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INTERSOLITON HOPPING TRANSPORT OF ELECTRONS IN QUASI 1-DIMENSIONAL MOLECULAR CRYSTALS

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Abstract Phonon-assisted electron hopping between solitons may contribute substantially to transport in the quarter-filled-band, quasi 1-dimensional (1d) compounds that exhibit large Coulomb repulsion between two electrons on the same site. We have calculated the intersoliton hopping rate for intramolecular- and acoustic-phonon-mediated hopping, and used this to find electron mobilities. Evaluation for the case of (N-methylphenazinium)$_{.54}$ (phenazine)$_{.46}$ tetracyanoquinodimethanide [(NMP)$_{.54}$(Phen)$_{.46}$TCNQ] gives a maximum mobility at 100K between .06 and 1.0 cm^2/V-sec, due to intramolecular-phonon-assisted hopping.

INTRODUCTION

Quarter-filled-band quasi-1d crystals with large Coulomb repulsion for two electrons on the same site ("large U" in the Hubbard model) have effectively a Peierls-distorted half-filled band of singly occupiable states. Such crystals, as Rice and Mele[1] have shown, can support the formation of singly occupiable soliton states in the Peierls gap.

An electron can make a phonon-assisted hop from an occupied to an empty soliton state and contribute to transport in these crystals. The analogous intersoliton electron hopping process in polyacetylene [(CH)$_x$] was studied by Kivelson.[2] We find significant differences between the hopping processes in the molecular crystals and in (CH)$_x$. In the following we outline the procedure used to

find intersoliton hopping rates, mobilities, and the thermopower due to hopping, and we evaluate the mobility for the case of the near-quarter-filled-band large-U crystal $(NMP)_{.54}(Phen)_{.46}TCNQ$ (a 4% donor-doped crystal which, according to the theory of Rice and Mele,[1] contains an 8% concentration of negatively charged solitons at T=0). A complete exposition of procedures and results can be found elsewhere.[3]

CALCULATION OF TRANSITION RATES

In calculating the intersoliton electron hopping rates, we make use of the method of Miller and Abrahams[4] for finding the hopping rate between defects in semiconductors. We consider two solitons, i and j, centered far enough away from each other so that overlap is small. One charged donor (or acceptor) is located nearby. Using the continuum Hamiltonian of Takayama, Lin-Liu, and Maki[5] we find a total Hamiltonian H for the system in the absence of phonons. When phonons are present, an additional term in H arises, and the matrix element $< H_q >$ of this term with the wavefunctions ψ_i and ψ_j determines the intersoliton hopping rate due to a phonon of wave vector q.

Transition rates $\nu_{ij}(E_j,E_i)$ from soliton i to soliton j are found by using Fermi's Golden Rule and inserting $< H_q >$ for either intramolecular or acoustic modes. These rates depend on E_i and E_j, the soliton energy levels on site i and site j, respectively; to find the total transition rate we sum over all allowed E_i and E_j for the transition with appropriate statistical weights. We have considered three different hopping processes, each with a different distribution of E_i and E_j:

1) hopping from a deep potential well around soliton i(strongly bound to a dopant) to soliton j, which in turn becomes bound to the dopant. The energy of the phonon assisting in the hop is taken up in the difference between initial and final vibrational levels on solitons i and j, respectively. This case will be applicable to solitons

strongly pinned to dopants (e.g. at low temperatures) such that an effective continuum of vibrational levels exists inside the potential wells (analogous to Kivelson's case for $(CH)_x$); 2) hopping of an electron from the potential well of soliton i (bound to a dopant) to soliton j which remains unpinned; 3) hopping from an unpinned soliton i with kinetic energy to an unpinned soliton j which then becomes bound in the final state to an oppositely charged dopant. These last two processes would be predominant either at high temperatures or in cases where solitons are weakly bound to dopants.

Using the total transition rates $\bar{\nu}$, we find the maximum mobility due to the electrons in the soliton levels from

$$\mu \simeq \frac{|e|\,\bar{\nu}\,R^2}{k_B T} \qquad (1)$$

where R is the average hopping distance (determined by soliton concentration) and $k_B T$ is Boltzmann's constant times temperature. This would be a maximum μ for the given spacing since it assumes that all sites are available to receive the electron.

MOBILITIES IN $(NMP)_{.54}(PHEN)_{.46}TCNQ$

The methods described above have been applied to the quarter-filled-band, large-U crystal $(NMP)_{.54}(Phen)_{.46}$ TCNQ, which has an 8% soliton concentration at all T's.[6] From the resultant mobilities we draw three principal conclusions:

1) Offchain (or 3-d) hopping is negligible compared to on-chain (1-d) hopping; $\bar{\nu}^{3d} \sim 10^{-4}\,\bar{\nu}^{1d}$ due to large interchain spacing in the molecular crystals; 2) Acoustic-phonon assisted hopping is quite ineffective, i.e., $\mu \sim 10^{-6}$ $cm^2/V\text{-sec}$ for this process, due to the large mass of the TCNQ molecule along the conducting chain, and weak coupling to the acoustic modes; 3) Intramolecular-phonon assisted hopping leads to substantial on-chain hopping mobilities; at T=100K,

these are in the range $\sim$ .06 to 1. cm^2/V-sec, depending on the exact process considered. Thus solitons may give a direct contribution to the conductivity.

THERMOPOWER DUE TO INTERSOLITON HOPPING

Following the method of Emin,[7] we have also calculated the contribution to the thermopower from intersoliton electron hopping in the molecular crystals. For hopping between a pinned soliton with binding energy E_b and a free soliton, we find the contribution to the thermopower, Q, to be

$$Q = \frac{k_B}{e}\left\{-\frac{E_b}{2k_BT} - \frac{\varepsilon_F}{k_BT}\right\} \quad , \qquad (2)$$

where ε_F is the Fermi energy of the system, and the electronic levels associated with the soliton are taken to be at midgap (the zero of energy). The "extra" term, $-E_b/2k_BT$, in addition to the usual hopping term, $-\varepsilon_F/k_BT$, reflects the fact that each soliton site has a multiplicity of possible energy levels (i.e., at $-E_b$ and at zero energy in this case). This term arises from the different spectrum of states for pinned and for free solitons. Thus the solitons may be expected to directly contribute to thermopower as well as conductivity.

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