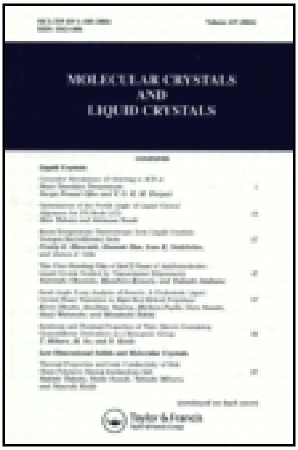

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CONFINED SOLITONS IN POLYACETYLENE

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Abstract The interchain coupling between neighboring chains in trans-polyacetylene gives rise to a confinement potential of $W\ell a^{-1}$ between a pair of solitons separated by distance ℓ, where W is estimated to be 30~3K. The effect of the confinement potential on neutral and charged solitons are studied theoretically. At low temperatures ($T\lesssim50$K) the neutral solitons are localized near the edge of polyacetylene crystal, which is consistent with a recent electron-nuclear triple spin resonance experiment. On the other hand the photogenerated charged soliton pair forms bound states due to the confinement potential. We predict that the radiative decay of highly excited bound pairs to lower excited pairs give rise to the photoluminescence at low temperatures.

INTRODUCTION

In spite of the theoretical elegance and the remarkable success of the soliton model of Su, Schrieffer and Heiger[1,2], the dynamical behavior of the soliton now appears to be more complicated than the simple theory predicts. For example, a NMR experiment at low temperatures indicated that most of neutral solitons in pristine trans-polyacetylene are trapped to some pinning centers.[3] We have shown recently that the interchain hopping of electrons give rise to the antiferromagnetic order between the dimerization patterns of the neighboring chains with the ordering energy of $-\ t_\perp{}^2/\pi t_0$ per carbon atom,[4] where $t_\perp$ is the transverse transfer integral while t_0 is the longitudinal transfer integral. Indeed such a transverse correlation has already been seen by a recent X-ray scattering experiment by Fincher et. al.[5] Furthermore the transverse correlation implies the soliton confinement;[4] a pair of solitons on the same polyacetylene chain experiences a confinement potential of $W|x|/a$ with $W=4t_{\perp}^2/\pi t_0$ and x is the distance between the pair. Here a factor of four arises as each polyacetylene chain is surrounded by four neighboring chains. Substituting values of $t_{\perp}$ and t_0 estimated from the band calculation,[6] we find W=30~3K. This value of W is consistent with that obtained by Baughman and Moss,[7] who modeled the interchain coupling in terms of Coulomb and dispersive force. We shall examine in some detail the effect of this confinement potential on soliton dynamics.[8]

NEUTRAL SOLITONS

In the presence of a confinement potential neutral solitons in crystalline polyacetylene cannot move around freely but they must be confined near the edge of the polyacetylene chain, when the mean distance of the soliton from the edge of the chain is larger than the soliton size (ξ~7a), the soliton can be treated as a particle in a confinement potential

$$H = \frac{1}{2M_s}P^2 + W\frac{x}{a} \tag{1}$$

where P and M_s ($\simeq 2m_e$) are the momentum and the mass of the soliton, and x is the distance measured from the edge of the $(CH)_x$ chain. Furthermore, since solitons cannot be located at the edge of the chain, we impose the boundary condition $\psi(0)=0$ for the soliton wave functions. The soliton distribution with the classical thermodynamics based on a similar Hamiltonian as Eq. (1) has been already carried out by Baughman and Moss.[7] However, we believe that such a classical approximation breaks down below $T\lesssim 150K$. In particular at lower temperatures the quantum nature of soliton becomes essential due to its small mass.

The eigen states of the above Hamiltonian are expressed in terms of Airy function.[9] The energies of the ground state and the first excited state are given by

$$E_0 = 2.3375\omega \qquad \text{and} \qquad E_1 = 4.088\omega \tag{2}$$

respectively with $\omega=(W^2/2M_s a^2)^{\frac{1}{3}}$. The spatial extension of the ground state wave function is given by

$$L = 2.34L_0 \qquad \text{with} \qquad L_0 = (a/2M_s W)^{\frac{1}{3}} \tag{3}$$

The predicted immobile soliton is not only consistent with the X-ray scattering result[5] but also with the bond lengths determined by nuclear spin nutation spectroscopy.[10] Immobility is also required to interpret the electron-nuclear triple resonance experiments.[11] The triple resonance experiment indicates[11] that the electron spin density at the carbon sites takes two distinct values $\rho_+=0.06$ and $\rho_-=-0.02$ of the full spin value. This spin density may be interpreted in terms of the neutral spin, if any appropriate Coulomb energy is incorporated[12] in the SSH model and if the soliton is localized with a potential well[13] of the length of 50a. If we assume that the above potential well is due to the confinement potential, we will obtain W=2.8K, which is quite consistent with the estimated one, though it may be somewhat smaller. If the present interpretation is correct the soliton becomes quite mobile above $T \simeq E_1-E_0=102$K, since above this temperature the soliton at the ground state can be easily excited into the higher levels by absorbing the thermal phonons. At even higher temperatures the confinement potential has little effect on soliton dynamics.

CHARGED SOLITONS

We shall limit ourselves to the photogenerated charged soliton pairs in pristine polyacetylene.[14,15] A pair of solitons are described by

$$H = \frac{1}{M_s}P^2 + W\frac{x}{a} + \frac{8}{\pi}\Delta e^{-2x/\xi} \qquad (4)$$

where P is the relative momentum of the pair and x(>0) is the distance between the pair. The last term in Eq. (4) is the short range repulsive potential between two solitons[16] as modified by Rice[17] who takes into account the proper symmetry of the electronic wave functions in the midgap states. The Hamiltonian (4) is similar to the one proposed by Rice[17] except that his long range Coulomb potential is replaced by the confinement potential. In any case we don't believe that the Coulomb potential has such a long range tail in polyacetylene. Due to the last term in Eq. (4), it is not easy to write down the energy spectrum of the bound pair. However, the energy difference between the gound state and the first excited state ΔE is given by

$$\Delta E = 2(W/a\xi M_s)^{\frac{1}{2}} \qquad (5)$$

If we identify this energy with the infrared mode at 500 cm^{-1} ($\simeq$725K) which appears in the pristine polyacetylene with photogenerated solitons[15] we will obtain W=18K. This W is about six times larger than the one deduced from the localization of the neutral soliton but is still within the theoretical estimate. Also the discrepancy of a factor of six may simply mean that one neutral soliton resides on polyacetylene chains with few neighboring chains. If this interpretation is correct we have a rather simple picture. At low temperatures most photogenerated pairs form bound states then they cascade down to the ground state by a series of radiative transitions to the ground state within 10^{-3} sec at least at low temperatures. This process gives rise to the photoluminescence with photon energies of the order of 100~200 cm^{-1}. The size of the ground state wave function is also estimated to be about 40a. The small saturation density $N_s = 5\times10^{17}\mathrm{cm}^{-3}$ observed for photogenerated soliton is still a mystery. We believe that the decay process $S^+S^- \to S^\circ S^\circ + h\nu$ proposed by Rice[17] is strictly forbidden. Furthermore, the decay time of the ground state should be much longer than $\tau_1 \simeq 10^{-3}$ sec, which is the radiative decay time of the first excited state. Therefore, it appears that the collision between these bound pairs will play an important role in conversing charged solitons into neutral solitons.

LIBERATION OF SOLITONS

There are experimental evidence indicating that the solitons at higher temperatures move more freely. For example, a recent experiment by Blanchet et. al.[18] shows that the photoconductivity drops abruptly around T=150K as the temperature is decreased. At the same time the infrared mode becomes active below this temperature. This phenomenon is most naturally interpreted as follows. For $T \lesssim 105K$ the confinement potential is strong; all the photogenerated pairs form bound states. Then the excited bound pairs cascade down to the ground state giving rise to photoluminescence. The excited level of the bound pairs with large quantum number n is approximately given by

$$E_n = (2n+1)^{\frac{2}{3}}\omega_0 \quad \text{with} \quad \omega_0 = (3\pi/8)^{\frac{3}{2}}(W^2/a^2M_s)^{\frac{1}{3}} \cong 222K \qquad (6)$$

Above T=150K, on the other hand, the confinement potential is weakened suddenly possibly due to thermal fluctuations, and solitons are liberated, which is seen by photoconductivity. A similar change is observed in the behavior of the neutral soliton in pristine trans-polyacetylene. Around T=150K the ESR signal associated with the solid state effect disappears completely.[19] We don't know the origin of this transition, although this transition appears to be a collective phenomenon.

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