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Statistics of solitons in quarter-filled-band, large-U quasi-one-dimensional crystals

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There is evidence that solitons are created by doping in certain of the quarter-filled-band semiconducting molecular crystals having large Coulomb repulsion for two electrons on the same site ("large U"). Since, as has been shown for polyacetylene, soliton concentrations depend on the concentrations of band carriers, it is necessary to know the chemical potentials of the solitons to find the electronic Fermi energy. We derive in this work the relations between soliton chemical potentials and the Fermi energy for quarter-filled-band, large-U semiconductors and use them to find concentrations of solitons, electrons, and holes as a function of temperature and chemical doping. Numerical results are presented for parameters appropriate to (N-methylphenazinium)$_x$(phenazine)$_{1-x}$tetracyanoquinodimethanide [(NMP)$_x$(Phen)$_{1-x}$TCNQ] for $x=0.50$ (exactly quarter-filled band) and $x=0.54$ (4% donor doping). The Fermi energy is found to be twice the chemical potential of the negatively charged solitons. For doped systems, the Fermi energy decreases approximately linearly with temperature at low temperatures, with a slope depending on the level of doping. At low temperatures we find also that the number of solitons will be less than twice the number of dopant molecules (their number at $T=0$ K) due to promotion of electrons from soliton levels to the conduction band and subsequent soliton recombination.

I. INTRODUCTION

It has been shown for polyacetylene, and should be generally true for soliton-containing semiconductors, that the soliton concentration in doped samples depends on the concentration of electrons in the conduction band or holes in the valence band.[1,2] As a consequence the Fermi energy depends on the chemical potentials of the solitons. To determine the Fermi energy it is therefore necessary to find the relations between the various chemical potentials and the dependence of the soliton chemical potentials on the soliton concentration. These relations, together with the charge balance or electrical neutrality equation, allow the determination of carrier concentrations. The various relations were obtained recently by Conwell for the case of polyacetylene[1,3] and used to determine the carrier concentrations for samples of different doping.[1]

In this work we apply this approach to the quarter-filled-band, large-U molecular crystals. In these systems, in the limit $U\rightarrow\infty$, the electronic states, while they have a spin degeneracy of 2, can only be singly occupied. Formation of a soliton-antisoliton pair involves removing one (filled) valence-band state and one (empty) conduction-band state to the middle of the Peierls band gap. The resulting soliton states have effective charges of $\pm|e|/2$, where e is the charge on the electron;[4] the plus sign corresponds to an empty soliton state, the minus sign to an occupied one. In contrast, in the polyacetylene case, the charges are $\pm|e|$ and 0. In thermal equilibrium, $(+|e|/2,-|e|2)$ pairs of solitons will be thermally created. Doping the system with a donor will produce, at $T=0$ K, a pair of negatively charged $(-|e|/2,-|e|/2)$ solitons for each electron added (acceptor doping would produce positively charged pairs).[4] For $T>0$ K, the solitons can exchange electrons (or holes) with the conduction band (or valence band); that is, an electron can be promoted from a $-|e|/2$ soliton to the conduction band, leaving a $+|e|/2$ soliton; likewise, an electron can drop from the conduction band into an empty soliton. Thus we can consider electrons, holes, and positive and negative solitons to be a system of interacting particles; a free energy F can be written for electrons, holes, and solitons, and a chemical potential μ found for each type of particle. In Sec. II of the present work we develop the relations between the various chemical potentials, find the free-energy contribution of the solitons to the system, and express the soliton concentrations in terms of the Fermi energy. In Sec. III this information is used, along with the charge-balance equation, to evaluate the Fermi energy and carrier concentrations for parameters appropriate to (N-methylphenazinium)$_x$ (phenazine)$_{1-x}$ tetracyanoquinodimethane [(NMP)$_x$ (Phen)$_{1-x}$ TCNQ], a quarter-filled-band, large-U compound for which it has been shown that solitons exist.[5] Conclusions are discussed in Sec. IV.

II. THEORY

In a quarter-filled-band, large-U semiconductor containing electrons, holes, and positive (empty) and negative (occupied) solitons four types of interaction can take place: (1) a conduction-band electron may recombine with a valence-band hole; (2) a positive and a negative soliton may recombine, releasing phonons; (3) an electron may drop from the conduction band into a positive soliton, producing a negative soliton; and (4) a valence-band hole may occupy a negative-soliton state, producing a positive soliton (that is, an electron may drop from a negative soliton into an empty valence-band state). Each of these reactions will give rise to a relationship between the chemical potentials of the constituents. The condition that the free energy F must be a minimum in equilibrium (we deal only with thermal-equilibrium situations) requires that[6]

$$\delta F=\sum_i \left[\frac{\partial F}{\partial n_i}\right]\Bigg|_{T,V} \delta n_i \equiv \sum_i \mu_i \delta n_i = 0 ,$$

where n_i is the number of particles of type i involved in a reaction and $\mu_i=(\partial F/\partial n_i)\,|_{T,V}$ is the chemical potential of the ith constituent. The reactions (1)—(4) then yield the relations

$$\mu_n+\mu_p=0 , \tag{2.1}$$

$$\mu^+ + \mu^- = 0 , \tag{2.2}$$

$$\mu_n + \mu^+ = \mu^- , \tag{2.3}$$

$$\mu_p + \mu^- = \mu^+ . \tag{2.4}$$

The fact that the electron-chemical potential (Fermi energy) μ_n is equal to and opposite in sign to the hole-chemical potential μ_p, Eq. (1), also follows directly from the definition of μ_i; the energy required to remove an electron from the system is minus the energy required to add it. μ^+ and μ^- are the chemical potentials for positive and negative solitons, respectively. Note that since the phonon chemical potential is zero, it does not explicitly appear in (2.2).

At this point we note also that solitons are produced in these systems in soliton-antisoliton pairs for topological reasons. Relations (2.3) and (2.4) could be written for antisolitons ($\bar{\mu}^+,\bar{\mu}^-$) as well as for solitons, and relation (2.2) must involve one soliton and one antisoliton, i.e., either $\bar{\mu}^+ + \mu^- = 0$ or $\mu^+ + \bar{\mu}^- = 0$. Elementary manipulation of these relations, however, shows that $\bar{\mu}^+ = \mu^+$ and $\bar{\mu}^- = \mu^-$. Therefore we will not subsequently distinguish chemical potentials of antisolitons from those of solitons. From Eqs. (2.1)—(2.4) we find that

$$\mu_n = 2\mu^- , \tag{2.5a}$$

$$\mu_p = 2\mu^+ = -\mu_n . \tag{2.5b}$$

We see that while, according to Eq. (1), electron- and hole-chemical potentials are equally spaced on opposite sides of midgap, the chemical potential of a negative (positive) soliton is halfway between midgap and the electron (hole) chemical potential.

To find the soliton concentrations in terms of μ^+ and μ^- (and thus in terms of μ_n) we need an expression for the free-energy contribution F_S of the solitons to the system. We can write

$$F_S = n_S E_c - kT \ln W_S \tag{2.6}$$

where $n_S \equiv n^+ + n^-$ is the total number of solitons in the system, the sum of the numbers of positive and negative solitons, E_c is the energy needed to create a soliton, and W_S is the number of distinct ways of arranging n_S solitons, n^+ positive and n^- negative, on a chain. It has been shown by Rice and Mele[4] that $E_c = \Delta/\pi$ for the quarter-filled-band large-U crystals, where Δ is half the Peierls band gap. This expression for F_S neglects the kinetic energy of the solitons, which we take to be small for reasons previously discussed.[7]

In calculating W_S it is necessary to ensure that soliton (S) and antisoliton ($\bar{S}$) alternate on the chain. We consider now what is involved in satisfying this condition. The Hamiltonian for this case may be written

$$\mathscr{H}=\sum_n \beta Q_n c_n^\dagger c_n - \sum_n t_0 (c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n) ,$$

where Q_n is the amplitude of the internal mode (we assume there is only one for simplicity) on the nth molecule or site, β the coupling constant to the internal mode and t_0 the transfer integral, independent of n since dimerization is negligible. This system does not have charge conjugation symmetry, as does polyacetylene, since a nonvanishing $\langle Q_n \rangle$, which could result from putting an electron on a soliton or removing it, adds to the soliton energy.[8] The result is that the energy levels of S^+ and S^- are no longer at midgap but separated from it by an energy $\pm\delta$.[8] We have shown that $|\delta|/kT$ is small for (NMP)$_x$ (Phen)$_{1-x}$ TCNQ over the important range of temperatures.[9] The wave function of a hole or electron on a soliton may be written

$$\psi_0^\pm = \sum_m a_m^\pm \,|\, m \rangle ,$$

where $|\, m\rangle$ represents a molecular orbital for a valence electron on site m. Evaluating $\langle n+1 \,|\, H \,|\, \psi_0 \rangle$, neglecting terms of order t_0^2 or βt_0, we obtain the recursion equation:

$$\pm \delta a_{n+1}^\pm = -t_0 (a_n^\pm + a_{n+2}^\pm) + \beta Q_{n+1} a_{n+1}^\pm .$$

In this equation βQ_{n+1} may be replaced by the staggered order parameter $(-1)^{n+1}\beta\widetilde{Q}$, which for large n, i.e., far from the soliton, approaches $\pm\Delta$.[9] The soliton solution of the resulting equation may be taken as that for which $\beta\widetilde{Q} \to -\Delta$ as $n \to -\infty, +\Delta$ as $n \to \infty$, the antisoliton solution that for which $\beta\widetilde{Q} \to +\Delta$ as $n \to -\infty$, $-\Delta$ as $n \to \infty$. These solutions clearly differ from those for the bond-distortion case in that there is no separation of even and odd terms.[10] Thus the amplitude of the wave function does not vanish on alternate sites as in that case. Nevertheless, when δ/kT is small and $t_0/\Delta > 1$, which should be true for the materials with which we are concerned, the envelope wave function should be given reasonably well by the continuum model.[9] Thus the length of the soliton l may be taken as $4t_0/\Delta$ in units of the lattice constant.

To calculate W_S we first determine W_n, the number of ways of arranging n_S solitons of length l on the chain without, of course, permitting overlap. If it takes equal energy to put either an S or an $\bar{S}$ on any set of l sites, the number of ways of arranging the solitons so that S and $\bar{S}$ alternate is just $2W_n$. This is so because once the sets of sites are selected, the solitons can be put down in only two ways: $S\bar{S}S\bar{S}$. . . or $\bar{S}S\bar{S}S$. . . . The number of ways could be different from $2W_n$ if, for example, an attractive impurity ion opposite a set binds S's, for example, much more strongly than $\bar{S}$'s. However, the binding energy E_b of either S or $\bar{S}$ to an impurity ion is $\lesssim 300$ K for the materials of concern here because l is fairly large.[9] The difference $E_b(S)-E_b(\bar{S})$ must then be small compared to kT. In addition to determining W_n we need to consider the distribution of charge among the solitons; the possible number of ways W_n of arranging n_S solitons on a chain is completely independent of the number of ways, $W_{(+-)}$, of designating n^- to be negative and n^+ to be positive. Thus we can write

$$W_S=2W_nW_{(+-)}\ . \tag{2.7}$$

If we designate the number of sites on a chain by N, we find that

$$W_n=\frac{(N/l)!}{n_S!(N/l-n_S)!}\ . \tag{2.8}$$

For $W_{(+-)}$ we find

$$W_{(+-)}=(2)^{n^-}\frac{n_S!}{(n^-)!(n^+)!}\ . \tag{2.9}$$

The factor $(2)^{n^-}$ in $W_{(+-)}$ results from the fact that an electron can be put into a soliton state either spin up or spin down, i.e., that there are two ways of creating a negative soliton. Substitution of (2.8) and (2.9) into (2.6), along with $E_c=\Delta/\pi$, gives us F_S in terms of n^+ and n^-. We can then find the chemical potentials μ^+ and μ^- by taking $(\partial F_S/\partial n^+)|_{T,V}$ and $(\partial F_S/\partial n^-)|_{T,V}$, respectively. Use of Stirling's approximation in evaluating factorials (we assume that $N,n^+,n^-\gg 1$) gives

$$\mu^-=\Delta/\pi+kT\ln[n^-/2(N/l-n_S)]\ , \tag{2.10}$$

$$\mu^+=\Delta/\pi+kT\ln[n^+/(N/l-n_S)]\ . \tag{2.11}$$

The relations $\mu^++\mu^-=0$ and $n^+=n_S-n^-$ can now be used to find n^+ and n^- in terms of n_S. We find

$$n^-=n_S/2\pm[(n_S/2)^2-2\exp(-2\Delta/\pi kT)(N/l-n_S)^2]^{1/2}\ . \tag{2.12}$$

Whether the + or − sign is applicable depends on whether the system in question is donor or acceptor doped. In either case, n^+ is found by taking the opposite sign. For a donor-doped crystal we know that $n^->n^+$, so the + sign pertains to n^-, the − sign to n^+. If the crystal is undoped, i.e., if there are thermal solitons only, we know that $n^+=n^-=n_S^{(i)}/2$ where $n_S^{(i)}$ is the number of solitons in an undoped crystal. We find this number by equating to zero the root in (2.12); this gives

$$n_S^{(i)}/N=(1/l)[1+(1/2\sqrt{2})e^{\Delta/\pi kT}]^{-1}\ . \tag{2.13}$$

From (2.10) we know that

$$n^-=2(N/l-n_S)\exp[(\mu^--\Delta/\pi)/kT]\ . \tag{2.14}$$

This expression can be equated to (2.12) to find the relation between n_S and μ^- for donor-doped (or undoped) crystals:

$$n_S/N=(1/l)\{1+\tfrac{1}{2}\exp[(\mu^-+\Delta/\pi)/kT]/[\tfrac{1}{2}+\exp(2\mu^-/kT)]\}^{-1}\ . \tag{2.15}$$

Comparison with (2.13) for undoped crystals shows that for the undoped case we must have $\mu^-=-(kT/2)\ln 2$ relative to the zero of energy at midgap. From (2.5a) this implies an electronic Fermi energy $\mu_n=-kT\ln 2$. This is the Fermi energy of an undoped quarter-filled-band large-U system in the absence of solitons;[11] as would be expected, the generation of thermal solitons alone does not affect the Fermi energy. The use of (2.14) and (2.15) now permits us to find n^- in terms of μ_n alone. The result is

$$\begin{aligned} n^-/N=(1/l)[1+\tfrac{1}{2}\exp(-\mu_n/kT)]\\ +\exp[(\Delta/\pi-\mu_n/2)/kT]^{-1}\ , \end{aligned} \tag{2.16}$$

and for n^+,

$$\begin{aligned} n^+/N&=(1/l)[1+2\exp(\mu_n/kT)]\\ &\quad+\exp[(\Delta/\pi+\mu_n/2)/kT]^{-1}\\ &=(n^-/2N)\exp(-\mu_n/kT)\ . \end{aligned} \tag{2.17}$$

To actually calculate n^-/N and n^+/N for a given crystal, we need the charge-balance equation. For a quarter-filled-band large-U crystal with a donor doping of (N_d electrons)/(lattice constant), charge neutrality can be expressed as[12]

$$p_v+N_d+(n^-+n^+)/2N=n_c+n^-/N\ , \tag{2.18}$$

where p_v and n_c are the valence-band hole and conduction-band electron concentrations (per lattice constant), respectively. The left-hand side of (2.18) is simply the total concentration of electrons available for distribution in the system, since $(n^-+n^+)/2N$ reflects the fact that one electron (and its electron state) is removed from the valence band for each pair of solitons created.[4] The right-hand side of (2.18) expresses the fact that these electrons are distributed on the conduction band and the negatively charged soliton states.

III. ILLUSTRATIVE NUMERICAL RESULTS

We have used (2.18), with n^-/N and n^+/N given by (2.16 and 2.17) to calculate electronic Fermi energies and carrier concentrations for $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}\mathrm{TCNQ}$, for $x=0.50$ (an exactly quarter-filled band) and for $x=0.54$ [4% doping, or $N_d=0.04$ in (2.18)]. Band electron and hole concentrations in (2.18) are taken from

$$n_c = (1/\pi)\int_{\pi/2}^{\pi} f_q^{+} d(qa) \tag{3.1}$$

and

$$p_v = (1/\pi)\int_{0}^{\pi/2} (1-f_q^{-}) d(qa)\ , \tag{3.2}$$

where

$$f_q^{\pm} = \{1+\tfrac{1}{2}\exp[(E_q^{\pm}-\mu_n)/kT]\}^{-1}$$

and

$$E_q^{\pm} = \pm[(2t)^2\cos^2(qa)+\Delta^2]^{1/2}$$

(Ref. 7). Here a is the lattice constant, q is the wave vector, and the bandwidth $4t \simeq 4500$ K for $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}\mathrm{TCNQ}$.[7] The factor $\frac{1}{2}$ in the distribution function $f_q^{\pm}$ is a manifestation of the doubly spin degenerate but "singly-occupiable" nature of the electronic states in large-U systems.

Results of the numerical calculations of n^-/N, n^+/N, n_c, and p_v for thermal solitons only ($x=0.50$) are shown in Fig. 1. For the undoped case, of course, $n_c = p_v$ and $n^-/N = n^+/N$ at all temperatures. Since the numerical calculations are intended to be illustrative, rather than exact, we have simplified them by keeping a fixed gap of $2\Delta = 1800$ K at all temperatures.[7] The thermal-soliton concentration is large relative to the band-carrier concentration due to the difference between the creation energy $2\Delta/\pi$ for a $S\bar{S}$ pair and the energy 2Δ needed to excite an electron-hole pair. At 300 K, for instance, $n_S/N \simeq 10^{-1}$, while $n_c + p_v \simeq 10^{-2}$ carriers per lattice site. Note that, according to (2.13), the total soliton concentration (n_S/N) is increasing at all temperatures, going to a limiting value of $\sim(1.36l)^{-1}$ as $T \rightarrow \infty$, if the gap is held constant with temperature. If Δ were allowed to decrease with increasing temperature (thus increasing band-carrier concentration), however, as would happen in a physical system, l would increase with temperature, and we would find a maximum in n_S/N for some finite temperature.[7]

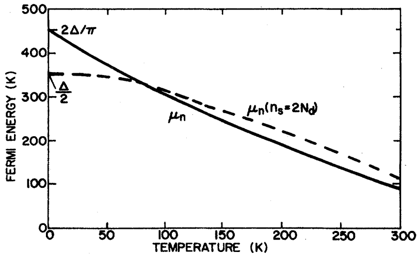

FIG. 2. Calculated electronic Fermi energies $\mu_n(n_S=2N_d)$ and μ_n for $(\mathrm{NMP})_{0.54}(\mathrm{Phen})_{0.46}\mathrm{TCNQ}$, for different statistics. Taking the solitons to be $2N_d$ ordinary impurity states at midgap leads to $\mu_n(n_S=2N_d)$ (dashed curve); the correct soliton statistics give μ_n (solid line) of Eqs. (2.5a) and (2.6). Parameters of the calculation are $4t=4500$ K and $\Delta=710$ K.

If we now consider $(\mathrm{NMP})_{0.54}(\mathrm{Phen})_{0.46}\mathrm{TCNQ}$, with 4% donor doping [that is, (0.08 solitons)/(lattice constant) at $T=0$ K], we find the results in Figs. 2 and 3. For these calculations the same parameters were used as for the undoped system, except that Δ was held constant at 710 instead of 900 K. This is a consequence of earlier work showing that Δ is reduced to this value from 900 K by the free-energy contribution of (0.08 solitons)/(lattice site) at $T=0$ K.[7] Figure 2 shows the electron Fermi energy versus temperature that results from the present statis-

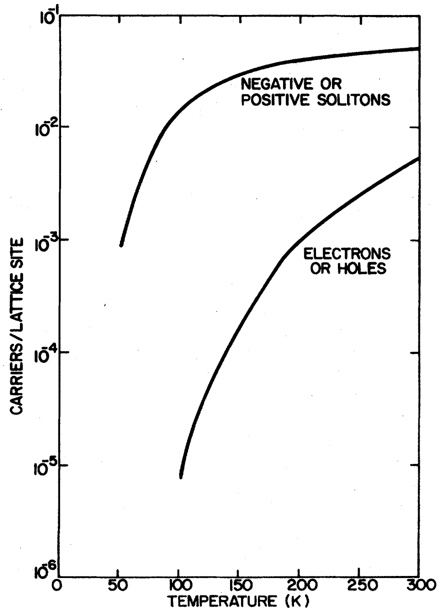

FIG. 1. Calculated carrier concentrations vs temperature for the case $(\mathrm{NMP})_{0.50}(\mathrm{Phen})_{0.50}\mathrm{TCNQ}$ (exactly quarter-filled band, thermal solitons only). Parameters are $4t=4500$ K, $\Delta=900$ K. The gap is held constant with temperature.

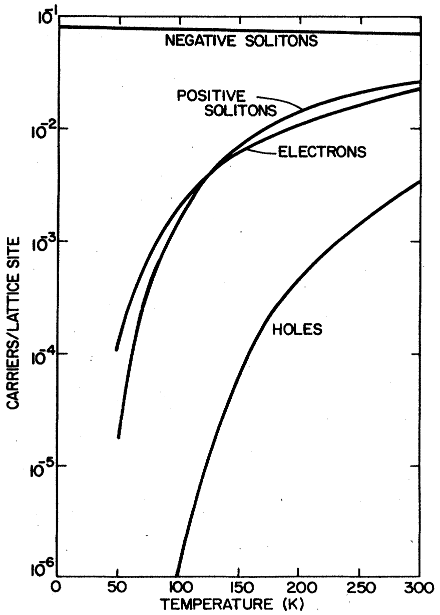

FIG. 3. Carrier concentrations vs temperature calculated for $(\mathrm{NMP})_{0.54}(\mathrm{Phen})_{0.46}\mathrm{TCNQ}$ (4% donor doping). Parameters are $4t=4500$ K and $\Delta=710$ K; the gap is kept constant with temperature.

tics. It also shows, for comparison, the Fermi energy $\mu_n(n_S=2N_d)$ that would result from the usual semiconductor statistics if the soliton levels were regarded as ordinary impurity levels, fixed at $2N_d$ in number. It will be shown shortly that, as anticipated, under the correct statistics n_S does not remain constant at $2N_d$. Consider first the behavior of the Fermi energy for temperatures low enough that holes and positive solitons may be neglected. For a semiconductor with $2N_d$ midgap levels the charge neutrality equation is

$$n \simeq 2N_d[1-f(0)]\ .$$

To obtain n as an explicit function of μ_n we integrate Eq. (3.1) for the Maxwell-Boltzmann limit with $kT \ll \Delta$ and f in the form appropriate for large U. This leads to

$$\mu_n(n_S=2N_d)\to\Delta/2+(kT/2)\ln[N_d/(kT\Delta/2\pi t^2a^2)^{1/2}] \qquad \text{as } T\to 0\,\mathrm{K}$$

after elimination of the effective mass m^* from the one-dimensional density of states by means of $m^*=\hbar^2\Delta/4t^2a^2$. The correct μ_n for the low-temperature limit may be obtained from Eq. (2.10) with $n^-=n_S=2N_d$. This leads to

$$\mu^-\to 2\Delta/\pi+2kT\ln[N_d/(N/l-2N_d)] \quad \text{as } T\to 0\ \mathrm{K}\ .$$

In agreement with these equations, it is seen in Fig. 2 that the correct μ_n goes to $2\Delta/\pi$ at $T=0$, while $\mu_n(n_S=2N_d)$ goes to $\Delta/2$ at $T=0$. As T increases from 0, the latter μ_n increases when $(kT\Delta/2\pi t^2a^2)^{1/2}<N_d$, which is for $T<2.7$ K for the present case, and then decreases. The correct μ decreases monotonically for $N_d<N/3l$. It is seen that except for temperatures $T\lesssim 100$ K, the correct μ_n lies below $\mu_n(n_S=2N_d)$, with the result that there are fewer band carriers in the correct case. At the higher temperatures, the slope versus temperature of the Fermi energy tends toward $-k\ln 2$; the numbers of positive and negative solitons approach each other, and the situation "looks" to some extent like the case of thermal solitons only, for which $\partial\mu_n/\partial T=-k\ln 2$.

Carrier concentrations for the 4%-donor-doped case are shown in Fig. 3. The positive-soliton concentration begins to become comparable to the negative-soliton concentration above $T\sim 150$ K. The negative-soliton concentration decreases continuously from its $T=0$ value of $n^-/N=0.08$, while concentrations of positive solitons, electrons, and holes are still rising at room temperature. The presence of extra electrons in the system drives the Fermi energy above midgap (at temperatures $\lesssim 350$ K) and causes the band-electron concentration to far exceed the band-hole concentration. At 100 K, for instance, there are ~ 2400 times as many electrons as holes. For low temperatures, the very low concentrations of band holes versus band electrons and of positive solitons compared to negative solitons mean that the charge-balance equation (2.14) can be written as

$$n^-/N\simeq 2N_d-2n_c\ . \tag{3.3}$$

Thus the soliton concentration will be *less* than $2N_d$ at low temperatures; for every electron entering the conduction band, two soliton states, one positive and one negative, recombine and are destroyed. The analogous process has been noted by Conwell[1,2] in $(\mathrm{CH})_x$; there two solitons recombine for every pair of electrons put into the conduction band.

IV. CONCLUSIONS

Consideration of the possible interactions between positively and negatively charged solitons, and conduction-band electrons and valence-band holes in a quarter-filled-band, large-U system, gives rise to a set of relations between the chemical potentials of these particles. Expressions for the chemical potentials of the solitons can be derived from an analysis of the possible number of arrangements of a set of positively and negatively charged solitons of finite length on a chain. Using these chemical potentials and the charge-balance equation, we can find the Fermi energy and carrier concentrations. We find the following to be true:

(1) The electronic Fermi energy is twice the chemical potential of the negatively charged solitons, and the chemical potential of the positive solitons is minus that of the negative solitons.

(2) In the absence of chemical doping but in the presence of a thermal-equilibrium soliton population, the Fermi energy is $-kT\ln 2$; in the presence of donor doping, the Fermi energy is $2\Delta/\pi$ at $T=0$ K and decreases linearly with temperature as $\sim 2kT\ln[N_d/(N/l-2N_d)]$ for low temperatures. At higher temperatures (such that the concentration of positive solitons becomes significant compared to the concentration of negative solitons) the Fermi energy is also linear with temperature, with a slope approaching $-k\ln 2$.

(3) For low temperatures, such that almost all solitons are filled, the charge-balance relation becomes $n^-\simeq 2N_d-2n_c$; for every electron that goes to the conduction band, two solitons are lost. Thus the number of solitons will be somewhat *less* than twice the number of dopants at very low temperatures.

(4) In donor-doped crystals, the fact that the Fermi energy lies below what we would expect for "ordinary" midgap impurity states leads to a lower-band electron concentration at temperatures above ~ 150 K. Concentrations of solitons are considerably higher than band-carrier concentrations (even in undoped systems) over a wide temperature range.

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