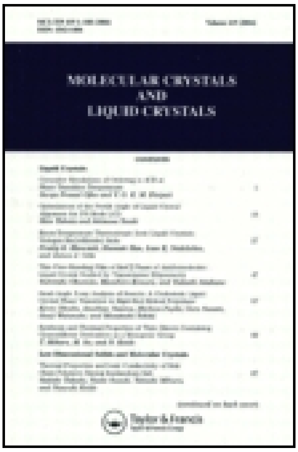

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Optical Conductivity for Possible Ground States of Dimerized Two-Band Pd(dmit) 2 Salts

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Optical Conductivity for Possible Ground States of Dimerized Two-Band Pd(dmit)$_2$ Salts

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We have studied the optical conductivity for possible ground states of Pd(dmit)$_2$ salts, exactly diagonalizing a two-band Hubbard model for a dimer. Our results reproduce dominant peaks of the optical spectra measured by Tajima *et al.* and confirm their argument from the strong-coupling viewpoint. Interaction strengths are estimated and used to study the stability of magnetic orders.

Keywords: Pd(dmit)$_2$, dimerization, two-band Hubbard model, exact diagonalization, optical conductivity, magnetic frustration

INTRODUCTION

Strongly dimerized, two-band systems are realized in (Et$_n$Me$_{4-n}$Z)[Pd(dmit)$_2$]$_2$ (Z=P,As,Sb), which have two-dimensional conducting layers and show insulating, metallic and superconducting phases under pressure[1, 2, 3]. In the insulating phase, an antiferromagnetic(AF) phase transition is experimentally observed at low temperature, except for Et$_2$Me$_2$Sb. The Néel temperature, T_N, is about 30K for Me$_4$P[4, 5] and 18K for Me$_4$Sb and Et$_2$Me$_2$P[6]. For Et$_2$Me$_2$Sb, the AF phase transition is not observed above 5K by the ESR measurement[7].

The energy difference between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital),

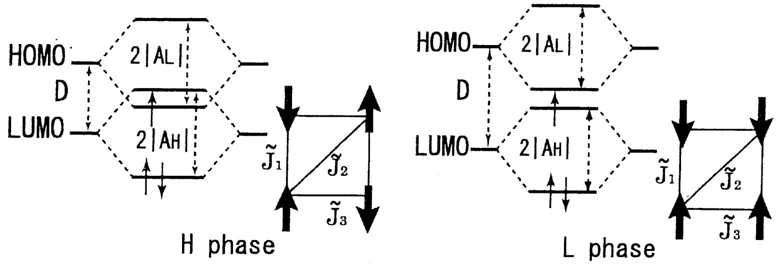

Figure 1: Electronic states in the hole picture and their corresponding magnetic orders.

D, is comparable to or smaller than $|A_H| + |A_L|$[8, 9], where A_H and A_L are the intra-dimer transfer integrals between the HOMOs and between the LUMOs, respectively. If D is small, the bonding LUMO and the antibonding HOMO are inverted, as shown in Fig.1[10, 11].

In our previous papers, we found that two different magnetic states are possible, depending on the degree of the level inversion, by using the Hartree-Fock approximation[12] and the strong coupling expansion[13]. However, we had no obvious proof to tell which magnetic state is realized in the compounds.

The optical conductivity, $\sigma(\omega)$, for the Me$_4$As and Cs salts are measured by Tajima *et al.*, and interpreted in the one-electron picture for a dimer as due to the level inversion[11]. The one-dimer model is useful to reproduce the overall structure of the optical spectra, since the intra-dimer transfer integrals, A_H and A_L , are an order of magnitude larger than the inter-dimer transfer integrals[8]. The peak position and the intensity are generally affected by electron-electron interactions. Then, in this paper, we calculate the optical conductivity of a dimer to clarify the role of electron-electron interactions by exactly diagonalizing a two-band Hubbard model. The interaction strengths are estimated and used in the estimation of effective exchange interaction strengths between dimers. The cation dependence of the magnetic properties is reconsidered.

GROUND STATES OF A DIMER

We use a two-band Hubbard model for a dimer,

$$H = H_t + H_U + H_{U'} + H_J, \tag{1}$$

$$
\begin{aligned}
H_t &= \sum_{\substack{\sigma=\uparrow,\downarrow \\ \nu=H,L}} A_\nu (c^\dagger_{1\nu\sigma} c_{2\nu\sigma} + H.c.) + D \sum_{i=1,2} n_{iL}, \\
H_U &= U \sum_{i=1,2} (n_{iH\uparrow} n_{iH\downarrow} + n_{iL\uparrow} n_{iL\downarrow}), \\
H_{U'} &= U' \sum_{i=1,2} n_{iH} n_{iL}, \\
H_J &= -J \sum_{i=1,2} [2 \overrightarrow{S}_{iH} \overrightarrow{S}_{iL} + \frac{1}{2} n_{iH} n_{iL}],
\end{aligned}
$$

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 $\overrightarrow{S}_{i\nu}$ is the spin operator for molecular orbital ν at site i. $\langle i, j \rangle$ denotes nearest-neighbor sites. U and U' are the repulsive interaction strengths between two electrons in the same and different orbitals, respectively, within a molecule. J stands for the Hund coupling. Below, we use the hole picture for convenience, *i.e.*, three holes in a dimer.

The possible ground states of a dimer are shown in Fig.1[13]. In the H (L) phase, the antibonding HOMO and the bonding LUMO are (are not) inverted, so that a hole enters into the HOMO (LUMO).

OPTICAL CONDUCTIVITY OF A DIMER

To estimate the interaction strengths, we calculate the "intensity parameters", I_σ, introduced in Ref.[11] as,

$$
\begin{aligned}
I_\sigma &= 8 \cdot \int_{6000\mathrm{cm}^{-1}}^{16000\mathrm{cm}^{-1}} d\omega \mathrm{Re}\, \sigma(\omega), & (2) \\
\mathrm{Re}\, \sigma(\omega) &= \frac{\pi}{V} \sum_n |\langle n | \hat{j} | 0 \rangle|^2 \frac{1}{\epsilon_{n0}} \left(\delta(\omega - \epsilon_{n0}/\hbar) + \delta(\omega + \epsilon_{n0}/\hbar) \right), & (3) \\
\hat{j} &= \mathrm{i} \frac{ed}{\hbar} \sum_{\substack{\sigma=\uparrow,\downarrow \\ \nu=H,L}} A_\nu (c^\dagger_{2\mu\sigma} c_{1\nu\sigma} - H.c.), & (4)
\end{aligned}
$$

where $\hat{j}$ is the current operator, and ϵ_{n0} is the absorption energy between the ground state and the nth excited state. The intra-dimer spacing is denoted by d. The peak positions, intensities and I_σ are plotted in Fig.2. These quantities do not depend on D. We used $A_H = -0.48$ eV and $A_L = 0.47$ eV that are obtained by Miyazaki *et*

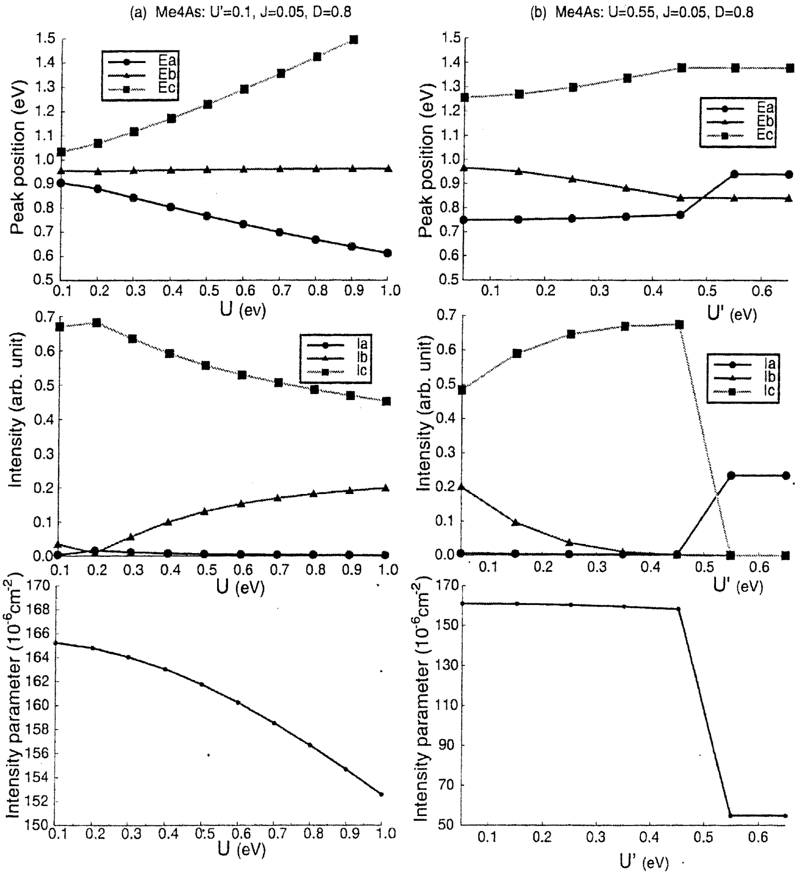

Figure 2: In the left (right) column, the peak positions, the intensities and the intensity parameter are plotted as a function of U (U').

al. on the basis of the density functional theory for the crystal structure of the Me$_4$N$\cdot$salt at room temperature[9]. These values should be valid, since the intra-dimer transfer integrals are little modified by changing the cation. The volume of a dimer and the component of the intra-dimer spacing parallel to the polarization direction are measured at room temperature by Kato *et al.* as 866.25 and 3.01, respectively[5]. The experimental values of I_σ range from 163 (room temperature) to 187 (20K), where the unit is 10^{-6} cm^{-2}[11].

In the L phase, there is only one peak and I_σ is about 55. Since this value of I_σ is much smaller than that observed in the experiment, the H phase has been proposed to be realized by Canadell *et al.*[10] and Tajima *et al.*[11]

First, we find that J should be smaller than 0.1 eV by taking account of the number of peaks and their intensities. Within this limitation and for $U' = 0.1$ eV, they are plotted in Fig.2(a) as a function of U. Since the dominant peak is measured at 1.3 eV, U should be about 0.6 eV. In the experimental spectra, a shoulder appears around 0.9 eV. This second peak intensity strongly depends on U' as shown in Fig.2(b), and we estimate U' to be about 0.2 eV. In summary, we can estimate the interaction strengths as, $U \sim 0.6$ eV, $U' \sim 0.2$ eV and $J \sim 0.1$ eV. Within this calculation, we cannot determine D.

As regards the effective exchange interactions, we use $D = 0.8$ eV and estimate $\tilde{J}_2/\tilde{J}_1 = 0.31$ and $\tilde{J}_3/\tilde{J}_1 = 0.81$ for the cation Me$_4$P, and $\tilde{J}_2/\tilde{J}_1 = 0.85$ and $\tilde{J}_3/\tilde{J}_1 = 0.98$ for Et$_2$Me$_2$Sb. The magnetic frustration is particularly important for the latter case, while the antiferromagnetic order survives in the former case within the linear spin wave theory. This cation dependence is consistent with the EPR measurement[7]. The salts with the other cations are located near the border between the spiral ordered state and the antiferromagnetically ordered state: *i.e.*, $\tilde{J}_2/\tilde{J}_1 = 0.55$ and $\tilde{J}_3/\tilde{J}_1 = 0.83$ for Me$_4$Sb; and $\tilde{J}_2/\tilde{J}_1 = 0.57$ and $\tilde{J}_3/\tilde{J}_1 = 1.03$ for Et$_2$Me$_2$P. Although the overall cation dependence of the magnetic properties is well explained, we need other factors such as three-dimensionality and itineracy of electrons to explicitly reproduce the Néel order and the Néel temperatures.

Acknowledgments

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