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Effect of solitons on Peierls gap in highly correlated quarter-filled-band crystals

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It has recently been proposed by Rice and Mele [Phys. Rev. B 25, 1339 (1982)] that fractionally charged solitons can exist in quarter-filled-band, quasi-one-dimensional crystals that are highly correlated, i.e., crystals in which the Coulomb repulsion U for a second electron on the same site is much larger than the bandwidth $4t$. In the limit $U/4t \rightarrow \infty$, the electronic states of the system are singly occupiable and solitons with charges $\pm |e|/2$ can be created. We have calculated the equilibrium soliton populations in such crystals, taking into account solitons generated both thermally and chemically (by doping). Thermally generated soliton populations are much larger than those expected in polyacetylene, for example, because of smaller Peierls gaps in the usual quarter-filled-band large-U crystals. We find also that the presence of solitons reduces both the zero-temperature value of the Peierls gap and the semiconductor-metal transition temperature. Comparison is made with recent conductivity data of Epstein *et al.* [Phys. Rev. Lett. 49, 1037 (1982)] for (N-methylphenazinium)$_x$(phenazine)$_{1-x}$tetracyanoquinodimethane [(NMP)$_x$(Phen)$_{1-x}$TCNQ] for $0.50 < x < 0.54$. Disappearance of the Peierls gap is predicted in the region where the experimental activation energy goes to zero.

I. INTRODUCTION

Rice and Mele[1] have suggested that quarter-filled-band, highly correlated, quasi-one-dimensional (quasi-1D) crystals can support the formation of solitons of fractional charge $\pm |e|/2$. These highly correlated systems can be viewed, in the large-U limit of the Hubbard model, as displaying a separation of spin and translational degrees of freedom, with the result that each electronic state can accommodate only a single electron. The wave vector of the Peierls transition in these systems of "spinless" fermions is thus shifted from $2k_F$ to $4k_F$, where k_F is the Fermi wave vector for the small-U case. As a result, the large-U quarter-filled-band quasi-1D crystals are, in the limit $U/4t \rightarrow \infty$, spinless analogs of half-filled-band quasi-1D systems such as polyacetylene [(CH)$_x$].[1]

Soliton excitations can be generated in these systems either thermally or chemically (i.e., by doping), as in (CH)$_x$; the "spinlessness" of the fermions, however, means that generation of a soliton-antisoliton pair requires taking only a single state from the valence band and one from the conduction band. A pair of midgap soliton states results, each capable of holding one electron; each is screened by a charge deficit of $|e|/2$ in the local valence-band charge density. Thus a filled soliton state will have a net charge of $-|e|/2$, while an empty state will have a charge of $+|e|/2$.[1] A thermally produced soliton-antisoliton pair will have charges of $(+|e|/2, -|e|/2)$, while addition of an electron (by doping with a donor, for instance) will create pairs of $(-|e|/2, -|e|/2)$ charged states. The creation energy for a soliton-antisoliton pair can be shown to be $2\Delta/\pi$,[1] where Δ is half the Peierls gap.

In contrast, for (CH)$_x$ formation of a soliton-antisoliton pair requires that a total of four states be taken from the electronic π bands, a spin-up—spin-down pair from both the valence and conduction bands.[2,3] The resulting midgap states are spin degenerate and can thus accommodate 0, 1, or 2 electrons. Since the soliton states are screened by a charge deficit of $|e|$ in the local valence-band charge density, a singly occupied soliton in (CH)$_x$ is neutral. Takayama, Lin-Liu, and Maki have shown that the creation energy for a pair of thermal (neutral) solitons in (CH)$_x$ is $4\Delta/\pi$.[4]

The existence of soliton states could be expected to have important effects on transport and other properties since it causes shifts in the Fermi energy with resulting changes in carrier concentrations and changes in the magnitude of the Peierls gap. Recent experimental data and theoretical work[5] tend to confirm the presence of solitons in at least one such system, (N-methylphenazinium)$_x$ (phenazine)$_{1-x}$ tetracyanoquinodimethane [(NMP)$_x$(Phen)$_{1-x}$ TCNQ] near $x = 0.5$ (the quarter-filled-band limit). This system will be discussed in more detail in Sec. V. The fact that the gaps are much smaller (typically $\Delta < 1000$ K) in the quarter-filled-band charge-transfer crystals than in $(CH)_x$ means that the creation energy for a soliton pair will be much lower. The equilibrium concentration of thermal solitons will then be substantially larger in the quarter-filled-band crystals, and their effects more pronounced.

In the following, the effects of solitons, either thermal alone, or chemical plus thermal, on the carrier concentrations and the Peierls gap in a quarter-filled-band, large-U crystal are explored. Section II explains in more detail the nature of the problem and sets up the appropriate charge-balance relations, from which the Fermi energy is determined. In Sec. III the free energy of a soliton-containing system is derived. The result is then used to find the thermal equilibrium number of solitons in the absence of chemical doping, and from this the temperature variations of the carrier concentrations and the Peierls gap are calculated. Section IV applies the same approach to the case of chemical-plus-thermal solitons. In Sec. V the $(NMP)_x(Phen)_{1-x}TCNQ$ system is discussed in light of the present calculations, and comparison is made with experimental results. Section VI presents conclusions.

II. CHARGE DISTRIBUTION AND FERMI ENERGY

A realistic treatment of soliton effects must include thermally generated soliton pairs along with chemical solitons. While the number of chemical solitons present in a system depends only on the level of doping, the number of thermal solitons must be determined by free-energy considerations. Another factor to be considered is that, if the presence of midgap states shifts the Fermi energy, it will affect the ratio of negatively charged (occupied) soliton states to positively charged (empty) states.

For large-U quarter-filled-band systems the Fermi energy ϵ_F, in the absence of defects, impurities, etc., lies at $\epsilon_F = -k_B T \ln 2$ below the middle of the Peierls gap,[6] which we take as the zero of our energy scale. Here T is temperature and k_B denotes Boltzmann's constant. The probability of occupation of a state with energy ϵ is given by[7]

$$f(\epsilon) = \{1 + \tfrac{1}{2}\exp[(\epsilon - \epsilon_F)/k_B T]\}^{-1}, \quad (1)$$

where the factor $\frac{1}{2}$ arises from the fact that, although the states are singly occupiable, they may be occupied by either a spin-up or a spin-down electron. For a defect-free semiconducting crystal with equal densities of states in conduction and valence bands, setting $\epsilon_F = -k_B T \ln 2$ in $f(\epsilon)$ leads to hole concentration equal to electron concentration.[6]

We now consider charge balance for the case in which no excess electrons or holes are put into the system, but ρ thermally generated soliton states per lattice site ($\rho/2$ soliton-antisoliton pairs) exist. For the quarter-filled-band system without solitons, the (filled) valence band contains $\frac{1}{2}$ electron per lattice site. The formation of each soliton pair removes one state and its electron from the valence band, as well as one state from the conduction band. The total concentration of charge taken from the filled valence band is therefore the hole concentration p_V, plus the concentration $\rho/2$ of charge removed in forming the thermal soliton states. This charge is distributed over the ρ soliton levels available plus the conduction-band states. If one denotes the distribution (1) for the midgap states as $f(0)$, then the concentration of occupied midgap states is $\rho f(0)$. Allowing the conduction-band electron concentration to be n_c, one can then write the charge-balance equation, which determines ϵ_F, as

$$n_c + \rho f(0) = p_v + \rho/2 \quad (2)$$

for the case of thermal solitons. In Eq. (2), as in the remainder of the present work, the soliton levels are assumed to be noninteracting, i.e., to lie at the center of the gap with zero bandwidth. This should be a good approximation if the soliton overlap is small and the bandwidth is a small fraction of the gap. Rice and Mele have shown[8] that the soliton band for a small-U case is very narrow below a critical concentration $c^* = 2\Delta/4t\pi$ of soliton levels per lattice site; for the large-U case, this becomes $c^* = \Delta/4t\pi$ solitons per lattice site.[5] Below this concentration and even a little above, the assumption of noninteracting solitons should be reasonable. In Sec. V we will show that the assumption is justified over the concentration range for which we apply the theory.

If N_d excess electrons per lattice site are put into the system, a total of $2N_d$ occupied chemical soliton states per lattice site will be formed at $T = 0$.[1] Each soliton-antisoliton pair formed will take one occupied state from the valence band and one empty state from the conduction band, just as in the thermal soliton case, so that a concentration N_d of charge is taken from the valence band when N_d electrons per lattice site are added. The N_d excess electrons occupy the N_d empty soliton levels, so that $2N_d$ electrons per lattice site are in the midgap states at $T = 0$. As the temperature is raised, electrons in these states may be ionized to the conduction band, or electrons may be promoted to these states from the valence band. Equating the number of electrons found in the conduction band and midgap levels to those available for distribution among those levels, we find that

$$n_c + 2N_d f(0) + \delta f(0) = p_v + 2N_d + \delta/2 \;, \tag{3}$$

where δ is the number of solitons in excess of $2N_d$ generated in thermal equilibrium. This will be discussed in Sec. IV of this paper.

III. FREE ENERGY AND GAP VARIATION—THERMAL SOLITONS ONLY

A. Free energy for n solitons on an N-site chain

The equilibrium number of solitons and the equilibrium Peierls gap for a system are found by minimizing the free energy with respect to the variable under consideration. The Helmholtz free energy F of a soliton-containing crystal can be calculated by considering all the possible arrangements of the soliton-antisoliton pairs on a chain.

In finding F several constraints must be introduced. The number of solitons (S) and the number of antisolitons ($\bar{S}$) must, of course, be equal. Solitons and antisolitons must be arranged in alternation ($S\bar{S}S\bar{S}$) along the chain, since two solitons (or two antisolitons) cannot be adjacent. In principle, according to a one-dimensional (1D) calculation,[2,9] a soliton may be centered at any point along the chain. Practically, however, there are other chains nearby and the solitons, being charged in this system, will have some interaction with the charges (e.g., NMP^+ ions) on the other chains. It is expected therefore that there be a preferred site for the soliton center within the unit cell. This need not be a lattice site, but for counting purposes it will be convenient to refer to it as such. Finally, the finite length l of the soliton is a factor that must be taken into account; this was not done in previous free-energy calculations.[10,11] We have required the solitons to be nonoverlapping, in agreement with our restriction to zero soliton bandwidth.

A final consideration in calculating the free energy is the mobility of the solitons. (It has been assumed in the foregoing that the solitons are immobile). There is evidence that neutral solitons in $(CH)_x$ are quite mobile at very low densities, whereas charged solitons created by interstitial doping molecules or atoms tend to be pinned near the dopant.[9] In the quarter-filled-band large-U systems, doping impurities between chains could also serve to pin solitons. If the "impurities" are NMP molecules one chain away, as in $(NMP)_x(Phen)_{1-x}$ TCNQ, the pinning would undoubtedly be less. Also for thermal solitons there are no pinning impurities. It must be remembered, however, that solitons are truly 1D objects. Thus any obstacle at all on a chain would serve to localize them. In particular, a soliton and antisoliton with like charge could neither go through each other nor recombine. We have therefore taken the solitons to be stationary objects in these calculations.

If there are n defects (including solitons and antisolitons) on a chain of N lattice sites, then the number of ways W_n of arranging these n objects, subject to the above constraints, is

$$W_n = \frac{[N-(l-1)][N-(3l-2)][N-(5l-3)]\cdots\{N-[(2n-1)l-n]\}}{2^{n-1}[(n/2)!]^2} \;. \tag{4}$$

The factor $(1/2)^{n-1}$ results from the condition that solitons and antisolitons alternate along the chain. The other factor in the denominator, $[(n/2)!]^2$, of (4) reflects the fact that there are $n/2$ solitons and $n/2$ antisolitons, each having $(n/2)!$ indistinguishable permutations. The numerator takes into account the nonoverlapping restriction. The $l-1$ lattice sites at the end of the chain must be excluded when placing the first defect on the chain; each subsequent defect added takes $2l-1$ more sites from those available. Of course, if the second defect added were placed on the chain as close to the first as possible, the total length of chain excluded from placement of subsequent defect centers would be only $4l-2$ and not $5l-3$. Choice of the latter to some extent takes into account the effect mentioned earlier of repulsion of the solitons, since most have like charge. In any case, the present expression for W_n should be accurate when the concentration of solitons is not large enough that significant numbers of them are in close-lying pairs, triplets, etc. Since W_n is small in the limit of such high soliton concentrations, it can be seen that (4) is adequate for our purposes.

Having found W_n, one can write the soliton free energy F_S as

$$F_S = n\Delta/\pi - k_B T \ln W_n \;, \tag{5}$$

recalling that the creation energy for a soliton-antisoliton pair is $2\Delta/\pi$. For $n \ll N$, Stirling's approximation may be used, and the result is that

$$\begin{aligned} F_S = n\Delta/\pi - k_B T\{ & n \ln[(2l-1)/n] + [N/(2l-1)]\ln[N/(2l-1)] \\ & -[(N-2nl+n)/(2l-1)]\ln[(N-2nl+n)/(2l-1)]\} \;, \end{aligned} \tag{6}$$

if one neglects l compared to N.

B. Number of solitons in thermal equilibrium

The equilibrium number of thermal solitons can be found by minimizing F_S in (6) with respect to n. This results in an equilibrium soliton concentration per lattice site, ρ, given by

$$\rho=e^{-\Delta/\pi k_B T}/[1+2l\,e^{-\Delta/\pi k_B T}]\ . \tag{7}$$

This result does not take into account the effect of interchain interactions on the concentration of thermal solitons, as done by Baughman and Moss[10] for $(CH)_x$. Such considerations will not be important for the cases studied here, however, due to the higher soliton densities involved. Also the fact that the Peierls transition in the crystals is stabilized by the internal modes rather than by molecular displacements means that mismatch of adjacent chains due to soliton creation will have less effect.

C. Peierls gap and carrier concentrations: Thermal solitons only

Having established the free energy (6) for solitons on a chain, one can find the equilibrium Peierls gap 2Δ for the soliton-containing system by setting up the total free energy—lattice, electronic, and soliton components—and minimizing with respect to Δ. The lattice component F_l is given by[12]

$$F_l=N\Delta^2/2t\pi\lambda\ , \tag{8}$$

where λ is the dimensionless electron-phonon coupling parameter to be further discussed in Sec. V. The electronic contribution F_e is

$$F_e=\epsilon_F N_e-k_B T\sum_k \ln\{1+2\exp[(\epsilon_F-E_k)/k_B T]\}\ , \tag{9}$$

where N_e is the total number of electrons in the system, and E_k is the energy of an electron with wave vector k. Within the valence and conduction bands, one can take (with the zero of energy at midgap)

$$E_k^{\pm}=\pm(\epsilon_k^2+\Delta^2)^{1/2}\ , \tag{10}$$

where $\epsilon_k=2t\cos(kb)$ is the tight-binding energy and b is the lattice constant for the undimerized (gapless) system. Equation (9) differs from the usual expression for Fermi statistics[13] in having the factor 2, the origin of which is the same as that of the $\frac{1}{2}$ in the distribution function (1).

Given this and the expression (6) for the soliton free energy, one can proceed to minimize $F=F_e+F_l+F_S$ by setting $\partial F/\partial\Delta=0$. The result, for thermal solitons only, is the gap equation

$$\Delta/\pi\lambda t+\rho/\pi+k_B T\left[\rho/\Delta+\left[\frac{1}{2l\Delta}\right]\ln(1-2l\rho)\right]$$
$$=(1/\pi)\int_{kb=0}^{kb=\pi/2} d(kb) f_k^{-}\Delta/(\epsilon_k^2+\Delta^2)^{1/2}-(1/\pi)\int_{kb=\pi/2}^{kb=\pi} d(kb) f_k^{+}\Delta/(\epsilon_k^2+\Delta^2)^{1/2}\ , \tag{11}$$

where $f_k^{\pm}$ is given by Eq. (1) with $\epsilon_k=E_k^{\pm}$. Equation (11) is to be solved self-consistently with Eq. (2), with the electron concentration in Eq. (2) taken as

$$n_c=(1/\pi)\int_{kb=\pi/2}^{kb=\pi} f_k^{+} d(kb)\ , \tag{12}$$

and the hole concentration as

$$p_v=(1/\pi)\int_{kb=0}^{kb=\pi/2}(1-f_k^{-})d(kb)\ . \tag{13}$$

In the absence of solitons, and in the limit $T\to 0$, Eq. (11) reduces to the gap equation in the limit $U\to\infty$,

$$2/\lambda=a\int_{kb=0}^{kb=\pi/2} d(kb)[1-a^2\sin^2(kb)]^{-1/2}$$
$$=K(a^2)\ , \tag{14}$$

where $a^2=4t^2/(4t^2+\Delta_0^2)$ and K is the complete elliptic integral of the first kind. This differs from the gap equation for a small-U system in not having on the right-hand side the factor 2 due to the summation over spins. Equation (14) gives the approximate relationship between the gap Δ_0 at $T=0$ and λ,

$$\Delta_0(U\to\infty)=8te^{-2/\lambda}\ , \tag{15}$$

whereas for small U,

$$\Delta_0(U\to 0)=8te^{-1/\lambda}\ . \tag{16}$$

The terms in brackets in Eq. (11) are those soliton terms which originate from the derivative of $\ln W_n$ when Stirling's approximation is used. When the soliton concentration ρ approaches $1/2l$ (or $\Delta/8t$), Stirling's approximation is inappropriate. The terms in (11) due to $\ln W_n$ diverge as $\rho\to 1/2l$, whereas it is obvious on physical grounds that $\ln W_n$ will tend to zero at high soliton concentrations since in the limit $\rho=1/2l$ there will be only one allowable distinguishable arrangement. Since $\ln W_n$ will then be very small at high concentrations as well as at low concentrations of solitons, the terms in brackets have been dropped from Eq. (11) in the numerical calculations.

Computations were carried out self-consistently using the parameters $\Delta_0/k_B=900$ K, $4t/k_B=4500$ K. As will be discussed in Sec. V, we believe these parameters describe $(NMP)_x(Phen)_{1-x}TCNQ$ near

$x = 0.50$. Results are shown in Fig. 1 for the variation of the normalized Peierls gap Δ/Δ_0 with temperature. The critical temperature in the absence of solitons is $T_c \simeq 505$ K. Included for comparison is Δ/Δ_0 vs T for the case of no solitons, that is, with all soliton terms omitted from Eqs. (2) and (11).

The presence of thermally generated solitons lowers the critical temperature by approximately 105 K for the parameters chosen. The gap reduction is due primarily to the energy required to create the solitons when the gap is formed. This in turn causes an increase in the number of free carriers, which serves to reduce the gap further. The disparity in the curves with and without solitons becomes significant as low in temperature as 50 K, where the soliton concentration deduced from Eq. (7) is 0.003 per lattice site, 7 orders of magnitude larger than the band electron or hole concentrations. Figure 2 compares the computed carrier concentrations with and without solitons. In both cases the Fermi energy $\epsilon_F = -k_B T \ln 2$; for the soliton-containing system this is evident from inspection of Eq. (2), where $n_c = p_v$ is a solution if $f(0) = \frac{1}{2}$, that is, if $\epsilon_F = -k_B T \ln 2$. Therefore the soliton levels are exactly half-occupied at all T's in the absence of chemical doping.

The thermal soliton concentration (in Fig. 2) does not increase monotonically with increasing temperature, but has a broad peak around 250 K and a gradual decrease at higher temperatures. The peak concentration for the parameters used was 0.063 solitons per lattice site at 250 K, over an order of magnitude larger than the electron or hole concentrations at the temperature. The decrease in soliton concentration at high temperatures is the result of the increase in l with decrease in Δ. As the gap decreases, the denominator of (7) will at some point begin to be dominated by l, and further reduction of Δ will decrease the soliton concentration. Physically, this means that the elongation of the solitons caused by the gap decrease has reached a point where further soliton formation is forbidden because there is no more room on the chain.

IV. FREE ENERGY AND GAP VARIATION: THERMAL-PLUS-CHEMICAL SOLITONS

A. Thermal equilibrium number of solitons

The case of crystals with chemical solitons is different in several important respects. First, the soliton concentration obviously can never fall below the level established by the chemical doping (as long as the temperature is below that at which the gap disappears); i.e., if N_d electrons per lattice site are added, there will be at least $2N_d$ solitons per lattice site. It is apparent that the lowest free energy is obtained by housing the N_d electrons on available, i.e., empty, thermal solitons. Thus if, at a given temperature, the thermal equilibrium concentration $\tilde{\rho}$ of solitons in the presence of extra electrons is greater than $2N_d$, no additional solitons will be generated. If, on the other hand, $\tilde{\rho} < 2N_d$, $2N_d - \tilde{\rho}$ solitons must be generated to house all the electrons. Thus δ in the charge balance Eq. (3) is given by

$$\delta(\Delta, T) = (\tilde{\rho} - 2N_d)\Theta(\tilde{\rho} - 2N_d) , \qquad (17)$$

where Θ is the unit step function. Here $\tilde{\rho}$ is given by the same expression [see Eq. (7)] as ρ (the thermal soliton concentration in the absence of doping).

According to our earlier considerations, the maximum concentration of solitons that can be fitted on the chain is $\simeq 1/2l$. As l increases with decreasing Δ, the maximum allowable concentration decreases.

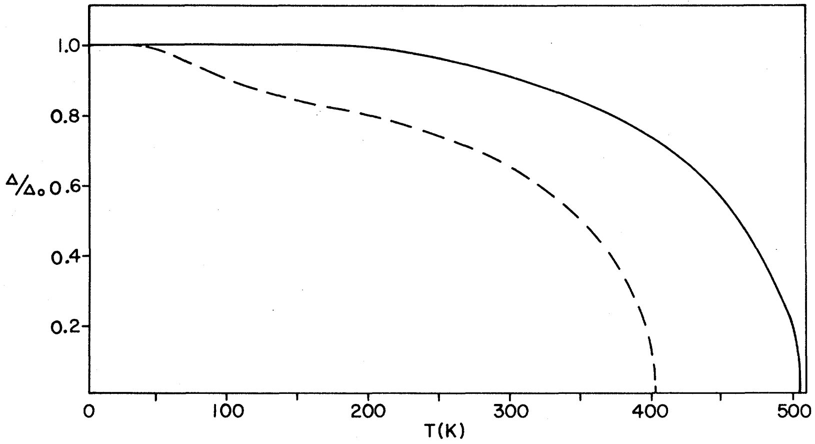

FIG. 1. Calculated temperature (T) dependence of the reduced Peierls gap (Δ/Δ_0) for a quarter-filled-band large-U crystal without (solid line) and with (dashed line) thermal solitons. Parameters are $\Delta_0/k_B = 900$ K, $4t/k_B = 4500$ K.

In the calculations we have kept the soliton concentrations constant at $2N_d$ per lattice site even when the concentration $1/2l$ is exceeded. Although the solitons begin to overlap past this point, their interaction should be small. For the range of soliton densities and gap values in the present work, we are not far from the isolated-soliton limit[14,15] even when the temperature is near the semiconductor-metal transition point. [Alternatively, we find $k \simeq 0.95$ in Eq. (20) of this paper, where $k \rightarrow 1$ is the isolated soliton limit.]

B. Peierls gap and carrier concentrations for thermal-plus-chemical solitons

When both thermal and chemical solitons are present, the gap equation will be identical to Eq. (11), except that ρ in that equation will be replaced by $2N_d+\delta(\Delta,T)$. The terms in brackets in Eq. (11), arising from the use of Stirling's approximation for $\ln W_n$, are omitted for the reasons discussed in the preceding section. The gap equation used for chemical-plus-thermal solitons is

$$\Delta/\pi\lambda t+[2N_d+\delta(\Delta,T)]/\pi=(1/\pi)\int_{kb=0}^{kb=\pi/2} d(kb)f_k^- \Delta/(\epsilon_k^2+\Delta^2)^{1/2}-(1/\pi)\int_{kb=\pi/2}^{kb=\pi} d(kb)f_k^+ \Delta/(\epsilon_k^2+\Delta^2)^{1/2} \ . \tag{18}$$

Equations (3) and (18) have been solved self-consistently for $N_d=0.02$ and $N_d=0.04$, with the same parameters previously used, $4t/k_B=4500$ K and $\Delta_0/k_B=900$ K. Results for the variation of the Peierls gap with temperature are shown in Fig. 3, compared to those previously presented for thermal solitons only.

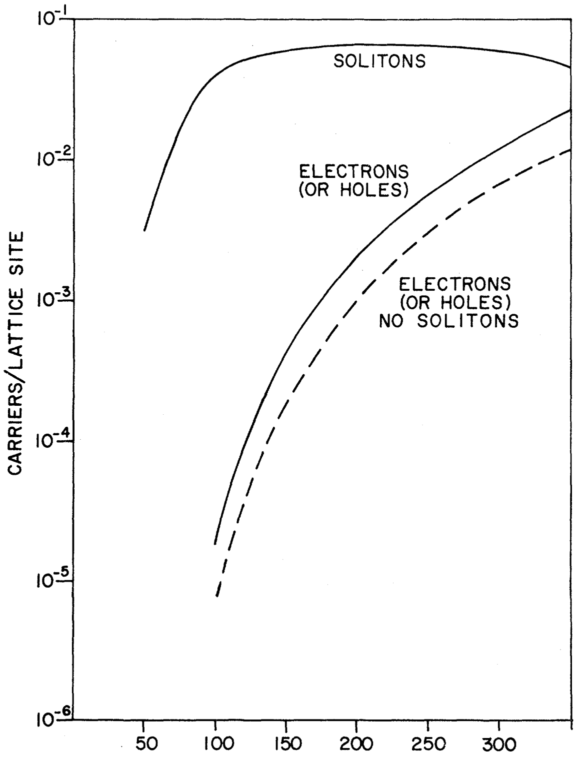

FIG. 2. Calculated electron, hole, and soliton concentrations as a function of temperature for a quarter-filled-band large-U crystal with (solid lines) and without (dashed line) thermal solitons. Parameters are identical to those used for Fig. 1.

It is apparent that at $T=0$ the magnitude of the gap is reduced when $N_d>0$, the reduction being greater for heavier doping. In physical terms, this happens because the gain in electronic energy due to the opening of the gap is partly offset by the free energy of the resulting solitons. For $N_d=0.02$, $\Delta(T=0)$ decreases to $\sim 0.9\Delta_0$, while for $N_d=0.04$, it drops to 0.79 Δ_0. Horovitz[15] has calculated the correction to Δ_0 due to a soliton lattice when the electron-phonon coupling is not weak but U is small. He finds that the reduced-gap parameter Δ_1 at $T=0$ is given in terms of Δ_0, the gap parameter for the soliton-free case, by

$$\Delta_1=\Delta_0[1-(E/K-\tfrac{1}{2}k'^2)\eta^2/k^2+O(\eta^4)] \ , \tag{19}$$

where $E(k)$ and $K(k)$ are the complete elliptic integrals. [The coupling parameter η ($\simeq\Delta_0/2t$) here is twice that of Horovitz[15] since for small U we obtain Eq. (16) instead of the more approximate result from the continuum model. Equation (19) should still, however, be approximately valid for large U.] The parameter k here is related to k' by $k'^2=1-k^2$, and is determined for the soliton lattice case by

$$1/n_s=(l/2)kK(k) \ , \tag{20}$$

with n_s the soliton density. Horovitz's gap parameter Δ_1 is related to the physical half-gap Δ by $\Delta=\Delta_1/k$. Using the parameters of the present calculation results in a predicted gap decrease $\Delta_1/\Delta_0=0.87$ for $N_d=0.04$. When the approximations made in both models are considered, this is in fair agreement with our numerically obtained result of $\Delta(T=0)/\Delta_0=0.79$ for the same case.

The computed gap curves become double valued

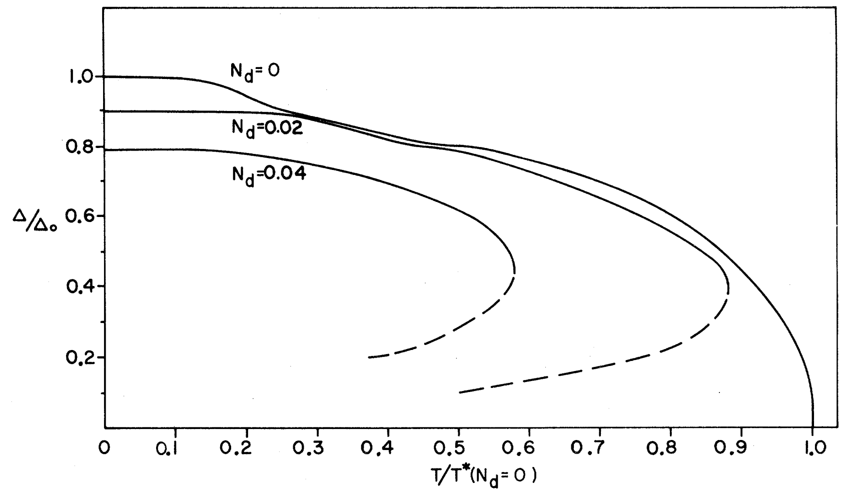

FIG. 3. Variation of the calculated reduced Peierls gap (Δ/Δ_0) with reduced temperature $[T/T^*(N_d=0)]$ for crystals containing thermal solitons only $(N_d=0)$ and chemical-plus-thermal solitons $(N_d=0.02$ and $N_d=0.04)$ at 2% and 4% donor doping levels. Here $\Delta_0/k_B=900$ K, $4t/k_B=4500$ K, and $T^*(N_d=0)$ is the critical temperature for a crystal with thermal solitons only. The dashed-line portions of the curves correspond to unphysical solutions.

for $N_d \neq 0$; in these cases the lower branch of the curve corresponds to a higher free energy for the Peierls-distorted state than for the metallic state, and is therefore unphysical. A similar behavior for the temperature dependence of the Peierls gap has been predicted previously[16,17] for the injection of excess electrons and holes into a uniform quasi-1D conductor. The critical temperature T^*, above which the gap disappears, decreases with an increasing level of doping N_d; for $N_d=0.02$, $T^* \simeq 355$ K, while for $N_d=0.04$, $T^* \simeq 240$ K. Increasing soliton length as the gap decreases "freezes out" the thermal solitons at some point below T^*. For $N_d=0.02$, for instance, this occurs at ~ 350 K.

Carrier and soliton concentrations are shown in Figs. 4 and 5 for $N_d=0.02$ and $N_d=0.04$, respectively. The presence of the excess electrons due to doping shifts the Fermi energy well above midgap for most of the temperature range studied; consequently, the number of band electrons exceeds the number of holes at all temperatures. The disparity in the electron and hole populations is markedly greater for higher doping levels. For $N_d=0.04$ at 100 K, for instance, the electron population is more than 10^3 times the hole population. For both the 2% and 4% doped systems, of course, the soliton concentration exceeds the electron and hole concentrations below T^*. The generation of excess thermal solitons above $2N_d$ has a greater effect on the total soliton population for lower doping levels, as would be expected; for $N_d=0.02$, the peak concentration of excess thermal solitons, which occurs at ~ 200 K, amounts to 57% of the chemical soliton population. At $N_d=0.04$, the chemical soliton concentration is $\sim 1/2l$ even at $T=0$; thus there are no thermal solitons.

The process of adding extra electrons or otherwise

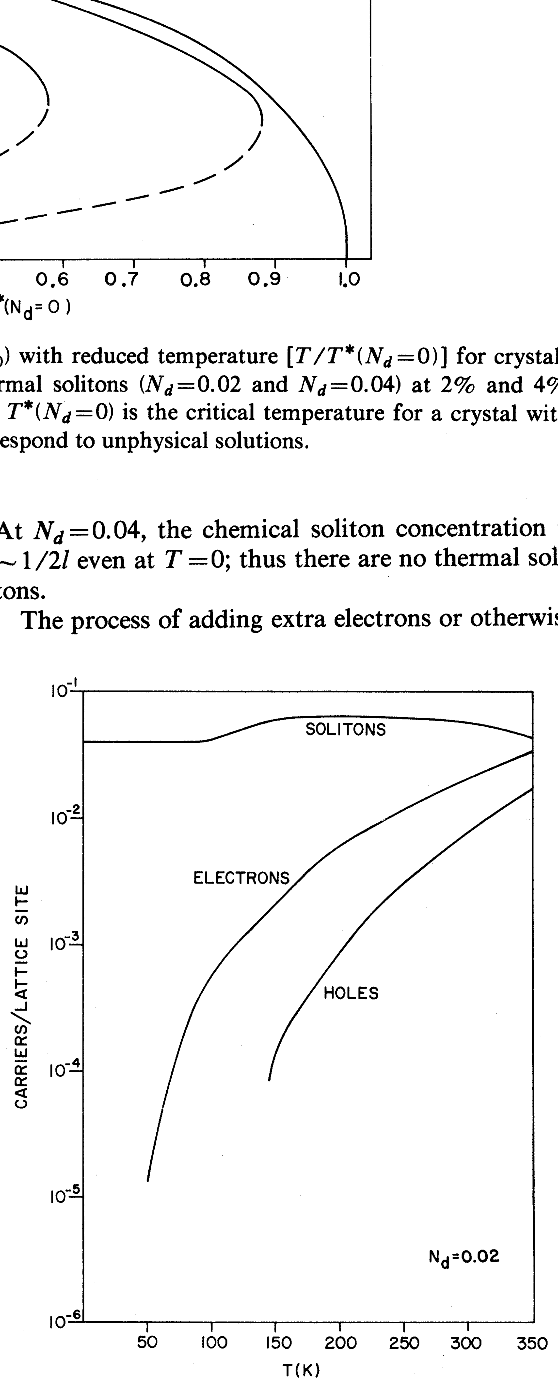

FIG. 4. Electron, hole, and soliton concentrations computed as a function of temperature T for a quarter-filled-band large-U crystal with 2% donor doping $(N_d=0.02)$. Parameters of Fig. 3 were used.

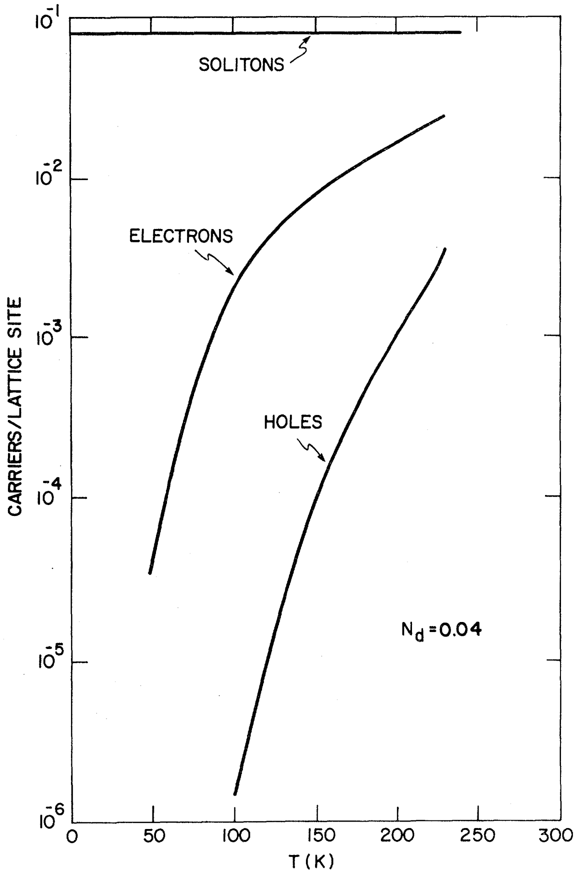

FIG. 5. Calculated electron, hole, and soliton concentrations as a function of temperature T for a crystal with 4% donor doping ($N_d=0.04$). Parameters of Fig. 3 were used.

creating solitons gives rise to disorder which tends to spread the midband levels and thus affect the gap. We have neglected this effect here since, although it has been shown to be of great importance for $(CH)_x$, it is much less so for the crystals we consider. The reasons for this will be taken up in the next section, after description of the crystals.

V. APPLICATION TO $(NMP)_x(Phen)_{1-x}TCNQ$

The model described in the previous sections can be applied to several systems of current experimental interest. One such system is $(NMP)_x(Phen)_{1-x}TCNQ$, $x \simeq 0.50$, which is formed from the charge-transfer compound NMP-TCNQ by substitution of up to half the NMP by the closed-shell molecule phenazine ($Phen^0$).[18,19] When half the NMP has been replaced by $Phen^0$($x=0.50$), each NMP donates one electron to the TCNQ chain, while $Phen^0$ donates no carriers; thus $(NMP)_{0.5}(Phen)_{0.5}TCNQ$ is a quarter-filled-band compound. The crystal structure remains basically that of NMP-TCNQ for up to half the NMP substituted by $Phen^0$. $(NMP)_{0.5}(Phen)_{0.5}TCNQ$ shows a dimerized ground state[18,20–24] with an average lattice spacing of 3.86 Å (Ref. 18) between molecules on the TCNQ chain. On the NMP-Phen chain, NMP and $Phen^0$ alternate; for $x>0.50$, i.e., for NMP concentrations slightly above the quarter-filled-band limit, the excess NMP molecules above $x=0.50$ are randomly inserted into the NMP-Phen alternating sequence. X-ray diffuse scattering appears only at $4k_F$ for $0.5 \leq x \leq 0.57$, indicating $U>4t$ in this range. This is borne out by optical,[25] thermoelectric power,[26] and magnetic studies.[24] From $x=0.57$ to 0.67 both $2k_F$ and $4k_F$ scattering, originating on the same TCNQ stacks, are observed,[20] suggesting $U \sim 4t$. Beyond $x=0.67$ only $2k_F$ scattering is observed.[20]

Diffuse x-ray measurements show that k_F does not change as x increases from 0.5 to 0.54, suggesting that beyond 0.5 the extra electrons go into soliton states.[1,5] Magnetic susceptibility and g-value measurements show that with increasing x in this range there is an increase in defects on the TCNQ chain, the amount of the increase correlating well with $x-0.5$.[5] The defects have spins uncoupled to the 1D antiferromagnetic ground state.[5] Thus the magnetic measurements are additional evidence that the extra electrons, up to $x=0.55$, go into soliton states. Beyond $x=0.55$ the concentration of defects seen in the susceptibility decreases, k_F changes,[20–22] and an incommensurate charge-density-wave state sets in.[5] At $x=0.57$, as can be seen from Fig. 6, the gap is comparable over a wide temperature range to that in an $x=0.51$ sample.

The behavior just described is, as noted above, quite different from that of $(CH)_x$ where the addition of comparable numbers of electron-(or hole-) donating impurities can to a large extent wipe out the effects of the gap. Calculations of Su *et al.*[27] show that the randomness of the soliton arrangement causes the soliton or condensate band to overlap the conduction band in $(CH)_x$ at 8% dopant concentration. Mele and Rice[28] find that the Coulomb field of the randomly arranged impurities causes a considerable spreading of the condensate band, the amount depending on the detailed model of the charged impurity. Both of these effects should be very much smaller for crystals such as $(NMP)_x(Phen)_{1-x}TCNQ$. Coulomb effects should be quite small since the dielectric constant parallel to the chains (the important one for screening since the solitons are quite extended along the chains) is typically greater than 1000 in this type of crystal as compared with 10 in $(CH)_x$. Also in $(NMP)_x(Phen)_{1-x}TCNQ$ the impurities are one

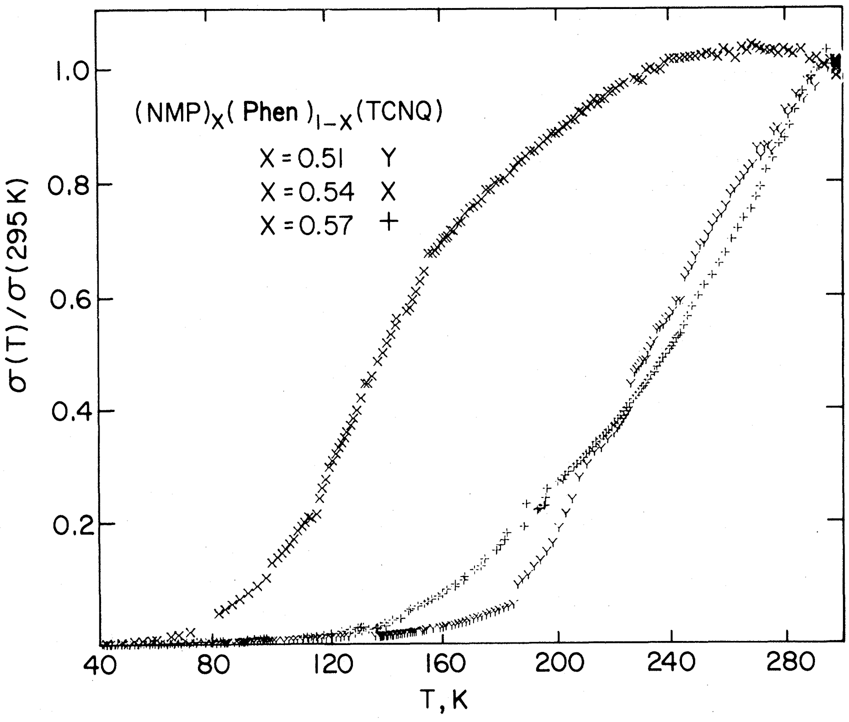

FIG. 6. Experimental a-axis conductivity vs temperature for $(NMP)_x(Phen)_{1-x}(TCNQ)$ for $0.50<x<0.60$ [After A. J. Epstein, J. W. Kaufer, H. Rommelmann, I. A. Howard, E. M. Conwell, J. S. Miller, J. P. Pouget, and R. Comes, Phys. Rev. Lett. 49, 1037 (1982)].

chain away (~8 Å) rather than $\sim\frac{1}{2}$ chain (~2 Å) as in $(CH)_x$. Randomness of the soliton arrangement will have less effect in the crystals for a given concentration since the solitons are shorter and will overlap less. Also, as noted earlier, they tend to avoid each other since the majority have like charge. In addition, the further contribution to randomness of three-dimensional (3D) effects, also discussed in Refs. 27 and 28, will be smaller in the crystals since the Peierls gap is stabilized principally by the interaction between electrons and internal modes in the crystals, with little if any dimerization. Proof of these contentions is found in the fact stated earlier, that for $x>0.55$ (i.e., >5% impurities), $(NMP)_x(Phen)_{1-x}TCNQ$ goes to an incommensurate Peierls transition, i.e., a coherent charge-density wave, whereas in $(CH)_x$, disorder only increases with increasing impurity concentration.

As is seen in Fig. 6, dc conductivity (σ) measurements show a more or less constant activation energy, determined from $\ln\sigma$ vs $1/T$ to be ~900 K, up to $T\sim270$ K for the $x=0.51$ and 0.57 samples. For $x=0.54$, however, σ shows a similar activation energy only below ~160 K. Above this temperature σ has a decreasing activation energy, culminating in a maximum near 240 K. The room-temperature conductivity for the $x=0.54$ sample is 37 (±50%) $\Omega^{-1}\text{cm}^{-1}$, as compared with 5 (±50%) $\Omega^{-1}\text{cm}^{-1}$ for the 0.57 sample. Thus its conductivity is always much larger than that of the 0.51 sample.

For the calculations the bandwidth (equal to $4t$) of the TCNQ chain in $(NMP)_x(Phen)_{1-x}TCNQ$ was chosen by comparison with tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). For the latter compound the TCNQ lattice spacing is 3.819 Å and the bandwidth is ~6000 K. Since the intermolecular distance on the TCNQ chain is somewhat larger for $(NMP)_x(Phen)_{1-x}TCNQ$, we chose $4t$ for the latter case as 4500 K. The parameters $4t$ and Δ_0 are the only ones, apart from x, at our disposal. Once these have been chosen λ is determined by Eqs. (15) or (16), as appropriate to the value of U. To satisfy Eq. (15) with $4t/k_B=4500$ K and $\Delta_0/k_B=900$ K requires $\lambda=0.85$. A more accurate value, from Eq. (14), is $\lambda=0.887$. The value of λ appropriate for a molecular crystal is greatly enhanced over that for coupling due to acoustic modes by the presence of internal modes.[27] The internal-mode contribution to λ is given by[27]

$$\lambda_i=E_p/\pi t\equiv\sum_{l=1}^{G}g_l^2/(\hbar\omega_l\pi t)\ . \qquad (21)$$

where E_p, the polaron binding energy, is, as shown, the sum over the internal modes (specifically over the G internal modes linearly coupled to the electrons) of a term for each mode involving the coupling constant g_l to the mode and its energy $\hbar\omega_l$. λ_i has been found experimentally for electrons on TCNQ in TTF-TCNQ to be 0.35.[28] Since E_p involves the interaction of electrons with internal modes, it is not unreasonable that it have a similar value for electrons on a TCNQ chain in $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}\mathrm{TCNQ}$. Taking into account the difference in values of t, we would then obtain for the latter case, using (21), $\lambda_i = 0.35(6000/4500) = 0.47$. The value of λ will be increased somewhat by the acoustic-mode contribution but is still well below that required to satisfy the gap equation (15), for $U \rightarrow \infty$. Comparison with Eq. (16) shows that a smaller value of λ would be required to satisfy the gap equation for $U \rightarrow 0$. Of course, U is not infinite for these crystals. In fact, as noted earlier, $2k_F$ x-ray reflections were seen as well as $4k_F$ for $x \geq 0.57$. The 0.57 sample, as is seen in Fig. 6, has the same (or perhaps smaller) Δ up to ~ 270 K as the 0.51 sample. (The difference above 270 K will be discussed below.) Thus part of the discrepancy is due to the assumption of infinite U. The remainder must be attributed to the approximate nature of the theory leading to Eqs. (14)–(16). It is well known that this theory leads to only qualitative agreement with experiment, having omitted to treat, among other things, the 3D nature of the transition.

Using Eq. (11) with $4t/k_B = 4500$ K and $\Delta_0/k_B = 900$ K, we obtain the results shown in Figs. 1–5. For $N_d = 0.04$, appropriate to $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}\mathrm{TCNQ}$ with $x = 0.54$, we find that the gap vanishes at about the temperature for which, according to Fig. 6, σ for $x = 0.54$ achieves its maximum. A maximum in the neighborhood of the gap vanishing is, of course, expected since σ decreases below due to decrease in carrier concentration and above due to decrease in mobility with temperature. The maximum is quite rounded, i.e., the variation in σ with T quite gradual, compared to that in nominally pure and perfect TTF-TCNQ,[29] for example. We attribute this to the disorder introduced by the solitons, which although not as serious as in $(\mathrm{CH})_x$ still can be expected to affect the 3D ordering. Indeed, σ vs T looks like that for moderately irradiated TTF-TCNQ.[30] It is interesting to note that in the as-grown state the familiar commensurate crystals—NMP-TCNQ,[31] quinolinium $(\mathrm{TCNQ})_2$,[32] acridinium $(\mathrm{TCNQ})_2$,[32] and acridizinium $(\mathrm{TCNQ})_2$ (Ref. 32)—all have rounded maxima of the type seen in Fig. 6 while the incommensurate crystals—TTF-TCNQ, tetraselenafulvalene-TCNQ and the numerous members of their family—have relatively sharp maxima. This suggests that there are usually impurities or other defects in all the commensurate crystals listed above which go into soliton states and affect the gap as we have discussed. For quinolinium-, acridinium-, and acidizinium-$(\mathrm{TCNQ})_2$, in fact, the results of this paper should be directly applicable since they are quarter-filled-band large-U crystals.

The large decrease in gap of the $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}\mathrm{TCNQ}$ sample with $x = 0.54$, as compared with the 0.51 or 0.57 samples, can account for most of the excess conductivity of the former. As noted earlier,[5] for $N_d = 0.04$ the change in gap at 150 K, for example, is sufficient to increase the number of conduction electrons and holes by a factor of 20. At lower temperatures the excess conductivity is expected to be at least partly due to a soliton contribution to σ. As discussed in Sec. III, we do not expect much soliton motion, but electron hopping from negatively to positively charged solitons can contribute to σ. The conductivity due to interchain hopping of this kind at very low soliton concentrations was calculated by Kivelson for polyacetylene.[33] For the much higher concentrations of our concern, intrachain hopping might be more important.

At the highest temperatures for which there are data in Fig. 6 it is seen that σ vs T for the 0.57 sample continues to rise steeply while that for 0.51 is beginning to flatten. This also is in agreement with our calculations. For $N_d = 0.01$, Δ vs T lies between the curves on Fig. 3 for $N_d = 0$ and 0.02, the shape being similar to that of the latter, and Δ vanishes at 385 K. Thus the gap has already decreased significantly by 280 K, accounting for the flattening seen in Fig. 6.

VI. CONCLUDING REMARKS

The effects of a soliton population on the Peierls gap and carrier concentrations in a quarter-filled-band, highly correlated quasi-1D crystal have been studied by self-consistent solution of the charge-balance equation and the gap equation. The results establish the following:

(1) The Peierls gap is decreased substantially at $T = 0$ by the presence of solitons, the reduction being greater for higher soliton concentrations (this point was previously established by Horovitz,[15] using different methods).

(2) The gap magnitude decreases faster with increasing temperature in soliton-containing systems than in soliton-free Peierls systems. The gap disappears above a certain critical temperature, which is lower for chemically doped crystals than for those containing only thermal solitons. In the latter case,

the gap goes smoothly to zero at the critical temperature; in the former, the gap has a nonzero value below the critical temperature and disappears above.

(3) Soliton-containing systems, with or without chemical doping, show a marked increase in the concentration of band carriers, and thus in the conductivity (at any temperature), over soliton-free Peierls systems.

(4) Over a wide range of temperatures, even in the absence of chemical doping, soliton concentrations are significantly higher than electron or hole carrier concentrations.

Although these results were derived for a specific case—quarter-filled band and large-U limit—they can be expected to hold, qualitatively, for any commensurate system, whatever the band filling and the magnitude of $U/4t$. The decrease in gap is due to the additional free energy of the solitons and to the extra band electrons and holes arising from the existence of a level in the forbidden gap. Both of these effects will occur in any commensurate quasi-1D system. The present calculations suggest that the presence of solitons should substantially affect the transport properties of the quarter-filled-band, highly correlated, quasi-1D crystals. Subsequent work will explore the nature of soliton effects on transport in these materials.

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