

## Effect of Lattice Zero-Point Motion on Electronic Properties of the Peierls-Fröhlich State

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We study the consequences of the previously overlooked fact that in most quasi-one-dimensional materials with a Peierls-Fröhlich ground state the lattice zero-point motion is comparable to the lattice distortion. The density of states deviates significantly from that of a rigid lattice, containing a tail of strongly localized states below the gap. Moreover, thermal lattice motion causes the tail to increase significantly with temperature. This is consistent with the subgap optical absorption seen in these materials.

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The wide range of quasi-one-dimensional materials with a Peierls-Fröhlich ground state continues to expand as new materials are synthesized. It has recently been predicted that fullerene tubules have a Peierls ground state [1]. Widely studied materials include inorganics [ $MX$  chains [2], the platinum chain compound  $K_2Pt(CN)_4Br_{0.3}$ , and the charge-density-wave compounds  $NbSe_3$  and  $K_{0.3}MoO_3$ ] and organics [*trans*-polyacetylene  $(CH)_x$  [3] and the charge-transfer salt TTF-TCNQ]. Below a three-dimensional transition at  $T_P$  each chain has a periodic lattice distortion with twice the Fermi wave vector,  $2k_F$ , resulting in a gap in the electronic spectrum at the Fermi surface. Although the lattice distortion increases the elastic energy, the gap preferentially decreases the electronic energy, making the Peierls-Fröhlich state energetically favored over the metallic state.

It is commonly held that the electronic properties of the three-dimensionally ordered state are well described by mean-field theory [4] and that the phonons can be treated in the mean-field approximation, i.e., a static lattice is assumed. However, we point out two discrepancies with experiment. (i) For all temperatures the optical absorption  $\alpha(\omega)$  is predicted to be zero for frequencies less than the gap,  $2\Delta$ , and contain an inverse-square-root singularity at  $\omega = 2\Delta$ . The observed optical absorption is quite different [5,6]. The singularity is absent, and there is a significant tail below the maximum. Furthermore, as the temperature increases, broadening of the spectrum occurs on an energy scale *much* larger than  $kT$ . (ii) The energy gap deduced from the absorption edge is smaller than the activation energy of the dc conductivity [6]. We also point out that there is no accepted theory of the temperature dependence of the lattice distortion and the gap parameter. Most measurements are compared to empirical formulas or the mean-field (BCS) form with a renormalized transition temperature [7]. Attempts have been made to explain some of these facts in terms of solitons [8], disorder [6], and imperfect nesting [9].

In this Letter, we show that the above properties can be consistently modeled, without invoking additional interactions such as disorder, Coulomb interactions, or inter-

chain hopping, by including the effect of the zero-point and the thermal lattice motion on the electronic properties. In polyacetylene the zero-point motion of the lattice  $\delta u$  is comparable to the lattice distortion  $u_0$  [10]. It has been shown [10–12] that this causes only a small reduction in the dimerization below the mean-field prediction. Table I shows that  $\delta u$  and  $u_0$  are also comparable in a *wide* range of materials. Furthermore, at temperatures comparable to the transition temperature the thermal lattice motion can be several times larger than  $u_0$ . Given that the size of the electronic gap is proportional to  $u_0$  [13], lattice fluctuations should have an important effect on the electronic properties. In fact, if  $\delta u \sim u_0$  one might wonder why there should be a clearly defined gap in the spectrum at all.

We show that the zero-point and the thermal lattice motions are a source of disorder: They have an effect on the electronic properties similar to that of a random potential with Gaussian correlations. For this latter model

TABLE I. Comparison of the magnitude of the measured lattice distortion  $u_0$  with the magnitude of the lattice zero-point motion  $\delta u$  for various quasi-one-dimensional materials. The zero-point motion is calculated from  $\omega_{2k_F}$ , the phonon frequency measured by neutron or Raman scattering, and the mass  $M$  displaced in the lattice distortion by  $\delta u = (\hbar/2M\omega_{2k_F})^{1/2}$ .

	$u_0$ (Å)	$\delta u$ (Å)
$K_2Pt(CN)_4Br_{0.3}$	0.03 <sup>a</sup>	0.04
$K_{0.3}MoO_3$	0.05 <sup>b</sup>	0.05
Pt(en)I	0.09 <sup>c</sup>	0.04
$(CH)_x$	0.03 <sup>d</sup>	0.03
TTF-TCNQ	0.01–0.02 <sup>e</sup>	0.04
Fullerene tubule	$\sim 10^{-6}$ <sup>f</sup>	$\sim 0.01$ <sup>f</sup>

<sup>a</sup>C. F. Eagan, S. A. Werner, and R. B. Saillant, Phys. Rev. B **12**, 2036 (1975).

<sup>b</sup>Reference [7].

<sup>c</sup>H. Endres *et al.*, Acta Crystallogr. Sect. B **36**, 35 (1980).

<sup>d</sup>C. R. Fincher, Jr., *et al.*, Phys. Rev. Lett. **48**, 100 (1982).

<sup>e</sup>Y. Bouveret and S. Megtert, J. Phys. (Paris) **50**, 1649 (1989).

<sup>f</sup>Based on theory in Ref. [1].

exact expressions for the energy dependence of the electronic density of states and of the localization length can be obtained analytically. For parameter values corresponding to actual materials, the fluctuations cause significant modification of the density of states: They remove the inverse-square-root singularity and produce a large tail of strongly localized states below the energy gap (Fig. 1). The spectrum varies on a temperature scale set by the frequency  $\omega_{2k_F}$  of the  $2k_F$  phonon. The zero-temperature lattice distortion and gap parameter are only slightly reduced below the mean-field predictions, in agreement with previous studies of the Su-Schrieffer-Heeger (SSH) model for polyacetylene [10–12]. However, the disorder due to the thermal lattice motion can destroy the Peierls-Fröhlich state at a temperature well below the mean-field transition temperature.

The low-lying excitations of the Peierls-Fröhlich state are phonons with wave vector near  $\pm 2k_F$  and electrons with wave vector near  $\pm k_F$ . The *phonons* can be described by a lattice distortion field  $u(x)$  which is complex (real) for an incommensurate (commensurate) lattice distortion. The *electrons* can be described by a spinor  $\Psi_s(x)$ , the upper and lower components for electrons with spin  $s$  moving with the Fermi velocity  $v_F$  to the right and left, respectively. The electronic part of the Peierls-Fröhlich Hamiltonian with electron-phonon coupling  $g$  can be written in the form [14]

$$H = \int dx \Psi_s^\dagger \left[ -iv_F \sigma_3 \frac{\partial}{\partial x} + \frac{g}{2} [u(x)\sigma_+ + u^*(x)\sigma_-] \right] \Psi_s.$$

Important energy and length scales are defined by the

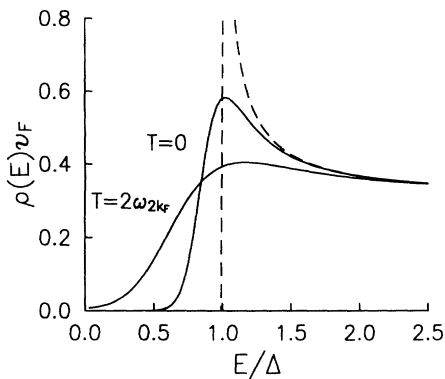


FIG. 1. Significant modification of the electronic density of states by lattice zero-point and thermal motion. The two solid curves correspond to a typical material at  $T=0$  and  $T=2\omega_{2k_F}$ . [The disorder parameter defined by Eq. (1) has values  $\eta=0.15$  and  $0.6$ , respectively.] The dashed curve ( $\eta=0$ ) corresponds to a rigid distorted lattice. The zero-point motion removes the inverse-square-root singularity in the density of states for the rigid lattice and produces a significant tail below the energy gap. The thermal lattice motion causes the broadening to increase with temperature. The results shown are for an incommensurate lattice distortion. Very similar results are obtained for the commensurate case of a half-filled band.

gap parameter  $\Delta \equiv gu_0$  and by the coherence length  $\xi_0 \equiv v_F/\Delta$ . The bandwidth  $W$  is defined by  $W = 2v_F/a \times \sin(k_F a)$ . The dimensionless electron-phonon coupling constant  $\lambda$  is defined [15] by  $\lambda \equiv 2g^2(\delta u)^2 a / \pi v_F \omega_{2k_F}$ . The zero-temperature mean-field gap parameter is given by  $\Delta_{MF} \equiv W[1 - \cos(k_F a)]e^{-1/\lambda}$ .

*Model of lattice fluctuations.*—Fluctuations in the lattice distortion field can be modeled by a static random potential [14] provided (i) the characteristic phonon energy is much smaller than the energy gap and (ii) the phonons are dispersionless. Both of these conditions are well satisfied for most materials *except* near the transition temperature. Condition (i) corresponds to the adiabatic or Born-Oppenheimer approximation. In particular, in a diagrammatic perturbation theory for the one-electron Green's function each phonon propagator  $D(q, t)$  can be replaced by the equal-time propagator  $D(q, t=0)$ . The perturbation theory is then identical to that for an electronic system where  $u(x)$  is a *random static* potential, with mean  $\langle u(x) \rangle = u_0$ . Furthermore, for dispersionless phonons [condition (ii)] the potential has Gaussian (white-noise) correlations:

$$\langle u(x)u^*(x') \rangle = u_0^2 + (\delta u)^2 \coth(\omega_{2k_F}/2T) a \delta(x - x').$$

Behavior consistent with this equation was observed in quantum Monte Carlo simulations [10,11] performed for the SSH model [3] of *trans*-polyacetylene. We find that the random configurations generated for a 16-site system are very similar to those found in Ref. [10].

The strength of the disorder is proportional to  $1/\tau$ , the electron-phonon scattering rate for states well above the gap. The dimensionless disorder parameter

$$\eta \equiv \frac{1}{\tau \Delta} = \lambda \frac{\pi \omega_{2k_F}}{2\Delta} \coth \left( \frac{\omega_{2k_F}}{2T} \right) \quad (1)$$

is central to this paper because it determines the properties of the subgap states. It can be shown that the fluctuations change the density of states on an energy scale  $\eta^{2/3}\Delta$ . We can also write  $\eta \sim (2\Delta/W)(\delta u/u_0)^2$  at  $T=0$ . Hence, when the bandwidth is much larger than the gap, as it usually is, the effect of the lattice fluctuations is reduced. This explains why a reasonably well-defined gap is still possible when  $\delta u \sim u_0$ . Based on Table I, measured energy gaps, and band-structure calculations of bandwidths we estimate that in most materials  $\eta \sim 0.05$  to  $0.2$  at zero temperature. For  $T > \omega_{2k_F}$ , the disorder parameter increases linearly with temperature ( $\eta \approx \pi \lambda T/\Delta$ ). If  $\omega_{2k_F} \sim 50$ – $100$  K, as it is in many materials,  $\eta$  can be of order unity at the transition temperature.

The model of static Gaussian disorder in the Peierls-Fröhlich state has been studied extensively. At the level of the self-consistent Born *approximation* the problem is mathematically equivalent to that of magnetic impurities in a superconductor. However, *exact* expressions for the density of states  $\rho(E)$  and the localization length  $L(E)$  can be obtained by several different techniques, for both

the case of an incommensurate lattice distortion [16] and the commensurate case of a half-filled band [17]. The two different cases give very similar results for weak disorder but differ qualitatively for strong disorder ( $\eta > 1$ ). The relevance of these exact solutions to understanding the effect of zero-point and thermal lattice motion in *perfect* crystals has not been pointed out previously.

The density of states has three important features if  $\eta > 0.1$  (compare Fig. 1). First, there is no large peak at the gap edges, in contrast to the inverse-square-root singularity which occurs in the absence of the zero-point motion. Second, the density of states is *nonzero for all energies* and has a substantial subgap tail. Third, when the temperature becomes of the order of the phonon frequency,  $\omega_{2k_F}$ , the disorder increases, and the smearing of the density of states increases considerably. These three features explain the discrepancy between static lattice calculations and the observed optical absorption [5,6] of many materials [8].

**Localization length.**—In our one-dimensional system all the electronic states are exponentially localized on a length scale  $L(E)$ . Figure 2 shows that the localization length is of the order of the coherence length  $\xi_0$  for the subgap states, and typically much larger [ $L(E) \approx 2\xi_0/\eta$ ] for states well above the gap. The strong energy dependence of the localization length near  $E = \Delta$  is somewhat similar to a mobility edge and will have an important effect on transport properties. Transport involving the subgap states will be suppressed. Consequently, we expect the gap deduced from the activation energy of the dc conductivity,  $\Delta_{dc}$ , should be larger than the gap deduced from the optical absorption threshold,  $2\Delta_{abs}$ . This is observed in many materials [6].

**Reduction of the gap parameter and lattice distortion at zero temperature.**—Figure 3 shows that the zero-point motion causes a small reduction in the order parameter

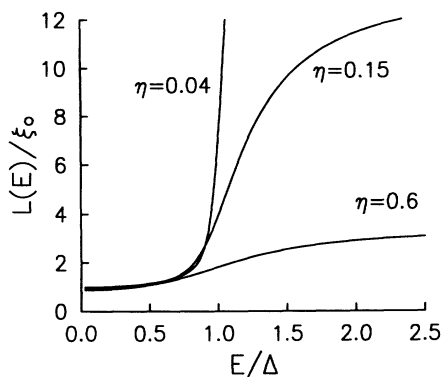


FIG. 2. Energy dependence of the localization length of the electronic states. Due to the one dimensionality all the electronic states are localized by the random potential resulting from the lattice fluctuations. For weak disorder the subgap states are much more strongly localized than the states well above the gap. The unit of length is the coherence length  $\xi_0$ . The results shown are for an incommensurate lattice distortion.

below the mean-field (i.e., static lattice) value. In general, we find that if  $\lambda\omega_{2k_F} < 0.3\Delta_{MF}$ , the reduction is small. For example, for a half-filled band with the SSH [3] parameter values for *trans*-polyacetylene we find  $u_0/u_{MF} = 0.9$ , a reduction consistent with values in the range 0.75 to 0.96 found in previous studies [10–12].

**Temperature dependence of the gap parameter and lattice distortion.**—We model the three-dimensionally ordered state by minimizing the free energy of a set of one-dimensional chains with infinite three-dimensional correlation length. Figure 3 shows that the reduction of the gap parameter below the mean-field (BCS) value increases with increasing electron-phonon coupling  $\lambda$ . The temperature dependence is not universal and deviates from the BCS form with a renormalized transition temperature. In particular, whereas the BCS curve is extremely flat for  $T < 0.3T_P$ , Fig. 3 shows a significant decrease in this range, as has been observed [7]. The reduction of the transition temperature  $T_P$  well below  $T_{MF}$  (Fig. 3, inset) is in contrast to the conventional view [4] that  $T_P$  is determined by the competition between quasi-one-dimensional thermodynamic fluctuations and interchain interactions. Our model neglects these fluctuations and so overestimates  $T_P$  [18]. Nevertheless, solely as a result of the thermal lattice motion, we can conclude that the ratio  $\Delta(0)/kT_P$  can be well above the mean-field value of 1.76.

Finally, we speculate that electron-electron interactions [13] will reduce the effect of the zero-point motion only when they provide the dominant contribution to the gap.

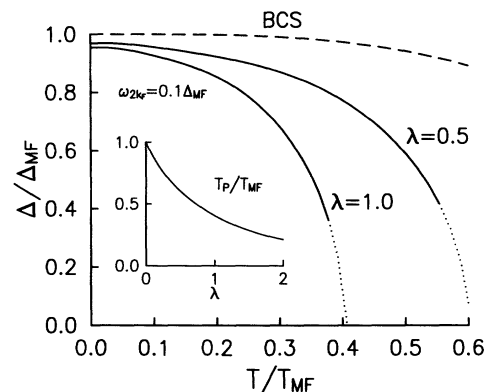


FIG. 3. Significant modification of the temperature dependence of the gap parameter and lattice distortion by thermal lattice motion.  $\Delta_{MF}$  and  $T_{MF}$  are the mean-field values of the zero-temperature gap and transition temperature, respectively. The enhanced reduction in the lattice distortion with increasing temperature is predominantly due to disorder from thermal lattice motion [cf. Eq. (1)] rather than thermal excitations across the gap (cf. mean-field case). The results shown are for an incommensurate lattice distortion. Our theory breaks down where the curves are dotted [18]; they can easily be extrapolated to the transition temperature  $T_P$ . Inset: Dependence of  $T_P$  on the dimensionless electron-phonon coupling constant  $\lambda$ .

In summary, in most Peierls-Fröhlich systems the zero-point motion is comparable to the lattice distortion. The resulting disorder causes the electronic properties to deviate significantly from those predicted for a rigid distorted lattice.

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- [18] In Fig. 3 we estimate the regime of invalidity of our theory (shown by the dotted lines) by (i) the region where  $\Delta$  is a few  $\omega_{2k_F}$ , so inelastic processes should be important, (ii) the fluctuation regime, calculated [4] taking into account interchain interactions, and (iii) the observed width of the transition in actual materials [for K<sub>0.3</sub>MoO<sub>3</sub>, see R. S. Kwok, G. Grüner, and S. E. Brown, *Phys. Rev. Lett.* **65**, 365 (1990)].