Theory of Metal-Insulator Transition in Peierls Systems with Nearly Half-Filled Bands

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It is shown that a metal-insulator transition takes place in a Peierls system with half-filled bands at a critical concentration, $c_{\rm cr}$, of excess electrons. At $c < c_{\rm cr}$ the electrons form pinned (chaotic) soliton states; at $c > c_{\rm cr}$ the solitons form an unpinned conducting lattice. We find $c_{\rm cr} = a^2/\pi^2 l_0^2$, where l_0 is the width of the solitons. The theory may explain the metal-insulator transition observed in doped polyacetylene at $c_{\rm cr} \sim 1\%$.

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Recently it has been proposed by several authors[1-6] that when a Peierls system with half-filled bands (and corresponding dimerization of the lattice) is chemically doped with donors or acceptors, the excess electrons or holes form localized soliton states rather than going into higher-lying bands. In the one-soliton state the lattice distortion at the nth site may be written

$$u_n = (-1)^n \Delta_0 \Delta_n, \qquad \Delta_n = \Delta(n) = \tanh(na/l_0), \tag{1}$$

where a is the lattice constant and Δ_0 the distortion in the dimerized state. The solitons are thus amplitude solitons with width l_0 rather than the phase solitons which are usually used to describe commensurate-incommensurate transitions.[7] The estimates of l_0 are in the range $2.8a < l_0 < 7a$.[1,2,6]

In this paper we show analytically and numerically that at a critical dopant concentration the system undergoes a transition from an insulating (or semiconducting) state where the solitons are pinned to the lattice, to a conducting state where the solitons form a regular lattice of their own. The critical concentration depends *only* on the soliton width, $c_{\rm cr} \sim a^2/\pi^2 l_0^2$. We believe that this may explain the metal-insulator transition observed in polyacetylene,[8] and the depinning transition in $\rm NbSe_3$.[9]

The energy of the system, expressed in terms of the lattice distortion, may be taken to be of the discrete φ^4 form

$$E = \sum_{n=-\infty}^{\infty} \tfrac{1}{2}\lambda(\Delta_n - \Delta_{n-1})^2 + V(\Delta_n), \tag{2}$$

where $V(\Delta_n)$ is the double-well potential

$$V(\Delta_n) = \gamma(\Delta_n^2 - 1)^2. \tag{3}$$

In the continuum approximation the energy becomes

$$E_{\rm cont} = \int_{-\infty}^{\infty} [\tfrac{1}{2}\lambda(d\Delta/dn)^2 + \gamma(\Delta^2 - 1)^2]\, dn. \tag{4}$$

The stable configurations fulfill the Euler-Lagrange equation[10]

$$\lambda d^2\Delta/dn^2 - 4\gamma\Delta(\Delta^2 - 1) = 0 \tag{5}$$

which has the soliton solution (1) with $l_0/a = (\lambda/2\gamma)^{1/2}$. In general, the solution to (4) is a soliton lattice with distance $l = a/c$ between solitons. The soliton lattice is conducting since the solitons are charged ($\pm e$) and the lattice can be shifted along x without any cost of energy. We shall now see that if the discreteness is taken into account this is not the case: If the solitons are too far apart (at low concentrations) the exponential repulsion between solitons cannot overcome the energy gain from locking the solitons to the lattice, and the solitons will be pinned. The analogous consideration relating to discrete sine-Gordon solitons was used by Pokrovsky.[11] A different approach leading to the conclusion about the pinning of the solitons was developed by Aubry.[12]

Let us first estimate analytically the critical concentration. The energy (2) is written as

$$E = \sum_{m=-\infty}^{\infty} \int dn\, E(n) \exp(i 2\pi nm) = \int_{-\infty}^{\infty} dn\, E(n) + 2\int_{-\infty}^{\infty} dn\, E(n) \cos(2\pi n) + \cdots, \tag{6}$$

with $E(n) = \frac{1}{2}\lambda(d\Delta/dn)^2 + V(\Delta(n))$. The first term is the continuum approximation. When $\Delta(n) = \tanh[(na - x_0)/l_0]$ is inserted, the second term is a periodic function of the soliton position x_0 which is maximized when $x_0 = 0$, and gives an estimate of the pinning energy

$$E_{\mathrm{pin}} = 2\int_{-\infty}^{\infty} 2V(\Delta(n))\,dn = 4\int_{-\infty}^{\infty} dn\,\frac{\gamma\cos(2\pi n)}{ch^4(na/l_0)} \sim \frac{16\pi^4}{3}\gamma\left(\frac{l_0}{a}\right)^4 \exp\left(\frac{-\pi^2 l_0}{a}\right) \tag{7}$$

for $l_0/a \gg 1$. The pinning energy thus decreases exponentially with l_0, as could be expected.[11] The soliton interaction energy can be derived by expanding the energy of the soliton lattice in terms of the soliton concentration c for small c (within the continuum approximation):

$$E = LcE_s[1 + C\exp(-a/l_0C) + \cdots]. \tag{8}$$

The second term is the soliton interaction, E_{int}, and $E_s = \frac{4}{3}(2\gamma\lambda)^{1/2}$ is the soliton energy. The transition takes place when $E_{\mathrm{pin}} = E_{\mathrm{int}}$ or, for $l_0/a \gg 1$,

$$c_{\mathrm{cr}} = a^2/\pi^2 l_0^{\,2}. \tag{9}$$

The critical concentration depends on nothing but the soliton width! At small l_0, Eq. (9) may underestimate c_{cr} because of the large numerical factor in Eq. (1).

The critical concentration can be found, probably more accurately, by numerical methods. The Δ_n's which minimize (2) are found among the solutions to an infinity of coupled difference equations

$$\begin{aligned}(\Delta_{n+1} - \Delta_n) - (\Delta_n - \Delta_{n-1})\\ = (4\gamma/\lambda)\Delta_n(\Delta_n^{\,2} - 1).\end{aligned} \tag{10}$$

Introducing $W_n = \Delta_n - \Delta_{n-1}$ this defines a recursion relation for W_n (and Δ_n):

$$\begin{aligned}W_{n+1} &= W_n + (4\gamma/\lambda)\Delta_n(\Delta_n^{\,2} - 1),\\ \Delta_{n+1} &= \Delta_n + W_{n+1}.\end{aligned} \tag{11}$$

Figure 1 shows the results of computer iterations for $l_0 = a(\lambda/2\gamma)^{1/2} = 4a$, which may be a good estimate for polyacetylene,[1,2,6] and for $l_0 = 1.5a$, where the effects of discreteness are more pronounced. Initial values of the parameters were chosen as regularly spaced points $(\Delta_{\mathrm{in}}, W_{\mathrm{in}})$ on the $W_n = 0$ axis. The interpretation of the various trajectories is quite analogous to the interpretation in the discrete sine-Gordon case.[11,13]

The fixed points P_1 and $P_2 = (\pm 1, 0)$ are the two symmetric dimerized states with no extra electrons or solitons. The closed orbits around (0, 0) are invariant trajectories associated with incommensurate conducting states. As the iteration proceeds, the points (Δ_n, W_n) form a continuous curve. The sliding mode can be described by simply choosing initial values of Δ_{in} and W_{in} which are slightly shifted along the trajectory. Since the curve which is eventually traced out is exactly the same, the energy of the shifted state is also the same. A charge $\pm 2e$ is associated with each revolution around (0, 0), and so the system exhibits Fröhlich conductivity. Near (0, 0) where the amplitude (the Peierls gap) is small, the lattice distortion is almost sinusoidal. The period is also small and so the state is highly incommensurate. As the amplitude becomes larger and larger, the invariant trajectories describe states which more and more take the form of soliton lattices, at least for $l_0 = 4a$, but the system is still conducting. The islands marked 1–8 for $l_0 = 1.5a$ describe a high-order commensu-

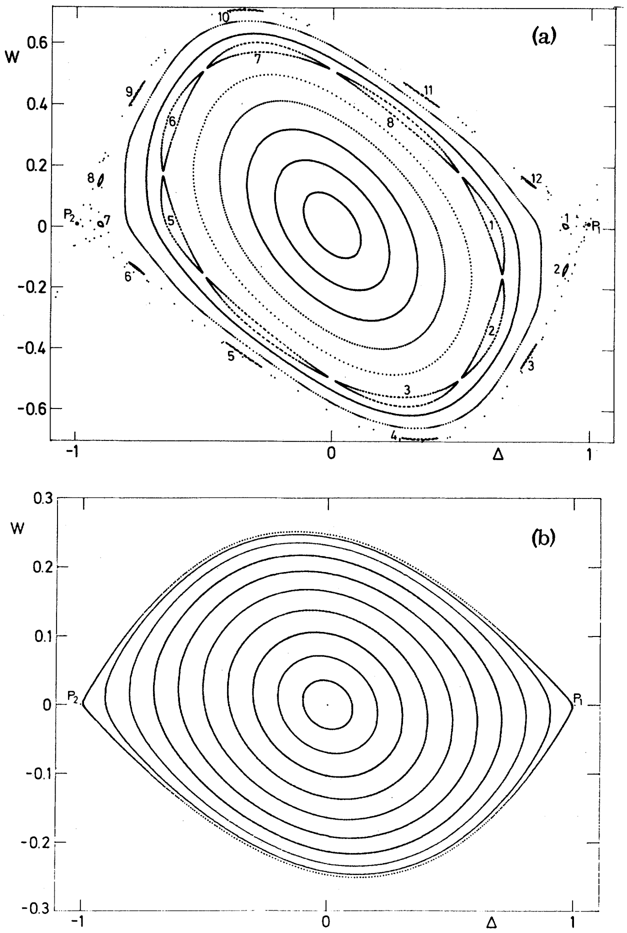

FIG. 1. Results of computer iterations of Eq. (11) for (a) $l_0 = 1.5a$ and (b) $l_0 = 4a$.

rate state where the distance between solitons is $4a$, which is stable for $c=\frac{1}{4}$.

When the average distance between solitons (for sufficiently large Δ_{in}) exceeds a critical value l_{cr} ($=a/c_{\text{cr}}$) no regular incommensurate solutions exist but the iterations exhibit *chaotic* behavior.[11,13] In the chaotic regime metastable states are formed by random distributions of pinned solitons. The lowest-energy states at a given concentration can be found by using methods developed in Ref. 11. These states are *insulating* since it is not possible to move the solitons without a cost of energy. The islands 1–12 in the chaotic regime describe a high-order commensurate phase which is not surrounded by conducting trajectories. This C phase is stable only for $c=\frac{2}{12}$. We find the following critical concentrations:

$l_0=1.5a$: $c_{\text{cr}} \sim 20\%$

$l_0=4a$: $c_{\text{cr}} \sim 1.78\%$.

These values are somewhat higher than the analytical estimate Eq. (9). The chaotic regime is extremely narrow for $l_0=4a$ and is not visible on the figure. The critical concentration compares very favorably with the one observed in *trans*-polyacetylene,[8] where at $c_{\text{cr}} \sim 1\%$ the conductivity changes by several orders of magnitude.

The pinning energy for $l_0=4a$ is extremely low ($\sim 10^{-5}\gamma$) and so for an *isolated* chain the solitons would be effectively depinned even at very low temperatures. However, three-dimensional interactions cannot be ignored, even in polyacetylene, and the pinning energy should be multiplied by an effective number of interacting chains. The solitons are walls rather than isolated kinks in a three-dimensional system.

An electric field will also depin the solitons. The critical field E_{cr}, above which the solitons are freely moving, is given by

$$E_{\text{cr}}a=E_{\text{pin}}. \tag{12}$$

The pinning energy is extremely sensitive to the soliton width, and it is difficult to give reliable estimates, say for polyacetylene. In the charge-density-wave system NbSe_3 a depinning transition at a critical field has actually been observed.[9] The wave vector is almost commensurate [$\vec{q}=(0, 0.243, 0)$][14] and the system could be in the chaotic regime. Our mechanism would then provide a simple explanation for this transition.

When applying the theory to polyacetylene it should be borne in mind that this material is far from an ideal crystalline system as assumed here. It has been suggested that the transition is actually a Mott-like transition, where the solitons are bound to impurities up to a critical concentration.[8,15] Beyond this concentration the bound states are destroyed. A transition based on this mechanism would probably be smeared, whereas the mechanism presented in this paper is intrinsic and gives a sharp transition like the one actually observed.

Finally we estimate the role of Coulomb interaction. One has to subtract the energy of the regularly arranged solitons from the total energy. The energy associated with the deviation u of a soliton from its equilibrium position is $E_Q=e^2u^2/2\epsilon l^4$ (per unit length), where ϵ is the dielectric constant. For $l_0=4a$ and $\gamma=\lambda/32$, $\epsilon\approx 10$, and with use of the previously obtained values, we find $E_Q/E_{\text{pin}}\approx 0.15$.

To summarize, we have shown that a Peierls system described by the phenomenological model defined by Eqs. (4) and (5) with half-filled bands necessarily undergoes a transition from an insulating phase to a conducting phase at a critical excess concentration of electrons. The theory gives a possible explanation of the metal-insulator transition in *trans*-polyacetylene and the depinning transition in NbSe_3.

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Role of Disorder in Photoelectrochemical Solar Cells with Polycrystalline Photoanodes

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This paper reports measurements of electrical impedance versus frequency on photoelectrochemical solar cells and metal-insulator-semiconductor junctions using polycrystalline, electrodeposited n-CdSe electrodes. A simple power law in frequency for the photoelectrochemical cell impedance is interpreted in terms of a percolation conduction at the semiconductor-electrolyte interface with use of arguments supported by measurements on this and related systems.

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Electrical impedance spectra with a simple power law in frequency have been observed for *bulk* systems such as composites exhibiting percolation conduction or semiconductors with random doping or potential distributions and exhibiting hopping conduction.[1] We report on the *in situ* complex electrical impedance-versus-frequency spectra for photoelectrochemical (PEC) solar cells with electrodeposited CdSe photoanodes in either polysulfide or sulfide-free electrolyte. The spectra for both systems are consistent with a percolation-dominated conduction. For the first time, we demonstrate a systematic experimental approach to locate the source of the disorder and determine that the semiconductor-electrolyte *interface* is responsible for the disorder-dominated conduction.

The PEC solar cells with a polysulfide ($S^{-2}/S/NaOH$ 1:1:1M) electrolyte and a Ni counterelectrode show promising stability and have approximately 80% peak quantum conversion efficiency. The best cells have achieved a simulated terrestrial efficiency of 6%. We show in Fig. 1 the impedance spectra for a PEC cell with an electrodeposited CdSe photoanode. These spectra cannot be described in terms of a finite, resolvable set of parallel, frequency-independent RC elements. However, these spectra are consistent with the