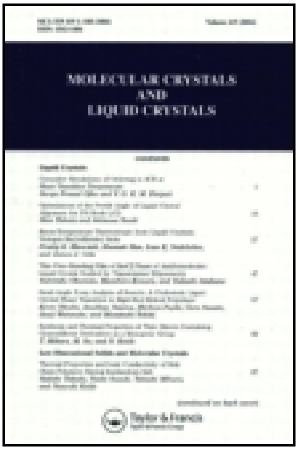

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ELECTRON-PHONON AND EXCHANGE INTERACTIONS IN THE ONE-DIMENSIONAL $\pi - d$ ELECTRON SYSTEMS

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Abstract A new model Hamiltonian is proposed for the suggestion of new one-dimensional (1D) π-d electron systems. The effects of the π-electron phonon interaction λ and the antiferromagnetic exchange interaction between nearest-neighbor π and d electrons, j_K, on the electronic states of these systems have been investigated. The case of a half-filled band has been studied by using a mean-field approximation and periodic boundary conditions. As the value of λ (j_K) is increased, the spin density and the energy gap of the π electron decrease (increase), while the dimerization increases (are almost constant). It turns out that the electron-phonon and exchange interactions are very important for the control of the electronic properties of the 1D π-d electron systems.

INTRODUCTION

The discovery of the giant DC conductivity of TTF-TCNQ[1] derived chemists and physicists to study the quasi-one-dimensional (1D) organic compounds. The 1D and 2D organic superconductors, e.g., $(TMTSF)_2PF_6$[2] and $(BEDT\text{-}TTF)_2ReO_4$[3], and polyacetylene[4] of the 1D π-electron system were synthesized. The charge-density wave, the spin-density wave and solitons of these conductors have been studied. Since the discoveries of fullerenes[5] and cuprates[6] of π and p-d electron systems, the strongly correlated electron systems have been investigated for the elucidation of the mechanism of high-temperature superconductivity. The spin gap and superconductivity of Sr_2CuO_4 with double chains have been discussed.[7] The p-d electron systems are similar to π-d electron systems. The study of the strongly correlated electron systems coupled to phonon and spin is now necessary. There are many organic compounds considered as π-d electron systems.[8] Previously, I have investigated the electronic states of the 1D π-d electron systems for the study of the electrical conductivity of the phthalocyanine salts.[9–11] Here, I propose a new model Hamiltonian of the 1D π-d electron systems for the suggestion of new 1D organic compounds. The effects of the electron-phonon and antiferromagnetic exchange interactions on the electronic states of these systems are investigated within a mean-field theory.

MODEL HAMILTONIAN

The 1D system composed of π and d electrons is considered. The π electrons with spin move itinerantly along the chain and interact mutually on the same site and with the lattice and the localized d-electron spins. The model Hamiltonian is written as

$$H = -\sum_{l,\sigma}[t + \alpha(u_l - u_{l+1})](c^\dagger_{l+1,\sigma}c_{l\sigma} + h.c.) + \frac{k}{2}\sum_l (u_l - u_{l+1})^2 + U\sum_l n_{l\alpha}n_{l\beta}$$

$$+J_{\mathrm{K}}\sum_l \mathbf{S}_l \cdot \mathbf{s}_l + J_{\mathrm{H}}\sum_l \mathbf{S}_l \cdot \mathbf{S}_{l+1}, \qquad (1)$$

where t is the transfer energy of a π-electron between nearest-neighbor sites, α describes the strength of the π-electron lattice coupling, u_l is the displacement of site l from the equilibrium position, k of the elastic energy of the second term is the spring constant. The operators $c^\dagger_{l\sigma}$ and $c_{l\sigma}$ create and annihilate a π-electron with spin σ (α and β are up and down spins, respectively) at site l, respectively. $n_{l\sigma}{=}c^\dagger_{l\sigma}c_{l\sigma}$ denotes the number operator of the π electron with spin σ at site l. $\mathbf{S}_l$ and $\mathbf{s}_l$ are the spin-1/2 operators of the localized d and itinerant π electrons at site l, respectively. U denotes the on-site Coulomb repulsion of the π electron. J_{K} is the antiferromagnetic exchange interaction between nearest-neighbor π and d electrons. J_{H} is the antiferromagnetic exchange interaction between nearest-neighbor d electrons.

The Hamiltonian and the parameters are normalized by t and are written as $h{=}H/t$, $u{=}U/t$, $j_{\mathrm{K}}{=}J_{\mathrm{K}}/t$, $j_{\mathrm{H}}{=}J_{\mathrm{H}}/t$, and the electron-phonon coupling is defined by

$$\lambda = 2\alpha^2/(\pi k t). \qquad (2)$$

I have computed self-consistently the total energy per site, the charge density, the spin density

$$\rho_s = |< n_{l\alpha} > - < n_{l\beta} >|, \qquad (3)$$

and the dimerization parameter

$$y = |\ y_l\ | = |\ \alpha(-1)^l(u_l - u_{l+1})/t\ | \qquad (4)$$

from the reduced Hamiltonian by using a mean-field approximation and periodic boundary conditions. I have evaluated the case of one d electron, $n_d = 1$, and one π electron, $n_\pi = 1$ per site, i.e., a half-filled band.

RESULTS

Figure 1 shows the energy gap of the π electron, E_g, as a function of the electron-phonon coupling λ for $j_{\mathrm{H}} = 0.1$ and $u = 2$ when $j_{\mathrm{K}} = 0.2$, 0.4 and 1. As the value of the electron-phonon coupling is increased, the value of the energy gap decreases gradually. The value of the energy gap is larger, when the antiferromagnetic exchange interaction between d and π electrons is stronger. Figure 2 depicts the spin density

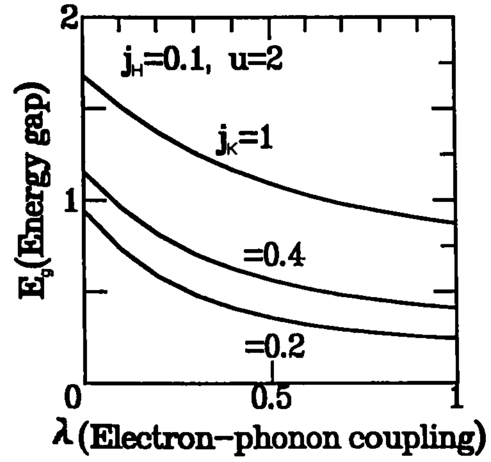

FIGURE 1 Energy gap E_g vs. electron-phonon coupling λ

of the π electron, ρ_s, as a function of the electron-phonon coupling λ for $j_H = 0.1$ and $u = 2$ when $j_K = 0.2$, 0.4 and 1. As the value of the electron-phonon coupling is increased, the value of the spin density decreases very slowly. The value of the spin density is larger, when the antiferromagnetic exchange interaction between d and π

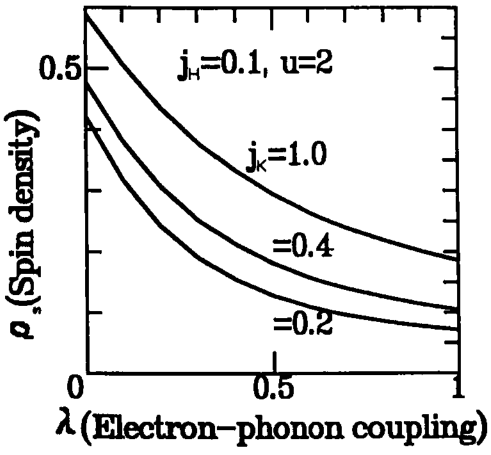

FIGURE 2 Spin density ρ_s vs. electron-phonon coupling λ

electrons is stronger. The up and down localized spins of the *d* electron align alternately and interact antiferromagnetically with the π-electron spins. The dimerization parameter y is shown as a function of the electron-phonon coupling λ for $j_H = 0.1$ and $u = 2$ when $j_K = 0.2$ and 1 in Fig. 3. As the value of the electron-phonon coupling is increased, the value of the dimerization parameter increases linearly and rapidly . The value of the dimerization parameter for $j_K = 0.2$ is a very little larger than that for $j_K = 1$. Figure 4 shows the energy gap of the π electron, E_g, as a

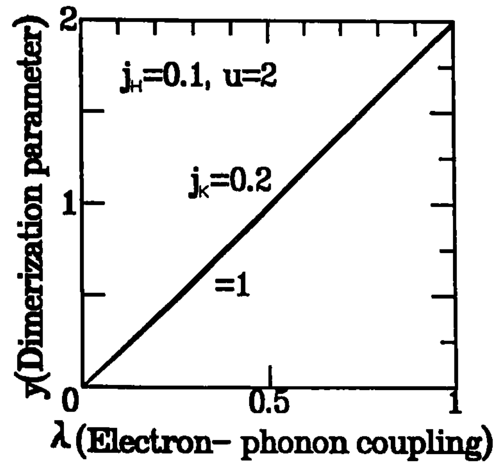

FIGURE 3 Dimerization paramerter y vs. electron-phonon coupling λ

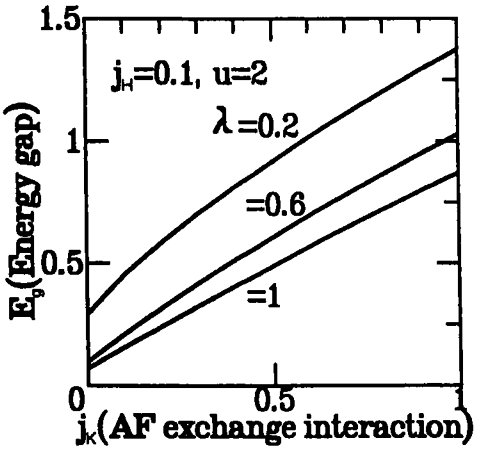

FIGURE 4 Energy gap E_g vs. antiferromagnetic exchange interaction j_K

function of the antiferromagnetic (AF) exchange interaction between d and π electrons, j_K, for $j_H = 0.1$ and $u = 2$ when $\lambda = 0.2$, 0.6 and 1. As the value of j_K is increased, the value of the energy gap increases gradually. The behavior of E_g vs. j_K is qualitatively different from the behavior of E_g vs. λ. The value of the energy gap is smaller, when the value of the electron-phonon coupling is larger. Figure 5 illustrates the spin density of the π electron, ρ_s, as a function of the antiferromagnetic

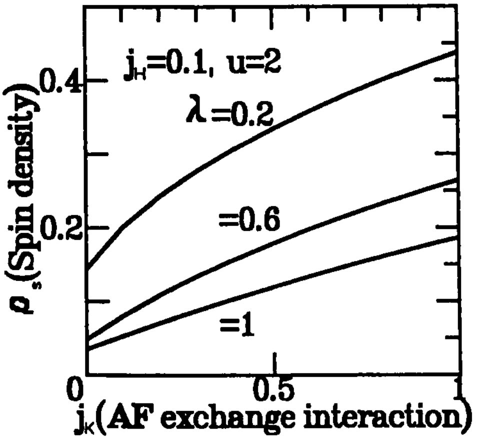

FIGURE 5 Spin density ρ_s vs. antiferromagnetic exchange interaction j_K

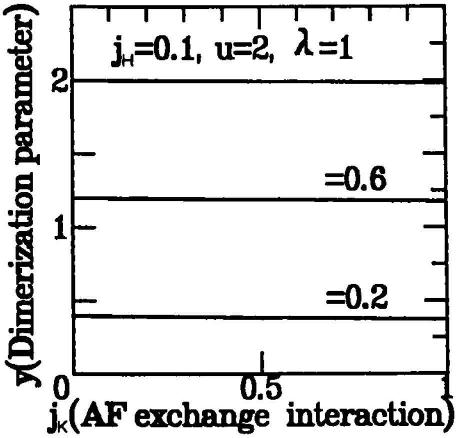

FIGURE 6 Dimerization paramerter y vs. antiferromagnetic exchange interaction j_K

exchange interaction between d and π electrons, j_K, for $j_H = 0.1$ and $u = 2$ when $\lambda = 0.2$, 0.6 and 1. As the value of j_K is increased, the value of the spin density increases gradually. The behavior of ρ_s vs. j_K is qualitatively different from the behavior of ρ_s vs. λ. The value of the spin density is smaller, when the value of the electron-phonon coupling is larger. The up and down localized spins of the d electron align alternately and interact antiferromagnetically with the π-electron spins. The dimerization parameter y is shown as a function of the antiferromagnetic exchange interaction between d and π electrons, j_K, for $j_H = 0.1$ and $u = 2$ when $\lambda = 0.2$, 0.6 and 1 in Fig. 6. As the value of j_K is increased, the value of the dimerization parameter seems to be almost constant but decreases very slightly. The value of the dimerization parameter is larger, when the value of the electron-phonon coupling is larger. The behavior of y vs. j_K is much different from the behavior of y vs. λ.

I have presented a new model Hamiltonian for the suggestion of new 1D π-d organic compounds. As the value of the electron-phonon coupling is increased, the energy gap of the π electron decreases. On the other hand , as the value the antiferrromagnetic exchange interaction between nearest-neighbor π- and d-electron spins is increased, the energy gap increaes. The distribution of the charge and spin densities of the π electron under the influence of phonons and localized spins along the chain decides the electronic states of 1D π-d electron systems. It turns out that the electron-phonon and antiferrromagnetic exchange interactions between π- and d-electron spins give important effects to the electric properties of 1D π-d electron systems with these interactions. In future, the efffects of the on-site Coulomb repulsion on the electronic states of these systems will be studied.

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