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HOPPING CONDUCTION IN LIGHTLY-DOPED POLYACETYLENE

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Résumé - Nous déduisons que le transport de charge dans le polyacétylène faiblement dopé met en jeu des états électroniques fortement localisés qui sont couplés aux mouvements atomiques.

Abstract - We conclude that the charge transport in lightly doped polyacetylene involves severely localized electronic states which are strongly coupled to the atomic motion.

INTRODUCTION

It appears that electronic transport in lightly doped polyacetylene proceeds by phonon-assisted hopping. Here we discuss general features of hopping transport and attempt to ascertain fundamental information about the hopping process in polyacetylene. Namely, are the electronic states that are involved in hopping severely localized (on the order of an interatomic separation) or are they only weakly localized? Concomitantly, are the localized electronic states between which hopping occurs coupled strongly or weakly to the atomic vibrational motion? We discuss the strength of the electron-lattice interaction and its relationship to general features of hopping conduction. Contrary to a prior work, we suggest that, as in many disordered materials in which hopping is observed above cryogenic temperatures (~10 K), the transport in lightly doped polyacetylene involves states which have strong coupling to the lattice. General principles of the thermoelectric power due to hopping conduction are briefly reviewed. It is pointed out that a recently proposed formula for the thermoelectric power violates these notions. Finally, it is noted that the frequency-dependent conductivity in lightly doped polyacetylene is like that of many hopping systems. Here a general analysis scheme which has been applied to other materials in which hopping occurs is applied to polyacetylene. In this approach, the frequency-dependent conductivity is determined by the dc conductivity and a dispersion parameter, n. Good fits to the experimental data are obtained. Here we suggest that the charge carriers are more strongly coupled to the atomic motion than has been suggested previously. Several possible strong-coupling (polaronic) hopping models are mentioned. However, in our opinion, the experimental and theoretical situation is not yet sufficiently delineated to permit us to advocate a specific picture.

THE ELECTRON-LATTICE INTERACTION

The electron-lattice interaction simply denotes the dependence of an electron's energy on the positions of the atoms surrounding it. Within the tight-binding picture this interaction manifests itself in 1) the dependence of the energy of an electron localized on a single site on the positions of the surrounding atoms, and 2) the dependence of the electronic transfer integrals which link electron sites on the separation between the sites. The first effect is termed diagonal since the associated term in the tight-binding Hamiltonian is diagonal in the electron's site-occupation amplitudes. It is this effect which is most often the object of polaron studies. The second effect, the nondiagonal effect, is responsible for the dimerization of polyacetylene within the SSH model. Most generally, both effects exist. Thus the effective electron-lattice coupling is larger than is inferred from
the SSH dimerization model alone. In particular, the energy and the spacial extent of a localized charge (e.g., as associated with a charged soliton) is generally reduced as a result of the diagonal electron-lattice interaction (the polaron effect). Thus charged solitons may be more severely localized than are neutral solitons.

The presence of disorder (as in doped polyacetylene) can also dramatically affect the nature of the electronic states. In particular, while disorder alone fosters electronic localization, in tandem with the electron-lattice interaction the effects are more than additive. Briefly, the synergistic effect results because of the feedback (nonlinear) nature of the polaron effect: with increasingly severe localization the polaronic effect is enhanced; but the polaron effect itself produces localization. Thus the imposition of disorder can serve to trigger extreme localization associated with the electron-lattice interaction. There are experimental observations of this phenomenon.

The polaron effect itself and the influence of disorder depends on the dimensionality of the electronic states. Due to the disordered morphology, dopants, unintentioned impurities, defects and possible crosslinks in lightly doped polyacetylene the electronic states and their dimensionality are uncertain. Hence, we simply analyze the temperature dependence of the hopping mobility to determine the severity of the states' localization and their coupling to the lattice.

**PHONON-ASSISTED HOPPING**

There are two types of phonon-assisted hopping: weak-coupling and strong-coupling. Weak-coupling hopping, as in shallow-impurity conduction in crystalline semiconductors, involves hopping between states of large radius. Concomitantly, the effective electron-lattice coupling is weak and the hops proceed with the absorption and emission of the minimum number of phonons consistent with the requirements of energy conservation. Alternatively, if the states are well-localized, the effective coupling to the lattice is strong and multiphonon processes predominate. In both cases the temperature dependence of the hopping mobility arises from the increase in the availability of phonons with rising temperature. However, in the weak-coupling case the temperature dependence depends critically on the dependence of the coupling function ( \( G \) of (2) or \( \gamma \) of (11)) on phonon energy. In standard models of the electron-lattice interaction (such as the deformation-potential model) the coupling function varies inversely with the phonon energy at low phonon energy. However, in (2) the coupling is assumed to rise as a high power (~9) of phonon energy. This gives rise to a very strong temperature dependence of the (weak-coupling) hopping mobility. In the absence of any justification we can only view this result as spurious.

On the other hand, with the strong coupling characteristic of well-localized states, the hopping rates generally rise strongly with temperature in a non-Arrhenius manner. The behavior ultimately becomes simply activated when the temperature exceeds the phonon temperature characteristic of the highest-energy phonons with which the electronic states interact appreciably. The observed mobilities in lightly-doped polyacetylene appear consistent with this hypothesis.

**THERMOELECTRIC POWER**

The Peltier heat, \( \pi \), related to the thermoelectric power, \( S \), by the Kelvin relation, \( \pi = qTS \), is the heat transport with a carrier of charge \( q \) as it moves. The Peltier heat generally consists of two terms. The first is the product of the temperature, \( T \), and the change of the entropy of the system upon the addition of a carrier. The second depends upon the details of the transport process. With a concentration of carriers, \( c \), localized among isoenergetic sites the entropy change for spinless particles is given by the Heikes formula: \( \pi = kT \ln[(1-c)/c] \). Particles of spin \( \frac{1}{2} \) yield \( \pi = kT \ln[(2-2c)/c] \) if the coulomb repulsion of the electrons is neglected. However, if double occupancy of a site is precluded by the intercarrier coulomb repulsion: \( \pi = kT \ln[2(1-c)/c] \). For hopping transport between sites with equivalent coupling to the atomic vibrations, as in (2), the second term vanishes since no
vibrational energy is transferred with a carrier as it hops. Then, the thermoelectric power is independent of the hopping process. Nonetheless, it is claimed that the resulting Peltier heat depends upon the electron-lattice coupling function $G$ in (2). Explicitly in (2) the Peltier heat depends upon the exponent with which the electron-lattice coupling function $G$ rises with phonon energy, $E$, at small $E$. To us this result is unphysical.

**AC CONDUCTIVITY**

In any dielectric which has mobile carriers, in addition to the hopping carrier's contribution to the dielectric loss $\varepsilon''(w)$ there is a residual or background contribution $\varepsilon''(w)$ from the dielectric lattice. This contribution, $\varepsilon''(w)$, is more or less independent of $w$ and has a weak temperature dependence. This is found in all dielectrics, including even crystalline materials. A contribution such as $\varepsilon''(w)$ will give rise to a residual AC conductivity, $\sigma_{\text{AC}}(w)$, that is approximately proportional to $w$ and weakly temperature dependent. Of diminishing the conductivity of the mobile carriers, the contribution to $\varepsilon''(w)$ from the carriers will eventually fall below $\varepsilon''(w)$. Hence for low conductivity materials such as NH$_3$ compensated (CH)$_n$, a-As$_2$, anthracene, or ionic conductors at low temperatures, etc., $\varepsilon''(w)$ dominates at sufficiently high frequencies and the AC conductivity $\sigma(w)$ reflects $\sigma_{\text{DC}}(w)$. Only when the conductivity level is sufficiently high as in trans-(CH)$_3$, the measured $\sigma(w)$ is due entirely to the hopping relaxation of the mobile carriers throughout the frequency measurement range (say 10 Hz to $10^6$ Hz). Even in this case, if measurements were made at higher and higher frequencies, the contribution $\sigma_{\text{AC}}(w)$ will eventually dominate. Thus the temperature dependence of $\sigma(w=10\text{ GHz})$ will be rather temperature insensitive reflecting the property of $\sigma_{\text{DC}}$ while $\sigma(w=30\text{ Hz})$ will be due to the charged carriers and has a strong T-dependence as that of $\sigma_{\text{DC}}$. This feature has been observed in trans-(CH)$_3$, and reported by Roth, Ehinger et al., in this Conference. The strong T-dependence of $\sigma(w)$ in trans-(CH)$_3$, is not unique to trans-(CH)$_3$, but is shared by other materials with high conductivity; with the dominance of the hopping relaxation, the usually strong T-dependence of the hopping conductivity manifests itself in the AC conductivity.

For hopping of mobile charged carriers in dielectrics, it is appropriate to consider the inverse complex permittivity or electric modulus: $M^e(w)=1/\varepsilon^e(w)=M^++iM^e=-M^+\text{d\tau}g(t)/[1+i\omega\text{t}]$. $M^e(w)$ reflects the "distribution" of hopping relaxation times, $g(t)$. The mean relaxation time, $\langle\tau\rangle_0=\int_0^\infty d\tau g(\tau)\tau_0$, yields the dc conductivity: $\sigma_{\text{DC}}=g_0/M\langle\tau\rangle$ where $M=1/\text{limc}$ for $\omega\tau>>1$. $M^e(w)$ gives not only the distribution of hopping times but also $\sigma(w)$ and $\sigma_{\text{DC}}$. Further $\sigma_{\text{DC}}$ is obtained from $\sigma(w)$ in the $w\rightarrow0$ limit. This should be contrasted with the rather ill-defined separation$^3$ of $\sigma(w)$ as the sum of $\sigma_{\text{DC}}+\sigma_{\text{AC}}$. There is a fundamental mechanism$^16$ that makes the hopping relaxation rate, $1/\tau_0$, time dependent and has the form of $\tau_0^{-1}(w\tau)$, where $w_0$ is an upper cut-off frequency and $0<\eta<1$. This leads to the fractional exponential decay function, $\phi(t)=\exp[-(t/\tau_0)^{1-\eta}]$ where $\tau_0=\left[(1-n)w_0\tau_0\right]/(1-n)$, to a homogeneous distribution of relaxation times; even $\tau_0$ has the same initial value for every hop. The mean relaxation time $\langle\tau\rangle_0$ is evaluated to be $\left[\tau_0/(1-n)\right]/(1-n)$. The $\sigma(w)$ calculated from the fractional exponential decay has a frequency independent value of $\sigma_{\text{DC}}$ at low frequencies ($\omega<<\omega_1=1/\tau_0$) and is proportional to $w_0$ for $\omega>>w_0$. The ability of the fractional exponential decay function to account for $M^e(w)$, $\sigma_{\text{DC}}$, and $\sigma_{\text{AC}}$ has been demonstrated repeatedly in the past.$^{15,16}$ We have fitted the $\sigma(w)$ data$^8$ for the NH$_3$ compensated trans-(CH)$_3$ and for trans-(CH)$_3$ with the $M^e$ approach and the fractional exponential decay function. The hopping contribution is separated from the background by replotting the $\sigma(w)$ data as $\varepsilon''(w)$ vs log $w$. At lower temperatures, $\varepsilon''(w)$ of the NH$_3$ compensated trans-(CH)$_3$ becomes frequency independent at high frequencies and there the measured $\varepsilon''(w)$ is entirely due to $\sigma_{\text{AC}}$. The magnitude of $\sigma_{\text{DC}}(w)$ at all frequencies is then estimated by the product $\omega D^e$ which has a slight T-dependence, and is depicted in Fig. 1 by the shaded portion. Measured $\sigma(w)$ can be ascribed to hopping relaxation only if its value is well above the shaded area. The set of solid curves are generated with $n=0.83$. Each solid
curve if continued to lower frequencies will level off to the $\sigma_{dc}$ value at that temperature. Thereby both $\sigma_{dc}$ and $\sigma_{ac}$ are obtained at the same time. The $\sigma(w)$ data of trans-(CH)$_2$ are well fitted with $n=0.58$ (Fig. 2). The background contribution in trans-(CH)$_2$ is lower than that in NH$_3$ compensated trans-(CH)$_2$, and an estimate of its maximum possible contribution is indicated by the shaded portion. Note that in the entire temperature and frequency ranges studied, the measured $\sigma(w)$ is well above the shaded portion; this clearly demonstrates that in trans-(CH)$_2$ the measured $\sigma(w)$ comes entirely from hopping relaxation. Whereas in NH$_3$ compensated trans-(CH)$_2$, the significant contribution to $\sigma(w)$ is from $\sigma_c$. This is the cause for the difference in the AC conductivity behaviors of the compensated and uncompensated materials.

CONCLUSIONS

We have commented on the electronic transport in lightly-doped polyacetylene. In particular, we conclude that the conductivity, dc and ac, is consistent with that expected, and often observed, for the (strong-coupling) hopping of carrier between severely localized states. However, not enough is known to permit us to deduce the nature of these states. Several possibilities are noted. Due to the presence of the diagonal electron-lattice interaction and disorder 1) charged soliton states, and perhaps even polaron states, may be sufficiently localized to move via (small-polaron-like) hopping; 2) the carrier may hop between impurity regions. This may, as in (2), involve solitons, or may simply be the strong-coupling impurity conduction.

We intend to prepare a detailed paper amplifying the present note.

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