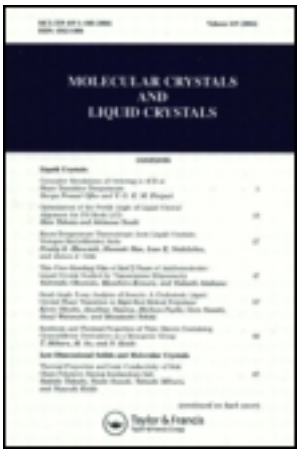

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STATISTICS AND FREE CARRIER CONCENTRATION IN HIGHLY DOPED SEMICONDUCTING TRANS-POLYACETYLENE

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Abstract Electrons in donor-doped trans-$(CH)_x$ are divided among soliton and polaron levels and the conduction band. In this paper the temperature dependence of these populations is discussed. Among the results obtained is the concentration of conduction electrons at 300K in a 5% donor-doped sample: $10^{18}/cm^3$. In materials where these electrons are not localized, which could include Na-doped $(CH)_x$, they could account for a major part of the conductivity at 300K.

1. INTRODUCTION

If a single impurity, capable of giving up one electron, were added to a trans-$(CH)_x$ sample, at temperature T=0 the excess electron would go into a polaron state. The polaron provides two levels for electrons, one above midgap into which the excess electron goes and another, equally far below midgap, which is filled by two electrons from the valence band. Calculations of Campbell and Bishop[1] place the upper level 0.2 eV below the conduction band in trans-$(CH)_x$. If a small number of additional donors were then added to the sample, the excess electrons would end up in negatively charged soliton states because the solitons have lower creation energy. The energy levels of the charged solitons states are, for low impurity concentrations, at midgap.[2,3] If the added donor concentration N_d is high enough there will also be at T=0 some electrons in polaron levels. When the temperature is raised above T=0 electrons are excited to higher levels and changes occur in the concentrations of solitons, polarons and electrons in the conduction band. It is the

purpose of this paper to consider the changes in the concentrations with temperature; some detailed calculations will be made for rather highly doped samples, with $\sim$4 to 5% donors. Although the discussion will be in terms of n-type samples, it applies also, with obvious modifications, to p-type samples. It will be assumed that the distribution of impurities is random.

The basic equation describing the populations of the various levels is the electrical neutrality equation:

$$p+N_d+n_S+2n_P=n+2n_S\langle f(E)\rangle_S+3n_P \qquad (1)$$

Here p and n are concentrations of holes in the valence band and electrons in the conduction band, respectively, and n_S and n_P the soliton and polaron concentrations. $\langle f(E)\rangle_S$ is the distribution function of the electrons averaged over the soliton levels. The right hand side represents the number of electrons found in the conduction band, on soliton levels and in polaron levels, while the left hand side represents the number of electrons available for distribution among the various energy levels. The valence band provides one for each soliton formed[2,3] and two for each polaron formed,[1] in addition to the p that leave behind holes.

Eq.(1) could be used to determine the Fermi energy μ_n. For the electrons Fermi-Dirac statistics give the relation to μ_n for a 1D case:

$$n=2(2\pi m^* kT/h^2)^{1/2}\exp\left[(\mu_n-\Delta)/kT\right], \qquad (2)$$

where Δ is the half-gap. It has been argued that the electrons cannot be treated as quasiparticles, and thus ordinary statistics should not apply, because of the short lifetime, 10^{-13} sec, for decay into a polaron.[4] Although this lifetime does result in some broadening of the energy levels, it is a quite typical lifetime for an electron in semiconductors such as CdS,[5] or impure GaAs or InP, with lower lifetimes being not unusual. Treatment of electrons as quasiparticles when the lifetime is 3 or 4×10^{-14} sec., for example, yields results in excellent agreement with

experiment in these semiconductors. Conduction electrons in $(CH)_x$ have, in fact, been treated as quasiparticles in the calculation of their lifetime for phonon scattering which is found also to be $\sim 10^{-13}$ seconds for thermal electrons.[6]

To simplify further discussion consideration will be limited to the case of fairly heavily doped samples, with $\sim$ 4-5% donors, in which essentially the full gap remains. In such samples the soliton ("midgap") absorption is found to be quite broad.[7] The causes of this breadth are overlap of the wavefunctions, Coulomb effects of the randomly distributed charged impurities and perhaps disorder resulting in different environments for different solitons. Whatever the causes, they should be at least as effective in causing the polaron levels to spread. In particular, the length of the polaron is 1.5 times that of the soliton, so overlap effects must be worse. Because the polaron levels are expected to be quite close to the band edge, comparable spreading would cause them to strongly overlap the conduction band. This would result in a mixing of the wavefunctions but, with the polarons being mobile and their mass comparable to m^*,[1] it would not have a great effect on properties of electrons near the band edge. It is therefore appropriate to modify Eq. (1) for this range of doping by dropping the n_p terms.

To determine μ_n from Eq. (1) it remains to express n_s as a function of μ_n. Consider first the relation between n_s and μ_s, the chemical potential for the solitons. For 4-5% doping the solitons are close to filling the chain, so that the number of possible configurations, and thus the soliton entropy, is relatively small. With essentially all the solitons negative, this leads to $\mu_s \simeq \mu_{s^-} \simeq E_s$ where E_s is the formation energy of a soliton. This relation leads directly to μ_n because for thermal equilibrium $\mu_{s^-} = \mu_n$.[8]

The foregoing results can be used to calculate the free carrier concentration at 5% doping, for example. Optical data[7]

give $\Delta \simeq 0.6$ eV at this doping level. For low doping $E_s = 2\Delta/\pi$, but it increases for high doping. Nakahara and Maki[9] find for a soliton lattice at 0K $E_s = 0.7\Delta$ at 5% doping. Using this value in Eq. (2), with m^* taken as the free electron mass, we obtain $n = 3 \times 10^{18}/cm^3$ at 300K for 5% doping. These electrons would need only $\mu = 20$ $cm^2/Vsec$, much less than the mobility calculated for phonon scattering,[6] to account for the observed conductivity in Na-doped samples at 300K. Note that the magnetic susceptibility for such a concentration of conduction electrons is about equal to that measured.[7] It may indeed be that the disorder in samples doped with large ions, such as I_3^-, AsF_6^- or ClO_4^-, is sufficient to localize all the conduction electrons.[10] However, this should not be true for $(CH)_x$ samples doped with Na. Although it is unlikely that free electrons are the only source of conduction in $(CH)_x$ doped with 5% N_a, it appears they could make a strong contribution around room temperature. Measurements of conductivity and susceptibility as a function of T for such samples would be helpful in elucidating the conduction mechanism.

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