Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: Zhao-Bin Su & Lu Yu (1985): Soliton and polaron generation in polyacetylene, Molecular Crystals and Liquid Crystals, 117:1, 219-225

To link to this article: http://dx.doi.org/10.1080/00268948508074628

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 219-225
0026-8941/85/1174-0219/$15.00/0

Printed in the United States of America

SOLITON AND POLARON GENERATION IN POLYACETYLENE

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Abstract The nonradiative decay of an e-h pair into soliton pair and that of an electron (hole) into polaron as well as the photoproduction of solitonpairs are considered using the lattice relaxation theory generalized to include the self-consistency of multi-electron states with the lattice symmetry breaking. The branching ratio of the photogenarated neutral to charged soliton pairs is estimated. The recent related experiments are discussed.

INTRODUCTION

Since the creation energy of a soliton pair $2E_s = 4\Delta/\pi$ is less than the energy of an e-h pair, the latter is metastable w.r.t. the former. Similarly, a single electron (hole) will decay into a polaron with energy $E_p = 2\sqrt{2}\,\Delta/\pi$. On the other hand, the soliton pair can be generated directly by absorbing a photon of energy less than the optical gap with the assistance of the lattice quantum fluctuation. The nonradiative decay of the e-h pair and that of the electron have been studied by Su and Schrieffer[1] on a discrete lattice. The photoproduction of the soliton pairs has been considered by Sethna and Kivelson[2] using the instanton technique. Both radiative and nonradiative processes of soliton and polaron generation as well as the life-time effects on the band-to-band and kink-to-band absorption have been studied by us[3,4] using the generalized theory of lattice relaxation.[5] In this paper we summarize our main results and compare them with the recent experiments.

NONRADIATIVE PROCESSES

The standard continuum version of the SSH Hamiltonian can be iden-

tically rewritten as

$$\mathcal{H} = \mathcal{H}_o^e + \mathcal{H}_o^{ph} + \mathcal{H}_{int} , \tag{1}$$

$$\mathcal{H}_o^e = \int dx \left[\psi^\dagger(x) \left(\frac{\hbar v_F}{i} \frac{d}{dx} \tau_3 + 4\alpha u_c(x) \tau_1 \right) \psi(x) + \frac{\rho}{2} \omega_b^2 u_c^2(x) \right], \tag{2}$$

$$\mathcal{H}_o^{ph} = \frac{\rho}{2} \int dx \left\{ \dot{u}(x) \dot{u}(x) + \omega_b^2 [u(x) - u_c(x)][u(x) - u_c(x)] \right\}, \tag{3}$$

$$\mathcal{H}_{int} = \int dx \left[4\alpha \psi^\dagger(x) \tau_1 \psi(x) + \rho \omega_b^2 u_c(x)] [u(x) - u_c(x)] \right], \tag{4}$$

where $\psi(x), \psi^\dagger(x)$ are spinor fermion operators, τ_1, τ_3 Pauli matrices, $u(x)$ staggered lattice displacement operator with $u_c(x)$ as its classical counterpart and $\dot{u}(x)$ as the velocity. Here v_F is the Fermi velocity and α the el-ph coupling constant. For simplicity we limit ourselves to the single frequency model ($\omega_b^2 = 4K/M$, K the spring constant, M the (CH) group mass) for the optical phonon. The linear density $\rho = M/a$, where a is the lattice constant. A summation over the spin index is understood where needed, while the x integration is taken over the chain length L.

In the Born-Oppenheimer approximation the state vector can be decomposed as

$$| \quad > = | e > \otimes | \tilde{n} > , \tag{5}$$

with $|e>$ diagonalizing the electron Hamiltonian and $|\tilde{n}>$ — the phonon part with shifted origin. Also, the diagonal matrix element of $\mathcal{H}_{int}$ should vanish for both $|e>$ and $|\tilde{n}>$. The nonradiative decay rate is then determined by the Golden rule using $\mathcal{H}_{int}$ as perturbation. It is essential to note, however, that the total $\mathcal{H}$ is split into interacting and noninteracting parts differently in the initial and the final states in accord with their own lattice relaxations $u_c(x)$ and $v_c(x)$. Therefore, they belong to different complete sets. Nevertheless, the result depends only on the transition amplitude but not on the overlap integral.

In the low temperature ($\hbar\omega_b \lesssim k_B T$) and strong coupling ($|S\hbar\omega_b - W_{if}| / S\hbar\omega_b \lesssim 1$) limit the probability of nonradiative

decay is given by

$$W = \frac{\pi\lambda v_F}{4}\left(\frac{2\pi}{S}\right)^{1/2} \exp\left\{-\frac{(W_{if} - S\hbar\omega_b)^2}{2S\hbar^2\omega_b^2}\right\} \sum_\nu |\langle e_f | K_\nu | e_i \rangle|^2 \qquad (6)$$

with

$$W_{if} = E_i - E_f , \qquad (7)$$

$$\lambda \equiv 32\alpha^2/\pi\rho\omega_b^2\hbar v_F , \qquad (8)$$

$$K_\nu \equiv \int dx\, \psi^\dagger(x)\tau_1\psi(x)\xi_\nu(x) + \rho\omega_b^2 u_\nu^c/4\alpha , \qquad (9)$$

$$S \equiv \frac{\rho\omega_b^2}{2\hbar}\int dx\,[u_c(x) - v_c(x)]^2 \qquad (10)$$

with $\xi_\nu(x)$ as eigenmodes and u_ν^c as the expansion coefficients for the lattice relaxation $u_c(x)$. Here the Huang-Rhys factor S is the average number of phonons needed to bring the initial lattice configuration into the final one.

Using the self-consistent solutions of the Bogoliubov-de Gennes equation and assuming the Hartree approximation for the electron states we have estimated the nonradiative decay rate for both polaron and soliton pair cases to be of order of 10^{13} sec^{-1} in agreement with the numerical calculation of Su and Schrieffer[1] with the same set of parameters, namely, $\Delta = 2$ eV, $\hbar\omega_b = 0.1$ eV, $\lambda = 0.62$, $L/\xi = 10$, where ξ is the coherence length.

It is worthwhile to point out that the nonradiative decay of e-h pair into soliton pair (either neutral or charged) would be forbidden, if there had been no term proportional to $\rho\omega_b^2 u_c(x)$ in $\mathcal{H}_{int}$ and the many-electron background effects had been ignored, because the term proportional to $\psi^\dagger(x)\tau_1\psi(x)$ in (4) is odd under charge conjugation, whereas the initial as well as the final states are charge conjugation even. As far as the $\rho\omega_b^2 u_c(x)$ term is present, the nonradiative decay is allowed in agreement with the calculation on the discrete model.[1] We would like to mention that this result differs from that of Ref. 6 where the el-ph interaction Hamiltonian does not account for explicitly the lattice symmetry breaking.

RADIATIVE PROCESSES

Within the framework of the lattice relaxation theory the multiphonon effects are included into radiative processes by calculating the Franck-Condon overlap integral. In the low temperature, strong coupling limit the cross section for the direct process of soliton pair photoproduction is given by[3,4]

$$\sigma^{d} = \frac{2\pi e^2 v_F^2}{c\omega\hbar\omega_b} \sum_{e_f} |\langle e_i | \hat{J} | e_f \rangle|^2 \left[\frac{2\pi}{S}\right]^{1/2} \exp\left\{-\frac{(\hbar\omega - \frac{4}{\pi}\Delta - S\hbar\omega_b)^2}{2S\hbar^2\omega_b^2}\right\} \quad (11)$$

where

$$\hat{J} \equiv \int dx\, \psi^{+}(x)\, \tau_3\, \psi(x). \quad (12)$$

c the speed of light, ω the photon frequency and S the lattice relaxation for the s-$\bar{s}$ pair. Notice that the frequency dependence of σ^{d} is Gaussian apart from the pre-exponential factor ω^{-1}. Such dependence agrees in essential features with what obtained by Mele[7] for the optical absorption curve of trans - $(CH)_x$ using the equation of motion method for the discrete lattice. The asymmetric tail at the high frequency end appearing there is due to the long time behavior of phonons which we do not consider here. To compare with the experimental results one needs to include higher excitations to be discussed later.

We would like to point out the selection rule which forbids the direct process of photoproducing neutral soliton pairs following from the symmetry arguments.[3,4] In fact, the current operator (12) is odd under space inversion whereas the filled valence band state as well as the neutral s-$\bar{s}$ pair configuration have even parity, so the matrix element $\langle e_f | \hat{J} | e_i \rangle$ vanishes. We should note that this conclusion is valid up to arbitrary order of multiphonon processes. This selection rule was also independently obtained by Ball, Su and Schrieffer using somewhat different arguments.[6]

There are two channels of photogenerating soliton pairs. One is the direct process we have just considered; the other is an indi-

rect process of first photoexciting the e-h pair and its subsequent decay into soliton pair via a nonradiative process. The band-to-band optical absorption with the life-time effects being accounted for is given by[3,4]

$$\sigma^{i} = \frac{4\pi^2 e^2 v_F^2}{c\omega} \sum_k \frac{\Delta^2}{\epsilon_k^2} \frac{1}{\pi} \frac{\Gamma_k/2}{(2\epsilon_k - \hbar\omega)^2 + \Gamma_k^2/4}, \tag{13}$$

where $\epsilon_k^2 = \hbar^2 v_F^2 k^2 + \Delta^2$ and Γ_k the line-width due to the nonradiative decay. Since the neutral and charged solitons are equally probable in the nonradiative decay, we can estimate the branching ratio of neutral to charged solitons in the photogeneration as[3,4]

$$\sigma^{i}/\sigma^{d} \simeq 10^{-3}. \tag{14}$$

To conclude this section we would like to mention that the above described calculations have been redone by Gu and Wang[8] using the Slater determinant wave functions for electrons instead of the Hartree approximation we have adopted. Although their numbers are somewhat different from ours, all basic features of the theory including the selection rules have been confirmed by numerical calculations.

COMPARISON WITH EXPERIMENTS

(i) We have previously compared[3,4] the cross section of soliton photogeneration given by (11) with earlier data on photoconductivity[9] and the agreement turns out to be good without adjusting parameters apart from the arbitrariness of the photocurrent units. Since photoconductivity is a complicated process one might question about the legitimacy of such comparison. However, Blanchet et al.[10] have found recently that the photoinduced (PI) IR absorption at 1370 cm^{-1} which should be observed only for charged defect states, has the same excitation frofile as the photoconductivity. This confirms the theoretical results in a more convincing way.

(ii) Very recently, Weinberger et al.[11] have shown using the photothermal deflection spectroscopy that the optical absorption has the same frequency dependence as the photocurrent and also that both of them display the typical Urbach tail structure well below the optical gap. These authors intend to interpret their data in terms of disorder effects. We would like to point out that these data are consistent with our theoretical results. First of all, these two curves should coincile with each other because the absorption edge is determined by the direct process of soliton pair generation. Moreover, there is no sharp threshold in the frequency dependence of (11) due to the life-time effects.

(iii) The upper bound for the branching ratio of PI neutral to charged soliton pairs found by Flood et al. [12] from the PI ESR experiments (2×10^{-3}) is consistent with our estimate (14). Recently, Orenstein et al.[13] found that the PI ESR signal decreases exactly the same way as the PI IR absorption increases, which means that, probably, the neutral solitons existed before become charged. This observation along with the fact that the nature of the PI absorption at 1.38 eV and 0.45 eV has not yet been fully understood[13,14], shows that the question whether the photocurrent is carried by charged soliton photogenerated directly or indirectly, is still open. In this connection we would like to mention that the neutral solitons are allowed in the indirect process and also that the selection rule which forbids the direct process of neutral pair photoproduction is very sensitive to the parity symmetry. In fact, this rule is strictly obeyed only for a ring consisting of $4N+2$ chains but not for rings of $4N$ chains[8] because the valence band is not strictly parity even for the latter case. The bleaching of 1.38 PI absorption at relatively high temperatures (200K)[14] might be associated with the charging process of the neutral pairs. However, to fully understand the experimental results one needs to include the correlation effects.

ACKNOWLEDGEMENTS

One of us (L.Y.) would like to thank S. Etemad, S. Kivelson, A.J. Heeger, E.J. Mele, J. Orenstein, J.R. Schrieffer and Z. Vardeny for stimulating discussions.

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