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Bipolarons in quinolinium di-tetracyanoquinodimethanide [Qn(TCNQ)$_2$] and (N-methylphenazinium)$_x$(phenazine)$_{1-x}$ tetracyanoquinodimethanide [(NMP)$_x$(Phen)$_{1-x}$(TCNQ)]

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Optical-absorption data have shown that Qn(TCNQ)$_2$ and (NMP)$_x$(Phen)$_{1-x}$(TCNQ) are semiconductors up to $T=300$ K, with gaps due mainly to Peierls distortion on the TCNQ chains. To explain the observed slow falloff of the Peierls gaps with temperature, there must be a small additional contribution to the gap due to the cation potential and perhaps Coulomb effects. As a result of the interchain potential, the stable soliton defects arising from electrons in excess of 0.5/TCNQ molecule are polarons rather than kinks. The stable polarons are found to consist of pairs of $-\frac{1}{2}e, -\frac{1}{2}e$ kinks or $+\frac{1}{2}e, +\frac{1}{2}e$ kinks, thus being bipolarons. The energy levels, creation energy, and length of the bipolarons are calculated in terms of the interchain potential Δ_e. To obtain an approximate value for Δ_e the Peierls portion of the gap Δ_0 is calculated as a function of temperature T for different Δ_e values and compared with the temperature variation of Δ_0 obtained from optical absorption. To carry this out it is necessary to determine the numbers of positive and negative bipolarons as functions of T. This is done by calculating their chemical potentials and relating these to the Fermi energy. It is found that the theoretical $\Delta_0(T)$ agrees best with experiment for a Δ_e/k_B value of ~ 25 K. The energy levels of the electrons bound in a bipolaron may then be calculated. Unambiguous evidence for the presence of bipolarons is not found in the optical absorption. Consideration shows that the bipolaron absorption may be quite broad, due to structural imperfections as well as to overlap, and therefore difficult to detect.

I. INTRODUCTION

Qn(TCNQ)$_2$ and (NMP)$_x$(Phen)$_{1-x}$(TCNQ) for $x \simeq 0.5$ are quasi-one-dimensional charge transfer salts characterized by a close to one-quarter-filled conduction band on the TCNQ chains, the only ones conducting, and large Coulomb repulsion (compared to the bandwidth) for a second electron on the same site ("large U"). Optical absorption of these materials has recently been found to vanish at low frequencies;[1] this shows that, contrary to the supposition of many earlier investigators,[2–5] they have gaps at the Fermi energy. The strong appearance in the absorption of the TCNQ a_g modes,[1] expected to be infrared inactive due to their symmetry, shows that at least a large part of the gaps results from Peierls distortion.[6] In the large-U limit the wave vector of the Peierls distortion is $4k_F$. For a quarter-filled-band material a $4k_F$ charge-density wave also results from Coulomb effects when $U>0$ and $V_1>2V_2$, where V_1 and V_2 are nearest-neighbor and next-nearest-neighbor repulsions, respectively.[7] Thus the gap could originate partly from Coulomb effects. If Coulomb effects were predominant, the gap would be due to V_1-2V_2 for the quarter-filled-band, large-U case.[7]

The change in the a_g modes from resonance to antiresonance is consistent with total gaps of ~ 1200 K in Qn(TCNQ)$_2$ and 1800 K in (NMP)$_x$(Phen)$_{1-x}$(TCNQ) for $x \simeq 0.5$,[1] in good agreement with the values deduced earlier from variation with temperature, T, of conductivity, σ.[8,9] The variation of the Peierls portion of the gaps with T may be obtained from the variation with T of the oscillator strengths of the a_g modes.[10,11] Some of the data[1] for Qn(TCNQ)$_2$ are reproduced in Fig. 1. As T increases from 6 K, the Peierls gap is seen to decrease fairly steeply up to ~ 100 K. Beyond 100 K it decreases quite gradually with further increase in T, about 25% remaining at 300 K. Similar results were obtained for (NMP)$_x$(Phen)$_{1-x}$(TCNQ), $0.50 \leq x \leq 0.56$, but the data show a great deal more scatter. The slow decrease of the gap is not what is expected from mean-field theory. If the gap were entirely of Peierls origin, it might be speculated that the Peierls transition actually occurs at ~ 150 K and the slow decrease thereafter is due to fluctuations, as was found to be the case for tetrathiafulvalene (TTF) in TTF-TCNQ.[11] However, the behavior of σ versus T indicates Qn(TCNQ)$_2$ is still a semiconductor above 150 K. A similar slow decrease in the a_g mode oscillator strength above ~ 150 K is seen for (NMP)$_x$(Phen)$_{1-x}$TCNQ with $0.50 \leq x \lesssim 0.53$,[1] where it is clear from the rapid decrease of σ with T up to 300 K that a sizable gap persists throughout the T range.[12] Thus we believe the slow gap decrease is due to the presence of an additional potential on the chain arising either from Coulomb effects or the cation chains. As will be discussed in more detail subsequently,[13] an additional potential Δ_{ad} supporting the gap stabilizes the Peierls distortion by keeping electrons from rising into the conduction band when T increases. Not surprisingly in view of the relatively small gaps in these materials, a small Δ_{ad} has a large stabilizing effect.[13] From the observed decrease of the Peierls gap to 300 K,

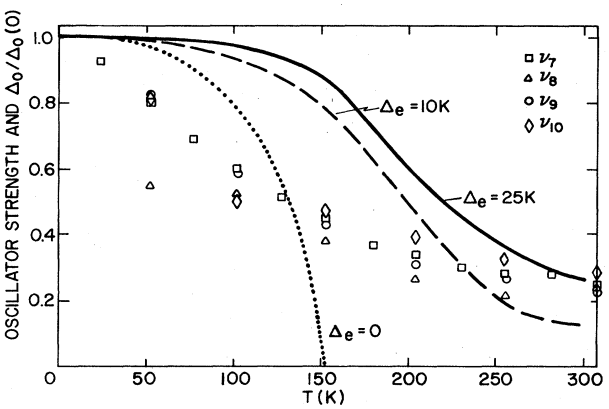

FIG. 1. Data points represent oscillator strength (normalized to the 6-K value) vs T, determined as described in Ref. 1, for the TCNQ a_g modes ν_7 (691 cm^{-1}), ν_8 (600 cm^{-1}), ν_9 (306 cm^{-1}), and ν_{10} (124 cm^{-1}) in Qn(TCNQ)$_2$. Because these modes are present only as a result of the Peierls distortion, their oscillator strength is proportional to the Peierls gap parameter Δ_0. The solid and dashed lines represent the calculated T dependence for Qn(TCNQ)$_2$ of Δ_0 (normalized to its 0 K value) for a $T=0$ gap in the absence of impurities of 1200 K, $t=1145$ K, a 4% donor concentration, and $\Delta_e=25$ K and $\Delta_e=10$ K, respectively. The dotted line represents the calculated Peierls gap dependence for $\Delta_e=0$ and all other parameters the same as for the other two lines.

Δ_{ad} must be less than 25% of the 0-K gap. It is our conclusion from the calculations to be discussed, the results of which are shown in Fig. 1, that for a Peierls gap of 1200 K Δ_{ad} can be no greater than ~ 25 K to allow the amount of decrease found experimentally for the a_g modes. Thus the data of Fig. 1 give essentially the decay of the total gap with T.

We note that the gap in Qn(TCNQ)$_2$ at room temperature is quite small, approximately a few hundred K. Evidence for this, apart from the gap decrease shown in Fig. 1, comes from the behavior of σ versus T. Above 240 K σ actually decreases with increasing T,[8] the T dependence of the mobility being stronger than that due to the variation of carrier concentration with T. If the gap were entirely due to Coulomb effects, this in itself would indicate that V_1-2V_2 is quite small. According to Ref. 7 reasonable values for V_1 and V_2 are $3\sqrt{2}t$ and $\sqrt{2}t$, respectively. With $t \sim 1100$ K for these materials,[8] V_1-2V_2 would then be ~ 1500 K. The fact that $4k_F$ diffuse x-ray scattering is seen from 25 K all the way to room temperature[14] does not mean $V_1-2V_2>0$; there could be a small external mode contribution to the Peierls distortion. The fact that the Peierls distortion is at $4k_F$ requires only that U be large. Evidence that U remains large to room temperature comes from thermoelectric power[15] and magnetic susceptibility,[16] for example. Small values of near-neighbor repulsions and large on-site repulsion can be accounted for by screening, which takes some distance to develop fully. At room temperature due to the small gap the carrier concentration in Qn(TCNQ)$_2$ is ~ 0.1 times that of metallic TCNQ compounds. Below room temperature, down to ~ 50 K, Qn(TCNQ)$_2$ is unusual in having a low-frequency dielectric constant parallel to the chains that is never less than 3×10^4 and reaches values greater than 10^5.[5] We conclude that, although the existence of the additional potential Δ_{ad} has important effects, almost the entire gap in Qn(TCNQ)$_2$ is due to Peierls distortion. Perhaps the Coulomb contribution to the gap is more important in (NMP)$_x$(Phen)$_{1-x}$(TCNQ) for x close to 0.5. Unfortunately the optical data on such samples raised questions about their quality. Nevertheless, for $0.53 \le x \le 0.57$, although, unlike Qn(TCNQ)$_2$, the decrease in a_g mode amplitude with increasing T showed a great deal of scatter, in no case was it less than what is shown in Fig. 1. This indicates that for this range of x the gap in (NMP)$_x$(Phen)$_{1-x}$(TCNQ) also was mainly a Peierls gap.

(NMP)$_x$(Phen)$_{1-x}$TCNQ is unique in that the number of electrons per site on the TCNQ chain, equal to x, may be varied in a controlled way by changing the phenazine concentration.[9] It was observed that k_F stays constant while x is increased from 0.50 to 0.56.[17] The suggestion has been made that this could be accounted for by the occurrence of configurations with electron pairs bound on adjacent sites due to Coulomb correlation.[7] Because the Coulomb effects that would create such pairs are apparently weak, as discussed above, it was concluded that in this doping range the defect states that accommodate any electrons beyond 0.50 per site are soliton states in the gap. The particular solitons we suggested[12] were kinks, domain walls interpolating between two degenerate arrangements of the Peierls-distorted TCNQ chain. The properties of these solitons for quarter-filled-band large-U-limit materials have been derived by Rice and Mele,[18] treating them as half-filled-band materials with $U=0$ and neglecting V_1, V_2, etc. Investigations of the effect of Coulomb correlations on solitons in the half-filled-band case, in particular polyacetylene, have shown that they survive the relatively large Coulomb correlations—$U \sim 2t$, $V_1 \sim t$—appropriate to polyacetylene.[19,20] From the small effect, if any, of V_1 and V_2 on the gap discussed earlier, it is expected that solitons would survive the effects of Coulomb correlations in these materials also. However, kink solitons will not survive even a small interchain potential with the periodicity of the Peierls distortion, as will now be discussed.

The combination of quarter-filled band, large U, and the Peierls distortion being a site distortion for these materials,[6] results in the Peierls-distorted chain consisting of molecules of two different shapes alternating.[21] Because the two shapes result from different amounts of frozen-in internal modes, to which the electrons are well coupled, along with shape alternation there is an alternation of the probability of finding a conduction electron on a site. Given one arrangement of the Peierls-distorted chain, a second, degenerate, arrangement may be generated by shifting the first arrangement by one molecule. The degeneracy is lifted, however, if there is an appropriate potential on the TCNQ chains due to the cation chains. In the case of (NMP)$_{0.5}$(Phen)$_{0.5}$(TCNQ) the NMP's, which are positively charged, and phenazines, which are neutral, alternate. The resulting potential on the TCNQ chains has the periodicity of the Peierls distortion. It is clear that the arrangement with the conduction electrons preferentially opposite the NMP$^+$'s has lower energy. If a pair of kinks were formed with the higher-energy lattice arrangement between them they would tend to come close together to minimize the energy of the system.[21] In this situation, as pointed out by Campbell and Bishop,[22] even in the limit of small external potential the stable excitation is another type of soliton, a bound-kink pair or polaron.

Qn(TCNQ)$_2$ cannot be doped in a controlled way but, because it has a Peierls gap, must have thermally generated solitons of some kind and most likely also has solitons due to accidentally incorporated impurities. The similarity of T variation of σ and thermopower[15] of typical Qn(TCNQ)$_2$ samples to samples of (NMP)$_{0.54}$(Phen)$_{0.46}$(TCNQ),[23,24] suggest that the Qn(TCNQ)$_2$ samples have $\sim 4\%$ donors. This donor concentration is consistent with x-ray measurements of the low-temperature correlation length along the chains of ~ 10 lattice sites,[14] as will be seen later. Of course there is no alternation of charge on the Qn chains as on the NMP$_{0.5}$Phen$_{0.5}$ chains, but it is well known that there is a random arrangement of the dipoles on the Qn molecules.[2] This will result in a Fourier component of the potential on the TCNQ chains with the periodicity of the Peierls distortion, making the stable solitons polarons. As has already been noted, the potential required to account for the observed slow-gap variation with temperature is quite small. The remaining Fourier components contribute to disorder on the TCNQ chains, but the existence of the Peierls distortion and $4k_F$ x-ray scattering indicate that the disorder effect is not significant.

In what follows we will first extend the present theory for polaron properties[22] to the quarter-filled-band large-U case. It will be found that the only stable polarons consist of pairs of charged kinks, thus bipolarons in the current terminology.[22] To avoid cumbersome notation, however, we will frequently refer to them as polarons. The theory leads to expressions for the creation energy of the bipolarons and their energy levels in the gap in terms of the interchain potential, to be denoted Δ_e. Because the effects of V_1 and V_2 are small, as has been seen, and difficult to treat, to obtain an approximate value for Δ_e we will assume that the non-Peierls part of the gap is entirely due to Δ_e. We can then obtain a value for Δ_e by calculating the variation of the Peierls gap with temperature, with Δ_e as a parameter, and comparing with the experimental results shown in Fig. 1. To calculate the gap we need expressions for the free energy and variation with temperature of positive and negative bipolarons, which will be obtained in Sec. III. Comparison of theory with experiment will be carried out mainly for Qn(TCNQ)$_2$ because, as indicated earlier, the optical data for (NMP)$_x$(Phen)$_{1-x}$(TCNQ) showed considerable scatter. Agreement of experiment with theory is good in many respects; we discuss reasons for the discrepancies.

II. PROPERTIES OF BIPOLARONS

Campbell and Bishop[22] found that the polaron excitation is a solution of the equations derived from the continuum Hamiltonian[25] for a Peierls dimerized chain. The polaron solution has gap parameter[22]

$$\Delta_P(y)=\Delta_0-\kappa_0 v_F\{\tanh[\kappa_0(y+y_0)] -\tanh[\kappa_0(y-y_0)]\}\ , \tag{2.1}$$

where, in the absence of an external potential, Δ_0 is the ground-state gap parameter, i.e., the Peierls gap parameter, and v_F the Fermi velocity. The quantity κ_0 is given by

$$\kappa_0 v_F=(\Delta_0^2-\omega_0^2)^{1/2}\ , \tag{2.2}$$

where $\pm\omega_0$ represents the distance from midgap of the two bound states in the gap corresponding to the polaron. The distance $2y_0$ between the centers of the two kinks bound in the polaron is given by the condition[22]

$$\tanh(2\kappa_0 y_0)=\kappa_0 v_F/\Delta_0\ . \tag{2.3}$$

In the spirit of the approximation that takes the length of a kink as $2\xi=4ta/\Delta_0$,[25] where t is the overlap integral and a the lattice constant, the length l of a polaron suggested by Eq. (2.1) is

$$l=2y_0+2/\kappa_0=2y_0+4ta/(\Delta_0^2-\omega_0^2)^{1/2}\ . \tag{2.4}$$

Equations (2.1)—(2.4) are written for the case of no external potential. When there is an external potential Δ_e, Δ_0 in these equations must be replaced by[22]

$$\tilde{\Delta}_0=\Delta_0+\Delta_e\ . \tag{2.5}$$

The creation energy of a polaron E_P is a sum of two terms: E_P^{latt}, the change in lattice energy due to the presence of a polaron, and E_P^{el}, the change in the total electronic energy due to the polaron. The former term is[22,25]

$$E_P^{\text{latt}}=\frac{1}{\pi\lambda v_F}\int_{-L}^{+L}[\Delta_P^2(y)-\Delta_0^2]dy\ , \tag{2.6}$$

where λ is the electron-phonon coupling constant. When the length L of the chain is allowed to go to ∞, for the case $\Delta_e\neq 0$ it is found

$$E_P^{\text{latt}}=-\frac{4}{\pi}\frac{\kappa_0 v_F}{\lambda}+\frac{4}{\pi}\gamma\tilde{\Delta}_0\tanh^{-1}\left[\frac{\kappa_0 v_F}{\tilde{\Delta}_0}\right]\ , \tag{2.7}$$

where

$$\gamma\equiv\Delta_e/\lambda\tilde{\Delta}_0\ . \tag{2.8}$$

This result is, as expected, the same for a quarter-filled-band, large-U case as for a half-filled-band case with $U=0$.[22]

One contribution to E_P^{el} comes from the valence electrons, whose wave vectors are changed due to a phase shift $\delta(k)$ of their wave functions in the presence of the polaron. A second contribution comes from the removal of an electron from the valence band in the formation of a pair of kinks in the $U\rightarrow\infty$ case.[18] Finally, there is the contribution due to the electrons in the bound states. In the $U\rightarrow\infty$ limit we obtain from these terms

$$E_P^{\text{el}}=\frac{1}{2\pi}\int_{-K}^{+K}\frac{\partial E_k}{\partial k}\delta(k)dk+\tilde{\Delta}_0 +[n(+\omega_0)-n(-\omega_0)]\omega_0\ . \tag{2.9}$$

The first term in (2.9) is formally the same as that in Ref. 25 [Eq. (A12)] for the case of the kink except that a factor 2 has been omitted here because there are half as many electrons in the valence band (spinless fermions). K is the cutoff wave vector, which will be allowed to go to ∞, and E_k is the ground-state energy for an electron with wave vector k,

$$E_k = -(\epsilon_k^2 + \tilde{\Delta}_0^2)^{1/2} . \tag{2.10}$$

The term $\tilde{\Delta}_0$ represents the energy lost when an electron is removed from the valence band to form the kink pair and the last term represents the energy of the electrons in the bound states, $n(+\omega_0)$ and $n(\omega_0)$ being the numbers in the upper and lower states, respectively.

Apart from the factor 2 the first term in (2.9) leads to the same result as obtained by Campbell and Bishop.[22] Combining (2.8) and (2.9) we obtain the total creation energy for the quarter-filled-band $U \rightarrow \infty$ case with $\Delta_e \neq 0$:

$$\begin{aligned} E_P = {} & [n(+\omega_0) - n(-\omega_0) + 1]\omega_0 + (2/\pi)\kappa_0 v_F \\ & - (2\omega_0/\pi)\tan^{-1}(\kappa_0 v_F/\omega_0) \\ & + \frac{4}{\pi}\tilde{\Delta}_0 \gamma [\tanh^{-1}(\kappa_0 v_F/\tilde{\Delta}_0) - (\kappa_0 v_F/\tilde{\Delta}_0)] . \end{aligned} \tag{2.11}$$

The quantities $\kappa_0 v_F$ and ω_0 must be chosen to minimize E_P. The relation (2.2) suggests that we choose

$$\kappa_0 v_F = \tilde{\Delta}_0 \sin\theta, \quad \omega_0 = \tilde{\Delta}_0 \cos\theta , \tag{2.12}$$

and, introducing these relations into (2.11), minimize E_P with respect to θ. This leads to the equation for θ:

$$\begin{aligned} 0 = \frac{2}{\pi}\sin\theta \{ & (\pi/2)[n(+\omega_0) - n(-\omega_0) + 1] \\ & - \theta - 2\gamma \tan\theta \} . \end{aligned} \tag{2.13}$$

Due to the spinlessness no more than one electron may populate a level. Restricting θ to the range 0 to $\pi/2$, we find that the case $n(+\omega_0)=0$, $n(-\omega_0)=1$ leads to $\theta=0$, for which $\omega_0 = \tilde{\Delta}_0$, i.e., the electron settles back into the ground state. For the case $n(+\omega_0)=1$, $n(-\omega_0)=0$ Eq. (2.13) can be satisfied for $\theta \neq 0$. However, this still does not lead to a stable polaron because the electron in the upper level can fall into the empty lower level, reducing this case to the previous one. The only stable polarons are found to be a negative bipolaron with $n(+\omega_0)=1$, $n(-\omega_0)=1$, and a positive bipolaron with $n(+\omega_0)=0, n(-\omega_0)=0$. In making a bipolaron in this $U \rightarrow \infty$ case one electron is removed from the valence band. The second electron in the negative bipolaron comes from a donor impurity; the bipolaron charge is only $-e$ nevertheless because of the screening charge of $+e$ from the missing electron in the valence band. To make a positive bipolaron the electron taken from the valence band must go into an acceptor impurity, leaving only the screening charge of $+e$ for the bipolaron. Alternatively, one may consider that the negative bipolaron is made up of two kinks each with $-\frac{1}{2}e$, while the positive bipolaron is made up of two $+\frac{1}{2}e$ kinks. For both of these bipolarons the equation for θ obtained from (2.12) and (2.13) is

$$\theta + 2\gamma \tan\theta = \pi/2 . \tag{2.14}$$

To determine κ_0 and ω_0 it is necessary to find the value of γ, which requires in turn the value of Δ_e.

III. BIPOLARON STATISTICS

For the calculation of the Peierls gap, and through it the determination of γ, it is necessary to know the numbers of positively and negatively charged bipolarons as functions of temperature. These numbers may be obtained from the free energy of the bipolarons, F_P. The form of F_P depends on whether or not the polarons are free to move among the lattice sites. In polyacetylene the solitons or polarons are free to do so even when bound because the impurities are interstitial and a bound pair of charged impurity and soliton or polaron can diffuse. Conceivably this model could hold for Qn(TCNQ)$_2$ because we do not know where the impurities are, but it is not valid for (NMP)$_x$(Phen)$_{1-x}$TCNQ; there only unbound polarons would be free to move among the lattice sites. This would include polarons of the same sign as the dominant impurities, and thermally generated polarons of either sign. Thus in a sample with background charged impurity concentration substantially smaller than the number of thermally generated polarons the polarons can move freely. The required maximum impurity concentration would be $\lesssim 1\%$ at room temperature, as will be seen, and smaller at lower temperatures.

When the number of polarons is comparable to or greater than the donor concentration and the donor impurities cannot diffuse, the dielectric constant determines whether or not the polarons are bound. For Qn(TCNQ)$_2$ the large value of $\epsilon_{\parallel}$, the dielectric constant parallel to the chains, and its temperature variation, make it difficult to decide this question. Starting from a value ~ 3000 at very low temperature, $\epsilon_{\parallel}$ for Qn(TCNQ)$_2$ increases with T to a peak value greater than 10^5 at ~ 90 K and then decreases, more or less linearly with T, to $\sim 3 \times 10^4$ at 300 K.[5] If the impurity could be considered a point charge and $\epsilon_{\parallel}$ attained its full value within a lattice constant, the polarons would be bound only at quite low temperatures, < 30 K.[26] We have made an estimate of the spatial variation of $\epsilon_{\parallel}$ based on the model of Ref. 5, in which the large value of $\epsilon_{\parallel}$ is due to the partial trapping of conduction electrons between barriers. With this we find that the negatively charged polarons would indeed be bound to donors at 90 K, for example, if the length of the polaron retained its low-temperature value. With decreasing gap, however, the polaron length increases, according to Eqs. (2.2)–(2.4); this causes the fraction of the polaron seeing an incompletely screened donor charge to grow progressively smaller. Because Δ_e is determined mainly by the gap variation in the region where the gap has decreased substantially, we have taken the polarons to be free for the calculation of F_P. The gap is in any case insensitive at low temperatures to the entropy term in F_P.[27]

On the assumption that the bipolarons are able to move freely the number of possible ways of arranging n_P of them on a chain with N molecules or sites is

$$W(n_P) = \frac{(N/l)!}{n_P!(N/l - n_P)!} . \tag{3.1}$$

The total number of configurations is the product of $W(n_P)$ and $W_{(+-)}$, the number of ways of designating n_P^- of the bipolarons to be negative and n_P^+ to be positive.[28] We find

$$W_{(+-)}=(4)^{n_P^-}\left[\frac{n_P!}{(n_P^-)!(n_P^+)!}\right] . \tag{3.2}$$

The factor $(4)^{n_P^-}$ results from there being two electrons on a negative bipolaron each of which may have two possible spin directions; thus there are four ways of creating a negative bipolaron. With this, the free energy of the bipolarons may be written

$$F_P=(n_P^+ + n_P^-)E_P - k_BT\ln W(n_P)W_{(+-)} . \tag{3.3}$$

Here we have neglected the kinetic energy contribution, which should be small compared to the other terms. Differentiating F_P with respect to n_P^- and n_P^+ we obtain the chemical potentials μ_P^- for negative bipolarons and μ_P^+ for positive bipolarons, respectively:

$$\mu_P^- = E_P - k_BT\ln\left[\frac{4(N-n_Pl)}{n_P^- l}\right] , \tag{3.4a}$$

$$\mu_P^+ = E_P - k_BT\ln\left[\frac{(N-n_Pl)}{n_P^+ l}\right] . \tag{3.4b}$$

The apparent asymmetry between negative and positive bipolarons, i.e., the difference of a factor 4 in the arguments of the logarithms, will be shown in Sec. IV to result from the condition $U\rightarrow\infty$.

Because a positive and a negative bipolaron may recombine, producing phonons whose chemical potential is zero,[29]

$$\mu_P^+ + \mu_P^- = 0 . \tag{3.5}$$

With (3.4) this leads to

$$n_P^- = \frac{n_P}{2}\pm\tfrac{1}{2}\{n_P^2-[4(N/l-n_P) \times\exp(-E_P/k_BT)]^2\}^{1/2} , \tag{3.6}$$

and a similar expression for n_P^+ with ± replaced by ∓. The upper signs hold for the case of donor doping, the lower for acceptor doping. To determine n_P^- at any given temperature it is still necessary to know μ_P^- because n_p is a function of μ_P^-. It is clear that μ_P^- must be related to μ_n, the Fermi energy, because electrons and holes interact with polarons. An electron may drop from the conduction band into a level of a positive bipolaron, resulting in an unstable neutral polaron that breaks up into phonons. Similarly, an electron may be thermally excited from a negative bipolaron into the conduction band and the unstable polaron left behind breaks up into phonons. From these "chemical reactions" we obtain the relation

$$\mu_P^- = -\mu_P^+ = \mu_n . \tag{3.7}$$

Thus Eqs. (3.4), (3.6), (3.7), and the corresponding equation for n_P^+ enable a determination of n_P^- and n_P^+ once μ_n is known.

To determine μ_n we make use of the electrical neutrality condition

$$p+N_d+n_P/N=n+2n_P^-/N , \tag{3.8}$$

where p, n, and N_d are hole, electron, and donor concentrations, respectively. If Eq. (3.8) is multiplied by N, the right-hand side gives the number of electrons actually found in the conduction band or on bipolarons, while the left-hand side gives the number available to go into the conduction band or bipolarons. It is assumed that each donor contributes one electron. The number of bipolarons appears on the left-hand side because one electron is withdrawn from the valence band for each bipolaron formed.

It is instructive to consider Eq. (3.8) in the low-temperature limit. In that limit p may be neglected and $n_P=n_P^-$. We then obtain from (3.8)

$$n_P^-/N\rightarrow N_d-n,\quad T\rightarrow 0 , \tag{3.9}$$

i.e., for every electron that goes into the conduction band a negative polaron is destroyed. The other electron in the bipolaron goes back into the valence band. Equation (3.9) does not hold, of course, at higher temperatures.

Use of Eq. (3.8) to determine μ_n requires knowledge of the relations between the various quantities and μ_n. The relations between n, p, and μ_n are[27]

$$n=(1/\pi)\int_{ka=\pi/2}^{ka=\pi} f_k^+ d(ka) , \tag{3.10a}$$

$$p=(1/\pi)\int_{ka=0}^{ka=\pi/2} f_k^- d(ka) , \tag{3.10b}$$

where f_k^+ and f_k^- are the distributions in the upper (conduction) band and lower (valence) band, respectively, and a is the lattice constant. The relations between n_P, n_P^-, and μ_n are given by (3.4), (3.6), and (3.7). N_d is determined by the doping of the sample. The only other quantity needed for Eq. (3.8) is the gap, whose determination we consider in the next section.

IV. GAP CALCULATION

The gap is found by minimizing the total free energy with respect to $\tilde{\Delta}_0$. The lattice portion of the free energy for a chain with N lattice sites is[27]

$$F_{\text{latt}}=N(\tilde{\Delta}_0-\Delta_e)^2/2\pi t\lambda . \tag{4.1}$$

For the case of site distortion[30]

$$\lambda=(1/\pi t)\sum_i (g_i^2/\hbar\omega_i) , \tag{4.2}$$

where g_i and ω_i are the coupling constant and frequency of the ith internal mode and the sum is over the symmetric modes. The electronic contribution is[27]

$$F_{\text{el}}=\mu_n nN-k_BT\sum_k \ln\{1+2\exp[(\mu_n-E_k)/k_BT]\} , \tag{4.3}$$

where E_k is given by Eq. (2.10). Differentiating the total free energy, which is the sum of (4.1), (4.3), and (3.3), with respect to $\tilde{\Delta}_0$, we obtain the gap equation

$$\frac{1}{\lambda t}\left[\frac{\tilde{\Delta}_0-\Delta_e}{\tilde{\Delta}_0}\right]+\frac{nPf(\theta)}{\tilde{\Delta}_0} = \int_0^{\pi/2}\frac{f_k^-}{|E_k^-|}dka-\int_{\pi/2}^{\pi}\frac{f_k^+}{E_k^+}dka\ , \qquad (4.4)$$

where

$$f(\theta)=\pi\cos\theta+2(\sin\theta-\theta\cos\theta)\ , \qquad (4.5)$$

θ being the solution of Eq. (2.14) and thus a function of γ.

The reason for the persistence of the gap when $\Delta_e \neq 0$ is readily seen from Eq. (4.4). The first term on the left may be thought of as representing a changed coupling to the acoustic modes, λ being replaced by $\lambda_{\rm eff}=\lambda/(1-\Delta_e/\tilde{\Delta}_0)$. As $\tilde{\Delta}_0$ approaches Δ_e, which is now the limiting value of the gap rather than zero, $\lambda_{\rm eff}$ increases rapidly; this increases the Peierls portion of the gap. In physical terms the presence of the interchain potential helps sustain the Peierls gap, without requiring a payment of lattice deformation, by keeping down the number of electrons that get to the conduction band and thus destabilize the gap. This allows the Peierls gap to decay more slowly as temperature increases. It is apparent from Eq. (4.4) that any Δ_e, no matter how small, will have this effect.

To determine the gap with Δ_e unknown we have used Δ_e as a parameter in solving Eq. (4.4) numerically, simultaneously with Eq. (2.14), which relates θ to Δ_e, and the electrical neutrality equation (3.8). There is only one parameter, t, to be chosen apart from Δ_e. This was taken as 1125 K, corresponding to a TCNQ bandwidth of 4500 K, somewhat smaller than that for TCNQ in (TTF)(TCNQ) because the intermolecular spacing is somewhat larger in Qn(TCNQ)$_2$. $\tilde{\Delta}_0$ for $T=0$ and $N_d=0$ was taken as 600 K, from optical[1] and σ-versus-T data.[8] The value of λ required to obtain this value of $\tilde{\Delta}_0$ for $T=0$ and $N_d=0$ from Eq. (4.4) with $t=1125$ K is 0.7, about 30% higher than the value expected from internal mode coupling.[11] This discrepancy may arise because other lattice modes also contribute to λ. It must be remembered, however, that there are many approximations made in the theory leading to the gap equation.[27]

The resulting values of the Peierls gap Δ_0, normalized to its low-temperature value, are shown as a function of T in Fig. 1 for Δ_e values of 25 and 10 K. The best fit to the data in the temperature range where the gap has decreased substantially is for Δ_e between these two values, although closer to 25 K. Some reasons why the fit at lower temperatures is poorer will be considered in the next section. Only the results for $N_d=0.04$ per lattice site are plotted because N_d values from 0 to 0.04 gave very similar results.

In Figs. 2 and 3 we show some by-products of the gap calculation, the concentrations of electrons, holes, and bipolarons as functions of temperature for $\Delta_e=25$ K. The results are quite similar for $\Delta_e=10$ K, the only significant difference being that the polaron concentrations fall off somewhat more rapidly above 200 K. Figure 2 is for the intrinsic case, $N_d=0$. In the large-U limit the Fermi energy is not at midgap in this case, but at $-k_BT\ln 2$.[31] Then by Eq. (3.7)

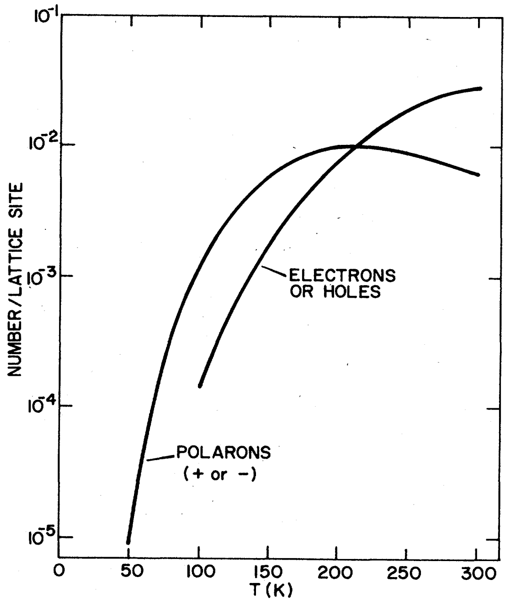

FIG. 2. Carrier and polaron concentrations calculated as functions of temperature for a quarter-filled-band, large-U crystal with a $T=0$ gap of 1200 K, $t=1125$ K, $\Delta_e=25$ K, and no donors.

$$\mu_P^- = -\mu_P^+ = -k_BT\ln 2 \ \text{ for } N_d=0\ . \qquad (4.6)$$

It is readily seen by using (4.6) in Eqs. (3.4a) and (3.4b) that this results in $n_P^+=n_P^-$, as expected for the intrinsic case. Thus, as noted earlier, the factor 4 in Eq. (3.4a), which does not appear in Eq. (3.4b), is needed to assure equal numbers of positive and negative bipolarons in the

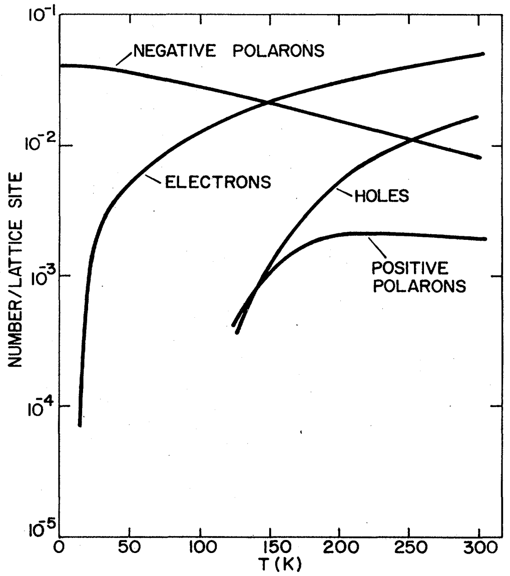

FIG. 3. Carrier and polaron concentrations calculated as functions of temperature for a crystal with 4% donors ($N_d=0.04$) and the other properties as described in the caption for Fig. 2.

$N_d=0$ case. It is seen in Fig. 2 that the numbers of electrons and holes, and of bipolarons, grow rapidly at low temperatures, the bipolarons more rapidly because the creation energy of a pair of bipolarons is less than $2\tilde{\Delta}_0$. However, the bipolaron concentration is seen to saturate at ~ 200 K and then decrease. This occurs because the length of a polaron increases as the gap decreases and fewer can fit on a chain. The decrease in n_P is more rapid for $\Delta_e=10$ K because the polaron length is larger for smaller Δ_e, as will be discussed in the next section. Figure 3 shows the concentration variation for $N_d=0.04$ per lattice site. In this case $n>p$ and $n_P^- > n_P^+$ throughout. Electron concentration grows rapidly at much lower temperatures than in the intrinsic case because the large n_P^- population results in μ_n being much closer to the conduction band. The n_P^- population decreases at low temperatures, before the gap has decreased materially, because the electrons are coming from polaron levels, as described by Eq. (3.9). This effect continues to decrease the n_P^- population at higher temperatures, although in that T region electrons also reach the conduction band from the valence band. At higher temperatures the n_P^- decrease is also partially due to the increasing length of the bipolarons as the gap decreases.

V. COMPARISON WITH EXPERIMENT

For $\Delta_e=25$ K, $\gamma \equiv \Delta_e/\lambda\tilde{\Delta}_0=0.06$. This value inserted in Eq. (2.14) leads to $\theta=1.23$ rad, with which Eq. (2.12) gives ω_0, the distance of the bipolaron levels from midgap, 200 K. From Eq. (2.11) we then obtain the creation energy for either negative or positive bipolarons as $0.735\tilde{\Delta}_0$ or 441 K. For $\Delta_e=10$ K $\gamma=0.023$, which leads to $\omega_0=125$ K and a creation energy of $0.687\tilde{\Delta}_0$ or 412 K. The creation energy for a kink in the large-U case is Δ_0/π,[18] which is 190 K for the present parameters. Thus the bipolaron creation energy for either $\tilde{\Delta}_e$ is somewhat more than that of two isolated kinks, as is also found for *cis*-$(\mathrm{CH})_x$.[22] The length of the bipolaron, defined by Eq. (2.4), for low temperatures is $14.5a$ for $\Delta_e=25$ K, $16.3a$ for $\Delta_e=10$ K. The increased length as well as the smaller creation energy are expected for the smaller Δ_e because it provides less confinement for the kinks. Both lengths are close to twice the length of a kink, the result of y_0 being fairly large, i.e., the kinks not well confined, due to the small value of γ. For $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$, if we arbitrarily take $\Delta_e=25$ K, we obtain quite similar values: $\omega_0=220$ K, $E_P=0.710\Delta_0$, and $l=11a$.

We are now able to show that, as noted earlier, $N_d=0.04$ per lattice site is consistent with x-ray measurements of the low-temperature coherence length along the chains of 40 Å or $\sim 10a$.[14] For $N_d=0.04$ per lattice site the distance between bipolaron centers averages $25a$. The bipolaron length between $14.5a$ and $16.3a$ derived above leaves just an average of $\sim 10a$ between bipolarons, in agreement with the x-ray data.

For $\Delta_e=25$ K the calculated energy levels, 200 K above and below midgap, combined with the low-temperature gap $\tilde{\Delta}_0=600$ K, lead to the prediction that at low temperatures and low concentrations there should be optical-absorption edges due to the polarons at 400 K, or 280 cm^{-1}, and 800 K or 560 cm^{-1}. For somewhat smaller Δ_e the lower absorption edge moves to higher frequency and the upper moves closer to it. At concentrations as high as 4% the absorption edges would be lower than calculated and probably somewhat smeared due to broadening of the bipolaron levels resulting from overlap. And finally we note that there should be corrections to the above calculations, which might be considerable, because the theory of Campbell and Bishop[22] is not complete. It does not take into account the Coulomb attraction of the charged donors for the bipolarons and the mutual repulsion of the two electrons (or holes) on the bipolaron. The latter is to some extent screened, presumably by $\frac{1}{2}$ hole for each electron, but there is also an exchange energy involved.

Optical absorption due to bipolarons is seen quite clearly in polypyrrole[32] and polythiophene,[33] to cite a couple of examples. In lightly doped samples of these polymers there is sizable background absorption below the gap and a well-defined absorption edge, close to 3 eV in the former case, 2 eV in the latter, where the absorption coefficient rises an order of magnitude, marking the gap. With increasing doping two separate absorptions attributable to bipolarons, each $\sim \frac{1}{2}$ eV wide, appear in the gap and grow. As these absorptions grow the absorption at the gap energy and beyond decreases.[32,33] For $\mathrm{Qn(TCNQ)_2}$,[1] and $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}\mathrm{TCNQ}$ for $0.50 \le x \le 0.56$,[1] a weak absorption starts at ~ 50 cm^{-1} and grows monotonically, except for a number of narrow peaks, to frequencies several times the gap. As noted earlier, optical determination of the gap is made, only approximately, by determining the frequency range in which the a_g modes change from resonance to antiresonance, ~ 800 cm^{-1} for $\mathrm{Qn(TCNQ)_2}$, ~ 1000 cm^{-1} for $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$, for $x \sim 0.5$. Presumably part of the broad background underlying the narrow peaks is the polaron absorption, greatly broadened. One source of such broadening is overlap. The data suggest other sources of broadening also. The large absorption starting well below the gap, and the lack of well-defined absorption edge to mark the gap (known from other measurements, such as σ versus T) are seen for semiconducting (TTF)(TCNQ),[34] which is incommensurate, and many other TCNQ compounds. On the evidence of x-rays (TTF)(TCNQ), $\mathrm{Qn(TCNQ)_2}$, $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$, etc., are far better ordered and purer materials than the polymers. We suggest that the broad background absorption and the smearing of the band edge are due to structural imperfections such as dislocations, inclusions, microchannels, etc. These have been studied in (TTF)(TCNQ),[35] and $\mathrm{(TEA)(TCNQ)_2}$,[36] and undoubtedly exist in all the crystals of this type including $\mathrm{Qn(TCNQ)_2}$ and $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}\mathrm{TCNQ}$. As discussed earlier,[37–39] due to the extremely large strain sensitivity of the gaps in these materials, dislocations are surrounded by regions in which the gap is spatially varying and either smaller or larger than the average value identified by the region of constant slope in $\ln\sigma$ versus $1/T$, for example. Similar considerations should hold for the other imperfections cited. Regions of varying gap provide barriers for electrons. There is strong evidence for the existence of barriers in the large values of static dielectric constant[5] of $\mathrm{Qn(TCNQ)_2}$, mentioned earlier.

For the barriers to exert a strong influence at 90 K and above, as observed in $\epsilon_{\parallel}$, some of them must be $\sim$200 or 300 K. The strain field around dislocations could probably account for such barriers.[37–39] The existence of a range of gap values in a sample, apart from broadening the intrinsic absorption, will clearly give rise to a range of bipolaron levels, thus additional broadening of the bipolaron absorption. The existence of barriers could occasion a further broadening due to transitions across the barriers. In short, the bipolaron transitions could be quite broad, independent of doping, and therefore difficult to see in the presence of a broad background that itself is not particularly dependent on doping according to the absorption spectra of $(\mathrm{NMP})_x\mathrm{Phen}_{(1-x)}(\mathrm{TCNQ})$ crystals for $0.5 \leq x \leq 0.59$.[40]

The agreement of the theory for $\Delta_0(T)$ with experimental data shown in Fig. 1 is reasonably good at high temperatures, as noted earlier, but not particularly good below $\sim$200 K. The gap decrease starts well below the temperatures at which it is predicted by the theory. We suggest that this also could be attributed to the existence of smaller gap regions; a smaller gap starts to decrease at lower temperatures. To do an accurate calculation in this T range one should also take into account the effects of the barriers. Nevertheless, as noted earlier, the Δ_e value should be reasonably good because it is determined by higher-temperature properties.

VI. SUMMARY

If the TCNQ chains in $\mathrm{Qn(TCNQ)_2}$ or $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$, $x \simeq 0.50$, were isolated, the stable soliton defects—those generated thermally or by the addition of electrons past the quarter-filled-band level—would be kinks with charge $+\frac{1}{2}e$ or $-\frac{1}{2}e$. However, the presence of even a small potential due to the donor chains with the spatial period of the Peierls distortion, $2a$, will make the stable defects bound pairs of kinks or polarons. Such a potential is expected in $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$ for $x \simeq 0.5$ due to the alternation of NMP^+'s and neutral phenazines. In $\mathrm{Qn(TCNQ)_2}$ the randomness of the dipole orientation on the Qn chains will result in a Fourier component of potential on the TCNQ chains with period $2a$. The observed gradual decrease of the Peierls gap with T is due to an additional potential which includes the interchain potential and perhaps some potential due to Coulomb repulsion. The bipolarons have been treated by adapting the formalism developed by Campbell and Bishop for *cis*-polyacetylene to the case of quarter-filled-band large-U materials. We find that neutral bipolarons, made up of a $+\frac{1}{2}e$ kink and a $-\frac{1}{2}e$ kink, are unstable. The stable polarons have charge $+e$ or $-e$. They have two levels in the gap, separated by $\pm\omega_0$ from midgap, that are each filled by a single electron in the $-e$ case, empty in the $+e$ case. The detailed properties of the bipolarons depend on the interchain potential Δ_e. This was determined, within the uncertainty in the size of the Coulomb potential, by calculating the Peierls gap variation with temperature for different Δ_e's and comparing with the experimental data of McCall and Tanner.[1] To calculate the gap it is necessary to know the numbers of positively and negatively charged bipolarons as functions of temperature. These numbers were determined from the free energy, calculated on the assumption that the bipolarons can move freely; this may not be true at low temperatures in doped samples, but has little effect on the calculation of the gap and Δ_e. Expressions were developed for the numbers of positive and negative bipolarons as functions of the length of the bipolarons, their creation energy and chemical potentials. As a result of the interactions between electrons and holes and bipolarons, for thermal equilibrium the chemical potential of the negative bipolarons must equal the Fermi energy, while that of the positive bipolarons is its negative.

The gap equation is set up by minimizing the total free energy—that of the periodic lattice distortion, the electrons, and the bipolarons—with respect to the gap. It is solved numerically, together with the equation for electrical neutrality, for different Δ_e values. A value between 25 and 10 K, closer to the former, gives the best agreement in the high-temperature range, where the gap variation is most sensitive to Δ_e. With $25 \geq \Delta_e \geq 10$ K, ω_0 lies between 125 and 200 K, the creation energy is not much more than the creation energy for two kinks, and the length, $14.5a$ to $16.3a$, is close to twice the kink length. Optical-absorption data for $\mathrm{Qn(TCNQ)_2}$ and $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$, $0.5 \leq x \leq 0.56$, show no structure corresponding to the expected bipolaron absorption. It is suggested that this is due to the absorption being broadened as a result of overlap and structural imperfections.

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