Thermoelectric Power of the Multi-Orbital Dimer Mott System, 
\( \beta-(\text{CH}_3)_4\text{N}[\text{Pd(dmit)}_2]_2 \)

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(CHA)_4[Ni(dmit)]_2 shows ordinary T-linear thermoelectric power of \(-40 \mu V/K\) at room temperature coming from the quasi-one-dimensional band, but \(\beta-(\text{CH}_3)_4\text{N}[\text{Pd(dmit)}_2]_2\) shows small negative thermoelectric power of \(-20\) to \(-10 \mu V/K\) at room temperature and T-inverse behavior at low temperatures. This is associated with the dimer Mott state, where the conduction band is derived from the half-filled highest occupied molecular orbital (HOMO). When the HOMO and the lowest unoccupied (LUMO) bands are taken as a whole, the lower HOMO bands afford negative thermoelectric power, whereas the upper two LUMO bands give positive thermoelectric power at the half-filling; this relation is maintained even after the order of the HOMO and LUMO bands is inverted. The inclusion of the Coulomb repulsion \(U\) accounts for the observed small room-temperature thermoelectric power and the low-temperature T-inverse behavior.

1. Introduction

Recently, increasing attention has been devoted to organic thermoelectric materials which enable direct conversion of thermal energy to electric energy around ambient temperature.\(^1\)–\(^9\) On the other hand, thermoelectric power of organic conductors has been widely used for a long time to estimate the bandwidth assuming the one-dimensional tight-binding band.\(^10\),\(^11\) We can extend this method to two-dimensional organic conductors, where the Seebeck coefficient is calculated using the Boltzmann equation on the basis of the band structure.\(^12\)–\(^14\) By adjusting the transfer integrals, we can find a set of transfer integrals that best reproduce the observed temperature dependence of the thermoelectric power. This method is insufficient for determining every detail of as many as typically five transfer integrals to represent the energy band, but it is sufficient to determine the overall bandwidth and anisotropy. Accordingly, this is a natural extension of the analysis based on the one-dimensional tight-binding band.

Band filling is another important factor of thermoelectric power. In polymers, maximum efficiency as a thermoelectric material has been achieved at a comparatively small doping level.\(^15\) In small-molecule organic conductors, band filling control is more difficult,\(^16\),\(^17\) and even if it is attained by anion exchange, the transport properties are sometimes susceptible to the anion size difference.\(^18\) In addition, band-filling control using a field-effect transistor has been reported.\(^19\),\(^20\) In ordinary cation-radical salts, thermoelectric power is positive, whereas it is negative if the average donor charge exceeds +1.\(^21\) However, even this simple expectation is sometimes violated depending on the band structures.\(^18\) It is therefore necessary to analyze the observed thermoelectric properties compared with the band structures.

In this connection, \([\text{Pd(dmit)}_2]_2^{2-}\) poses another problem as a multi-orbital system (dmit: 1,3-dithiole-2-thione-4,5-dithiolate).\(^22\) Some of \([\text{M(dmit)}_2]_2\) compounds are superconductors, and except for \(\text{C}_6\text{O}_{6}\), these are the only organic superconductors mediated by anionic species. For example, \((\text{CH}_3)_4\text{N}[\text{Ni(dmit)}_2]_2\) and \(\beta-(\text{CH}_3)_4\text{N}[\text{Pd(dmit)}_2]_2\) exhibit superconductivity respectively at 5 and 6.2 K under pressures of 7 and 6.5 kbar.\(^23\),\(^24\) Since the lowest unoccupied molecular orbital (LUMO) of \([\text{Ni(dmit)}_2]_2\) makes the conduction band, \((\text{CH}_3)_4\text{N}[\text{Ni(dmit)}_2]_2\) shows a negative thermoelectric power with the room-temperature value of \(-40 \mu V/K\) and metallic (T-proportional) temperature dependence.\(^25\),\(^26\) The Pd analog has strong dimerization,\(^27\) and the bonding combination of the LUMO (\(\psi^{-}\)) appears below the antibonding combination of the highest occupied molecular orbital (HOMO) (\(\psi^{+}\)).\(^28\) Such a HOMO–LUMO inversion has been confirmed by the tight-binding calculation,\(^28\) the first principle calculation,\(^29\)\(^31\) and the optical spectroscopy.\(^28\),\(^32\),\(^33\) Since the conduction band is maintained by the HOMO (\(\psi^{+}\)), it arises a naive question whether the thermoelectric power becomes positive or negative.

Owing to the \(-1\) charge on a \([\text{Pd(dmit)}_2]_2\) dimer, these compounds are regarded as a dimer Mott insulator.\(^34\) When P, As, and Sb cations are used instead of ammonium, approximately triangular lattice is achieved, and a spin-lattice state is realized.\(^35\),\(^36\) The paramagnetic state is, however, competitive with a charge-ordered state.\(^37\),\(^38\) In addition, the possibility of intramolecular charge disproportionation has been suggested\(^31\) so that it may be sometimes more appropriate to choose independent dmit ligand as a starting unit instead of the \([\text{Pd(dmit)}_2]_2\) molecule (fragment molecular orbital approach).\(^39\)

The present work reports thermoelectric power of \(\beta-(\text{CH}_3)_4\text{N}[\text{Pd(dmit)}_2]_2\) in comparison with \((\text{CH}_3)_4\text{N}[\text{Ni}-
(dmit)$_2$. Although the composition is the same, the Pd compound is not isostructural to the Ni compound. The Pd compound has a strong dimerization, whereas the dimerization of the Ni compound is small. The observed thermoelectric power is interpreted on the basis of the energy band considering the Coulomb repulsion $U$. Interpretation of thermoelectric power is still challenging in multi-orbital systems, particularly in dimer Mott systems.

2. Experiment

Crystals of (CH$_3$)$_4$N[Ni(dmit)$_2$] and $\beta$-(CH$_3$)$_3$N-[Pd(dmit)$_2$] were black hexagonal plates with the typical length and width of 0.6 and 0.4 mm. Temperature dependence of the resistivity was measured by the conventional four-probe technique down to the measuring limit coming from the high resistance. To measure the thermoelectric power, the sample was attached to copper blocks via gold foils by carbon paste, and the copper blocks were alternately heated by applying voltages to the resistors to generate a temperature gradient. The thermocouple was Re-Fe versus chromel thermocouple. The thermo-electric power was measured using the four-probe technique down to the measuring limit coming from the high resistance.

Table 1. Transfer integrals (meV) of (CH$_3$)$_4$N[Ni(dmit)$_2$] and $\beta$-(CH$_3$)$_3$N-[Pd(dmit)$_2$].

<table>
<thead>
<tr>
<th>$t$</th>
<th>Ni</th>
<th>$\beta$-(CH$_3$)$_3$N-[Pd(dmit)$_2$]</th>
<th>H-H</th>
<th>$\beta$-(CH$_3$)$_3$N-[Pd(dmit)$_2$]</th>
<th>L-L</th>
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<td>354</td>
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<tr>
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<tr>
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<td>54</td>
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<td>-7</td>
<td>18</td>
<td>20</td>
</tr>
</tbody>
</table>

a) Values in parentheses are constructed from Table II. b) Transfer integrals between the adjacent LUMOs, c) HOMOs, and d) HOMO and LUMO.

In $\beta$-(CH$_3$)$_3$N[Pd(dmit)$_2$], the stacks run in two different directions, [110] and [110], which are equivalent but make different layers alternately arranged along the $c$ axis (Fig. 2). Instead of the original $C$-centered unit cell, the lattice is transformed to the primitive cell [Fig. 2(c)] according to

$$a_p = (a + b)/2$$

and

$$b_p = b$$

for the band calculation. The calculations were done for the lattice including the [110] column, where the $k_{\phi}$ direction corresponds to the average stacking direction ($\phi$, whereas the $k_p$ direction is tilted from the principal direction. The latter was transformed to the principal values, and the results correspond to the values along the original $a$ and $b$ axes.

From this, thermoelectric power $S$ was evaluated according to the Boltzmann equation,

$$S = -\frac{1}{[\epsilon/ T K_0]}. \tag{1}$$

$$K_0 = \frac{1}{4\pi^3 h} \int \frac{\epsilon}{\partial E} \frac{dS_E}{\epsilon} \frac{dE}{\epsilon}. \tag{2}$$

$$K_1 = \frac{1}{4\pi^3 h} \int \frac{\epsilon}{\partial E} \frac{dS_E}{\epsilon} \frac{dE}{\epsilon}. \tag{3}$$

Here, $h$ is the Planck constant divided by $2\pi$, $\tau$ is the carrier velocity, and $v_k = \partial(E)/\partial k$ is the perpendicular component. These quantities were calculated from the band structure, $E(k)$. $f^0$ is the Fermi distribution function, and the relaxation time $\tau$ is assumed isotropic. The integration is done along the Fermi surface $s_F$, but $-\partial f^0/\partial E$ is nonzero only around the Fermi level, $E_F$, with the energy width of about $T$, from which the temperature dependence emerges.

Recently, similar calculations have been reported starting from various band structures, but here we have taken the tight-binding HOMO and LUMO bands into account.

Fig. 2. (Color online) Crystal structure of the $\beta$-(CH$_3$)$_3$N[Pd(dmit)$_2$] viewed along (a) the $b$ and (b) the $c$ axes. (c) Molecular arrangement and transfer integrals viewed along the molecular-short axis. The gray, yellow, and blue atoms correspond to the C, S, and Pd atoms, respectively.
Temperature dependence of resistivity and thermoelectric power is depicted in Fig. 3. The resistivity of the Ni compound decreases down to around 100 K, though there is somewhat hysteresis in the heating and cooling runs.\(^{27,49}\) Thermoelectric power of the Ni compound is \(-40 \mu \text{V/K}\) at room temperature, and shows T-linear dependence down to low temperatures in agreement with the previous result.\(^{25,26}\) It is noteworthy that the thermoelectric power exhibits T-linear dependence even in the low temperature region in which the resistivity increases. Assuming the one-dimensional quarter-filled band, this leads to the bandwidth of 0.52 eV.\(^{10,11}\) This value is basically in agreement with the calculated transfer integrals of 102–108 meV [Table I and Fig. 2(c)].\(^{40}\) The dimerization gap \(2|t_A - t_B|\), which gives the \(\psi^- - \psi^-\) splitting in Fig. 1, is practically zero. The HOMO–LUMO gap \(\Delta\) [Fig. 1(b)] has been estimated to be 0.5 eV from the semi-empirical band calculation,\(^{28}\) or 0.73 eV from the first-principle band calculation.\(^{29}\) Accordingly, the situation of Fig. 1(a) is realized, where the conduction is maintained by the LUMO band. The Ni compound is not far from the ordinary quasi-one-dimensional metal.

Thermoelectric power of the Pd compound is largely different [Fig. 3(b)]; it is \(-20 \text{ to } -10 \mu \text{V/K}\) at room temperature, and diverges to the positive direction at low temperatures. Room-temperature \(S\) is somewhat different along the \(a\) and \(b\) axes, but the zero crossing occurs at similar temperatures. The low-temperature divergence is attributable to the Mott-insulating character coming from the strong dimerization.

Arrhenius plot of the resistivity is shown in Fig. 3(c). The activation energy for the \(a\) and \(b\) directions are respectively estimated to be 91 and 59 meV below 150 K. An increase of the activation energy in the thermoelectric power [Fig. 3(d)] corresponds to the development of an insulating state, where the activation energies are 38 and 71 meV below 90 K. The activation energy, however, shows somewhat sample dependence. The low-temperature thermoelectric power is not represented by such a simple form as \(S = S_0 + E_a/T\) or \(S = aT + E_a/T\); extrapolation of the low-temperature \(E_a/T\) term leads to a large negative \(S_0\) at high temperatures [Fig. 3(d)]. This seems to be associated with disappearance of \(E_a\) around 150 K. A phase transition at 120 K has been suggested from the \(^1\text{H}-\text{NMR}.\(^{50}\) Since the comparatively small high-temperature \(S\) is characteristic of the Pd complex, we may have to treat the low and high-temperature parts independently.

In order to show this more clearly, thermoelectric power is calculated from the energy band. The transfer integrals defined in Fig. 2(c) are calculated as listed in Table I.\(^{42}\) These transfer integrals are basically the same as the previous calculation.\(^{49}\) In contrast to the Ni complex, the intradimer transfer \(t_A = 398 \text{ meV}\) is overwhelmingly large. The interdimer interaction \(t_B\) is not largely different from the interchain interactions \(t_c\), \(t_p\), and \(t_q\), and results in the two-dimensional Fermi surface [Fig. 4(a)], in agreement with the previous report.\(^{49}\) Here, \(\Delta = 0.42 \text{ eV}\) is assumed on the basis of the extended Hückel calculation,\(^{28}\) where the Fermi surface comes from the HOMO \(\psi^-\) band. This diagram contains four bands because the considered primitive cell includes two molecules, and both of which have HOMO and LUMO. As shown in Fig. 1, the whole band is \(5/8\) (= 0.625) filling. Note that the LUMO \(\psi^+\) conduction band is realized at large \(\Delta\) [Fig. 1(a)], whereas small \(\Delta\) makes HOMO \(\psi^-\) the conduction band [Fig. 1(b)]. Here, \(\Delta = 0.42 \text{ eV}\) is obviously

![Fig. 3](image-url)  (Color online) Temperature dependence of (a) resistivity, and (b) thermoelectric power of (CH\(_3\))\(_4\)N[Ni(dmit)\(_2\)]\(_2\) (Ni) and \(\beta-(CH_3)_4N-[Pd(dmit)_2]_2\) (Pd). (c) Arrhenius plot of the resistivity and (d) thermoelectric power against the reciprocal temperature in \(\beta-(CH_3)_4N[Pd(dmit)_2]_2\).

![Fig. 4](image-url)  (Color online) (a) Energy band of \(\beta-(CH_3)_4N[Pd(dmit)\(_2\)]_2\) at \(\Delta = 0.42 \text{ eV}\), and the Fermi surface at the 0.625 filling (solid line) coming from the HOMO \(\psi^-\) band. (b) Thermoelectric power calculated from various starting units together with the observations. (c) Calculated thermoelectric power when the Fermi energy is located at the centers of HOMO \(\psi^+\) (0.125), \(\psi^-\) (0.625), LUMO \(\psi^+\) (0.375), and \(\psi^-\) (0.875) bands. (d) Calculated thermoelectric power at other band fillings in the HOMO \(\psi^-\) band. Solid and broken curves correspond to the results along the \(a\) and \(b\) axes, respectively.

3. Results

Temperature dependence of resistivity and thermoelectric power is depicted in Fig. 3. The resistivity of the Ni compound decreases down to around 100 K, though there is somewhat hysteresis in the heating and cooling runs.\(^{26,40,48}\) The resistivity of the Pd compound gradually increases from room temperature.\(^{27,49}\) Thermoelectric power of the Ni compound is \(-40 \mu \text{V/K}\) at room temperature, and shows T-linear dependence down to low temperatures in agreement with the previous result.\(^{25,26}\) It is noteworthy that the thermoelectric power exhibits T-linear dependence even in the low temperature region in which the resistivity increases. Assuming the one-dimensional quarter-filled band, this leads to the bandwidth of 0.52 eV.\(^{10,11}\) This value is basically in agreement with the calculated transfer integrals of 102–108 meV [Table I and Fig. 2(c)].\(^{40}\) The dimerization gap \(2|t_A - t_B|\), which gives the \(\psi^- - \psi^-\) splitting in Fig. 1, is practically zero. The HOMO–LUMO gap \(\Delta\) [Fig. 1(b)] has been estimated to be 0.5 eV from the semi-empirical band calculation,\(^{28}\) or 0.73 eV from the first-principle band calculation.\(^{29}\) Accordingly, the situation of Fig. 1(a) is realized, where the conduction is maintained by the LUMO band. The Ni compound is not far from the ordinary quasi-one-dimensional metal.

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smaller than the dimerization gap $2|t_1 - t_b| \approx 0.7$ eV, and the latter situation is realized. Although the Fermi level is located in the HOMO band, the calculated thermoelectric power is negative [Fig. 4(b)], and shows ordinary metal-like behavior.

In order to interpret the negative $S$, $S$ at other virtual band fillings are considered [Fig. 4(c)]. Starting from the energy level order in Fig. 1(b), band fillings, 0.125 and 0.625, corresponds to centers (half fillings) of the two HOMO bands [Fig. 4(a)], whereas band fillings, 0.375 and 0.875, are at the centers of the two LUMO bands. The actual filling corresponds to 0.625. As shown in Fig. 4(c), the HOMO bands afford negative thermoelectric power, while the LUMO bands give positive thermoelectric power. This is opposite to the ordinary definition of HOMO and LUMO, but when the four energy bands are taken as a whole, the lower two HOMO bands afford negative thermoelectric power, and the upper two LUMO bands give positive thermoelectric power. This is more straightforward when the HOMO and LUMO bands are entirely separated at large $\Delta$ [Fig. 1(a)], but also holds even after the HOMO $\psi^-$ is located above the LUMO $\psi^+$. The observed negative thermoelectric power [Fig. 4(b)] is consistent with the HOMO $\psi^-$ conduction band.

Figure 4(d) shows $S$ at various band fillings in the HOMO $\psi^-$ band. The filling 0.625 corresponds to the half filling, which is identical to Fig. 4(c). The upper quarter filling (0.6875) leads to positive $S$, whereas the lower quarter filling (0.5625) results in negative $S$. For respective bands, the upper half is basically hole like, while the lower half shows ordinary electron-like $S$. The above discussion for Fig. 4(c) concerns to half fillings of the respective bands, where $S$ is not exactly zero depending on the location in the entire band.

We have also investigated the fragment molecular orbitals. Since the population of the HOMO and LUMO on the metal atom is small (Fig. 1), the ligand orbital (dmit$^{2-}$-HOMO) is chosen as the starting orbital. The intermolecular interactions are decomposed to these ligand orbitals as shown in Fig. 5, and the resulting transfers are calculated as listed in Table II. Since $\psi^-$ and $\psi^+$ are represented by using the dmit fragment orbitals $\chi_1$ and $\chi_2$ as $\psi^\pm = (\chi_1 \pm \chi_2)/\sqrt{2}$, the transfers in Table I are estimated from $t = (t_{11} \pm t_{12} \pm t_{21} \pm t_{22})/2$. These values are listed in the parentheses in Table I. Since these values are not largely different from the ordinary monomer calculation, we can conclude both methods afford basically the same result.

The resulting calculated thermoelectric power is depicted in Fig. 4(b) together with the observations. The calculation successfully gives negative thermoelectric power though the absolute value is larger than the observations. The fragment orbital calculation affords almost the same result as the ordinary monomer calculation, because the Fermi surface is exclusively derived from the HOMO. Since the dimerization is strong, we have also estimated transfer integrals starting from the dimer [Pd(dmit)$_2$]$_2$ unit. The resulting Fermi surface and the thermoelectric power are unchanged [Fig. 4(b)], and we obtain basically the same result starting from the dimer orbital as well.

Since band calculation including the Coulomb repulsion $U$ has been attempted recently, thermoelectric power along the $b$ axis shifts to positive direction. Therefore, $U = 0.15 - 0.2$ eV seems necessary to reproduce the observed small room-temperature $S = -20$ to $-10$ $\mu$V/K particularly along the $b$ axis. This is basically unchanged for $\Delta$ up to 0.7 eV. Although we have not optimized average number of electrons $\langle n_i \rangle$ on the molecule $i$, the obtained $U$ corresponds to the diagonal term $\sum_i U_0 \langle n_i \rangle \langle n_i \rangle$. For half filling, $\langle n_i \rangle$ is 0.5 on an average, so that the absolute value of $U_0$ for a single molecule is expected to be 0.6 - 0.8 eV. The resulting band is still in the correlated metal region. The Mott–Hubbard gap opens above $U \sim 0.4$ eV, where $|S|$ shows $T$-inverse divergence. The low-temperature thermoelectric power is attributed to opening of the Mott–Hubbard gap; we have to assume an increase of $U$ below 150 K, and the resulting development of the Hubbard gap. This happens associated with the increasing imbalance of $\langle n_i \rangle$ and the spin polar-
The temperature dependence of thermoelectric power is too sensitive to parameters for the quantitative estimation. Among other dimer Mott systems, $\kappa-(ET)_{2}\text{Cu(SCN)}_{2}$ affords a small thermoelectric power of $+10$–$20\,\mu\text{V/K}$ at room temperature together with the comparatively high conductivity (ET: bis(ethylenedithio)tetrathiafulvalene), whereas $\beta-(ET)_{2}\text{AuCl}_{4}$ shows a large thermoelectric power of $400\,\mu\text{V/K}$ together with the semiconductor behavior. Though temperature dependence of thermoelectric power is related well to the resistivity, the magnitude varies largely depending on the subtle change of the electron correlation in dimer Mott systems. In this sense, thermoelectric power is a good measure of electron correlation.

4. Summary

$\beta-(\text{CH}_{3})_{4}\text{N}[\text{Pd(dmit)}]_{2}$ exhibits comparatively small negative thermoelectric power. This is consistent with the HOMO $\psi^{-1}$ band including $U$. The negative thermoelectric power is not disagreeable to the HOMO conduction band because when the HOMO and LUMO bands are considered as a whole, the lower two HOMO bands afford negative thermoelectric power at the half filling, while the upper two LUMO bands give positive thermoelectric power; this relation is maintained even when the order of the central HOMO and LUMO levels is inverted. In the present metal complexes, the starting unit of calculation is potentially chosen as a single molecule, a ligand corresponding to a half molecule, and a dimer composed of two molecules, but these three methods afford practically the same results. The observed small room-temperature thermoelectric power and the low-temperature $T$-inverse dependence are consistent with the dimer Mott state.

Acknowledgments

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