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Michiyasu Mori [a], Kenji Yonemitsu [a] & Hiori Kino [b]

[a] Institute for Molecular Science, Okazaki, 444-8585, Japan

[b] Joint Research Center for Atom Technology, Tsukuba, 305-8562, Japan

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Role of Dimensionality in Dimerized Two-Band Systems

MICHIYASU MORI[a], KENJI YONEMITSU[a] and HIORI KINO[b]

[a]*Institute for Molecular Science, Okazaki 444–8585, Japan and* [b]*Joint Research Center for Atom Technology, Tsukuba 305–8562, Japan*

We have studied the ground state properties of $Pd(dmit)_2$ salts using an effective dimer model. This model describes low-energy excitations of the two-band Hubbard model and is derived by a strong coupling expansion. Dimensionality of the Fermi surface, density-of-states singularity, and magnetic frustration in the dimer model are simultaneously controlled by substituting the cation.

Keywords: $Pd(dmit)_2$; dimerization; two-band system; strong coupling expansion; dimensionality; frustration

INTRODUCTION

The assembled metal complexes $(Et_nMe_{4-n}Z)[Pd(dmit)_2]_2$ (dmit=1,3-dithiol-2-thione-4,5-dithiolate, Z=P,As,Sb) exhibit insulating, metallic and superconducting phases at low temperatures under pressure, depending on the counter-cation[1]–[7]. They show only an insulating phase at ambient pressure. The metallic phase appears for cations Et_2Me_2As and Et_2Me_2Sb[7]. In addition to the metallic phase, the superconducting phase appears for cations Me_4Sb and Et_2Me_2P[4]–[7]. In the insulating phase, the antiferromagnetic (AF) phase transition is experimentally observed. The Néel temperature, T_N, is about 30K for Me_4P[5] and 18K for Me_4Sb and Et_2Me_2P[7, 8]. In the case of Et_2Me_2Sb, the AF phase transition is not observed above 5K by the ESR measurement[8]. In this paper, we will study such a cation effect on the transport and magnetic properties.

These salts $(Et_nMe_{4-n}Z)[Pd(dmit)_2]_2$ have conduction $Pd(dmit)_2$ layers and insulating cation sheets. The conduction layers are separated from each

other by the cation sheet and are composed of two $Pd(dmit)_2$ molecules per unit cell. The molecules compose a dimer unit. The intra-dimer transfer integral between the HOMOs (highest occupied molecular orbitals) A_H and that between the LUMOs (lowest unoccupied molecular orbitals) A_L are an order of magnitude larger than the inter-dimer transfer integrals[4]-[6],[9]. The energy difference, D, between the HOMO and the LUMO is comparable to or smaller than $|A_H| + |A_L|$[4],[10]-[13]. Thus, we take account of two orbitals at each $Pd(dmit)_2$ molecule. Since the formal charge of the acceptor molecule $Pd(dmit)_2$ is $-1/2$, there is additional one electron per dimer. The insulating phase at ambient pressure would be a Mott insulator originating from strong correlation. It is noted that, though the crystal structure of $(Me_4N)[Ni(dmit)_2]_2$[14] is similar to that of $Pd(dmit)_2$ salts, the dimerization in the Ni complex is so weak that the LUMO makes a quasi-one-dimensional half-filled band.

EFFECTIVE DIMER MODEL

In order to study the strongly correlated two-band systems, we have adopted the two-band Hubbard Hamiltonian,

$$
\begin{aligned}
H &= H_t + H_U + H_{U'} + H_J, \qquad (1)\\
H_t &= \sum_{\substack{<i,j>,\sigma=\uparrow,\downarrow\\ \mu,\nu=H,L}} t_{i,\mu;j,\nu}(c^{\dagger}_{i\mu\sigma}c_{j\nu\sigma} + H.c.) + D\sum_i N_{iL},\\
H_U &= U\sum_i (n_{iH\uparrow}n_{iH\downarrow} + n_{iL\uparrow}n_{iL\downarrow}),\\
H_{U'} &= U'\sum_i N_{iH}N_{iL},\\
H_J &= -J\sum_i [2\vec{S}_{iH}\vec{S}_{iL} + \frac{1}{2}N_{iH}N_{iL}],
\end{aligned}
$$

where $c^{\dagger}_{i\nu\sigma}(c_{i\nu\sigma})$ is the electron creation (annihilation) operator for molecular orbital ν with spin σ at site i, $n_{i\nu\sigma}$ is the electron number density, $N_{i\nu} = n_{i\nu\uparrow} + n_{i\nu\downarrow}$, and $\vec{S}_{i\nu}$ is the spin operator for molecular orbital ν at site i. $\langle i,j\rangle$ denotes nearest neighbor sites. $t_{i,\mu;j,\nu}$ stands for the transfer integral between orbital μ at site i and orbital ν at site j. U and U' are the repulsive interaction between two electrons in the same and different orbitals, respectively, at site i. J stands for the Hund coupling.

For low-energy excitations of Eq.(1), an effective dimer model is derived by a strong coupling expansion[15]. First, we solve a one-dimer system with

three holes, whose ground state determines the reduced space on which the effective Hamiltonian operates and corresponds to a quasiparticle on the dimer. Two different ground states are possible depending on A_ν, U, U' and J[15]. One is called H phase, in which the HOMO composes a half-filled effective band. The other is called L phase, in which the LUMO constitutes another half-filled effective band. The experiments[10, 11] and the first-principle calculation[13] suggest that the HOMO contributes to a half-filled band. Below, we study the low-energy excitations only in the H phase. The L phase will be studied elsewhere[15].

Next, we calculate the effective transfer integrals between the dimers $\tilde{t}_{ij}$ and the effective interaction strength $\tilde{U}$ on the dimer to derive an effective Hamiltonian,

$$\begin{aligned}
\tilde{H} &= \tilde{H}_{\tilde{t}} + \tilde{H}_{\tilde{U}}, \qquad (2)\\
\tilde{H}_{\tilde{t}} &= \sum_{\substack{<i,j>\\ \sigma=\uparrow,\downarrow}} \Big[\tilde{t}_{ij}\tilde{n}_{i\bar{\sigma}}\tilde{n}_{j\bar{\sigma}}(\tilde{c}^{\dagger}_{i\sigma}\tilde{c}_{j\sigma} + H.c.) + \tilde{t'}_{ij}(1-\tilde{n}_{i\bar{\sigma}})(1-\tilde{n}_{j\bar{\sigma}})(\tilde{c}^{\dagger}_{i\sigma}\tilde{c}_{j\sigma} + H.c.)\\
&\quad + \tilde{t''}_{ij}(\tilde{n}_{i\bar{\sigma}}(1-\tilde{n}_{j\bar{\sigma}}) + \tilde{n}_{j\bar{\sigma}}(1-\tilde{n}_{i\bar{\sigma}}))(\tilde{c}^{\dagger}_{i\sigma}\tilde{c}_{j\sigma} + H.c.)\Big],\\
\tilde{H}_{\tilde{U}} &= \tilde{U}\sum_{i}\tilde{n}_{i\uparrow}\tilde{n}_{i\downarrow},
\end{aligned}$$

where $\tilde{c}^{\dagger}_{i\sigma}$ ($\tilde{c}_{i\sigma}$) is the creation (annihilation) operator for the quasiparticle on the dimer with total spin z-component σ, and $\tilde{n}_{i\sigma}$ is the quasiparticle number density. In deriving Eq.(2), we consider only the ground states with two, three and four holes in the dimer and neglect those states whose energy is at least an order of A_ν^2/U higher than the ground state energy. Then, the triplet dimer states are excluded. The two and four holes in the dimer correspond to the empty and the doubly occupied dimer sites, respectively. We do not distinguish $\tilde{t}_{ij}$, $\tilde{t'}_{ij}$ and $\tilde{t''}_{ij}$ to have a rough idea of the cation dependence and evaluate only $\tilde{t}_{ij}$.

EFFECTIVE FERMI SURFACE AND DENSITY OF STATES

The effective transfer integrals $\tilde{t}_{ij}$ are evaluated by using the bare transfer integrals obtained by Rouzière *et al.* from the structural analysis at 8K[9] and adopting U=5.0 eV, U'=1.0 eV and J=0.5U'. Then, we calculate the effective bandwidth $\tilde{W}$. The effective interaction strength $\tilde{U}$, $\tilde{W}$ and $\tilde{U}/\tilde{W}$ are listed in Table I. The ratio of $\tilde{U}$ to $\tilde{W}$ is regarded as one of criteria for the metal-insulator transition as the case for κ-BEDT-TTF salts[16]. The ratio

TABLE I Effective interaction $\tilde{U}$ and effective bandwidth $\tilde{W}$ (eV)

	$\tilde{U}$	$\tilde{W}$	$\tilde{U}/\tilde{W}$
Me_4P	0.600	0.132	4.55
Me_4Sb	0.599	0.124	4.83
Et_2Me_2P	0.591	0.113	5.23
Et_2Me_2Sb	0.580	0.099	5.86

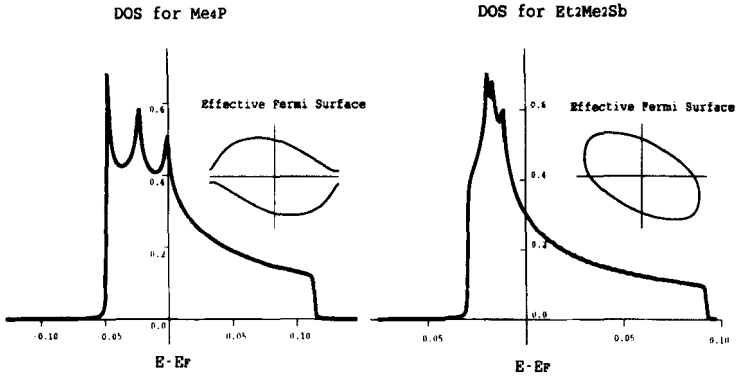

FIGURE 1 Effective Fermi surface and DOS for Me_4P and Et_2Me_2Sb.

$\tilde{U}/\tilde{W}$ decreases as the cation becomes small, suggesting that the smaller cations favor the metallic behavior. On the contrary, the experiments show that the salts with the smaller cations are insulating even under pressure.

Then, we calculate the effective Fermi surface and the density of states (DOS) for qualitative studies of the metal-insulator transition and plot them in Fig. 1 for the smallest cation Me_4P and the largest cation Et_2Me_2Sb. Dimensionality of the effective Fermi surface and the DOS at the effective Fermi level sensitively depend on the cation. For the cation Me_4P, the effective Fermi surface has much better nesting property and the effective Fermi level is located in the vicinity of the van Hove singularity. For the cation Et_2Me_2Sb, the effective Fermi surface is rather isotropic and the effective Fermi level is far from the singularity. Such cation dependence implies that the salt with Me_4P (Et_2Me_2Sb) prefers an insulating (metallic)

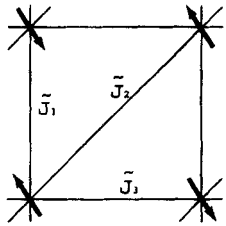

FIGURE 2 Magnetic order on the anisotropic triangular lattice.

phase. Thus, we conclude that the cation dependence of the transport properties mainly originates from the dimensionality and the singularity of the quasiparticle band.

MAGNETISM

Finally, we study the insulating phase in which three holes per dimer are localized[15]. The dimers constitute a spin-1/2 Heisenberg model on the anisotropic triangular lattice as shown in Fig.2. The effective exchange couplings $\tilde{J}_i$ are calculated within the second order perturbation theory with respect to the inter-dimer transfer integrals. Since $\tilde{J}_3 > \tilde{J}_1 > \tilde{J}_2 > 0$, the magnetic moments can be ordered as shown in Fig.2. For the cation Me_4P, $\tilde{J}_2/\tilde{J}_1 = 0.29$ and $\tilde{J}_3/\tilde{J}_1 = 1.05$. Meanwhile, $\tilde{J}_2/\tilde{J}_1 = 0.85$ and $\tilde{J}_3/\tilde{J}_1 = 1.35$ for Et_2Me_2Sb, so that the magnetic frustration is important[9] and can destroy the magnetic order. We calculate a sublattice magnetization at zero temperature for each cation, using the linear spin wave theory, and find that reduction of the sublattice magnetization due to quantum fluctuations is divergent for Et_2Me_2Sb. This result indicates that the magnetic frustration destroys the AF order in the Et_2Me_2Sb salt. For the smaller cations, Me_4P, Me_4Sb and Et_2Me_2P, reduction of the sublattice magnetization is smaller than 1/2, indicating that the AF order is stable. These results are consistent with the ESR results[8].

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