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AMPLITUDE SOLITONS IN INCOMMENSURATE PEIERLS SYSTEMS: IMPLICATIONS FOR TTF–TCNQ

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Amplitude soliton excitations are described for both dimerized [i.e. commensurate with $2k_f = (\pi/a)$] and incommensurate charge-density-wave (CDW) ground states. For the dimerized case the soliton excitations can have charge $+e, 0, -e$ with spin $0, \pm\frac{1}{2}, 0$ depending on the occupancy of the localized gap state. For the incommensurate case only the neutral spin-$\frac{1}{2}$ soliton exists. Utilizing the results of Takayama, Lin-Liu and Maki, we show that $E_s = (2/\pi)\Delta$ where 2Δ is gap for electron–hole excitations ($\Delta_i = W \exp(-1/\lambda)$ for the incommensurate case and $\Delta_c = W \exp(-\frac{1}{2}\lambda)$ for the dimerized case where λ is the electron–phonon coupling constant and W is the bandwidth). We suggest that neutral soliton excitations may make significant contributions to the magnetic susceptibility of incommensurate CDW systems, and that this may be the origin of observed differences between the low-temperature magnetic and transport activation energies in TTF–TCNQ.

RECENTLY there has been significant progress in the theoretical description of the interacting electron–phonon system in quasi-1d materials which exhibit Peierls-charge-density wave (CDW) instabilities. Su, Schrieffer and Heeger [1] (SSH) and Rice [2] discussed the formation of solitons in the half-filled band case [$2k_f = (\pi/a)$] where the electron concentration is such that the Fermi vector is exactly commensurate with the chain periodicity, as is the case for polyacetylene. They concluded that an amplitude soliton could exist with order parameter $\Delta(n) = \Delta_0 \tanh(na/l)$, where a is the lattice constant, l is the half-width of the soliton, and n denotes the position along the chain. With the formation of such a soliton (either as a defect, a thermal excitation or through doping) there is an associated electronic bound state at an energy in the middle of the Peierls gap. Depending on the occupancy, the electronic state could have charge $0, \pm e$ with spin $\frac{1}{2}, 0$ respectively. The "neutral-spin $\frac{1}{2}$" soliton could contribute to magnetic susceptibility, but not to electrical conduction. The SSH calculation was carried out in detail in a cell-localized basis set, from which the order parameter and electronic Green's functions can be obtained for either the spatially uniformly dimerized system, or for one with a soliton (antisoliton, or pair).

An alternative approach to this class of problems has been via the Luttinger double linear-band basis [3–5], using a two-state spin or electronic wave function which slowly modulates the Fermi-level electronic states in a continuum representation. The coupled ion-displacement and electron Green's-function equations of motion are derived and depend on an order parameter $\tilde{\Delta}(x)\, e^{i\tilde{\varphi}(x)}$. In the mean-field approximation for the electrons, and to leading order in time and space derivatives, approximate differential equations governing $\tilde{\Delta}$ and $\tilde{\varphi}$ have been derived and solved [5] (and references therein); but these differential equations involve approximations that are invalid if $\tilde{\Delta} - 0$. Unfortunately, the amplitude soliton demands just this condition at its center. Takayama, Lin-Liu, and Maki [6] (TLM), have recently solved directly the integral equation resulting from the equations of motion and the self consistency condition on the electron distribution by methods analogous to those used for the Bogoliubov–de Gennes equation [7]. Of central importance in our discussion here is that: first, TLM find that a neutral-spin $\frac{1}{2}$ gap soliton with $\tilde{\Delta}(x) \propto \tanh(x/l)$ is indeed a proper solution (without derivative approximations); second, upon examination we now conclude that their calculation is applicable with slight modification to both the incommensurate and commensurate cases (as we will discuss below); third, TLM's computed neutral soliton energy $E_s = (2/\pi)\Delta_i$ implies a low-temperature paramagnetic susceptibility with an activation energy of $(2/\pi)\Delta_i$ where $2\Delta_i$ is the energy gap for excitation of

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electron–hole pairs. We suggest this is a possible solution to the long standing question of the observed differences between the low temperature magnetic and transport activation energies in TTF–TCNQ. One of us (B.H.) [8] has also extended the treatment to include Coulomb effects in the Hartree–Fock approximation; the results imply that the gap soliton solution survives in this more general case and $E_s = (2/\pi)\Delta_i$ still applies.

In the continuum limit, the electron field operator in the two branch basis is written as

$$c_{n,s} = u_s(n)\, e^{ik_f na} - iv_s(n)\, e^{-ik_f na} \tag{1}$$

and the ion displacement field is taken to be a classical field

$$F_n = A[\Delta^+(n)\, e^{i2k_f na} + \Delta(n)\, e^{-2ik_f na}]. \tag{2}$$

In the limit where the spinor $\Psi \equiv (u_s, v_s)$ and Δ^+, Δ vary slowly with site n one replaces na by the continuous variable x; A is defined by an electron–phonon coupling parameter α. In this representation the Hamiltonian written in terms of intersite hopping matrix elements modulated by ion displacements is transformed to ($\hbar = 1$)

$$\begin{aligned} H = \sum_s \int dx \Bigg\{ & -iv_f \left[u_s^+(x) \frac{\partial}{\partial x} u_s(x) - v_s^+(x) \frac{\partial}{\partial x} v_s \right] \\ & + [\Delta^+(x) + \eta\Delta(x)]\, u_s^+(x) v_s(x) + [\Delta(x) \\ & + \eta\Delta^+(x)]\, u_s^+(x) v_s(x) \Bigg\} + (2\pi\lambda v_F)^{-1} \\ & \times \int dx [2\Delta^+(x)\Delta(x) + \eta\Delta^2(x) + \eta\Delta^+(x)^2]. \end{aligned} \tag{3}$$

In the above, v_F is the Fermi velocity and λ is the dimensionless electron–phonon coupling parameter $(4\alpha^2 a/\pi v_F k)$, where k is the phonon elastic stiffness. For the commensurate case, $2k_F = \pi/a$ (e.g. the dimerized structure of $(CH)_x$) and $\eta = 1$, while for the incommensurate case $\eta = 0$. This difference can be traced to the extra contribution of umklapp terms near the commensurate condition. Note that for $\eta = 0$ the Hamiltonian is identical to that studied by TLM.

The equations of motion of the single-particle wave function (indices: "l" level, "s" spin) take the form

$$\begin{aligned} -iv_f \frac{\partial}{\partial x} u_{l,s}(x) + \tilde{\Delta}^+(x) v_{l,s} &= \epsilon_l u_{l,s}(x) \\ iv_f \frac{\partial}{\partial x} v_{l,s}(x) + \tilde{\Delta}(x) u_{l,s} &= \epsilon_l v_{l,s}(x) \end{aligned} \tag{4a}$$

where $\tilde{\Delta}(x) = \Delta(x) + \eta\Delta^+(x)$, (4b)

Summing on occupied states, the variation of H with respect of $\tilde{\Delta}$ yields the self-consistency condition

$$\tilde{\Delta}(x) = -\lambda\pi v_f \left[\sum_{l,s} (u_{l,s}^* v_{l,s} + \eta u_{l,s} v_{l,s}^*) \right]. \tag{5}$$

Equation (4) is identical in form to that given by TLM [their equation (7)]; however their consistency condition [their equation (8)] corresponds to the incommensurate case with $\eta = 0$. Thus, the mathematical analysis of TLM can be taken over exactly to the incommensurate case, and the amplitude soliton thus found leads to the bound state

$$u_b(x) = iv_b(x) = (\Delta_i/4v_f)^{1/2} \operatorname{sech}(\Delta_i x/v_f), \tag{6a}$$

$$\Delta(x) = \Delta_i \tanh(\Delta_i x/v_f), \tag{6b}$$

$$\Delta_i = W e^{-(1/\lambda)} = \tilde{\Delta} = \text{real}. \tag{6c}$$

Here W is the nominal band width and Δ_i is the incommensurate case Peierls gap. The excitation energy of this state relative to the ground state as calculated by TLM is $(2/\pi)\Delta_i$, and the consistency condition, equation (5) can be satisfied with Δ_i real only for the neutral soliton. That is, if the bound state is singly occupied with either spin then the sum over band states just cancels the imaginary term $[u_b^*(x)v_b(x)]$. Multiply occupied, charged, solitons cannot be described by equations (6) in this incommensurate case. Instead, $\tilde{\Delta}$ must be complex, consistent with the known result that excess charge density may be defined by the gradient of the phase of the order parameter of in an incommensurate Peierls condensate with $|\Delta| = \text{constant}$.

Consistency in the dimerized commensurate case is more straightforward; $\eta = 1$ in equation (4b) implies $\tilde{\Delta}(x)$ is manifestly real and the TLM soliton solutions are valid for occupancies 0, 1, 2 corresponding to charges $+e$, 0, $-e$ and spin 0, $\frac{1}{2}$, 0 respectively (within the present one-electron approximation, which may be quite good if the soliton state is rather spread out). The (real) ion displacements are directly proportional to $\tilde{\Delta}(x)(-1)^n$ [by substitution in equation (2)]; the bound state has the form $\Delta_c \tanh(x/l)$ where

$$\Delta_c = W e^{-1/2\lambda}. \tag{7}$$

This gap is larger than that of the incommensurate case by the factor $(e^{1/2\lambda})$. These results are, of course, just those of SSH.

Summarizing briefly, we envisage several types of excitations: charged or neutral gap-solitons in dimerized commensurate materials, and neutral gap-solitons (magnetically active). Charged phase solitons may be induced in an incommensurate Peierls chain by an additional periodic field [5, 9].

The possibility of neutral solitons in dimerized polyacetylene has been discussed extensively [10]. However, the experimental consequences of neutral amplitude solitons in an incommensurate CDW system such as TTF–TCNQ have not yet been explored. The existence

of such neutral spin $\frac{1}{2}$ excitations would lead to a contribution to the paramagnetic susceptibility of the form

$$\chi = N_s(T)\mu_B^2/kT \tag{8}$$

per chain of unit length where $N_s(T)$ is the number of thermally excited amplitude solitons given by

$$N_s(T) = \frac{\sigma}{a}\exp\left(-\frac{2}{\pi}\Delta/kT\right) \tag{9}$$

where a is the lattice constant and σ is an entropy factor. Including the number of chains per unit area, the molar susceptibility is written.

$$\chi = N(\mu_B^2/kT)\exp\left[-\frac{2}{\pi}\left(\frac{\Delta}{kT}\right)\right] \tag{10}$$

where N is Avogadro's number.

The circumstantial evidence in support of the idea of neutral paramagnetic solitons in the low temperature semiconducting phase of TTF–TCNQ is interesting. Schultz and Craven [11] review the experimental evidence on conductivity and magnetic susceptibility, particularly in the range $10\,\text{K} \lesssim T < 39\,\text{K}$ where ordering in the low temperature phase is complete. Studies of (TTF–TSeF) TNCQ alloys [11–14] have been particularly useful in establishing that the TTF chains dominate the low temperature electronic properties. In the low-temperature regime, the conductivity is activated with $\Delta = \frac{1}{2}E_g = 200 \pm 25\,\text{K}$ [11]. On the other hand, the magnetic susceptibility, which is dominated by the TTF chains, has a smaller activation energy measured by various groups to be 125 [13], 140 [15] and 150 K [14b]. Taking the view that the conductivity has activation energy Δ_t and that the magnetic susceptibility is due to neutral paramagnetic solitons with activation energy $(2/\pi)\Delta_t$, one would expect a magnetic activation energy of 127 K, in tempting agreement with experiment. Moreover, the absolute magnitude of the measured susceptibility is in agreement with the prefactor of equation (10). On the other hand, the susceptibility from band excitations would have a prefactor smaller by a factor of order $(2\Delta/W) \sim 10^{-2}$ for TTF–TCNQ. We note that the neutral magnetic solitons would have a half-width of $l \sim \hbar v_F/\Delta \sim 30$ Å, and being extended objects might be quite mobile.

A number of additional theoretical and experimental factors must be considered to clarify the possible role of neutral soliton excitations in the incommensurate CDW states of the quasi-1*d* charge transfer salts. The model presented above represents a single chain. While the amplitude soliton under consideration is both globally and locally neutral (SSH), the moment of the local charge distribution changes sign between opposite sides of the soliton. Thus, interchain effects must be given serious consideration. Indeed, the need for broader considerations is required by the experimental results on $(TTF_{1-x}TSeF_x)(TCNQ)$ alloys; the experiments show that in TSeF–TCNQ, $\Delta_{cond} \simeq \Delta_{mag}$. However, it is also true that the low-temperature ordering is different (period of $4a$ for TTF–TCNQ and $2a$ for TSeF–TCNQ) and the local fields therefore must differ [16].

We recognize the need for addressing analytically such further properties as interchain effects, soliton interactions, multiple soliton states, and the energetics of phase vs. amplitude solitons in incommensurate systems; however, for now we prefer simply to air the main idea of amplitude solitons in incommensurate materials.

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NOTE ADDED IN PROOF

Dr. S. Brazowski, (Landau Institute of Theoretical Physics, USSR) has called our attention to his work on this subject. In an earlier paper, *JETP Lett.* [*Sov. Phys. JETP Lett.* 606 (1979)], he discusses tight-binding polarons in the Peierls state and shows that in the Fröhlich model an amplitude soliton solution, with zero charge and spin $\frac{1}{2}$ is obtained; its energy is different from ours, being at the middle of the gap (rather than $2/\pi$ of the gap). In a subsequent paper *JETP* 78, 677 (1980) he provides extensive further discussion and addresses interchain effects. He addresses the consequences for optical, electrical, and magnetic properties. In the main his views coincide with ours, and we are happy to acknowledge his prior work on this problem.