence of the stack dimerization (top), the static magnetic susceptibility (middle), and the real part of dielectric constant (bottom) for each compound. The degree of stack dimerization was estimated by the normalized intensity (*A*) of a_g molecular vibrations in infrared-absorption spectra, which are originally optically inactive, but become strongly active in the dimerized stack due to the coupling with the CT excitation.[13] Among the data shown in Fig. 2, the results for the infrared-absorption intensity (*A*) and the magnetic susceptibility (χ) of TTF-BA are quoted from the paper by Girlando, Pecile, and Torrance.[11] We confirmed nearly identical behaviors using our own TTF-BA samples, on which we measured the dielectric constant and conductivity as well. Measurements of dielectric response were made on single crystals, if available, to examine the dielectric anisotropy, and otherwise on polycrystalline pellets. The dielectric constant in the frequency range of 100 Hz–10 MHz was deduced from the ac complex conductivity measured by using an *LCR* meter and an impedance analyzer.

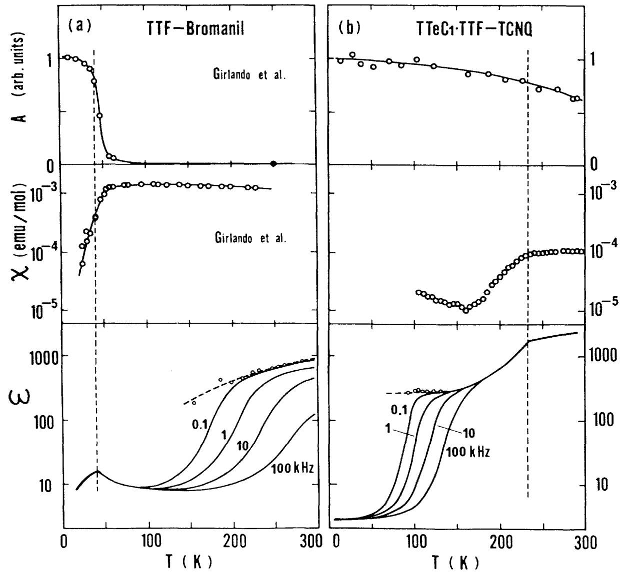

FIG. 2. Temperature dependence of the stack dimerization (top), the magnetic susceptibility (middle), and the real part of dielectric constant (bottom) in (a) TTF-BA and (b) TTeC$_1$TTF-TCNQ. Open circles connected by dashed lines in ϵ plots indicate the extrapolated value of dc ($f=0$) dielectric constant (see text).

First, concerning the temperature variation of the dimeric BOW distortion, these two compounds show contrasting behavior: In TTF-BA the BOW distortion (*A*) rises steeply around $T_c = 50$ K, whereas in TTeC$_1$TTF-TCNQ the distortion exists over the whole temperature range and shows little temperature dependence. In the former compound, the D^+A^- stack is essentially uniform well above T_c. Reflecting this, the magnetic data show fairly large χ values ($>10^4$ emu/mol) above T_c, which are well fitted by assuming the 1D spin-fluid state, such as by the Bonner-Fischer formula.[11] Below T_c, χ begins to decrease steeply, which is evidently correlated with the onset of dimeric distortion in the stack. This phenomenon is quite analogous to the spin-Peierls transition as first suggested by Torrance and co-workers.[2,11] On the other hand, χ in TTeC$_1$TTF-TCNQ is smaller by 1 order of magnitude at room temperature than that in TTF-BA, showing much decreased freedom of spins due to the formation of intradimer singlet pairs. However, the χ values above T_c remain nearly constant and are still too high to be ascribed to thermally excited triplet excitons within the static dimers. This implies that there is no long-range order in the BOW state at high temperatures, allowing generation of a number of spin-carrying defects. Also in TTeC$_1$TTF-TCNQ, we have observed the existence of a critical temperature T_c ($=240$ K), below which the magnetic susceptibility sharply decreases. Considering that there occurs no critical change in the local lattice distortion (*A*) at T_c, this phase change can be characterized by an order-disorder–type phase transition, in which the "liquid" state of the DA dimer condenses into the three-dimensionally ordered state.

The dielectric constant ϵ measured on polycrystalline samples of TTF-BA shows a cusplike anomaly at $T_c = 50$ K, as shown at the bottom of Fig. 2(a). Since polar stacks are generated by the dimerization of *DA* stacks below T_c, the observed sharp but not divergent ϵ hump implies antiferroelectric (out-of-phase) coupling between the neighboring polar *DA* stacks. On the other hand, in TTeC$_1$TTF-TCNQ the extremely large dielectric constant ($>10^3$) sharply drops at T_c ($=240$ K) in accord with the critical change in χ. The huge anisotropy ($\epsilon_{\parallel}/\epsilon_{\perp} > 50$) of the dielectric constant with respect to the direction of the stack axis is observed in a single crystal of TTeC$_1$TTF-TCNQ. [Figure 2(b) shows the parallel component $\epsilon_{\parallel}$.] Therefore, the large dielectric response in the disordered BOW state above T_c can be unambiguously attributed to the field-induced polarization change of fluctuating BOW clusters. Again, no divergent trend is observed at T_c, indicating that the low-temperature phase is of an antiferroelectric nature with 1D ferroelectricity.

Within the measured frequency (f) range between 10^2 and 10^6 Hz, remarkable f-dependent features in the dielectric response appear above T_c (=50 K) in TTF-BA and below T_c (=240 K) in TTeC$_1$TTF-TCNQ, giving rise to a seemingly f-independent feature near T_c in both cases. In the case of TTeC$_1$TTF-TCNQ [Fig. 2(b)], the dielectric response above T_c is very fast and is independent of f below 1 MHz. This indicates that the fluctuation of BOW domains is so rapid that its f-dependent feature is hardly detected. With decreasing temperature below T_c, however, the dielectric response slows down enough to be observed in the frequency range below 1 MHz, as seen in Fig. 2(b). The low-frequency component of ϵ maintains its large anisotropy ($\epsilon_{\parallel}/\epsilon_{\perp} > 50$) even below T_c, and hence such a temperature-dependent dynamical response must be correlated with the temperature-dependent motion of kink-type domain walls in the ordered BOW state. The f dependence of ϵ approximately obeys the Debye law, and its relaxation time (τ) shows thermal activation-type behavior with an activation energy (E_τ) of ≈ 0.15 eV, as expressed by $\tau^{-1} = \tau_0^{-1}\exp(-E_\tau/k_BT)$.

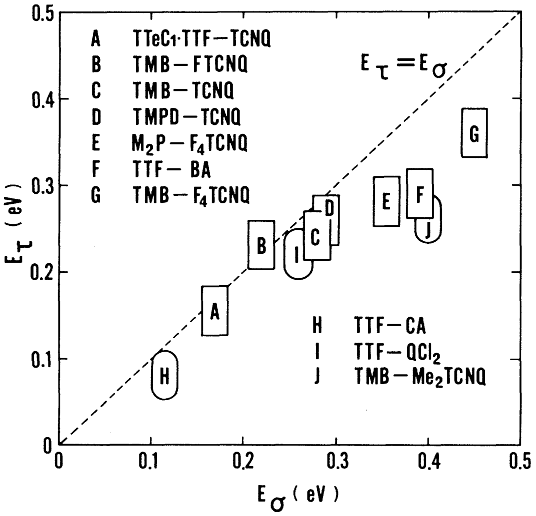

FIG. 3. Correlation between the thermal-activation energies for the low-field dc conductivity (E_σ) and for the dielectric relaxation time (E_τ) in CT compounds with quasi-ionic (rectangular box) and quasineutral (ellipsoid) DA stacks. Abbreviations: TMB=3,3′,5,5′ teteramethylbenzidine, M$_2$P=dimethylphenazine, TTeC$_1$TTF=tetrakis(methyltelluro)tetrathiafulvalene. CA=chloranil, BA=bromanil, xTCNQ=x-substituted TCNQ. TMPD=tetramethylphenylenediamine.

Such a thermal activation-type response has been commonly observed in a number of mixed-stack DA compounds (see Fig. 3) over a wide temperature range. Dashed lines connecting open circles in the ϵ plots of Figs. 2(a) and 2(b) represent the estimated dc ($f=0$) dielectric constants, which were obtained by an extrapolation procedure using the extended Debye formula.[14] In TTF-BA [Fig. 2(a)], the large low-frequency component of ϵ moves down to the f range below 100 Hz at temperatures below 150 K. Quite a similar dielectric response has been commonly observed in the other ionic DA compounds with nominally uniform stacks above T_c, a typical example being M$_2$P (dimethylphenazine)-TCNQF$_4$ (T_c=120 K).[15] In these CT compounds, the constituent molecules are centrosymmetric, and hence the observed large ϵ values cannot be attributed to the dielectric response of polar molecules nor side groups. Furthermore, the undamped low-frequency component of ϵ measured on single-crystal specimens, for example, on M$_2$P-TCNQF$_4$ crystals, shows a large anisotropy ($\epsilon_{\parallel}/\epsilon_{\perp} > 50$) at 300 K ($>T_c$).[16] These observations strongly suggest that even in nominally uniform DA stacks there exist charged-defect pairs, such as the charged solitons shown in Figs. 1(b) and 1(c), which may strongly respond to the electric field parallel to the stack axis. This phenomenon appears to be inherent to the large 1D fluctuation and will be hardly detected, for example, by ir spectroscopy, as a macroscopically observable BOW distortion except near above T_c [see Fig. 2(a)]. In this context, at low temperatures near T_c (=50 K) the domain-wall-type excitation in TTF-BA can no longer respond to the field for frequencies above 100 Hz and the ϵ anomaly observed around T_c is simply attributed to the softening of the ionic DA lattice as observed in conventional ion-displacement-type (anti)ferroelectrics.

In addition to these two kinds of BOW-related dielectric transitions, i.e., displacement- and order-disorder-type transitions, there is another important aspect in the organic CT dielectrics. That is the effect of the CT instability leading to the so-called neutral-ionic (N-I) transition.[9,10,17,18] When the compound is in the quasineutral but located sufficiently close to the N-I phase boundary, excitation of fluctuating ionic domains or equivalently pairs of neutral-ionic domain walls (NIDW's)[8] are possible due to the near degeneracy of the I phase and N phase as schematically shown in Fig. 1(d). The motion of NIDW's is expected to cause the large dielectric response as well as the effective transport of the domain-wall charges, just like the spin-0 solitons in the ionic BOW phase. A typical example is TTF-CA, which shows an N-I phase transition at T_c=81 K. A divergently increasing dc dielectric constant (more than 10^3 for the $E\parallel$stack component) is observed in the neutral phase with temperature decreasing toward T_c.[19] In fact, the existence of ionic domains or NIDW's has been confirmed in TTF-CA by spectroscopic methods.[17] Several neutral *DA* solids near the N-I phase boundary show a similar frequency- and temperature-dependent anisotropic dielectric response originating from the CT instability, although its effect is not so drastic as in TTF-CA. In those cases, the dielectric relaxation time relevant to the NIDW motion again obeys the thermal activation-type behavior.

As a final remark, we point out a significant experimental correlation between the activation energies for the dc conductivity (E_σ) and for the dielectric relaxation time (E_τ). (Note here that E_τ is *not* for ϵ itself, but for τ.) In Fig. 3 we have plotted the correlation between the two activation energies for the mixed-stack CT compounds we investigated. The straight line represents the relation $E_\sigma = E_\tau$, on which most of the data points approximately fall. This implies that pairs of oppositely charged species, such as BOW solitons and NIDW's, are responsible for the unusually large dielectric response when they are bound, and also for the charge transport when they are dissociated. This result leads us to the significant conclusion that the charge transport in *DA* mixed-stack compounds is primarily determined *not* by the *number* of thermally activated carriers, but rather by the thermally activated *motion* of existing charge carriers. The confinement of charged defect pairs is likely caused by the electrostatic interstack interaction of antiferroelectric nature. This assertion is consistent with the recent observation[10] that in all the *DA* CT crystals listed in Fig. 3 the electrical conductivity increases strikingly with the field (up to 10^4 times the low-field value), which has been explained in terms of field-induced decoupling of bound carriers. In accordance with this, the dielectric constants in the CT compounds show a strongly nonlinear dependence on the field and even change sign to be negative at low frequencies,[16] indicating the dissociation of confined domain walls into unbound free carriers under a strong electric field.

We thank Dr. H. Takagi and Professor S. Uchida for their help in the magnetic measurement. We acknowledge enlightening discussions with Professor T. Mitani, Dr. N. Nagaosa, and Dr. J. B. Torrance. This work was partly supported by a Grant-In-Aid from the Ministry of Education, Culture and Science, Japan.

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