CHARGE TRANSPORT IN CHARGE TRANSFER SALTS BY ORDER PARAMETER FLUCTUATIONS

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ABSTRACT

The conduction mechanism in Charge Transfer Salts (CTS) with 1:2 donor to acceptor ratio is investigated. These systems can be characterized by two different order parameters, each corresponding to different realisations of a gap at the Fermi surface. One is the usual Peierls dimerization, the other corresponds to a uniform shift of donor molecules, which induces an alternating potential on the acceptor chain. We show that small, coherent variations of these two-fold order parameter provide a cooperative charge transport mechanism. We argue that this mechanism accounts for some anomalous electrical transport phenomena recently found in substituted morpholinium TCNQ₂ compounds.

INTRODUCTION

This paper deals with charge transfer salts with 1:2 donor to acceptor ratio, complete charge transfer and TCNQ as acceptor [1]. In this case the electron-electron interaction (Hubbard's U) is much larger than the bandwidth [2], which justifies us in taking the limit of infinite interaction. The proper Hamiltonian reads [3]

$$\mathcal{K} = \sum_i (t + (-1)^i \tau) (c_{i+1}^\dagger c_i + \text{h.c.}) + E \sum_i (-1)^i n_i \quad (1)$$

where τ is related to an alternation of the charge transfer integral within the unit cell due to a distance alternation between adjacent TCNQ molecules. E denotes the alternation in local potential, which is a consequence of an asymmetric positioning of the donor molecule with respect to the neighbouring acceptor

molecules. Fig. 1 shows the generalized schematic configuration within the unit cell together with the phonon spectrum. The gap, Δ , in the electron spectrum is

$$\Delta = 2(4\tau^2 + E^2)^{\frac{1}{2}} \quad (2)$$

and the electron distribution in the ground state is given by

$$\rho_{e/o} = \frac{1}{2} \pm \frac{1}{\pi} \left(\left(\frac{2t}{E} \right)^2 + 1 \right)^{-\frac{1}{2}} K \left(\frac{1 - \left(\frac{\tau}{t} \right)^2}{1 - \left(\frac{E}{2t} \right)^2} \right) \quad (3)$$

where K is a complete elliptic integral of the first kind. Fig. 2 shows the electron distribution and its dependence on both τ and E .

Consider a system in which E and τ are constant over a (microscopically) large region, the initial state being $(\tau - \frac{1}{2}\delta\tau, E - \frac{1}{2}\delta E)$ with an electron occupation of ρ on odd-numbered sites and $1-\rho$ for even sites. Now, a change in the order parameters $\tau - \frac{1}{2}\delta\tau \rightarrow \tau + \frac{1}{2}\delta\tau$ and $E - \frac{1}{2}\delta E \rightarrow E + \frac{1}{2}\delta E$ will result in an electron occupation of $\rho + \delta\rho$, resp. $1-\rho - \delta\rho$. Since for all sites the overlap with the left-hand neighbour differs 2τ from the right-hand overlap, the charge flow which establishes the new equilibrium will have a preferential direction, i.e., will result in a current. This statement can be made quantitative by using Fermi's golden rule: the transition probability for an electron to hop from one site to another is proportional to the square of the overlap. This implies that the prob-

Fig. 1. Model for the 1:2 CTS lattice and its phonon spectrum.

Fig. 2. (E, τ) -parameter space. The drawn lines are contours of equal ρ for the ground state. Revolution along Γ produces a net charge flow as seen from the insert. Fat (thin) arrows indicate large (small) transfer integrals.

ability difference for charge flow from an even-numbered site to the left or right equals

$$P(\leftarrow) - P(\rightarrow) = \frac{(t + \tau)^2 - (t - \tau)^2}{(t + \tau)^2 + (t - \tau)^2} = \frac{4t\tau}{2t^2 + 2\tau^2} \approx \frac{2\tau}{t} \text{ for } \tau < t$$

Since in the above-described change in the parameter space an amount of charge $d\rho$ is redistributed we have for the amount of charge (δQ) that passes along all even sites:

$$\delta Q = \delta\rho \cdot (P(\leftarrow) - P(\rightarrow)) = \delta\rho \cdot \frac{2\tau}{t} \quad (4)$$

Or, more general

$$\Delta Q = 2 \int_{\text{parameter space}} d\rho \cdot \frac{\tau}{t} \quad (5)$$

where the integral is taken over parameter space and its value will depend not only on the end and starting points but also on the path in between. Note that for odd sites both $d\rho$ and $(P(\leftarrow) - P(\rightarrow))$ change sign, which implies that δQ is site-independent and an overall shift of the electron gas is accomplished. It is important that generally Q is non-zero if one integrates over a closed loop in parameter space, as the reader may verify by considering fig. 2. For a small closed trajectory one has

$$q_{\text{eff}} = \oint d\rho \frac{2\tau}{t} = \oint \frac{2\tau}{t} \left[\left(\frac{\partial \rho}{\partial E} \right) \cdot dE + \left(\frac{\partial \rho}{\partial \tau} \right) \cdot d\tau \right] \approx \left(\frac{\partial \rho}{\partial E} \right) \frac{2A}{t} \quad (6)$$

where q_{eff} is the transported charge and A the area of the closed loop. Since charge is transported by going along any closed trajectory, an electric field will manifest itself as a force in (E, τ) -space.

We conclude that coherent variations of the two order parameters τ and E can give rise to the cooperative motion of the electron gas, which is impossible for a commensurate system with just a single order parameter.

OPTICAL PHONONS

So far, we have dealt with a hypothetical chain with a charge density distortion which was correlated over the entire chain. In the actual situation of a CTS, the ground state will be characterized by a set of order parameters E^* and τ^* , and at finite temperature lattice vibrations will cause small, local fluctuations of these order parameters. Since τ and E can be defined at unit cell level and are determined by intra unit cell distances, variations of τ and E should be attributed to optical phonons. As a consequence of the above discussed charge transport arising from variations in E and τ , the optical phonon modes with τ - and E -character respectively will be coupled by the electric

field. If we treat the phonons classically, we can write the local, time-dependent order parameters in terms of phonon contributions:

$$\tau(\mathbf{x}, t_R) = \sum_k \tau_k \sin(k\mathbf{x} - \omega_{\tau,k} t_R + \phi_{\tau,k}) \quad (7a)$$

$$E(\mathbf{x}, t_R) = \sum_k E_k \sin(k\mathbf{x} - \omega_{E,k} t_R + \phi_{E,k}) \quad (7b)$$

The phonons themselves are - for the unperturbed lattice - solutions of the equations of motion

$$M_{\tau} \ddot{\tau}(\bar{\mathbf{x}}) - K_{\tau} \tau_{\mathbf{xx}}(\bar{\mathbf{x}}) + M_{\tau} \omega_{\tau, \text{opt}}^2 \tau(\bar{\mathbf{x}}) = 0 \quad (8a)$$

$$M_E \ddot{E}(\bar{\mathbf{x}}) - K_E E_{\mathbf{xx}}(\bar{\mathbf{x}}) + M_E \omega_{E, \text{opt}}^2 E(\bar{\mathbf{x}}) = 0 \quad (8b)$$

M_{τ} , M_E denote effective masses; K_{τ} , K_E are spring constants. $\bar{\mathbf{x}}$ denotes the two-vector of place ($\mathbf{x}$) and time (t_R), while $\tau_{\mathbf{xx}}$ and $E_{\mathbf{xx}}$ are the second derivatives of τ and E with respect to position. If an electric field is present, an external force F_{τ} (F_E) will appear on the r.h.s. of eq.(8a,b) as a consequence of electron-phonon coupling. For the external force (exerted by an electric field) on a generalized coordinate q , one has $F_q = -dW/dq$, where dW is the work done by the electric field (ϵ), which equals $\epsilon \cdot \delta Q$ and δQ is given by eq.(5). This yields

$$\begin{aligned} F_{\tau}(\bar{\mathbf{x}}) &= \lim_{\Delta\tau(\bar{\mathbf{x}}) \rightarrow 0} - \frac{\Delta W}{\Delta\tau} = \lim_{\Delta\tau(\bar{\mathbf{x}}) \rightarrow 0} - \frac{2\epsilon}{t \cdot \Delta\tau(\bar{\mathbf{x}})} \int_{(E, \tau)}^{(E, \tau + \Delta\tau)} d\rho(\bar{\mathbf{x}}) \cdot t(\bar{\mathbf{x}}) \\ &= - \frac{2\epsilon\tau(\bar{\mathbf{x}})}{t} \cdot \left(\frac{\partial \rho}{\partial \tau} \right)_{\tau(\bar{\mathbf{x}}), E(\bar{\mathbf{x}})} \end{aligned} \quad (9a)$$

and likewise

$$F_E(\bar{\mathbf{x}}) = - \frac{2\epsilon\rho(\bar{\mathbf{x}})}{t} \left(\frac{\partial \rho}{\partial E} \right)_{\tau(\bar{\mathbf{x}}), E(\bar{\mathbf{x}})} \quad (9b)$$

Combining (9) and (8) and transforming to k -space we find that the phonon modes obey the relations:

$$\ddot{\tau}_k(t_R) + \omega_{\tau,k}^2 \tau_k(t_R) = \frac{-2\epsilon}{M_{\tau} t} \left(\frac{\partial \rho}{\partial \tau} \right)_{\tau^* E^*} \cdot \tau_k(t_R) \quad (10a)$$

$$\ddot{E}_k(t_R) + \omega_{E,k}^2 E_k(t_R) = \frac{-2\epsilon}{M_E t} \left(\frac{\partial \rho}{\partial E} \right)_{\tau^* E^*} \cdot E_k(t_R) \quad (10b)$$

Let us restrict ourselves to the case where $\tau^* = E^* = 0$, for which $(d\rho/d\tau) = 0$. Then (10a,b) simplify to

$$\ddot{\tau}_k + \omega_{\tau,k}^2 \tau_k = 0 \quad (11a)$$

$$\ddot{E}_k + \gamma \dot{E}_k + \omega_{E,k}^2 E_k = \frac{-2\epsilon}{M_E t} \left(\frac{\partial \rho}{\partial E} \right)_{0,0} \cdot \tau_k \quad (11b)$$

where we have introduced a dissipative term in (11b) to avoid unphysical results (γ is inversely proportional to the phonon life time). Note that the asymmetry in (11) with respect to E and τ , could already be anticipated by examining figure 2: the field-induced force will always be perpendicular to contours of equal ρ as a consequence of (5). The situation is similar to oscillators, of which one (τ) serves as the driving force for the other (E). The solution of (11) is

$$\tau_k(t_R) = A \sin(\omega_{\tau,k} t_R) \quad (12a)$$

$$E_k(t_R) = \tilde{E}_k \sin(\omega_{\tau,k} t_R + \tilde{\phi}_k) \quad (12b)$$

where

$$\tilde{E}_k = \frac{2\epsilon A}{M_E t [(\omega_{E,k}^2 - \omega_{\tau,k}^2) + \gamma^2 \omega_{\tau,k}^2]} \quad \tilde{\phi}_k = \frac{\gamma \omega_{\tau,k}}{[\omega_{\tau,k}^2 - \omega_{E,k}^2]}$$

The physical interpretation of the above is the following: due to an electric field, part of the E -mode oscillation amplitude is transferred to frequency ω_{τ} while being phase-coupled to the τ -mode oscillation. We see that the coupling of optical phonons in the presence of an electric field gives indeed rise to coherent variations of τ and E , which was shown earlier to be the condition for charge transport. Using eqs.(5) and (7) one finds for the current

$$I = \sum_k \left(\frac{\partial \rho}{\partial E} \right)_{E^* \tau^*} \tau_k \tilde{E}_k \omega_{\tau,k} \frac{1}{t} \sin(\tilde{\phi}_{E,k}) \quad (13)$$

DISCUSSION

It is possible to give an order of magnitude estimate for the current resulting from a pair of coupled phonons. Let us look more closely at two phonons, each of a different branch and ideally coupled in phase. We recall that this phonon pair will cause the system to make tiny revolutions around the ground state configuration (E^*, τ^*). Using eq.(13) we can write

$$I = \omega_k u_{\tau,k}^m u_{E,k}^m \left(\frac{\partial \rho}{\partial E} \right) \left(\frac{\partial \tau}{\partial u_{\tau}} \right) \quad (14)$$

where u_{τ}^m and u_E^m are the vibrational amplitudes of both modes for a single phonon, which is (quantum mechanically [4])

$$u_{\lambda}^m = \left(\frac{\hbar}{M n \omega_{\lambda}} \right)^{\frac{1}{2}}; \quad \lambda = \tau, E \quad (15)$$

In calculating the actual contribution to the conductivity we take a chain system with 10^7 unit cells per cm and 10^{14} chains per cm^2 . The reduced mass M , involved in the oscillations will be 10-100 a.m.u. $d\rho/du_E$ and $d(\tau/t)/du_{\tau}$ are

expected to be of the order of $1 \text{ \AA}^{-1}$, which implies that a change in the molecular positions of $1 \text{ \AA}$ would reverse the charge distribution or dimerization. Using these numerical data, we estimate the current for a system with one coupled pair or phonons per chain to be $0.1\text{--}1 \text{ \AA}/\text{cm}^2$. In actual systems for which the model may be applicable (like substituted morpholinium TCNQ_2 compounds, the room temperature conductivity is of the order of $1\text{--}10 (\Omega\cdot\text{cm})^{-1}$. At this temperature, optical phonons are rather abundant and one finds that only 1 in every 10^5 phonons need to be coupled by an electric field of $1 \text{ V}/\text{cm}$. Another, perhaps more physical way of expressing the power of the mechanism is to say that the field-induced admixture of one phonon mode into the other at $1 \text{ V}/\text{cm}$ needs to be only 10^{-5} to account for the observed conductivities.

In conclusion we state that the model presented in this paper is able to account for the conductivities found in the class of morpholinium TCNQ_2 salts [5]. Moreover, it predicts temperature-activated conductivity, just as the single electron model does, but here the activation energy is not dependent on the electron gap but rather on the optical phonon energy. It should therefore be expected to contribute whenever single particle conductivity fails because of a large gap-value or low carrier mobility. This different origin of the activation energy would explain the absence of any correlation between the calculated gap (using eq.(2)) and the observed activation energy [6]. Although at present it is not possible to give an explanation for the anomalous field and frequency dependence of the conductivity observed in a number of substituted morpholinium TCNQ_2 salts, examination of the data indicate that the origin is most likely to be found in lattice-coupled charge transport [7] for which our model is certainly a good candidate.

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