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Quantum fluctuation and CDW in MX chain complex

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Abstract

The effect of quantum fluctuation on the CDW state of the MX chain complex is studied with the Green Function method, which can deal with any phonon frequency and infinite chain. It is shown that the effect is dependent on the electron-phonon coupling. For strong coupling, the CDW amplitude is only slightly reduced; but for weak coupling, the reduction becomes so serious that the CDW is almost destroyed.

The quantum fluctuation has important effect on the CDW state of the halogen-bridged mixed-valence transition metal (MX) complex [1]. The luminescence and resonance Raman spectrum in Pt-Cl complex demonstrate that, in contrast to the conjugated polymer, its tail of localized states below the energy gap originates from the zero-point lattice motion rather than the static structural disorder [2]. The effect of the quantum fluctuation on the CDW amplitude of the MX chain complex has been calculated by using the quantum variational principle in the antiadiabatic limit for a short chain [3]. This paper further studies the dependence of the effect on the electron-phonon coupling by using the Green Function technique, which is able to deal with infinite chain and any phonon frequency.

The CDW in the MX chain complex can be described by the Holstein model [4]

$$H = -t\sum_{l\sigma}(c^\dagger_{l\sigma}c_{l+1\sigma}+h.c.)+\frac{1}{2}\sum_l(\dot{Q}_l^2+\omega_0^2Q_l^2) + g\sum_{l\sigma}(Q_l-Q_{l-1})n_{l\sigma} \quad (1)$$

where $c^\dagger_{l\sigma}$ ($c_{l\sigma}$) is the creation (annihilation) operator of an electron at site l with spin σ, $n_{l\sigma}=c^\dagger_{l\sigma}c_{l\sigma}$, t the hopping constant, ω_0 and Q_l the phonon frequency and displacement coordinate of the halogen ion X, g the electron-phonon coupling.

In the case of half-filled band, the condensation of the breathing mode of X ion's vibrations produces a dimerization Q_0 in the X sublattice, and the CDW is established by the charge transfer between the even and odd M ions [5]. Then

$$Q_l=(-1)^lQ_0+\phi_l\ , \quad (2)$$

ϕ_l is the lattice fluctuation with quantum nature, which is neglected in the adiabatic approximation. Q_0 measures the amplitude of CDW and is determined by the condition

$$<\phi_l>=0\ . \quad (3)$$

After dimerization, the original half-filled band is split into valence band and conduction band, and the Hamiltonian (1) becomes

$$H=2\sum_{k\sigma}(a^\dagger_{1k\sigma}\ a^\dagger_{2k\sigma}) \begin{pmatrix} t_k(c_k^2-s_k^2)+2gQ_0s_kc_k & 2t_ks_kc_k-gQ_0(c_k^2-s_k^2) \\ 2t_ks_kc_k-gQ_0(c_k^2-s_k^2) & -t_k(c_k^2-s_k^2)-2gQ_0s_kc_k \end{pmatrix} \begin{pmatrix} a_{1k\sigma} \\ a_{2k\sigma}\end{pmatrix} + \frac{g}{\sqrt{N}}\sum_{kk'\sigma}(a^\dagger_{1k\sigma}\ a^\dagger_{2k\sigma})S_1(k,k')\begin{pmatrix} a_{1k'\sigma} \\ a_{2k'\sigma}\end{pmatrix} (1-e^{i(k'-k)})\phi(k-k') + \frac{g}{\sqrt{N}}\sum_{kk'\sigma}(a^\dagger_{1k\sigma}\ a^\dagger_{2k\sigma})S_2(k,k') \begin{pmatrix} a_{1k'} \\ a_{2k'}\end{pmatrix}(1+e^{i(k'-k)})\phi(k-k'-\pi)\ , \quad (4)$$

where $\phi(k)=\frac{1}{\sqrt{N}}\sum_l e^{ikl}\phi_l$, $t_k=t\sin k$, $s_k=\sin\theta_k$ and $c_k=\cos\theta_k$ are the transformation coefficients from $c_{k\sigma}$ to $a_{k\sigma}$, and

$$S_1(k,k')=\begin{pmatrix} c_kc_{k'}+s_ks_{k'} & c_ks_{k'}-s_kc_{k'} \\ s_kc_{k'}-c_ks_{k'} & s_ks_{k'}+c_kc_{k'}\end{pmatrix}\ , \quad (5)$$

$$S_2(k,k')=\begin{pmatrix} c_ks_{k'}+s_kc_{k'} & s_ks_{k'}-c_kc_{k'} \\ s_ks_{k'}-c_kc_{k'} & -s_kc_{k'}-c_ks_{k'}\end{pmatrix}\ . \quad (6)$$

The electron self-energy Σ induced by the electron-phonon interaction can be obtained by the Green Function technique [6], in on-shell scheme

$$\Sigma(k) = (\alpha_k\epsilon_k+\beta_k\sin\varphi_k+\gamma_k\cos\varphi_k)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} - (\beta_k\cos\varphi_k-\gamma_k\sin\varphi_k)\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\ , \quad (7)$$

where

$$\alpha_k=\frac{g^2}{\pi\omega_0}\int\frac{dk'}{\epsilon_k^2-(\epsilon_{k'}+\omega_0)^2}\ , \quad (8)$$

$$\beta_k = \frac{g^2}{\pi\omega_0}\int dk' \frac{(\epsilon_{k'}+\omega_0)\sin\varphi_{k'}}{\epsilon_k^2-(\epsilon_{k'}+\omega_0)^2} , \quad (1)$$

$$\gamma_k = -\frac{g^2}{\pi\omega_0}\int dk' \frac{(\epsilon_{k'}+\omega_0)\cos\varphi_{k'}\cos(k'-k)}{\epsilon_k^2-(\epsilon_{k'}+\omega_0)^2} . \quad (2)$$

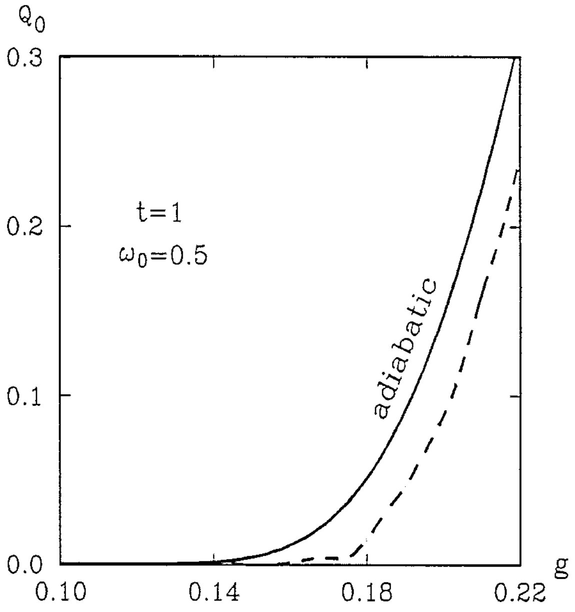

Figure 1 The dependence of CDW amplitude Q_0 on the electron–phonon coupling g .

Making the diagonalization of the renormalized electron energy, the electronic spectrum ε_k and the transformation coefficient θ_k can be determined by the combined equations

$$\epsilon_k = \alpha_k\epsilon_k + (2gQ_0+\beta_k)\sin\varphi_k + (2t\sin k+\gamma_k)\cos\varphi_k , \quad (3)$$

$$(2gQ_0+\beta_k)\cos\varphi_k + (-2t\sin k-\gamma_k)\sin\varphi_k = 0 , \quad (4)$$

Then the Eq. (3) gives

$$\omega_0^2 Q_0 = -\frac{2g}{N}\sum_{l\sigma} < (-1)^l n_{l\sigma} >= 4g\int dk \sin\varphi_k . \quad (5)$$

The CDW amplitude Q_0 can be calculated by self-consistently solving the Eqs. (8)–(13). The dependence of Q_0 on the electron-phonon coupling g for $t = 1$ and $\omega_0 = 0.5$ is shown in Fig. 1, where the solid curve is the adiabatic result and the dashed one is the result with the quantum fluctuation. It is seen that the relative reduction of CDW very much depends on the coupling. For strong coupling, the CDW is only slightly reduced; but for weak coupling, the reduction is so serious that the CDW is almost destroyed. The physics reason for this behavior is understandable by noticing the following facts. In contrast to the SSH model of the conjugated polymers, the renormalized frequencies of the optical phonons of the CDW model (1) don't change too much from the bare one ω_0, especially in the limit of coupling $g \to 0$, the frequency of the optical phonon approaches ω_0 rather zero. It is well known, for the SSH model, the optical branch starts from the zero in the limit $g \to 0$ [7]. It means that, in the case of CDW, the zero-point lattice motion will not decrease even if the coupling g goes to zero. On the other hand, the dimerization becomes smaller if g decreases. Then it is obvious that, when the coupling g is getting weaker, the CDW will be more suppressed by the quantum fluctuation.

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