VOLUME 50, NUMBER 24 PHYSICAL REVIEW LETTERS 13 JUNE 1983

Diatomic Polymers, Mixed-Stack Compounds, and the Soliton Lattice

B. Horovitz and B. Schaub

Department of Nuclear Physics, The Weizmann Institute of Science, Rehovot, Israel

(Received 9 March 1983)

The continuum electron-phonon system is studied for $(AB)_x$-type polymers with an average charge of $1+\hat{\rho}$ per site. For $\hat{\rho}=0$ spontaneous bond dimerization and soliton excitations are possible if $\alpha<\Delta_0$, where α is the intrinsic gap and Δ_0 is the spontaneous dimerization gap when $\alpha=0$. Recently observed neutral-to-ionic transitions in mixed-stack organic compounds are reinterpreted as the onset of such bond dimerization. For $\hat{\rho}\neq 0$ spontaneous order and a soliton lattice are found even if $\alpha \geqslant \Delta_0$. The electronic gap then has a maximum at a finite $\hat{\rho}$.

PACS numbers: 72.15.Nj, 64.70.Kb, 71.38.+i, 72.80.Le

Phase transitions and soliton excitations in both polymers and charge-transfer organic compounds are of considerable recent interest.[1] Theoretical predictions[2-5] that solitons exist in *trans*-polyacetylene have considerable support from both doping and photogeneration experiments.[1] The theoretical model for polyacetylene has been recently extended by Rice and Mele[6] to describe $(AB)_x$-type polymers; solitons then have irrational charge values.

The analog of an $(AB)_x$ polymer for a charge-transfer compound is a mixed-stack compound, where donor and acceptor molecules alternate along the stacking direction. It was recently found that such compounds undergo a "neutral to ionic" phase transition as a function of pressure or temperature.[7,8] Theories for such a transition consider the competition of the difference in on-site potentials (2α) with Coulomb energies,[7-9] predicting usually a first-order transition. Experimentally, however, the transition is continuous and involves an intermediate region where neutral and ionic features coexist. In particular tetrathiafulvalene-chloranil[8] shows a new infrared "ionic" mode coexisting with the "neutral" mode. This also implies a change in crystal symmetry.

Extensive early studies on a similar system, tetramethylphenylenediamine-chloranil,[10] revealed also a phase transition. From the splitting in the ESR line and its anisotropy it was concluded[10] that this transition also involves a symmetry change, namely a rotation of the chloranil ions. Here, however, optical absorption indicates that the system is "ionic" both below and above the transition.

Transfer integrals in these systems are fairly large[10] compared with α and the concept of "neutral" or "ionic" is not precise.[7,8] We propose instead that the order parameter for these transitions is bond dimerization, i.e., that donor-acceptor transfer integrals have alternating values. The charge is then continuously transformed from sites to bonds; this amounts to a change in the degree of ionization which is consistent with the changes in the optical absorption.[7,8] The driving force is the electron-phonon coupling, rather than Coulomb interactions.

The proposed transition does not involve a change in translation symmetry since the unit cell contains donor-acceptor pairs in both phases. Instead inversion symmetry at the center of a donor (or acceptor) molecule is broken. The existence of this inversion above the transitions[10,11] guarantees equal transfer integrals. Its absence below the transitions is consistent with the infrared[8] and ESR[10] data and it naturally explains why the Raman and infrared frequencies coincide.[12] This symmetry change is further supported by tetrathiafulvalene-fluoranil with only $P\bar{1}$ as space group[11]; the most likely symmetry to be broken (excluding translation[10]) is inversion.

The proposed (T,α) phase diagram is shown in Fig. 1; Δ_0 is the dimerization gap if all the molecules were equivalent ($\alpha=0$). The imposed site order competes with the spontaneous bond order and eliminates it if $\alpha>\Delta_0$. Under pressure Δ_0 can increase, by an increase in the transfer integral or electron-phonon coupling, and the system becomes ordered. For compounds with $\alpha<\Delta_0$ also reduction of temperature leads into the ordered phase.

These ideas are evaluated explicitly for the continuum model of $(AB)_x$ polymers, neglecting Coulomb interactions.[6] The model is solved also for the incommensurate system with an average charge density $\rho_0+\rho$, where ρ_0 corresponds to one electron per site. We find exact soliton lattice solutions which describe the $\rho\neq 0$ system. These solutions exist even if $\alpha\geqslant\Delta_0$, i.e., the commensurate ($\rho = 0$) system is *not* dimerized. Thus, solitons are self-generated—both the order parameter and the modulation in it which defines solitons are formed simultaneously.

We start from the continuum model of polyacetylene[5] describing electrons coupled to the acoustic ion displacement field $\Delta(x)$ in the adiabatic limit. The electrons are described by a spinor field $\psi_s^\dagger(x) = (u_s^\dagger(x), v_s^\dagger(x))$ of right- and left-moving electrons with spin s. The Hamiltonian is[5]

$$H_0 = \sum_s \int dx\, \psi_s^\dagger(x)[-iv_F\sigma_3\partial/\partial x + \Delta(x)\sigma_1]\psi_s(x) + \int dx\, \Delta^2(x)/2\pi v_F\lambda, \tag{1}$$

where σ_i are Pauli matrices, v_F is the Fermi velocity ($v_F = 1$ below), and λ is the dimensionless electron-phonon coupling. The ground state of this system has a gap $\Delta_0 = 2\Lambda\exp(-1/2\lambda)$ where Λ is a momentum cutoff. ($\frac{1}{2}v_F\Lambda$ is the A-B transfer integral.)

In the $(AB)_x$ polymer the alternating on-site energies $\pm\alpha$ lead to a gap 2α which is orthogonal to $\Delta(x)$; α favors a charge-density wave centered on the sites, while Δ favors it on the bonds. The total Hamiltonian is then

$$H = H_0 + \alpha\sum_s \int dx\, \psi_s^\dagger(x)\sigma_2\psi_s(x). \tag{2}$$

The ground state has an order parameter $\bar{\Delta} = (\Delta_0^2 - \alpha^2)^{1/2}$ for $\alpha < \Delta_0$ and no order ($\bar{\Delta} = 0$) for $\alpha \geq \Delta_0$. At a finite temperature T, $[\bar{\Delta}^2(T) + \alpha^2]^{1/2}$ follows the BCS gap equation and the transition temperature occurs when this gap equals α (Fig. 1). The transition is of second order, in agreement with data on mixed-stack compounds.[8,10] When $\alpha > \Delta_0$ reduction of temperature is not sufficient to induce the phase transition, but increase of Δ_0 (e.g., by pressure) is sufficient.

For $\bar{\Delta} \neq 0$ the ground state is twofold degenerate corresponding to $\pm\bar{\Delta}$, and solitons are possible excitations.[6] The soliton charge Q is readily evaluated from the counting rule[13]: If $\Delta\theta$ is the change in phase of the off-diagonal term $\Delta(x) + i\alpha$ between degenerate ground states then $Q = \Delta\theta/\pi$. Since here α is constant and $\Delta(x)$ changes between $\pm\bar{\Delta}$, we obtain $Q = \pm(2/\pi)\tan^{-1}(\bar{\Delta}/\alpha)$, in agreement with the direct derivation.[6] Additional 2π rotations do not change the topology, and amount to ± 2 additions to the soliton charge. The additional rotation can be made for only one spin component, resulting in ± 1 additions to the soliton charge and the presence of spin $\frac{1}{2}$. Thus the counting rule is an efficient method for evaluating soliton charges.

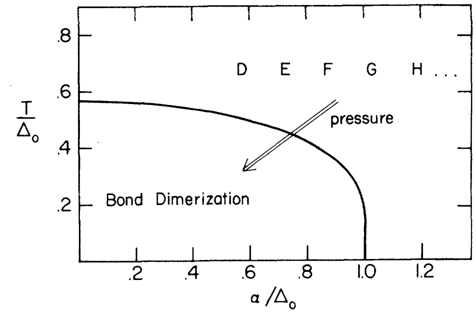

FIG. 1. T,α phase diagram for Eq. (2) in the commensurate case. Compounds $A-Z$ are defined in Table I of Ref. 7. They are placed at their expected position at room temperature. A phase transition is induced by either temperature change in compounds D (Ref. 10) and F (Ref. 8) or by pressure change in compounds $E-L$, N, and Q (Ref. 7).

Soliton lattice solutions can be found by a mapping into the sine-Gordon system.[14] Define $f_n(x) = u_n(x) + iv_n(x)$ for the electron eigenfunctions with eigenvalues ϵ_n. The electron equations of motion reduce to

$$[\epsilon_n^2 + \alpha^2 + \partial^2/\partial x^2 - \Delta^2(x) + \Delta'(x)]f_n(x) = 0, \tag{3}$$

with the normalization $\int |f_n(x)|^2 dx = (\epsilon_n + \alpha)/\epsilon_n$ and eigenvalues restricted to $|\epsilon_n| \geq \alpha$. The equation of motion for $\Delta(x)$ in the adiabatic limit is $\delta\langle H\rangle/\delta\Delta(x) = 0$. This yields the self-consistency equation,

$$\Delta(x) = -\pi\lambda[\Delta(x) + \tfrac{1}{2}\partial/\partial x]\sum_n{}' |f_n(x)|^2/(\epsilon_n + \alpha), \tag{4}$$

where the prime indicates summation on occupied states and $\epsilon_n + \alpha \neq 0$.

The potential in Eq. (3) is given in terms of a solution of the classical sine-Gordon equation[14] with Eq. (4) determining its mass parameter Δ_1. In terms of the Jacobian elliptic function $\mathrm{sn}(u, k)$ with parameter k we obtain

$$\Delta(x) = \frac{\Delta_1 k}{1 + k'}\,\mathrm{sn}\left(\frac{x\Delta_1}{k}(1 + k'), \frac{1 - k'}{1 + k'}\right). \tag{5}$$

$\Delta(x)$ has a periodicity of $l = 2kK/\Delta_1$ where $K = K(k)$ is a complete elliptic integral. In each period $\Delta(x)$ vanishes twice, representing two solitons with charges Q (or $-Q$) and $2 - Q$ (or $Q - 2$). The average charge density (added to ρ_0) is then $\rho = \pm 2/l$.

The electronic spectrum has three gaps with valence band, conduction band, and two midbands. The midbands are separated from each other by a gap 2α at wave vector $q=0$, and from the valence or conduction bands by a gap $E_g=\Delta_1 k/(1+k')$ at $q=\pm\pi/l$. The midbands are generated either empty or full so as to accomodate precisely the charge $\rho=\pm 2/l$; the valence band is full and the conduction band is empty.

By use of the known eigenfunctions[15] of Eq. (3) it is straightforward to see that Eq. (4) is valid, with the parameter Δ_1 satisfying

$$\ln\frac{\Delta_1}{\Delta_0}=-\frac{\alpha^2 k^4}{2\Delta_1^{\,2}}\int_0^1\frac{x}{R^3(x)(1-k'^2x^2)^{1/2}}\ln\frac{1+x}{1-x}\,dx. \tag{6}$$

Here

$$R(x)=[1-k'^2x^2+(k\alpha/\Delta_1)^2(1-x^2)]^{1/2}$$

and $k'^2=1-k^2$; finite-cutoff effects[14] are neglected, implying weak coupling, $\lambda \ll 1$.

The gap $E_g=\Delta_1 k/(1+k')$ can be considered as the order parameter of the system. The solutions of Eq. (6) for E_g as a function of $\rho=\Delta_1/kK$ are plotted in Fig. 2. For $\alpha<\Delta_0$, $E_g(0)=\overline{\Delta}\neq 0$ and decreases as a function of ρ, except for $0.98<\alpha/\Delta_0<1$ where $E_g(\rho)$ has a maximum at a finite ρ.

The most interesting situation is found for $\alpha \geqslant \Delta_0$. In this case the commensurate system is not ordered ($\overline{\Delta}=0$), and the charged excitations are extended electrons or holes. However, as soon as $\rho\neq 0$ a finite order parameter representing localized solitons is generated. It reaches a maximum at a finite ρ (Fig. 2). Thus the addition of charge to a nondimerized system enables the bond ordering to be spontaneously formed.

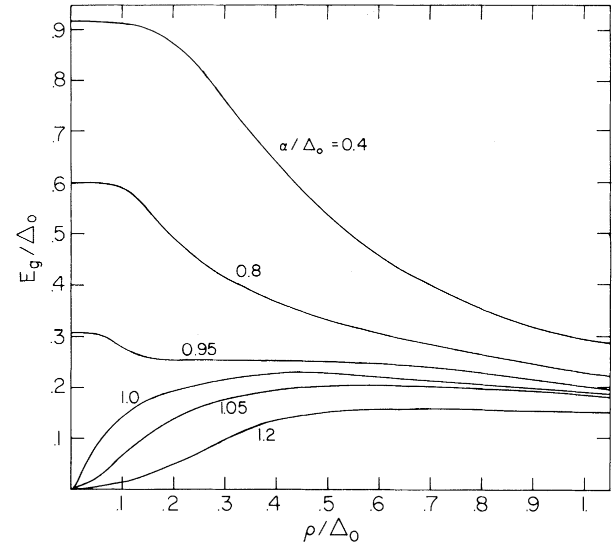

FIG. 2. Gap in the electron spectrum at the Fermi level as function of the excess charge density ρ. (Note $v_F=1$.)

We can understand this peculiar behavior by considering momentum space where the gap E_g is formed at $q=\pm\pi\rho/2$ while the gap 2α remains at $q=0$. Thus for $\rho\neq 0$ the competition between the gaps E_g and α is weakened and a finite E_g appears.

Consider next the energy of the soliton lattice E_{s1}, relative to the energy of the commensurate ($\rho=0$) phase. A straightforward summation, $\sum' \epsilon_n$, with the lattice energy yields

$$\begin{aligned}E_{s1}={}&\frac{2\Delta_1^{\,2}}{\pi k^2}\left(\frac{E}{K}-\frac{1}{2}k'^2\right)+\frac{1}{2\pi}(\Delta_0^{\,2}-\alpha^2-\Delta_1^{\,2})+\frac{\alpha^2}{\pi}\ln\frac{\Delta_1}{k\Delta_0}\\&+\frac{\theta(\alpha-\Delta_0)}{2\pi}\left(\alpha^2-\Delta_0^{\,2}-2\alpha^2\ln\frac{\alpha}{\Delta_0}\right)+\frac{\Delta_1^{\,2}}{\pi k^2}\left(1+k'^2-\frac{2E}{K}\right)\ln\frac{\Delta_1}{\Delta_0}\\&+\frac{\alpha^2k^2}{\pi}\int_0^1 dx\left\{-\frac{1}{2}\left(1+k'^2-\frac{2E}{K}\right)\frac{x}{R(x)(1-k'^2x^2)^{3/2}}\ln\frac{1+x}{1-x}\right.\\&\left.+\frac{(1+k^2\alpha^2/\Delta_1^{\,2})(1+k'^2x^2)-2k'^2x^4(k'^2+k^2\alpha^2/\Delta_1^{\,2})}{R^3(x)(1-k'^2x^2)^2}\,k\ln\frac{k+(1-k'^2x^2)^{1/2}}{(1-x^2)^{1/2}}\right\},\end{aligned} \tag{7}$$

where E, K are complete elliptic integrals and $\theta(\alpha-\Delta_0)$ is a step function. A low-density expansion of Eqs. (6) and (7) yields for the energy per soliton (here $\alpha<\Delta_0$)

$$\frac{E_{s1}}{\rho}=\frac{2\overline{\Delta}}{\pi}+\frac{2\alpha}{\pi}\sin^{-1}\frac{\alpha}{\Delta_0}+\frac{8\overline{\Delta}^2}{\pi\alpha}\sin^{-1}\frac{\alpha}{\Delta_0}\exp\left(\frac{-2\overline{\Delta}}{\rho}\right)\quad(\rho\to 0). \tag{8}$$

The first two terms are the single soliton energy (average of the two types) while the last term represents the long-range interaction between solitons. This interaction is exponential and repulsive; it tends to zero as $\alpha\to\Delta_0$ for a fixed overlap between solitons (i.e., fixed $\rho/\overline{\Delta}$). The energy per soliton from Eq. (7) is plotted in Fig. 3 as function of ρ/Δ_0 and of $\rho/\overline{\Delta}$. In the latter case the weaker repul-

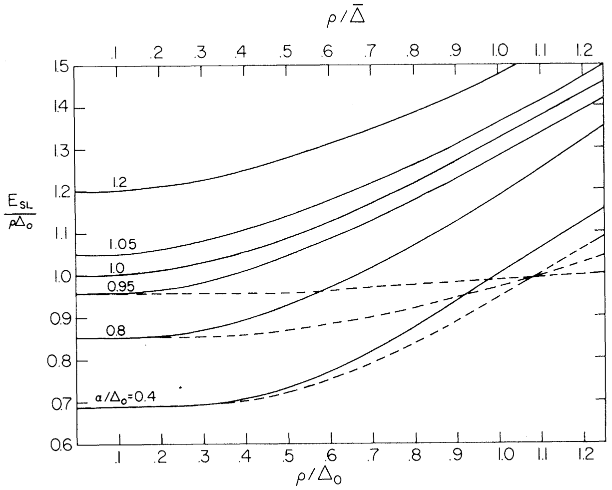

FIG. 3. Energy of the soliton lattice per soliton as function of ρ/Δ_0 (full curves) and as function of $\rho/\bar{\Delta}$ (dashed curves).

sion as $\alpha \to \Delta_0$ is apparent. For $\alpha > \Delta_0$ and $\rho \to 0$ the curves approach $E_{sl}/\rho = \alpha$, the energy of adding a single electron or hole to the nondimerized ($\bar{\Delta} = 0$) system.

Finally, we discuss the experimental relevance of these results. Solitons in general and fractional charge in particular are intriguing possibilities in $(AB)_x$ polymers or in mixed-stack compounds. An efficient method for detecting such charged excitations is their infrared activity.[6,16] Their thermal excitation should lead to new infrared modes whose intensity is *temperature activated.* This activity is in fact consistent with the large dielectric constant of tetrathiafulvalene-chloranil and its decrease with lowering temperature.[17] The split ESR line may also indicate the presence of such solitons.[9]

Most of the relevant systems (e.g., see Fig. 1) have $\alpha > \Delta_0$ and do not order at low temperatures. Upon doping with excess donors or acceptors we expect a phase transition at low temperatures into an incommensurate charge-density wave. The transition temperature and the electronic gap at low temperatures should both have a maximum at a finite doping level.

We wish to thank D. Mukamel for very helpful discussions and J. B. Torrance for a useful correspondence. This research was supported in part by a grant from the U. S.–Israel Binational Science Foundation, Jerusalem, Israel, and by the Minerval committee.

---

[1] For recent reviews, see Proceedings of the International Conference on Synthetic Low Dimensional Conductors and Superconductors, Les Arc, 1982 (to be published).

[2] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979), and Phys. Rev. B 22, 2099 (1980).

[3] S. A. Brazovskii, Pis'ma Zh. Eksp. Teor. Fiz. 28, 656 (1978) [JETP Lett. 28, 606 (1978)], and Zh. Eksp. Teor. Fiz. 78, 677 (1980) [Sov. Phys. JETP 51, 342 (1980)].

[4] M. J. Rice, Phys. Lett. 71A, 152 (1979).

[5] H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B 21, 2388 (1980); B. Horovitz, Phys. Rev. B 22, 1101 (1980).

[6] M. J. Rice and E. J. Mele, Phys. Rev. Lett. 49, 1455 (1982).

[7] J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, Phys. Rev. Lett. 46, 253 (1981).

[8] J. B. Torrance, A. Girlando, J. J. Mayerle, J. I. Crowley, V. Y. Lee, P. Batail, and S. J. LaPlaca, Phys. Rev. Lett. 47, 1747 (1981).

[9] J. B. Torrance, in Ref. 1.

[10] G. T. Pott and J. Kommandeur, Mol. Phys. 13, 373 (1967).

[11] J. J. Mayerle, J. B. Torrance, and J. I. Crowley, Acta Crystallogr., Sec. B 35, 2988 (1979).

[12] A. Girlando, R. Bozio, C. Pecile, and J. B. Torrance, Phys. Rev. B 26, 2306 (1982).

[13] Y. Frishman and B. Horovitz, Phys. Rev. B 27, 2565 (1983); T. L. Ho, Phys. Rev. Lett. 48, 946 (1982); B. Horovitz, Phys. Rev. Lett. 48, 1416 (1982).

[14] B. Horovitz, Phys. Rev. Lett. 46, 742 (1981).

[15] A. L. Fetter and M. J. Stephen, Phys. Rev. 168, 475 (1968); B. Sutherland, Phys. Rev. A 8, 2514 (1973).

[16] E. J. Mele and M. J. Rice, Phys. Rev. Lett. 45, 926 (1980); B. Horovitz, Solid State Commun. 41, 729 (1982).

[17] G. Gruner and J. B. Torrance, private communication.