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ELECTRONIC STATES IN STRONGLY CORRELATED ORGANIC CONDUCTOR DCNQI-Cu

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Abstract The periodic Anderson model with both the electron-phonon interaction and the interchain hopping has been examined in terms of the slave-boson method to understand the metal-insulator transition in DCNQI(dicyanoquinonediimine)-Cu salts. Strongly correlated states are studied by calculating the phase diagram and the density of states consisting of the incoherent (localized) component and the coherent (band) component.

INTRODUCTION

Organic conductors DCNQI(dicyanoquinonediimine)-Cu undergo the metal-insulator (M-I) transition where the structure shows an array of one-dimensional (1D) chains consisting of π-electron in DCNQI-molecule and localized d-electron in Cu-atom [1, 2]. The hybridization between the π-electron and the d-electron is important due to $Cu^{+4/3}$ on an average. In the insulating state, a three-fold lattice distortion and a local spin appear simultaneously and then lead to the three-fold periodicity of the valence expressed as Cu^{+}, Cu^{+} and Cu^{++} along the chain [3]. The local spin of Cu^{++} indicates the M-I transition in the presence of the strong correlation.

The M-I transition of DCNQI-Cu salt has been studied theoretically by use of the periodic Anderson model with the electron-phonon (e-p) interaction [4]. In terms of the hole picture [5], the slave-boson method was applied to take account of the strong correlation [6]. Within the slave-boson mean-field theory, the phase diagram on the plain of the e-p coupling constant and temperature has been calculated for both one-dimensional (1D) model [7] and three-dimensional (3D) model [8].

In terms of the 1/N-expansion which treats the local constraint strictly [9, 10], we study the M-I transition and the electronic density of states [11] for both the π-electron and the strongly correlated d-electron.

FORMULATION

By assuming the three-fold periodicity along the 1D-axis, we consider the 3D

model given by (j=1,2, and 3) [8]

$$
\begin{aligned}
H_\lambda &= \frac{N_1 N_\perp W^2}{g} + \sum_{\vec{k}} \sum_{\sigma} \Big[\Psi^+_{\vec{k}\sigma} (H_0(k) - \mu) \Psi_{\vec{k}\sigma} + \overline{\Psi}^+_{\vec{k}\sigma} (H_0(k) - \mu) \overline{\Psi}_{\vec{k}\sigma} \\
&+ \sum_{mj} \sum_{\vec{s}} \Big[\sqrt{\frac{3}{N_1 N_\perp}} V(\vec{p}) \left(C^+_{\vec{k}j\sigma} f_{mj\sigma}(\vec{s}) b^+_{mj}(\vec{s}) \mathrm{e}^{-ik\cdot(3m)} \mathrm{e}^{-i\vec{p}\cdot\vec{s}} + h.c. \right) \Big] \Big] \\
&+ \sum_{mj} \sum_{\vec{s}} \Big[(\varepsilon_j - \mu + \lambda_{mj}(\vec{s})) \sum_{\sigma} f^+_{mj\sigma}(\vec{s}) f_{mj\sigma}(\vec{s}) + \lambda_{mj}(\vec{s}) b^+_{mj}(\vec{s}) b_{mj}(\vec{s}) \Big] \ , \quad (1)
\end{aligned}
$$

where $(H_0(k))_{jj'} = \delta_{jj'} 2W \cos Qj + \delta_{j,j'\pm 1} + \delta_{j3}\delta_{j'1} \mathrm{e}^{i3k} + \delta_{j1}\delta_{j'3} \mathrm{e}^{-i3k}$, $\varepsilon_j = \varepsilon_d - 2W_d \cos Qr_j$, $Q = 2\pi/3$ and k is the 1D wave number. $\Psi^+_{\vec{k}\sigma} = (C^+_{\vec{k}1\sigma}, C^+_{\vec{k}2\sigma}, C^+_{\vec{k}3\sigma})$ and $\overline{\Psi}^+_{\vec{k}\sigma} = (\overline{C}^+_{\vec{k}1\sigma}, \overline{C}^+_{\vec{k}2\sigma}, \overline{C}^+_{\vec{k}3\sigma})$ where $\Psi^+_{\vec{k}\sigma}$ and $\overline{\Psi}^+_{\vec{k}\sigma}$ are bonding and nonbonding operators of π-electron. $\vec{k} = (k, \vec{p})$, $\vec{p} = (p_x, p_y)$ and $V(\vec{p}) = 2V \left[(\cos(p_x/2))^2 + (\cos(p_y/2))^2 \right]^{1/2}$. The index of the 1D lattice (the square lattice) with the total number N_1 ($N_\perp$) is given by $l = 3m + 1$ ($\vec{s}$). The lattice constant and the hopping energy are taken as unity. The V-term is an energy of the hybridization between π electron and d electron with a localized energy level ε_d. In the insulating state, there appear molecular fields W and W_d for π and d electrons respectively due to the Peierls transition where g is the coupling constant of the e-p interaction. The elastic energy is given by $N_1 N_\perp W^2/g$. These fields are determined so as to minimize the total energy with the fixed W_d/W. The strongly correlated state of d electron is examined by use of the slave-boson method with the operators of the slave-boson, $b_l(\vec{s})$, and the pseudo-fermion, $f_{l\sigma}(\vec{s})$, where $d^+_{l\sigma}(\vec{s}) = f^+_{l\sigma}(\vec{s}) b_l(\vec{s})$ [9]. The local constraint is treated by introducing the Lagrange's multiplier $\lambda_{mj}(\vec{s})$. which is taken infinity in the end.

Green functions of the bonding π electron, slave-boson and pseudo fermion are expressed respectively as

$$
G_{jj'\sigma}(\vec{k}, i\omega_n) = \left(\left[i\omega_n + \mu - H_0(k) - \frac{a_j V(\vec{p})^2}{i\omega_n + \mu - E_j} \right]^{-1} \right)_{jj'} \ , \quad (2)
$$

$$
B_j(i\nu_n - \lambda_{mj}(\vec{s})) = \left[i\nu_n - \lambda_{mj}(\vec{s}) - \int_{-\infty}^{\mu} \mathrm{d}z \frac{8V^2 \tilde{\rho}^c_j(z)}{z + i\nu_n - \lambda_{mj}(\vec{s}) - \varepsilon_j} \right]^{-1} \ , \quad (3)
$$

$$
F^0_{j\sigma}(i\omega_n - \lambda_{mj}(\vec{s})) = \left[i\omega_n + \mu - \lambda_{mj}(\vec{s}) - \varepsilon_j \right]^{-1} \ , \quad (4)
$$

where j=1,2 and 3, and $\beta^{-1}(= T)$ is the temperature. In Equations (2)-(4), $\omega_n = \pi T(2n + 1)$ and $\nu_n = 2n\pi T$ with the integer n. After performing the analytical continuation, $i\omega_n \to \omega + i\delta, (\delta > 0)$, one obtains

$$
\tilde{\rho}^c_j(\omega) = -\frac{3}{\pi N_1 N_\perp} \sum_{\vec{k}} \left(\frac{V(\vec{p})}{2V} \right)^2 \mathrm{Im} G_{jj\sigma}(\vec{k}, \omega - \mu + i\delta) \ . \quad (5)
$$

The quantity $\tilde{\rho}_j^c(\omega)$ denotes the effective density of states of π electron per spin at the j-th site and is different from the actual density of state, $\rho_j^c(\omega)$, which is defined by putting $V(\vec{p})/2V \to 1$ in Equation (5). Equation (3) is calculated as[10]

$$\frac{-1}{\pi}\mathrm{Im}B_j(\nu + i\delta) = a_j\delta(\nu - \varepsilon_j + E_j) + C_j(\nu) \ , \tag{6}$$

where the first term comes from the pole of $B_j(\nu)$ at $\nu = \varepsilon_j - E_j$ and quantities a_j and E_j are determined self-consistently. The density of states $\rho_j^d(\omega)$ in the case of $\omega < \mu$, which belongs to the d electron in the ground state, is obtained as [11]

$$\rho_j^d(\omega) = C_j(-\omega + \varepsilon_j) \ , \tag{7}$$

for $a_j = 0$ and

$$\begin{aligned} \rho_j^d(\omega) &= -8V^2 a_j \int_{-\infty}^{\mu} \mathrm{d}z' \left(-\frac{1}{\pi}\right) (\mathrm{Im}B_j(-\omega + z' - i\delta + \varepsilon_j - E_j)) \frac{\tilde{\rho}_j^c(z')}{(z' - E_j)^2} \\ &\equiv \rho_{j1}^d(\omega) + \rho_{j2}^d(\omega) \ , \end{aligned} \tag{8}$$

for $a_j \neq 0$. The first and second terms in Equation (8) denote coherent (band) and incoherent (localized) components of d electrons since the former and the latter are derived from the pole and the continuum of Equation (3) respectively.

M-I TRANSITION

We examine the M-I transition by taking parameters as ε_d =0.88 V = 0.3 and $W_d/W = 0.7$ which lead to $X \simeq 4/3$ for Cu^X in the metallic state at T=0.

In Figure 1(a), the phase diagram on the plane of g and T is shown where $a_1 = a_2 = a_3 \neq 0$ and $W = 0$ for the metallic state and $a_1 = a_2 \neq 0$, $a_3 = 0$ and $W \neq 0$ for the insulating state. There is a large hysteresis due to the first order phase transition followed by the entropy of the local spin [5]. The lower bound of the magnitude of g for the insulating state comes from the fact that the energy gain by the Peierls gap competes with the vanishing of the coherent energy of the hybridization in the case of $a_3 = 0$. Phase transitions as a function of T are classified into three groups; metallic state down to zero temperature in the case of $0 \leq g < 0.51$ (group I), metallic state into insulating state in the case of $0.54 < g$ (group II) and the reentrant transition given by M-I-M in the case of $0.51 < g < 0.54$ (group III). Further the antiferromagnetic state exists in the hatched region when the exchange interaction with J=0.05 is added. In Figure 1(b), self-consistency solutions for the M-I transition at $T = 0$ is shown as a function of g. There is the small variation of valence, X_j, of Cu^{X_j}. The quantity X_j jumps at the M-I transition and decreases slightly by the increase of g. The insulating state is always followed by $a_3 = 0$ due to the large jump of W at the M-I transition.

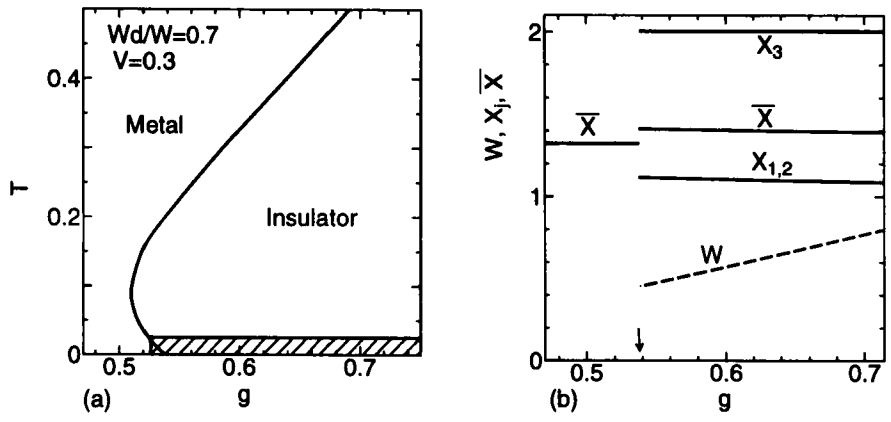

FIGURE 1 Phase diagram on the plain of g and T (a) and self-consistency solutions $X_j(=2-a_j)$, (j=1,2 and 3) and W at $T=0$ (b) in the case of V=0.3 . $\overline{X}$ and arrow denote the average of X_j and the M-I boundary respectively.

DENSITY OF STATES

We examine $\rho_j^d(\omega)$ of the metallic state (insulating state) by choosing $W=0$ ($W=0.7$), which corresponds to $g=0$ ($g=0.66$). In these cases, self-consistency solutions are given by $a_1=a_2=a_3\simeq 0.68$, $E_j=1.25$ and $\mu=0.94$ for $W=0$ and $a_1=a_2\simeq 0.91, a_3=0, E_1=E_2\simeq 1.61$ and $\mu=0.92$ for $W=0.7$.

In Figure 2(a), the density of state of the π-electron, $\rho_j^c(\omega)$, for the metallic (insulating) state is shown by the solid (dashed or dotted) curve. The density of states $\rho_j^d(\omega)$ is calculated from Equations (7) and (8) and then the characteristic of $\rho_j^d(\omega)$ which expresses the model of DCNQI-Cu salts is included in $\tilde{\rho}_j^c(\omega)$ and $\rho_j^c(\omega)$.

First we calculate $\rho_j^d(\omega)$ for $W=0$ and then $\varepsilon_j=\varepsilon_d$. The spectral weight of the slave-boson obtained from Equation (6) is shown in Figure 2(b). The bound state corresponding to the pole of $B_j(\nu)$ appears at $\nu=\varepsilon_j-E_j(<0)$. The incoherent component, which exists only for $\nu>\varepsilon_j-\mu$, spreads in a wide range of the order of the band width. The dotted curve is obtained from the constant $\rho_j^c(\omega)$ which is given by $1/(2\omega_0)$ for $|\omega|<\omega_0$,($\omega_0=2.5$) and zero otherwise. The density of states $\rho_j^d(\omega)$ is shown in Figure 3(a) where the hatched part denotes the incoherent component $\left(\rho_{j2}^d(\omega)\right)$ and the other part denotes the coherent component $\left(\rho_{j1}^d(\omega)\right)$ in Equation (8). From Equation (8), $\rho_{j2}^d(\omega)$ exists only for $\omega<2\mu-E_j$. The inequality, that $2\mu-E_j(=0.63)<\varepsilon_j(=0.88)$, indicates the large energy gain by the incoherent electrons where the energy is located far below the original level ε_j. Such a shift is attributable to the large V in addition to $a_j\simeq 2/3$. For the comparison with the solid curve, $\rho_j^d(\omega)$ obtained from the constant $\rho_j^c(\omega)$ is shown by the dotted curve.

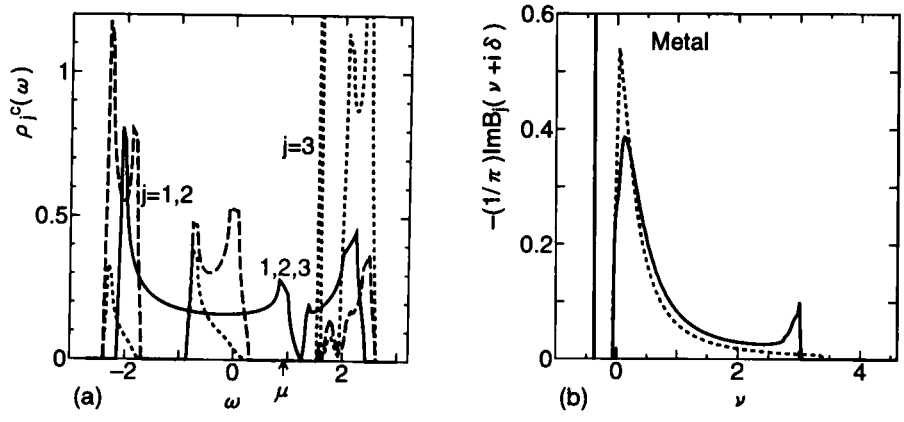

FIGURE 2 Density of states of the π electron, $\rho_j^c(\omega)$, where the solid (dashed or dotted) curve belongs to the metallic state with $W = 0$ (insulating state with $W = 0.7$) (a). The spectral weight of the slave-boson for the metallic state where the dotted curve is obtained from the constant $\rho_j^c(\omega)$ (b).

Next we calculate $\rho_j^d(\omega)$ for $W = 0.7$. There are two kinds of local fields which come from the three-fold periodic potential with W and W_d in Equation (1). From Equation (6), one obtains that $C_1(\nu) = C_2(\nu) \neq 0$ in the regions of $1.03 < \nu < 2.21$ and $3.04 < \nu < 3.75$ and $C_3(\nu) \neq 0$ in the regions of $-0.41 < \nu < 0.75$ and $1.59 < \nu < 2.29$. Then the electronic states for j=1,2 are different from that for j=3. In Figure 3(b), the averaged quantity, $\bar{\rho}^d(\omega)$ ($\equiv \sum_j^3 \rho_j^d(\omega)/3$), is shown by the solid curve. The hatched (other) part denotes the incoherent (coherent) component. The hatched part around $\omega = \varepsilon_3$ is determined by $\rho_3^d(\omega)$ in which all the states are incoherent due to $a_3 = 0$. Two islands correspond to those of $\rho_j^c(\omega)$ below the chemical potential in Figure 2(a). In the case of j=1 and 2, there are both the coherent and incoherent components.

SUMMARY

We have examined the electronic density of states of the d electron by use of the 3D model for DCNQI-Cu salts. In the metallic state ($a_j \simeq 2/3$), the coherent electron exists just below the chemical potential and the incoherent electron is located far below the original localized level due to $a_j \sim o(1)$. The weight of the former state is twice as large as that of the latter one. In the insulating state, most of d electrons belong to the incoherent state which are located around $\omega = \varepsilon_3$, i.e., the new localized level at j=3 in the presence of W_d. Thus we obtained the strongly correlated state for the d electron in the insulating state.

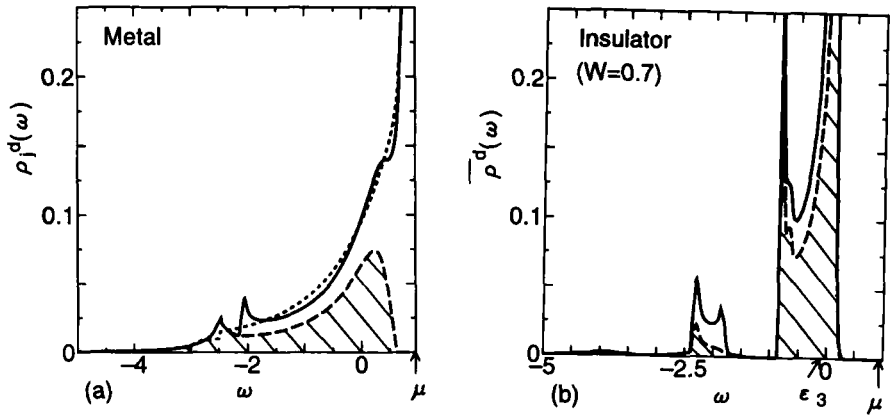

FIGURE 3 Density of states of the d electron for the metallic state $W = 0$(a) and the insulating state $W_d/W = 0.7$(b). $\bar{\rho}^d(\omega) = \sum_j^3 \rho_j^d(\omega)/3$. The hatched region denotes the incoherent part. The dotted curve in (a) denotes $\rho_j^d(\omega)$ obtained from the constant $\rho_j^c(\omega)$.

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