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Statistics for electrons, solitons, and polarons in *trans*-polyacetylene and consequences for conductivity

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The equations that govern the temperature variation, in thermal equilibrium, of electron populations in soliton (kink) and polaron levels and the conduction band are set up for *trans*-polyacetylene. These are the electrical neutrality equation, the relations between chemical potentials of electrons, holes, solitons, and polarons, and the relations between the chemical potentials and the concentrations of the different excitations. It is pointed out that the lifetime predicted for a conduction electron against dropping into a polaron level, short though it is, is comparable to scattering times for conduction electrons in some typical three-dimensional (3D) semiconductors; it therefore does not preclude treatment of electrons in the conduction band of polyacetylene as quasiparticles. From the relations derived for the concentrations of solitons and polarons it is deduced that in *trans*-$(CH)_x$ polaron concentration is negligible compared with soliton concentration in thermal equilibrium within the range of doping where both can exist, i.e., up to $\sim 5\%$ or 6%. The 300-K conduction-electron concentration in *trans*-$(CH)_x$ with 5% doping is found to be $\sim 10^{18}/\mathrm{cm}^3$. On theoretical grounds, and according to x-ray and other types of evidence, dopant ions are, however, generally not random in their distribution as was assumed in the calculation of the thermal-equilibrium level populations. As a result a 5% dopant concentration, say, and correspondingly high electron concentration might be achieved in some local regions when the average doping is much less than 5%. With much lower doping in the surrounding regions, however, a local high electron concentration would not have much effect on dc conductivity. It could, however, contribute to high-frequency conductivity. Recent measurements of Genzel *et al.* may show this contribution.

I. INTRODUCTION

The existence of solitons and polarons in a quasi-one-dimensional (1D) semiconductor results in some significant differences in the statistical mechanics from that for typical three-dimensional semiconductors. In this paper the statistics for a 1D semiconductor with a two-fold-degenerate ground state, exemplified by *trans*-polyacetylene [$(CH)_x$] will be examined. Consideration will be limited to samples with impurity concentration low enough [$\lesssim 5\%$ or 6% in the usual *trans*-$(CH)_x$ sample] so that essentially the full gap remains, although it may contain many localized states. To simplify the discussion it will be assumed that (1) the impurities are randomly distributed, and (2) the material is not so disordered that it does not have reasonably well-defined conduction- and valence-band edges. How well these two conditions are satisfied in currently available polyacetylene samples will be considered in Sec. V. They should hold literally in Li-doped samples and probably no others. Nevertheless, it will be seen that many of the results to be derived are applicable even when these conditions are not well satisfied.

In the development of the statistics the case of donor impurities will be the one considered, but the results clearly apply to acceptor impurities with the obvious modifications. It is expected that an impurity commonly cited as a donor transfers all or almost all of an electronic charge to a polyacetylene chain. The theory to be presented will apply only to such impurities. In these cases, the electron will go into a soliton level on the chain.[1-3] For a 1D semiconductor with doubly degenerate ground state the soliton may be a kink, i.e., a domain wall that interpolates between the two degenerate arrangements, or a polaron, which may be thought of as made up of two kinks, one charged and one neutral.[4] At first sight it might appear that for the 1D semiconductor one could take over the statistics for the 3D case, simply replacing the donor level for that case by the soliton level or appropriate polaron level. That is not so, however, because the number of solitons or polarons is not a constant, as is the number of donors, but varies with temperature. Pairs of neutral or oppositely charged solitons may recombine; a negative polaron that gives up an electron is unstable and decays,[4] etc. It is clear therefore that new statistics must be developed for the 1D case. That has already been done for the one-quarter-filled-band case with Coulomb repulsion U for a second electron on a site much greater than the transfer integral t.[5] In this paper the statistics are developed for the half-filled-band case with $U < t$, as is appropriate for *trans*-$(CH)_x$.[6,7]

In the next section I set up the charge-neutrality condition for this case and consider its implications. This equation can be used to find the Fermi energy μ_n provided the concentrations of electrons, holes, solitons, and polarons can be expressed in terms of μ_n. In Sec. III a step is taken toward this goal by deriving the relations between chemical potentials of electrons, holes, solitons, and polarons. The chemical potentials must then be related to the concentrations. In deriving the chemical potential for the solitons the question of the number of possible configurations W_S of the solitons on a chain is discussed. For low soliton concentrations two different expressions are obtained for W_S, one based on the premise that soliton (S) and anitsoliton ($\bar{S}$) may be centered on any site, the other on the premise that S and $\bar{S}$ must be centered on sites of different parity. The chemical potential μ_S is obtained for both cases because it is not clear which actually applies for *trans*-(CH)$_x$. μ_S is also obtained for high soliton concentrations, where both premises lead to the same W_S. The chemical potential μ_P for polarons is also obtained. From the relations between μ_S and μ_P a relation is obtained between soliton and polaron concentrations n_S and n_P, respectively. For *trans*-(CH)$_x$ this leads to the conclusion that $n_P \ll n_S$ independent of doping, provided, of course that the doping is not so high as to preclude the existence of solitons and polarons. The various relations are used in Sec. IV to estimate the conduction-electron concentration in *trans*-(CH)$_x$ with 5% doping. In Sec. V the applicability to presently available samples, *trans*-(CH)$_x$ made by the Shirakawa process[8] and doped with various donors or acceptors, is considered. As will be discussed in that section, there are reasons for the impurity distribution to be nonrandom. Li doping is the one case cited for a random impurity distribution, while many other dopants have been shown by x rays and other types of evidence to be distributed nonrandomly. On such evidence a sample with average impurity concentration as low as 1%, say, might have regions with ~5% doping and, therefore, large free-electron concentration. In Sec. V I will consider the contribution of such regions to dc and ac conductivity. Conclusions will be presented in Sec. VI.

II. CHARGE-NEUTRALITY CONDITION

The basic equation relating the populations of the electronic levels in and above the valence band is the electrical neutrality equation

$$p+N_d+n_S+2n_P=n+2n_S\langle f(E)\rangle_S+3n_P \ . \qquad (2.1)$$

Here, p and n are concentrations of holes in the valence band and electrons in the conduction band, respectively, N_d the donor concentration, and $f(E)$ the distribution function of the electrons. The distribution is averaged over the soliton levels in Eq. (2.1) to allow for their being spread in energy. The right-hand side of Eq. (2.1) represents the number of electrons found in the conduction band, in soliton levels and polaron levels. The polaron term has the factor 3 because donor-doped *trans*-(CH)$_x$ will have only negative polarons, which are each occupied by three electrons; two electrons, taken from the valence band, occupy a level at an energy ω_0 below midband and the third electron, from a donor, occupies a level ω_0 above midband.[4] The soliton levels differ from polarons in that they can exist unoccupied, or occupied by one or two electrons;[2,3] thus the number of electrons in a soliton level of energy E is $2f(E)$. The left-hand side of Eq. (2.1) represents the number of electrons available for distribution among the various energy levels: from the valence band, two for each polaron formed, one for each soliton formed,[2,3] and p that leave behind holes, plus N_d from the donors.

Before discussing some consequences of Eq. (2.1), I note that it has been argued that electrons cannot exist in the conduction band of polyacetylene because they will rapidly self-trap, i.e., drop into polaron states, due to the nature of the electron-phonon coupling in this material. Of course, in thermal equilibrium, if μ_n is close enough to the band edge, there must be electrons in the conduction band. For any actual semiconductor sample, 1D or 3D, there are always empty states in the gap or in the valence band for conduction electrons to fall into. The important question is what is the lifetime of an electron in a conduction-band state. If that lifetime is too short the resultant level broadening will, of course, be too large for the electrons to be treated as quasiparticles. Evidence that it is not intrinsic to a Peierls-distorted semiconductor that the conduction-electron lifetime against polaron or soliton formation be so short as to invalidate quasiparticle treatment is provided by the semiconducting 1D molecular crystals. In (NMP)$_x$(Phen)$_{1-x}$TCNQ, to cite an example that is a (CH)$_x$ analog,[9] over a considerable T range the log of the conductivity σ is proportional to $-(1/2kT)$ times the (optically) measured gap, indicating that conduction electrons and holes are responsible for at least the major part of σ.[10,11] Further, the mobility of these carriers is of the order of that expected for a TCNQ chain due to phonon scattering of quasiparticles.[10] Many other examples of this kind in the 1D molecular crystals can be cited. The electron-phonon coupling constant λ in the TCNQ-based crystals is ~0.35,[12] almost identical with the value of 0.38 given for *trans*-(CH)$_x$.[13] The significant difference between these crystals and *trans*-(CH)$_x$ is the smaller energy gap. Indeed, conduction-electron lifetimes in 3D semiconductors are strongly dependent on the size of the gap, decreasing rapidly as the gap increases. For the parameters of *trans*-(CH)$_x$ a calculation of Su and Schrieffer gives the lifetime due to polaron formation of $\sim 10^{-13}$ sec for a single extra electron at the band edge.[14] To decide whether this is too short to make quasiparticle treatment valid, one may look to 3D semiconductors. It is found that 10^{-13} sec is a typical lifetime for a conduction electron in a 3D semiconductor, with shorter lifetimes quite common. Calculating the average lifetime τ (in semiconductor terminology, "scattering time") from the measured mobility μ and measured effective mass m^* ($\tau=\mu m^*/e$), one finds, for example, at 300 K, τ for holes in undoped CdS is 3×10^{-14} sec,[15] while τ for conduction electrons in GaAs,[16] or InP,[17] with 10^{19} impurities/cm,[3] is 4×10^{-14} sec. The level broadening in these cases is ~200 K. Nevertheless, very careful detailed calculations of mobility from the known scattering mechanisms, with the electrons or holes treated as quasiparticles, give results in excellent agreement with experiment for the three cases just cited.[15–17] Thus a lifetime of 10^{-13} sec, or even somewhat less, for decay into levels in the gap does not rule out quasiparticle treatment. It should be noted also that in heavily doped (CH)$_x$ samples ($N_d \sim 5\%$), where the chains are already close to filled with solitons and polarons, the lifetime for such decay is undoubtedly longer than 10^{-13} sec. That is significant because, as will be seen, only in such heavily doped samples or regions of samples would n be sizeable. Conduction electrons in *trans*-$(\mathrm{CH})_x$ have, in fact, been treated as quasiparticles in the calculation of their lifetime for acoustic- and optical-phonon scattering. That lifetime is also found to be $\sim 10^{-13}$ sec at 300 K for thermal electrons.[18]

Equation (2.1) is a generalization of the equation used to determine the Fermi energy in 3D semiconductors. As a preliminary to using it for that purpose here, the next section will be devoted to expressing the various quantities in the equation in terms of μ_n. The remainder of this section will be devoted to a useful deduction that can be made from Eq. (2.1) for the low-temperature limit. In that limit the polaron terms in Eq. (2.1) are negligible and, because p may be neglected in an n-type $(\mathrm{CH})_x$ sample, Eq. (2.1) yields

$$n_S=(N_d-n)/[2\langle f(E)\rangle_S-1]\rightarrow N_d-n \quad \text{as } T\rightarrow 0\ , \qquad (2.2)$$

because in the $T\rightarrow 0$ limit the soliton levels should be essentially filled. It is seen from this equation that, when electrons go into the conduction band, solitons are lost. In detail, on electron excitation into the conduction band the neutral solitons left behind recombine in pairs. This loss of solitons results from the requirement of minimum free energy.

III. CHEMICAL POTENTIALS OF THE EXCITATIONS

As the first step toward determining n_S and n_P as functions of μ_n, the relations between the chemical potentials of the solitons, polarons, and electrons will be determined. In doing this it is convenient to consider electrons, holes, positive solitons (S^+), negative solitons (S^-), neutral solitons (S^0), positive polarons (P^+), and negative polarons (P^-) as independent particles, each with its own chemical potential. Because adding a hole to the system is equivalent to subtracting an electron,

$$\mu_p=-\mu_n\ . \qquad (3.1)$$

To determine the other relations between the chemical potentials we use the technique of reaction kinetics.[19] From the reaction of S^+ and S^- to form $2S^0$'s there results[20,21]

$$\mu_{S^+}+\mu_{S^-}=2\mu_{S^0}\ . \qquad (3.2)$$

μ_{S^0} is conveniently determined by using the fact that when $2S^0$'s recombine, phonons are produced. The chemical potential for phonons is zero,[19] because the thermal-equilibrium number of phonons is determined by minimizing the free energy F with respect to that number. Thus $\mu_{S^0}=0$.[22] This implies that neutral solitons, like phonons, are thermally activated. It has been deduced, however, from the fact that spins are found in *trans*-$(\mathrm{CH})_x$ isomerized from *cis*-$(\mathrm{CH})_x$, although the original *cis*-$(\mathrm{CH})_x$ contained no spins,[23] that the isomerization process introduces some neutral solitons. These S^0's do not arise thermally and cannot recombine. It will therefore be considered that these S^0's are outside these statistics. In practice, there is no problem in doped samples because even moderate doping causes the residual spins, and thus presumably the S^0's created in the isomerization process, to decrease greatly in number. If Eq. (3.2) is then combined with the relation derived from $S^++n=S^0$ or $S^-+p=S^0$, one obtains

$$\mu_{S^-}=-\mu_{S^+}=\mu_n\ . \qquad (3.3)$$

In the case of polarons only P^+ and P^- are stable. Thus an electron added to a P^+ or removed from P^- causes disintegration into phonons. This leads to

$$\mu_{P^-}=-\mu_{P^+}=\mu_n\ . \qquad (3.4)$$

The significance of Eqs. (3.3) and (3.4) is that, because no change in F results from introducing a neutral soliton at thermal equilibrium, the change in F on introducing an S^- or P^- is just that required to add an electron.

The chemical potential of a type of particle or excitation is related to the concentration of particles of that type. To obtain this relation I neglect the kinetic energy, which should be small compared to the other energies involved. The chemical potential for excitations of the ith kind may then be taken as

$$\mu_i=E_i-kT\frac{\partial}{\partial n_i}(\ln W_i)\ , \qquad (3.5)$$

where E_i is the creation energy and W_i the number of possible configurations. In connection with the calculation of W_i it is noted that the excitations themselves, or the combination of an excitation and an ion to which it is bound, are mobile. This must be true because doping occurs through diffusion.

In the case of solitons W_i ($\equiv W_S$) must satisfy the requirement that S and $\bar{S}$ alternate on the chain. If l_S, the length of a soliton or antisoliton in units of lattice sites, were unity, this requirement could only be satisfied by having S's on even sites and $\bar{S}$'s on odd sites, or vice versa. If all S's and $\bar{S}$'s were bound to ions, the requirement that the ion be in an interchain position opposite the soliton or antisoliton would mean that not all possible ion configurations would be allowed; configurations in which adjacent ions were opposite sites of the same parity would not be permitted. The W_S that results in this case for $n_S \ll N$, the number of sites on the chain, is[24]

$$W_S=\frac{1}{2^{n_S-1}}\left[\frac{(N/2)!}{(N/2-n_S/2)!(n_S/2)!}\right]^2 \quad \text{for } n_S\ll N \text{ and } l_S=1\ . \qquad (3.6)$$

The expression in large parentheses is the number of ways of putting $n_S/2$ S's on even sites and $n_S/2$ $\bar{S}$'s on odd sites. The factor $1/2^{n_S-1}$ selects the fraction of those ways which have S and $\bar{S}$ alternating. In the limit where n_S approaches N, the factor outside the large parentheses approaches unity because, as the sites fill up, there are progressively fewer chances for violating the $S\bar{S}$ sequence. With this factor unity, W goes to unity when $n_S=N$, as indeed it should. (Actually, W should go to 2 when $n_S=N$, but for $n_S<N$ this makes little difference in $\ln W$, and none in μ_S.)

For $l_S \neq 1$ the situation is quite different in that it is possible to create either an S or an $\bar{S}$ for either parity of the central site,[25] i.e., the site opposite the ion. In the SSH model[2] S has nonvanishing amplitude on sites of one parity, say even, while $\bar{S}$ has nonvanishing amplitude on sites of the other parity. For the ion opposite a site of even parity, for example, an S wave function is created by choosing maximum amplitude on the site opposite the ion, while an $\bar{S}$ wave function may be created by choosing zero amplitude at that site and maxima at the two adjacent sites.[25] If the ion location is taken as $x=0$, the former case corresponds, in the continuum version of the SSH model,[13] to a wave function

$$\psi_S = \left[\frac{2}{l_S a}\right]^{1/2} \operatorname{sech}\left[\frac{2x}{l_S a}\right] \cos\left[\frac{\pi x}{2a}\right] , \tag{3.7}$$

while the latter corresponds to

$$\psi_{\bar{S}} = \left[\frac{2}{l_S a}\right]^{1/2} \operatorname{sech}\left[\frac{2x}{l_S a}\right] \sin\left[\frac{\pi x}{2a}\right] , \tag{3.8}$$

a being the lattice constant. In principle, one would expect the binding energy for the cosine configuration, $E_b(S)$, to be larger, corresponding to a lower energy. The difference between $E_b(S)$ and $E_b(\bar{S})$ might not be large, however, because the solitons extend over many lattice sites. If $E_b(S)-E_b(\bar{S}) \ll kT$, the requirement of alternating S and $\bar{S}$ could, unlike the case $l_S=1$, be satisfied for any configuration of the ions, provided, of course, they are not closer than $l_S a$. In that case the number of possible configurations for n_S solitons plus antisolitons on a chain with N sites, $N \gg n_S l_S$ is [26]

$$W_S^{\mathrm{I}} = (l_S)^{n_S} \left[\frac{(N/l_S)!}{(N/l_S - n_S)!\,n_S!}\right]$$
$$\text{for } n_S \ll N/l_S \text{ and } E_b(S)-E_B(\bar{S}) \ll kT . \tag{3.9}$$

The factor in large parentheses is the number of configurations that would be obtained if the chain were rigidly divided into boxes l_S sites long, starting at the first site, into which S's and $\bar{S}$'s must be put. The factor $(l_S)^{n_S}$ allows for the fact that each box could have l_S discrete positions, i.e., new configurations could be obtained by starting the boxes at the second site, the third site, etc., through the (l_S-1)th site. When n_S is not negligible compared to N_S/l_S, however, not all of these different configurations can be realized, and in the limit $n_S \rightarrow N/l_S$ the factor $(l_S)^{n_S}$ should be replaced by unity. Again, this permits W_S^{I} to go to unity in the limit $n_S = N/l_S$.

If the difference $E_b(S)-E_b(\bar{S})$ were large compared to kT, the requirement that S and $\bar{S}$ alternate would necessitate that, as in the $l_S=1$ case, S and $\bar{S}$ each peak opposite the binding ion, and the sites opposite which the ions sit alternate in parity. The number of configurations would then be

$$W_S^{\mathrm{II}} = \frac{(l_S)^{n_S}}{2^{n_S-1}} \left[\frac{(N/2l_S)!}{(N/2l_S - n_S/2)!\,(n_S/2)!}\right]^2$$
$$\text{for } n_S \ll N/l_S \text{ and } E_b(S)-E_b(\bar{S}) \gg kT . \tag{3.10}$$

This expression reduces to (3.6) for $l_S=1$. In the limit where n_S approaches N/l_S the factor outside the large parentheses should be replaced by unity as discussed for the two earlier cases.

To determine $E_b(S)-E_b(\bar{S})$ a more careful calculation of the binding energy has been done,[27] specifically for the case of a Na^+ ion, which can reasonably be represented as a point charge. The distance of the ion from the chain is 2.97 Å.[28] The wave functions for S and $\bar{S}$ were taken as (3.7) and (3.8) respectively. With $\epsilon_{\parallel}=7$, $\epsilon_{\perp}=1.8$, obtained from recent measurements of the infrared refractive index on fully oriented, highly crystalline *trans*-$(\mathrm{CH})_x$,[29] it was found that $E_b(S)$ and $E_b(\bar{S})$ are both 1.1 eV. Taking into account the incomplete screening close to the ion, we obtained[27] $E_b(S)=1.4$ eV, $E_b(\bar{S})=1.3$ eV. The difference $E_b(S)-E_b(\bar{S})$ is indeed larger than kT at room temperature and below. However, the calculated values of the binding energies are very much larger than one would infer from optical-absorption data. The absorption that releases an electron from an S^- or a hole from an S^+ in a pristine sample is centered at ~ 0.45 eV,[30] while in a Na-doped sample it is centered at ~ 0.7 eV.[31] This would suggest that the binding energy is ~ 0.3 eV. One conclusion that could be drawn from these considerations is that the wave function of a charged soliton bound to an ion is not well approximated by Eqs. (3.7) or (3.8), which represent wave functions for a neutral soliton. Although many authors have suggested that this is the case, a definitive model for a charged soliton bound to an impurity ion has not yet emerged. Another possible conclusion, as will be discussed later, is that nonrandom arrangements of the ions mean that the interaction of a number of ions and solitons must be taken into account even at very low average doping. In any case, it is not possible to say whether W_S^{I} or W_S^{II} is the correct form for W_S, and further calculations will be done here for both.

With the expression (3.9) for W_S^{I}, and the use of Stirling's approximation, Eq. (3.5) leads to the soliton chemical potential

$$\mu_S^{\mathrm{I}} = E_S + kT \ln[n_S/(N-n_S l_S)] \quad \text{for } n_S \ll N/l_S . \tag{3.11}$$

When W_S is taken as W_S^{II}, Eq. (3.10), the soliton chemical potential becomes

$$\mu_S^{\mathrm{II}} = E_S + kT \ln[2n_S/(N-n_S l_S)] \quad \text{for } n_S \ll N/l_S . \tag{3.12}$$

One may use Eq. (3.11) or (3.12) to calculate n_S^{th}, the number of thermally generated neutral solitons, by equating μ_S^{I} or μ_S^{II} to zero. For case I, which yields the larger number, one finds

$$n_S^{\mathrm{th}} = N e^{-E_S/kT} / (1 + l_S e^{-E_S/kT}) . \tag{3.13}$$

For $E_S = 2\Delta/\pi$,[13] this equation leads to n_S^{th} smaller by 4 orders of magnitude than the background neutral solitons before doping.

When a *trans*-$(\mathrm{CH})_x$ sample is donor-doped, essentially all the solitons will be negatively charged and μ_S may be set equal to μ_n, according to Eq. (3.3). With this, for the large-soliton-concentration limit, i.e., $n_S \sim N/l_S$, where, as discussed earlier, W_S^{I} and W_S^{II} are given by the factors in large parentheses in Eqs. (3.9) and (3.10), Eq. (3.5) gives

$$\mu_S^{\mathrm{I}}=\mu_S^{\mathrm{II}}=\mu_n=E_S+kT\ln\left[\frac{n_S l_S}{N-n_s l_S}\right] \quad \text{for } n_S \sim N/l_S\ . \tag{3.14}$$

According to Eq. (3.14), $\mu_n > E_S$ for $n_S > N/2l_S$. For $l_S = 14$,[2] $\mu_n > E_S$ for a soliton concentration of 3.5% or more. If $l_S = 10$, the value obtained for a charged soliton bound to an impurity ion,[2,32,33] $\mu_n > E_S$ for 5% doping or more.

Consider now the chemical potential for polarons. If only polarons were present the number of possible configuration would be given by Eq. (3.9) with S replaced by P. However, with both solitons and polarons present it is necessary to correct Eq. (3.9) for the excluded volume due to solitons as well as that due to polarons. Also, because $E_P > E_S$, it is appropriate to use the form of Eq. (3.9) for large soliton concentration. It is then found that

$$\mu_P=E_P+kT\ln\left[\frac{n_P l_P}{N-n_S l_S-n_P l_P}\right]\ . \tag{3.15}$$

For a donor-doped sample μ_P may be taken equal to μ_{P-} and, according to Eq. (3.4), $\mu_{P-}=\mu_n$. Because $\mu_{S-}=\mu_n$ also Eqs. (3.14) and (3.15) may be equated. After correction of the ln term in (3.14) for the excluded volume due to polarons, this leads to the thermal equilibrium ratio of soliton to polaron concentrations,

$$n_S/n_P=(l_P/l_S)e^{(E_P-E_S)/kT}\ . \tag{3.16}$$

Thus the ratio of these populations is independent of doping unless E_P and E_S are doping dependent. Calculations neglecting overlap and Coulomb effects, both of the impurity ion and of the electrons internal to each excitation, give $E_S = 2\Delta/\pi$,[13] and $E_P = 2^{3/2}\Delta/\pi$.[4] Taking $l_P = 2x_0 + 2/\kappa_0$, in the notation of Ref. 4, one obtains $l_P \simeq 4l_S$. With this and the values of E_S and E_P obtained neglecting overlap and Coulomb effects, one obtains $n_S/n_P = 4\times10^3$ at 300 K, and greater below. Consideration of Coulomb effects leads to the conclusion that the actual ratio must be even larger. From optical absorption in doped samples it has been deduced that the energy to create a charged soliton is ~0.5 eV greater than that to produce a neutral soliton.[32] The difference is attributed mainly to the localization of two electrons, or two holes, on the soliton.[32] However, as indicated earlier, the occurrence of the peak of the charged soliton absorption at midgap suggests that this increase in E_S is largely cancelled by the lowering of the bound-electron-energy levels in the attractive field of the impurity ion. Thus the average E_S, when overlap effects are neglected, should still be $\sim 2\Delta/\pi$. Comparable information concerning E_P is not available. With a negatively charged polaron containing three electrons, however, the Coulomb correction should be at least as large as for the soliton. This will also be counteracted to some extent by the attraction of the impurity ion, but the binding to the impurity must be smaller than for the soliton because the polaron length is greater. As a result, even at small polaron concentrations the average E_P is probably significantly larger than the $2^{3/2}\Delta/\pi$ obtained with Coulomb interactions neglected. From these considerations, the ratio of soliton to polaron population must be greater than the 4×10^3 calculated earlier neglecting Coulomb interactions. When overlap is sufficient so that repulsive soliton-soliton and soliton-polaron interactions become significant, both E_P and E_S should increase. The increase should begin at lower doping concentration for the polarons because of their greater length. Thus the difference $E_P - E_S$ should, if anything, increase due to overlap effects, increasing n_P/n_S further. This small proportion of polarons in thermal equilibrium is consistent with the results of infrared absorption and susceptibility measurements on *trans*-$(\mathrm{CH})_x$ up to 5% or 6% doping. In what follows polarons will be neglected.

IV. FREE-ELECTRON CONCENTRATION IN HIGHLY DOPED CRYSTALS

In this section the results of the preceding sections are utilized to calculate μ_n and n in crystals with 4—5 % doping. One additional relation is needed, that between μ_n and n. In Sec. II it was pointed out that, despite a calculated lifetime for decay into polarons of $\sim 10^{-13}$ sec, conduction electrons could be treated as quasiparticles. That conclusion is even more valid at high doping because, as seen earlier, the presence of 4—5 % solitons excludes most of the volume of the chain for polaron production, increasing the lifetime. The relation between n and μ_n is then the standard one for Maxwell-Boltzmann statistics,

$$n=2(2\pi mkT/h^2)^{1/2}e^{(\mu_n-\Delta)/kT}\ , \tag{4.1}$$

where m is the effective mass of a conduction electron, including a contribution from electron-phonon coupling.[18] Note that this result does not depend on doping being random.

To obtain μ_n for large doping I use Eq. (3.14). Because of the large gap in *trans*-$(\mathrm{CH})_x$, $n_S \simeq n_{S^-}$ is well approximated by N_d, giving

$$\mu_n=E_S+kT\ln\left[\frac{N_d/N)l_S}{1-(N_d/N)l_S}\right]\ . \tag{4.2}$$

For $N_d/N = 0.05$ and $l_S = 10$ the ln term vanishes and $\mu_n = E_S$. For $N_d/N = 0.04$, Eq. (4.2) gives $\mu_n = E_S - 0.4kT$. With $E_S \simeq 2\Delta/\pi$, which is 5160 K for $\Delta = 0.7$ eV, it is clear that μ_n barely moves below E_S over the entire temperature range for such heavy doping. This conclusion must be true regardless of the detailed form of W_S, because when the solitons are close to filling a chain, the number of possible arrangements is small.

Having μ_n, one may substitute in Eq. (4.1) to obtain n. With $E_S = 2\Delta/\pi$, $\Delta = 0.7$ eV, and m the free electron mass, n for 5% doping is found to be $5\times10^{16}/\mathrm{cm}^3$ at 300 K. At such large doping, however, soliton interactions are expected to result in larger E_S. For a 5 mol % concentration of solitons on a lattice, Nakahara and Maki[33] calculated an increase in E_S from $2\Delta/\pi$ to 0.7Δ, and very little increase in the gap. This leads to $n \lesssim 10^{18}/\mathrm{cm}^3$ at 300 K. If the soliton concentration were as high as 6.67 mol %, n would still be close to $10^{18}/\mathrm{cm}^3$ because the increase in E_S is offset by the increase in the gap.[33] It should be noted that the magnetic susceptibility χ for a

Maxwell-Boltzmann distribution of electrons with this concentration in the entire sample is a little less than the measured χ for 5 at. % Na doping.[31] Greater χ is found for *trans*-(CH)$_x$ samples with 5% or less of other dopants. Thus a free-electron concentration of $10^{18}/\text{cm}^3$ is not in contradiction with magnetic susceptibility measurements. If such a free-electron concentration occurred in an ordered sample, with the mobility $\mu = 600\ \text{cm}^2/\text{V sec}$ calculated for phonon scattering,[18] it would lead to a conductivity of the order of a hundred $\Omega^{-1}\,\text{cm}^{-1}$.

V. EXPERIMENTAL CONSEQUENCES

The foregoing development leaves two important questions: (1) To which, if any, of the currently available *trans*-(CH)$_x$ does the theory apply? (2) If it does apply, can any of the observed conductivity be attributed to free-electron transport? These questions are addressed in this section.

As mentioned earlier, one of the assumptions underlying the validity of most of the theoretical development is that of randomness of the impurity distribution. Baughman *et al.*, however, have pointed out that strains due to the large size of the dopants and mixing entropy favor dopant aggregation.[28] Randomness is predicted and observed, so far, up to ~5% concentration, only for (CH)$_x$ doped with Li whose small size allows it to fit between the chains with little distortion. The small distortion should also result in the second assumption, the existence of reasonably well-defined band edges, being satisfied. Thus the theory developed here should apply to Li-doped *trans*-(CH)$_x$. Unfortunately, there are few data for such material. In one study, including samples with up to 3 at. % Li,[34] it was found that the conductivity σ versus doping percentage was identical with that for Na-doped *trans*-(CH)$_x$ over the same range. The values for the Na-doped material were, however, lower by a factor 100 than others reported in the literature.[31]

X-ray data indicate that the alkali metals other than Li form tetragonal channel complexes in which columns of alkali-metal ions are each surrounded by four polyacetylene chains.[28,35] Particularly for doping by potassium, whose van der Waals volume is very close to the volume available in the tetragonal channel, extensive staging, i.e., the growth of ordered phases, has been found.[35–37] Baughman *et al.* conclude that there is evidence for the existence of such ordered phases in some portion of the sample over the attainable doping range, 0.5% to ~17%.[36] Phases of the type $(\text{C}_n\text{H}_n)_m\text{K}$, where n ranges from 3 to 5 and m from 2 to 4, are consistent with the x-ray data and energetic considerations.[36] The higher values of n and m are found at lower impurity concentrations. Typical coherence lengths were 60–100 Å perpendicular to the chains and greater than 45 Å along the chain direction.[35] Similar phases have been found to exist for *trans*-(CH)$_x$ doped with Na, the lowest concentration phase being $(\text{C}_5\text{H}_5)_3\text{Na}$.[37,38]

On the evidence of the very small magnetic susceptibility for Na doping up to close to 6%,[31] the electrons are mainly paired, which may be taken as evidence for solitons. This is consistent with the existence within such samples of a phase such as, for example, $(\text{C}_5\text{H}_5)_3\text{Na}$, corresponding to 6.67 at. % Na. With three polyacetylene chains per Na channel such a phase would allow sufficient space for the electron from each ion to form an independent soliton. For the average impurity concentration $\bar{y} < 5$ or 6%, this phase could exist only in part of the sample, not necessarily in contiguous regions. Within this part of the sample overlap of the solitons is clearly much greater than if the same soliton concentration were distributed randomly throughout the sample. Overlap, it it known, causes the soliton energy levels to spread.[39,40] With such ordered phases, having actual Na concentration $y > \bar{y}$, formed for $\bar{y}$ as low as 0.5%,[38] the increased overlap could account for the observation that the optical absorption attributable to charged solitons extends over most of the gap for these low dopings. At 0.7 at. % Na, for example, the lowest doping for which optical-absorption data are given,[31] the absorption spreads from 0.6 eV, the lowest photon energy at which measurements were taken, to ~1.4 eV, close to the band edge. Theoretical calculations[39,40] indicate that such a spread is characteristic of ~5–6% doping. Equally broad optical absorption associated with charged solitons is found for other dopants, e.g., 0.1 mol % AsF$_5$,[41] 0.8 mol % I,[42] and 0.3 mol % ClO$_4$.[43] X-ray studies give evidence for clustering of these dopants also. In the case of iodine, x-ray and other data point to the existence of first- and third-stage phases, in which, respectively, one and three close-packed planes of polyacetylene chains lie between each dopant.[28,44–46] Baughman *et al.* point out that the interpretation of the iodine-doped (CH)$_x$ data is complicated by the coexistence of phases with different doping levels.[28] For AsF$_5$ there are x-ray data consistent with a first-stage structure.[28] Intercalation of ClO$_4^-$ ions to form ordered phases extending over about 40 Å in the [100] direction and 20 Å in the [001] direction, is inferred from x-ray data for *trans*-(CH)$_x$ doped with an average ClO$_4$ concentration of ~6 mol %. Evidence for clustering of ClO$_4^-$ ions is found also at lower concentrations.[47] It should be remembered that broadening of the soliton absorption lines requires only clustering of the dopant; ordered phases are not necessary and may not occur to any great extent for bulky anions such as AsF$_5^-$.

In the presence of inhomogeneous doping the portions of the conducting path with lower doping and therefore higher resistivity will dominate the measured σ. This seems particularly clear for Na-doped samples where, although χ increases by orders of magnitude for 5–6% doping, σ continues its relatively slow increase without a ripple.[31] The inhomogeneity makes it difficult to ascertain, from measurements of dc current versus voltage, the origin of the increase in σ with y—whether due to enhanced hopping, larger free-carrier contribution, or charged soliton conduction. However, in any case, the free-carrier contribution to σ_{dc} is likely to be small. If there exists an ordered region with $y \sim 5\%$, and thus sizeable n, adjacent to a region with smaller doping, a barrier will be set up between the two regions, tending to keep the electrons in the larger-y region.

The situation could well be different, however, for σ_{ac}, because electrons need not cross barriers. Conductivity measurements on I- and AsF_5-doped *trans*-$(CH)_x$ have recently been extended to the millimeter range.[48] Earlier measurements of σ_{ac} on samples with $<1-2.5$ at. % I doping showed no frequency dependence up to 500 MHz.[49] Genzel *et al.*[48] found that σ for samples with 1.1 at. % I or AsF_5 doping decreased as ω went from 10 to $\sim 10^2$ GHz, after which it increased with further increase in ω Because σ_{ac} must increase with ω for hopping conduction, although the increase may not be large for variable-range hopping,[50] Genzel *et al.* proposed that the decrease in σ_{ac} with ω arises from free-electron conduction. Above $\sim 10^2$ GHz, this contribution to σ_{ac} has apparently decreased to the extent that hopping again dominates σ_{ac}. Comparing their experimental results with simple Drude theory, Genzel *et al.* found that at 300 K $n \sim 10^{15}/\text{cm}^3$ and μ is between 4×10^3 and $1.5\times10^4 \text{cm}^2/\text{V sec}$. The μ values are considerably larger than the 600 $\text{cm}^2/\text{V sec}$ calculated for phonon scattering of conduction electrons in *trans*-$(CH)_x$.[18] However, the values deduced from σ_{ac} must be considered very approximate, because, among other things, the authors have not taken into account the nonuniform dopant distribution, and therefore σ, expected in this dopant range.

VI. CONCLUSIONS

It has been argued that electrons cannot exist in the conduction band of polyacetylene because electron-phonon coupling will cause them to self-trap in a very short time. The calculated lifetime for this self-trapping is, however, of the order of the scattering time in typical 3D semiconductors for $(CH)_x$ with little doping, and should be considerably longer for the several percent doping required for a sizeable conduction-electron population. Thus it is reasonable to treat conduction electrons in *trans*-$(CH)_x$ as quasiparticles.

The electrical neutrality condition, relating electron populations in the conduction-band, soliton, and polaron levels to the donor concentration, has been derived. From this equation it was deduced that at low temperatures, when electrons are excited into the conduction band, solitons are lost. The chemical potentials of negatively charged solitons and polarons were shown to equal μ_n, the Fermi energy, while those for positively charged solitons and polarons equal $-\mu_n$. In deriving the relations between the chemical potentials and concentrations of the excitations, the question of the possible number of configurations W_S of solitons on a chain was discussed. There are two possible forms for W_S at low soliton concentration, differing on whether the requirement that S and $\bar{S}$ alternate necessitates that S's be centered on sites of one parity, $\bar{S}$'s on the other. Better knowledge of the wave function of a bound soliton is necessary before one can decide which of these two forms is correct. Fortunately, for large soliton concentrations the two forms are essentially the same. Using the relations between chemical potentials and numbers of excitations, and the fact that $\mu_{S^-}=\mu_{P^-}$, one finds that in thermal equilibrium for *trans*-$(CH)_x$ the number of polarons is negligible compared to the number of solitons, independent of dopant concentration, provided it is low enough that solitons can exist. For crystals with 4 to 5% doping the various relations may be simplified, leading to $\mu_n \simeq E_S$, the creation energy of a soliton. With this it is found that for 5–6 % doping $n \simeq 10^{18}/\text{cm}^3$.

Due to strain and entropy considerations, most actual samples should have nonrandom dopant distributions, contrary to what was assumed in deriving the thermal-equilibrium relations. On the evidence of x-ray and electrochemical studies, and the large spread in charged-soliton "midgap" absorption at dopings as low as tenths of a percent, it appears that for many types of dopant the distribution is nonrandom even at such low concentrations. High free-carrier concentration and resulting large conductivity in a local region due to a local aggregation of impurities is not expected to have much effect on dc conductivity; it might, however, be seen in ac conductivity. Millimeter wave σ measurements by Genzel *et al.* on *trans*-$(CH)_x$ samples with 1% doping may have detected this conductivity.

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