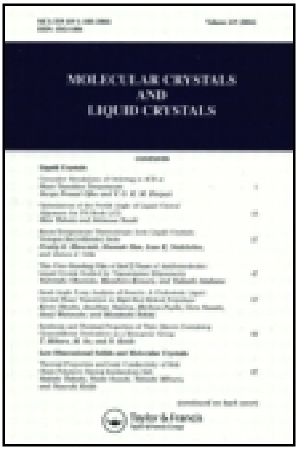

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E. M. Conwell [a] & I. A. Howard [a]
[a] Xerox Webster Research Center, Webster, N.Y., 14580
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EFFECTS OF SOLITONS ON GAP AND TRANSPORT IN $Qn(TCNQ)_2$ AND $(NMP)_x(Phen)_{1-x}TCNQ$

E.M. CONWELL AND I.A. HOWARD
Xerox Webster Research Center, Webster, N.Y. 14580

Abstract Optical absorption data show that $Qn(TCNQ)_2$ and $(NMP)_x(Phen)_{1-x}TCNQ$, $x \simeq 0.5$, have Peierls gaps to 300K.[2] The variation of the gaps with temperature deduced from these measurements requires that there be a potential on the TCNQ chains, due to the donor chains, with the same periodicity as the Peierls distortion. As a result of this potential, the localized soliton states into which excess (over the number required for the quqrter-filled band) electrons go are not kinks, but bound pairs of charged kinks, or bipolarons. The effect of these states on the gap variation with temperature is shown to be in good agreement with the optical data. There is evidence that these states affect transport. Also, they may provide the barriers needed to explain the large low-frequency dielectric constant observed in $Qn(TCNQ)_2$.

$Qn(TCNQ)_2$ and $(NMP)_x(Phen)_{1-x}TCNQ$, $x \simeq 0.5$, are characterized by close to 1/4 filled bands on the TCNQ chains and large Coulomb repulsion for a second electron on the same site ("large U"). Optical absorption of these materials vanishes at low frequencies, indicating they have gaps.[1] The prominent appearance in the absorption of the TCNQ a_g modes,[1] normally infrared inactive, means that the gaps are due to the Peierls distortion.[2] The change in these modes from resonance to anti-resonance indicates gaps of $\sim$ 1200K in $Qn(TCNQ)_2$, $\sim$ 1800 K in $(NMP)_x(Phen)_{1-x}TCNQ$,[1] in good agreement with values deduced earlier from conductivity σ variation with temperature T.[3,4] The variation of these gaps with T may be deduced from the variation with T of the oscillator strengths of the resonances or anti-resonances. From these we find that, as T increases from 4K, the Peierls gap in both materials decreases fairly sharply up to $\sim$ 100K and then quite gradually with further increase in T. We show first that this type of behavior, quite different from the prediction of mean field theory, is due to the presence of an interchain potential.[5]

When there is an interchain potential, Δ_e, the gap parameter $\tilde{\Delta} = \Delta_o + \Delta_e$, where Δ_o is the contribution due to the Peierls distortion. Using the expressions for free energy of the lattice and of the conduction electrons,[6] and minimizing the total free energy with respect to $\tilde{\Delta}$, we obtain the gap equation

$$\frac{\pi}{\epsilon_p}\left(\frac{\tilde{\Delta} - \Delta_e}{\tilde{\Delta}}\right) = \int_0^{\pi/2} \frac{f_k}{E_k^-}\, d(kb) - \int_{\pi/2}^{\pi} \frac{f_k}{E_k^+}\, d(kb) \qquad (1)$$

Here ε_p is the electron-phonon coupling energy. For the cases where the Peierls distortion is stabilized by internal modes, ε_p is given by the sum over the internal modes of $g_i^2/\hbar\omega_i$, where g_i and ω_i are the coupling constant to, and the frequency of, the i^{th} mode, respectively. For the cases where the Peierls distortion is due to acoustic modes $\varepsilon_p = \pi\lambda t$, where λ is the dimensionless electron-acoustic phonon coupling constant and t the transfer integral. In the terms on the right f_k is the distribution function and $E_k^{\pm} = \pm(\varepsilon_k^2 + \tilde{\Delta}^2)^{1/2}$, the energy of an electron with wave vector k in the conduction or valence band, ε_k being the one-electron energy in the undistorted lattice. The first term on the right of Eq. (1) is the contribution of the valence band, the second that of the conduction band. When $\Delta_e = 0$ Eq. (1) is the usual gap equation in the absence of solitons.[6] For $\Delta_e \neq 0$ it may be considered that there is an "effective phonon coupling" constant $\varepsilon_p\tilde{\Delta}/(\tilde{\Delta} - \Delta_e)$. As $\tilde{\Delta}$ decreases, approaching Δ_e (its minimum value), the "effective phonon coupling" increases, causing $\tilde{\Delta}$ and therefore Δ_o to decrease more slowly. In essence, the presence of Δ_e, by decreasing the number of electrons that can get into the conduction band and thereby destabilize the Peierls transition, helps sustain the Peierls distortion and Δ_o.

In $(NMP)_x(Phen)_{1-x}TCNQ$ the number of electrons on the TCNQ chain can be increased by making a sample with larger x. From the fact that the Fermi wave vector k_F stays constant when the number of electrons per TCNQ is increased from 0.5 to $\sim$ 0.56, by increasing x from 0.5 to $\sim$ 0.56, we have deduced that in this doping range the electrons are going into soliton states in the gap.[4] "Soliton" is a generic name for a localized excitation, arising from a nonlinear equation, that can propagate without change of shape. The particular solitons we suggested were kinks, which interpolate between one degenerate lattice arrangement and another. When the Peierls distortion is due to the internal modes, as is the case for $(NMP)_x(Phen)_{1-x}TCNQ$, $Qn(TCNQ)_2$, TTF-TCNQ and many other molecular crystals where x-rays show no lattice distortion, it consists of a periodic arrangement of molecules with different amounts of frozen-in internal modes, i.e., different shapes. For the 1/4-filled-band large-U case $k_F= \pi/2b$, rather than $\pi/4b$, where b is the lattice constant, and the perfect Peierls-distorted lattice consists of molecules of one shape alternating with molecules of another shape. For convenience in talking about them we may label these shapes as "fat" and "thin". If we think about an isolated chain, there are then two degenerate arrangements consisting of:(A) "fat" molecules on odd sites, "thin" ones on even sites and (B) "fat" molecules on even sites, "thin" ones on odd sites. The kink is a domain wall interpolating between these two arrangements. However, when we take into account the presence of the $(NMP)_x(Phen)_{1-x}$ chains, we see that these two arrangements are no longer degenerate. Because of the coupling of the electrons to the internal modes, electrons have different energies on the "fat" molecules and "thin" molecules. Let us assume the latter energy to be smaller, so the electrons are preferentially on "thin" molecules. For x=0.5 NMP^+'s alternate with neutral phenazine molecules. The resulting potential on the TCNQ chain will lower the energy of the arrangement where the "thin" molecules, which are more likely to have an electron, are opposite the NMP^+'s and the "fat" molecules opposite the phenazines. For specificity we take this as arrangement A. Let us now imagine that we increase x to create a pair of kinks, with arrangement A to the left of the first kink and to the right of the second and arrangement B between them. Because B has higher energy than A, the lowest energy configuration would have the kinks as close together as possible. In this situation, the stable excitation is another type of soliton, a bound kink pair.[7] Because in the $U \to \infty$ limit the spin degrees of freedom are separated from the kinetic degrees of freedom the kinks in the 1/4-filled-band large-U materials have charge $\pm$ e/2.[8] The stable excitations therefore have charge $\pm$ e and, consisting of two charged kinks, are called bipolarons.[7]

It should be noted that, although NMP^+'s and phenazines do not strictly alternate for $x > 0.5$, there will always be a Fourier component of their potential with the periodicity of the Peierls distortion. In the case of $Qn(TCNQ)_2$ such a Fourier component will result from the random orientation of the dipoles on the Qn molecules. As will be seen, the required potential is quite small.

The theory for the wavefunctions and energies of the polarons has been worked out for the ideal case of an isolated polaron on a chain.[7] The situation in the materials under discussion differs from this in that (1) the polarons are probably bound by the attraction of the NMP^+ ions and (2) the polaron concentrations are generally large, which would cause overlap and spreading of the level into a band of energies. Nevertheless it is of some interest to compare experimental results with the theory.

According to the theory, there are associated with each polaron two electronic states located symmetrically about midgap at energies $\pm\ \omega_o$. The gap parameter variation for the polaron is given by[7]

$$\Delta(x) = \Delta_0 - \kappa_0 v_F \left\{ \tanh(x+x_0) - \tanh(x-x_0) \right\} \quad (2)$$

where $\kappa_0 v_F = (\Delta_0^2 - \omega_0^2)^{1/2}$, v_F being the Fermi energy, and $2x_0$, the distance between the confined kinks, is a function of κ_0, Δ_0 and ω_0.[7] The formation energy E_p of a polaron in the presence of an interchain potential has been calculated for the case of fermions with spin.[7] Generalizing this to the case of spinless fermions we obtain

$$E_p = (n_+ - n_- + 1)\hbar\omega_0 + \frac{2}{\pi}\hbar\kappa_0 v_F - \frac{2\hbar\omega_0}{\pi}\tan^{-1}\left(\frac{\kappa_0 v_F}{\omega_0}\right)$$

$$+\frac{4}{\pi}\tilde{\Delta}_0\gamma\left[\tanh^{-1}\frac{\kappa_0 v_F}{\tilde{\Delta}_0} - \frac{\kappa_0 v_F}{\tilde{\Delta}_0}\right], \quad (3)$$

where n_+ and n_- are the numbers of electrons in the levels $+\omega_0$ and $-\omega_0$, respectively, and $\gamma = (\Delta_e/\tilde{\Delta}_0)(\pi t/\varepsilon_p)$. The quantities κ_0 and ω_0 must be chosen to minimize $\tilde{E}_p$. Because they are related, we may take $\kappa_0 v_F = \tilde{\Delta}_0 \sin\theta$, $\omega_0 = \tilde{\Delta}_0 \cos\theta$ and minimize E_p with respect to θ. The result is that the only stable polarons are those with charge $-e$, where $n_+ = n_- = 1$, and those with charge $+e$, where $n_+ = n_- = 0$. For both of these the equation that determines ω_0 is

$$\theta + 2\gamma\tan\theta = \pi/2 \quad (4)$$

It is possible to obtain a value of Δ_e, and therefore of γ, by comparing the optical data for the variation with T of Δ_0 with the calculated $\Delta_0(T)$ for various Δ_e's. This has been done so far only for kinks, but we expect the results to be quite similar for bipolarons. To calculate $\Delta_o(T)$ we add to the left of the gap equation (1) the term n_k/Δ, where n_k is the kink concentration, from the free energy of the kinks. The resulting equation must be solved together with the electrical neutrality condition,[6] which determines the Fermi energy E_F. In doing this, it must be remembered that, because electrons, holes and kinks interact, n_k is a function of E_F.

Numerical integration was carried out for $Qn(TCNQ)_2$ for different values of the number of donors N_d. There are only two parameters in the calculation, $\widetilde{\Delta}(0)$ at N_d=0, and 4t, which were chosen as 600K and 4500K, respectively. The calculated values of $\Delta_o(T)/\Delta_o(0)$ are plotted in Fig. 1 for Δ_e=25K. It is seen that the agreement of experiment and theory is reasonably good. Note that the results are not very sensitive to the Δ_e value; it could be larger or smaller by as much as 50%.

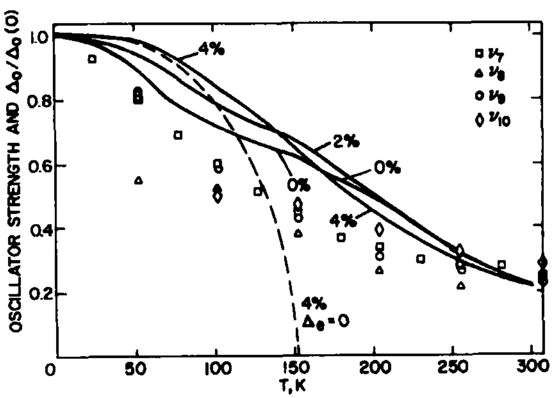

FIGURE 1. The lines represent the calculated T-dependence for $Qn(TCNQ)_2$ of the Peierls portion of the gap (normalized to its 0K value) for the % donor concentration indicated and Δ_e= 25K (solid lines), Δ_e= 0 (dashed line). The data points represent oscillator strength (normalized to the 6K value) vs T, determined as described in reference 1, for the TCNQ a_g modes ν_7

$(691 cm^{-1})$, ν_8 $(600\ cm^{-1})$, ν_9 $(306\ cm^{-1})$ and ν_{10} $(124\ cm^{-1})$ in $Qn(TCNQ)_2$.

With Δ_e=25K, and the value of $\varepsilon_p/\pi t$ required by the relation between $\Delta_o(0)$ and 4t to be 0.7, we obtain γ =0.06. This leads to ω_o=200K. With $\tilde{\Delta}_o(0)$=600K, this value would suggest a low-temperature optical absorption edge at 400K. The edge actually observed is $\sim$ 150K. As anticipated, the theory does not apply to the samples used.

At temperatures above $\sim$ 100K, where the concentrations n of conduction electrons and p of holes are large, it is difficult to separate the contributions to transport of bipolarons and free carriers. It is clear, however, from the thermopower Q measured in this range that the bipolarons do have an effect. If the latter provide a conductivity σ_{bp} and thermopower contribution Q_{bp}, Q may be written

$$Q = (\sigma_n Q_n + \sigma_p Q_p + \sigma_{bp} Q_{bp})/(\sigma_n + \sigma_p + \sigma_{bp}) \qquad (5)$$

At 300K n $\simeq$ p, and if $\sigma_n \simeq \sigma_p$ and the bipolaron contribution is negligible, due to large U Eq. (5) would lead to Q $\simeq$ -60 μV/K.[9] This is in fact observed in $(NMP)_{0.54}$ $(Phen)_{0.46}$ TCNQ and $Qn(TCNQ)_2$.[1] As T goes below 300K E_F moves higher in doped samples and electrons increasingly outnumber holes. However, Q is found to stay at $\sim$ -60 μ V/K in these samples, indicating either (1) the bipolarons are making a contribution to Q, which would be positive since their electronic levels lie below E_F or (2) σ_n is not larger than σ_p because, although n > p, the mobility of electrons falls below that of the holes. This behavior would also result from the presence of bipolarons since, being predominantly negative in charge, they would tend to block electrons on the chain but not holes. It is likely that both of these effects are operating. The blocking effect of the bipolarons, which could be greatly enhanced by clustering where there is a cluster of donors, may provide the barriers needed to explain the large low frequency dielectric constant observed in $Qn(TCNQ)_2$.[10]

In summary, we have shown that the slow decrease in the gap as T increases in $Qn(TCNQ)_2$ and $(NMP)_x(Phen)_{1-x}TCNQ$, $x \simeq 0.5$, is due to an interchain potential of $\sim$ 25K. This potential causes the stable soliton defects in these materials to be bipolarons with charge $\pm e$. The bipolarons may both contribute to transport and affect the contribution of conduction electrons by decreasing their mobility. They may also give rise to the barriers required to explain the large dielectric constant.

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