Midgap State in Nearly Commensurate Charge-Density Waves

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The mean-field Fröhlich Hamiltonian in one dimension is diagonalized numerically in a self-consistent manner for systems with a nearly $\frac{1}{2}$-, $\frac{1}{3}$-, or $\frac{1}{4}$-filled band. Near the Fermi energy, midgap states are present inside the main gap, and the location of the midgap states is not right in the center of the main gap. Recent absorption experiments on orthorhombic TaS_3 are analyzed in terms of the above results.

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The energy-gap structure of the one-particle excitation spectrum near the Fermi level is one of the most fundamental quantities in condensed-matter physics. This is particularly true for ordered states such as charge- or spin-density waves. It is generally believed that even incommensurate ordered states possess essentially the same single-energy-gap structure near the Fermi level as do commensurate states. We demonstrate here that such "common sense" is not true.

Much attention has been focused on incommensurate states in various research fields. In particular, the charge-density-wave (CDW) states in quasi-one-dimensional materials such as TaS_3, $NbSe_3$, and $K_{0.3}MoO_3$ have attracted much interest in connection with their non-Ohmic conduction mechanisms.[1] In spite of intensive theoretical and experimental efforts the energy-gap structure of the incommensurate charge-density wave (ICDW) state has not been fully elucidated yet, partly because of the difficulty of making a good sample. Recently a remarkable experiment on orthorhombic TaS_3 has been reported[2]: Itkis and Nad' observe sharp absorption lines (at energies of ~ 62 and 125 meV) inside a fundamental absorption edge (~ 184 meV) corresponding to the Peierls gap at $T=98$ K, a temperature which is below the Peierls transition temperature $T_0 \sim 215$ K and just above the commensurate-incommensurate lock-in transition.[3,4] They suggest the presence of a midgap state in the ICDW state.

The aims of the present paper are twofold: One is to show that the electronic density of states in the nearly commensurate CDW of one-dimensional systems indeed possesses the midgap state inside the Peierls gap quite generally, which is in marked contrast to the commensurate CDW state in which the simple BCS-like gap exists near the Fermi level. The other aim is to find the detailed nature of the midgap state, such as the position of the midgap band relative to the Peierls gap and its wave function. We also compute the spatial modulation of the electron density and the lattice distortion, and confirm that the midgap band is due to the soliton (discommensuration) lattice structure of such spatial modulations. By exact diagonalization of the mean-field Fröhlich Hamiltonian in one dimension, including all higher harmonics inevitably arising from a self-consistent condition,[5] we numerically study the ICDW systems with a nearly $\frac{1}{2}$-, $\frac{1}{3}$-, or $\frac{1}{4}$-filled band. In the nearly $\frac{1}{2}$-filled-band case an analytic solution is known[6] to yield a narrow band of midgap states located at the center of the Peierls gap, thus serving as a check for our calculation. In other cases[7,8] of electron filling the detailed gap structure remains to be studied, although their single-soliton structures as fractionally charged objects have been investigated extensively.[9] Previously Le Daëron and Aubry[10] have studied the ICDW problem by diagonalizing a model numerically in real space in a self-consistent manner. This is complementary to our momentum-space approach. Brazovskii, Dzyaloshinskii, and Kirchever[11] have studied the ICDW problem analytically, but their model is a specialized one.

We start with the standard Fröhlich Hamiltonian in one dimension and treat it in k space (we neglect electron spin):

$$H=\sum_k \epsilon_k c_k^\dagger c_k+\sum_k \omega_k b_k^\dagger b_k + \frac{1}{\sqrt{N}}\sum_k g_k(b_k+b_{-k}^\dagger)\rho_k ,$$

with $\rho_k=\sum_q c_q^\dagger c_{q+k}$, where $c_k^\dagger$ ($b_k^\dagger$) is the creation operator of an electron (phonon). Applying the mean-field approximation, we obtain $H=H_{\rm el}+H_{\rm ph}$:

$$H_{\rm el}=\sum_k \epsilon_k c_k^\dagger c_k+\sum_k \langle\hat{\Delta}_k\rangle\rho_{-k} ,$$

$$H_{\rm ph}=\sum_k \omega_k b_k^\dagger b_k+\sum_k \langle\rho_{-k}\rangle\hat{\Delta}_k ,$$

where $\langle\hat{\Delta}_k\rangle=g_k(\langle b_k\rangle+\langle b_{-k}^\dagger\rangle)/\sqrt{N}$ and $\langle\rho_k\rangle$ is the expectation value of ρ_k. The diagonalization of the phonon Hamiltonian $H_{\rm ph}$ yields a self-consistent equation: $\langle\hat{\Delta}_k\rangle=-(2|g_k|^2/N\omega_k)\langle\rho_{-k}\rangle$. The lattice displacement u_n at the nth site is given by $u_n=\sum_k[\langle\hat{\Delta}_k\rangle/g_k(2M\omega_k)^{1/2}]\exp(ikR_n)$, with M being the ion mass.

Let us consider the system with the electron number

ν per site ($0<\nu<1$). Lattice distortion due to the Peierls instability and described by the fundamental wave number $Q=2k_F$ (the Fermi wave number is $k_F=\pi\nu/a$ and a is the lattice constant) occurs spontaneously in the ground state. This distortion necessarily induces higher-harmonic distortions ($\langle\hat{\Delta}_{2Q}\rangle$, $\langle\hat{\Delta}_{3Q}\rangle$, etc.) through the self-consistent condition. Thus the effective mean-field electron Hamiltonian is reduced to $H_{el}=\sum_k \epsilon_k c_k^\dagger c_k + \sum_{l=1}^{\infty}\Delta_l\rho_{-lQ}$ with the self-consistent equation $\Delta_l=\langle\hat{\Delta}_{lQ}\rangle=-(2|g_{lQ}|^2/N\omega_{lQ})\langle\rho_{lQ}\rangle$.

When ν is rational, i.e., $\nu=m/n$ (m and n are prime to each other), the problem is reduced to diagonalization of a $n\times n$ matrix (n is called the commensurability index). Our calculations were performed by a simple iteration method: We first assume a set of the values Δ_l ($l=1,2,\ldots,n$). Then diagonalizing the Hamiltonian matrix to obtain the eigenvalues and eigenfunctions for certain points in the Brillouin zone, we obtain a new set of Δ_l and substitute these into the self-consistent equation to check the self-consistency. This step is repeated until the self-consistency is attained. We choose $\epsilon_k=-\cos k$ (the energy unit is twice the transfer integral of the tight-binding model and length is scaled by a) and introduce α ($\alpha^2=2|g_{lQ}|^2/\omega_{lQ}$). We assume that $|g_k|^2/\omega_k$ is independent of k for the convenience of computation although it is easy to relax this in our calculation. We mainly focus on the systems with a nearly quarter-filled band, $\nu=(1/n)\times(1+\delta)$, where $n=4$ and δ is small, although we have done calculations for the nearly half-filled ($n=2$) and one-third-filled ($n=3$) cases. The maximum n that we have treated is about 100. In this case our calculation is effectively of an infinite system with an effective unit cell of size about 100 sites. We have checked our calculations by comparing them with the previous cases[7] with lower commensurability indices.

Figure 1(a) shows the overall band structure in the reduced-zone scheme for the nearly $\frac{1}{4}$-filled case ($n=4$, $\delta=\frac{1}{95}$) where the band is split into four bands on the whole, opening up the Peierls gaps. Note that the self-consistent requirement of our problem keeps the number of visible gaps small[12] (compare with the case by Prange, Grempel, and Fishman[5]). In Fig. 1(b) we can clearly see the extra band situated inside the main gap. Such a midgap state always appears.

In Fig. 2 we depict traces of the gap edges near the Fermi level as a function of the deviation δ from quarter-filled. As the system approaches the commensurate state, or $|\delta|$ decreases, the midgap band becomes narrower and clearly split off from the main bands while the magnitude of the main gap remains constant, tending smoothly to the commensurate gap. The location of the midgap state depends on the sign of δ; when δ is positive (negative), it is situated near the occupied (unoccupied) band or valence (conduction) band and is occupied (unoccupied) by electrons.

This feature of the existence of the midgap state appears for other values of the electron-phonon coupling

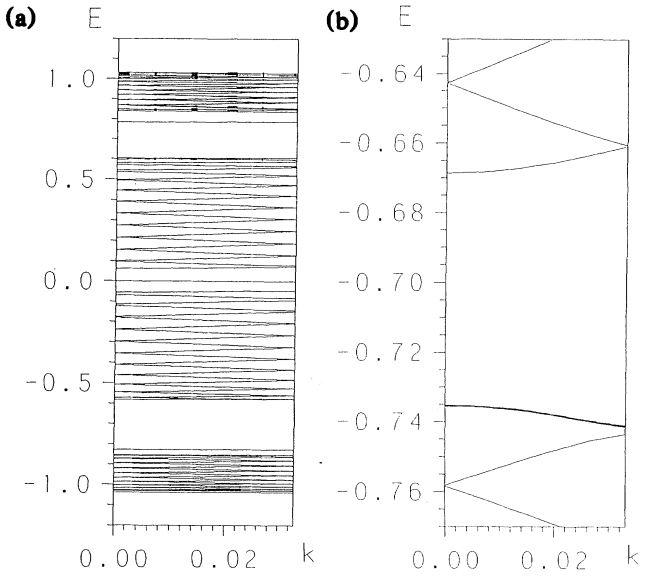

FIG. 1. (a) Dispersion relation (energy E vs wave number k) in the reduced-zone scheme for the nearly quarter-filled case; $\nu=\frac{24}{95}$, $\delta=+\frac{1}{95}$, and $\alpha=1.15$. The energy band below $E=-1/\sqrt{2}$ is occupied by electrons. (b) Enlarged figure of the dispersion relation near the Fermi level for $\nu=\frac{24}{95}$, $\delta=+\frac{1}{95}$, and $\alpha=1.0$. Note that the midgap state at $E\simeq-0.74$ denoted by the thick line is split off from the valence band and is occupied by electrons.

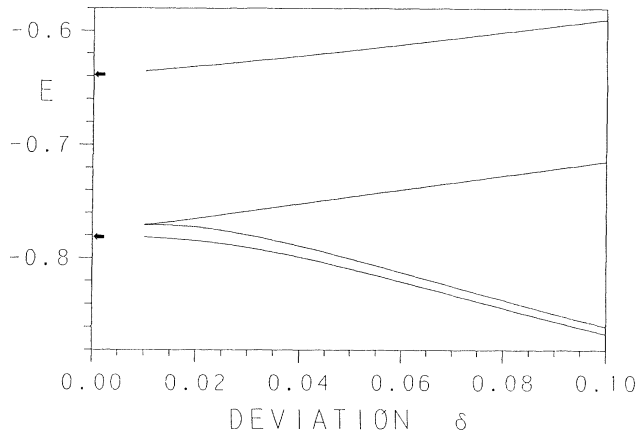

FIG. 2. Traces of the band edge near the Fermi level as a function of the deviation δ from quarter-filled ($\alpha=1.08$). The lowest (highest) curve indicates the top (bottom) of the valence (conduction) band. The midgap band is clearly seen between the valence and conduction bands. The arrows indicate the gap in the commensurate state.

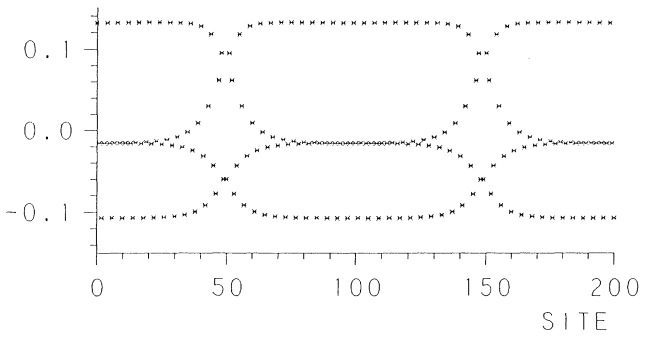

FIG. 3. Electron density variation as a function of the lattice site for the nearly quarter-filled case ($\nu = \frac{25}{99}$, $\delta = +\frac{1}{99}$, and $\alpha = 1.08$). The period of the variation is 99 sites. Rapid changes of the variation at around the 50th and 150th sites indicate solitons. In between, electron density modulation with periodicity of four sites is seen, corresponding to the commensurate CDW state.

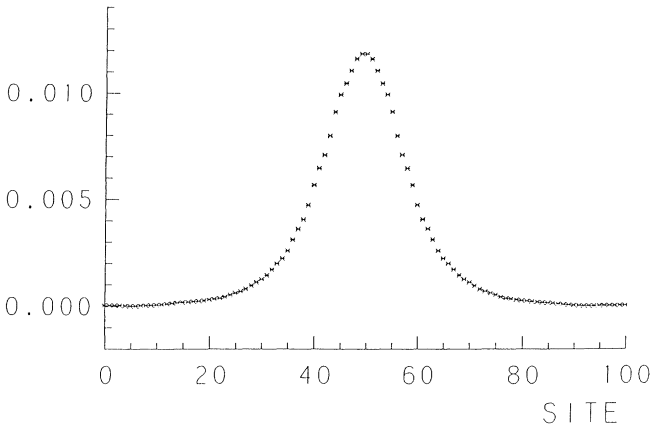

FIG. 4. Local electron density averaged over the nearest six lattice sites ($\nu = \frac{25}{99}$, $\delta = +\frac{1}{99}$, and $\alpha = 1.08$). The ordinate indicates the deviation from the mean electron density. The excess electrons are accumulated at the soliton sites, carrying a fractional charge. The total area under the curve is $\frac{1}{4}$, which corresponds to the excess charge. (Note that the electron spin is neglected.)

constant α and is also seen in the nearly $\frac{1}{2}$- and $\frac{1}{3}$-filled cases. We note, however, that upon decreasing α and also increasing n ($n = 2$, 3, and 4), we have to decrease δ to approach a "nearly commensurate" situation.

The electronic charge-density modulation is shown in Fig. 3. It is seen that the fourfold-degenerate ground states are connected through a soliton or domain wall which spreads over ~ 20 lattice sites. Between the solitons, which are placed regularly to form a soliton lattice, an almost commensurate state is realized. The excess (deficit) charge density for the $\delta > 0$ ($\delta < 0$) case is accumulated at the soliton sites as shown in Fig. 4, accommodating a fractional charge of $e/4$. The width of the excess (or deficit) charge density coincides approximately with that of the soliton as shown in Fig. 3.

The resulting eigenfunctions obtained after diagonalization of the Hamiltonian self-consistently reveal that while the eigenfunctions in the conduction or valence bands are extended over a whole system, the eigenfunction corresponding to the midgap state is *localized exponentially* at the soliton site as long as δ is small as is seen from Fig. 5. Therefore, the soliton is responsible for the appearance of the midgap state.

Let us briefly examine the experiments on a quasi-one-dimensional CDW system, orthorhombic TaS_3. The wave number[3,4] of the ICDW along the chain axis or c axis continuously decreases from $\sim 0.255c^*$ at the onset, $T_0 = 215$ K, to $0.250c^*$ at the lock-in transition, ~ 90 K. Therefore TaS_3 is an ideal system with a nearly $\frac{1}{4}$-filled band ($\delta > 0$). The fundamental absorption spectrum[2] at $T = 98$ K consists of three peaks at $h\nu_1 = 184$ meV, $h\nu_2 = 125$ meV, and $h\nu_3 = 62$ meV. Since the energy of the $h\nu_1$ peak roughly coincides with the activation energy estimated[2] from the conductivity, we can identify it as the absorption across the main Peierls gap. As is seen in Fig. 2 [the deviation δ from quarter-filled in TaS_3 at $T = 98$ K is estimated[3] as $\delta \simeq 0$ (0.01)], we expect two more absorptions in the ICDW, namely, the electronic transition from the occupied midgap state to the conduction band and the other process from the valence band to the midgap state. An applied electric field[2] or thermal effect makes the latter process possible. We notice that $h\nu_1 - h\nu_2 \cong 59$ meV is roughly equal to $h\nu_3 = 62$ meV, coinciding with our assignment of the peaks. In experimental data[2] taken under other experimental conditions the essential feature mentioned above is

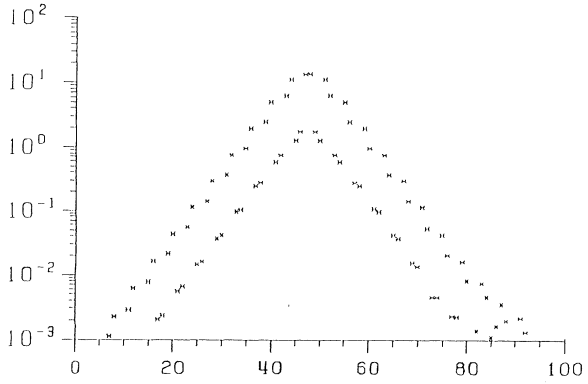

FIG. 5. Amplitude of the wave function corresponding to the midgap state as a function of the lattice site ($\nu = \frac{24}{95}$, $\delta = \frac{1}{95}$, and $\alpha = 1.15$). The wave function of the midgap state is localized exponentially at the soliton sites.

preserved. Therefore, we conclude that the ICDW in TaS_3 possesses a midgap state.

We mention additional evidence of the midgap state in other systems. The half-filled case is rather exceptional and different from the other fillings; the position of the midgap state is approximately at the center of the main gap, which implies that the absorption consists of two peaks ($h\nu_1$ and $h\nu_2 = h\nu_3$) instead of three. This fact has been observed[13] in the incommensurate spin-density-wave state of Cr which has been proved to be mathematically equivalent to the ICDW with a $\frac{1}{2}$-filled band.

The midgap state which we have demonstrated to exist in nearly commensurate CDW states is observable in other low-dimensional CDW materials such as $K_{0.3}MoO_3$ or $(TaSe_4)_2I$. If we focus on the temperature near a lock-in transition, we *always* get a "nearly commensurate" situation in which the bandwidth of the midgap band becomes narrow enough to be easily accessible experimentally.

In summary, we have confirmed the general existence of the midgap band due to the soliton lattice in nearly commensurate Peierls systems by fully self-consistent calculations.

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