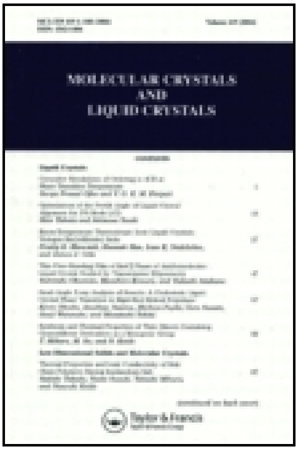

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Nonlinear Conduction in Quasi-1D Organic Systems

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Abstract Two theoretical models for the linear and nonlinear response of quasi-1D organic systems are critically investigated in comparison with experiments. The anomalous dielectric properties and the nonlinear switching phenomenon are discussed from the viewpoint of the soliton motion and the interchain coupling.

INTRODUCTION

The magnetic, electric, dielectric and optical properties of the charge transfer organic salts have been extensively studied experimentally as well as theoretically. We focus, in this paper, on the dielectric response[1] and the nonlinear transport properties[2] which has recently been observed in mixed-stack as well as segregated-stack charge transfer compounds. The basic picture we propose is that the kinks or the solitons (antikinks or the antisolitons) on the 1D chain carry charge and/or spin and invert the polarization[3]. The motion of these object gives rise to the d.c.current and the central peak in the dielectric function. The interchain interaction, on the other hand, confines the kink-antikink pair (soliton-antisoliton pair), reduces their number and hinders their free motion. The competition between these two, i.e., the thermal disordering due to the excitation of the kinks and solitons along the chain and the ordering effect due to the interchain interaction $J_\perp$, determines the 3D transition temperature T_c [3]. It should be noted that T_c is only weakly dependent on $J_\perp$, and $J_\perp$ can be order of magnitude smaller than T_c. The energy scale E_1 coming from the the applied electric field E is of the order of eEa where e is the minus of the electron charge, a is the lattice constant. Putting $E \sim 500\text{V/cm}$ and $a \sim 5\text{Å}$, we obtain the $E_1 \sim 0.2\text{K}$ which is quite smaller than the temperature

$T \sim 100\mathrm{K}$ at which the typical experiment is performed. The energy of the soliton E_S is of the order of 1000K and even larger than T. Then it is surprising that such a small energy triggers the switching at which the current jumps about two orders of magnitude. Then we look for other smaller energy scales. There is an energy scale which appears in the transfer matrix fromalism of the statistical mechanics of 1D chain. It is the " tunneling matrix element" $Q(\propto \exp(-E_S/T)$ between the two potential valleys , which represents the thermal disordering by the solitonic excitations. This Q competes with $J_\perp$ to determine T_c as discussed above. In summary, the relative magnitudes of the energy scales are

$$Q \sim J_\perp \sim E_1 << T << E_{\mathrm{soliton}}, \tag{1}$$

We discuss in this paper the dynamical aspects of the competition among the three lowest energies.

MODEL AND ITS LINEAR RESPONSE

The electron system interacting with each other and/or with the lattice can be described by the phase Hamiltonian;

$$\begin{aligned} H = \int \mathrm{d}x \Bigg[& A_\rho \left(\frac{\mathrm{d}\theta(x)}{\mathrm{d}x}\right)^2 + C_\rho p(x)^2 - B_\rho \cos 2\theta(x) \\ & + A_\sigma \left(\frac{\mathrm{d}\phi(x)}{\mathrm{d}x}\right)^2 + C_\sigma m(x)^2 + B_\sigma \cos 2\phi(x) \\ & + \sqrt{S} u(x) \cos\theta(x) \cos\phi(x) + u(x)^2 - \Delta \sin\theta(x) \cos\phi(x) \Bigg], \end{aligned} \tag{2}$$

where θ is the charge phase and ϕ is the spin phase. The slowly varing part of the polarization $P(x)$, the charge density $\rho(x)$ and the current densty $J(x)$ are given by $(e/\pi)\theta$, $-(e/\pi)\mathrm{d}\theta/\mathrm{d}x$ and $(e/\pi)\dot{\theta}$, respectively. If the inversion symmetry with respect to the midpoint between the neighboring molecules is absent as in the case of DA compounds, there appears also the polarization by the dimerization P_{dim} which is represented by $P_{\mathrm{dim}} \propto u(x) \propto \cos\theta \cos\phi$. In the case of segregated-stack charge transfer compounds, P_{dim} is absent. The coupling with the electric field $H_{\mathrm{electric\ \ field}}$ is given by

$$H_{\text{electric field}} = -\frac{eE}{\pi}\int dx\theta(x), \tag{3}$$

The possible ground states are represented as the points in the $\theta - \psi$ plane where the potential has a local minimum, while the soliton structures as the lines connecting these points. It should be noted that the neighboring ground states have the opposite sign of the dimerization, which are denoted by A and B phases, respectively.

Before going into the nonlinear conduction, we discuss the linear response. Tokura et al.[1] revealed the appealing relationship between the two activation energies E_σ and E_τ for the d.c.conductivity and for the inverse of the relaxation time τ^{-1} appearing in the Debye formula for the dielectric function, respectively. They found the approximate relationship $E_\sigma = E_\tau$ for the wide range of the charge transfer compounds includng both mixed-stack and segregated-stack types. They suggested that this activation energy is that of the hopping motion of the solitons assuming that the number of the solitons is temperature independent [Model 1]. However, the soliton number is temperature independent only in the two extreme cases. One is when the excitation energy of the soliton E_S is much smaller than the thermal energy, but the system should be disordered and we can not expect a three dimensional order in this case. The other case is the opposite limit, and one assumes that the soliton is introduced in an extrinsic way, e.g., in the process of the crystal growth. To sustain the d.c.current, however, the soliton should be continuously created because the initially existing solitons will annihilate. We persue another possibility as follows [Model 2]. We assume that the motion of the solitons can be treated in the continuum approximation, and the temperature dependence of its mobility is at most power behavior. In this picture, the peak in the dielectric response function is regarded as the central peak due to the inversion of the polarization which occurs every time the soliton passes the observation point. It is nescessary that the confining energy $J_\perp < u >$, where $< u >$ is the dimensionless dimerization order, is less than Q in order for this mechanism to be effective. The characteristic rate τ^{-1} is proportional to the number of the solitons and to $\exp(-E_S/kT)$ in the ideal soliton gas approxmation. In the overdamped case, the motion of the solitons becomes diffusive, and the average distance l which the soliton travel within the time t is proportional to $t^{1/2}$. Hence τ^{-1} is proportional to $\exp(-2E_S/kT)$. Because the d.c.conductivity σ is proportional to $\exp(-E_S/kT)$, one may be tempted to conclude that the relation $E_\sigma = E_\tau$ means that the motion of the solitons can be described in the ideal gas approximation. However, the above discussion can be applied only to the simple periodic potential where there is only one kind of the soliton. In the more realistic model, there are two kinds of the solitons, i.e., the charge soliton and the spin soliton with the energy E_{CS} and E_{SS}, respectively. The inversion of the polarization is possible by only one kind of the soliton with the lowest energy, but the d.c.conductivity is possible with the combination of the charge and spin solitons in the case of DA compounds. Hence $E_\sigma = \max(E_{CS}, E_{SS})$ while $E_\tau = b \cdot \min(E_{CS}, E_{SS})$ where $b = 1$ in the underdamped case and $b = \ \ 2$ in the overdamped case. Then it is possible that the motion of the soliton is diffusive ($b = \ \ 2$) and E_σ and E_τ represent the different soliton energies. In this case, the correlation of E_σ and E_τ is not so universal and we should look for a microscopic model which relates E_{CS} and E_{SS}. Another difficulty for this central-peak model [Model 2] is that the pronounced frequency dependence of the dielectric function is observed in the high temperature phase ($T > T_c$) of TTF-Bromanil[1] where the dimerization is already absent even locally. It may be possible that there remains the local dimerization which can not be detected by the infrared optical spectra, but the the recovery of the magnetic susceptibility χ above T_c will still remain a mystery. Lastly, the phenomenon is observed also for the segregated-stack spin-Peierls systems, which is also unfavorable for Model 2. However, the dimerization at low temperature is large in these systems, and maybe the inversion symmetry is broken. The detailed structural analysis at low temperature is desirable.

NONLINEAR SWITCHING PHENOMENON

Next we discuss the nonlinear response of the system to the electric field. The basic idea is as follows. Because the continuous flow of the θ phase is nescessary for the d.c.current, the phase changes as $\cdots \rightarrow \mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{A} \rightarrow \mathrm{B} \rightarrow \cdots$. In the low-conductive state, each single chain is under the influence of the ordering field from the other chains, which favors for example A phase than B phase. Then, the two solitons are somehow confined to reduce the B phase region. The thermal density of this combined object is determined by the sum of the two soliton energies $E_{A\to B}+E_{B\to A}$ which enters into the exponent as the activation energy. Also the nucleation process occurs directly from A to A or from B to B skipping the intermediate phase. Then the nucleation rate R for the soliton-antisoliton pair is proportional to $\exp(-2(E_{A\to B}+E_{B\to A})/T)$. The current I is proportional to $R^{1/2}$ and hence $\exp(-(E_{A\to B}+E_{B\to A})/T)$, which is the same temperature dependence as the thermal density of the combined solitons. In the high-conductive state, on the other hand, the ordering field is reduced and both the A and B phases are available. In this case, the solitons are deconfined to move independently, and the thermal density of the soliton from A(B) phase to B(A) phase is $E_{A\to B}$ ($E_{B\to A}$). The nucleation rate R is proportional to $\exp(-2E_{A\to B}/T)$ or $\exp(-2E_{B\to A}/T)$, and the activation energy for the current is $E_{A\to B}$ or $E_{B\to A}$ whichever is larger. Then we expect a jump in I of the order of $\exp(E_{A\to B}/T)$ or $\exp(E_{B\to A}/T)$, whichever is smaller. It should be noted that the high density of solitons, the high rate of nucleation, the equal probability of A and B phases and the small ordering field on each chain in the high-conductive state are self-consistently realized. Then, it is probable that the low- and high-conductive states are stable locally to result in the hysteresis of the $I-V$ curve. The above scenario assumes the continuum model [Model 2]. The dynamics when the discrete nature of the lattice is important ([Model 1]) will be more complicated, and further studies are needed in this direction.

In conclusion, we have discussed the linear and nonlinear response of the quasi-one-dimensional compounds. The solitons on the chain are assumed to be responsible for the peculiar features of the dynamics in these materials. Two models are compared with experiments, and each of them has its weak points. Further studies from both experimental and theoretical sides are highly desirable to have a clear picture of these phenomena.

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