"Pudding Mold"-type Band as an Origin of Large Thermopower in \(\tau\)-type Organic Conductors

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Abstract

We study the origin of the large thermopower in quasi-two-dimensional \(\tau\)-type organic conductor, \(\tau\)-(EDO-S,S,DMEDT-TTF)\(_2\)(AuBr\(_2\))\(_{1+y}\) \((y \leq 0.875)\), from the view point of a "pudding mold"-type band structure. We calculate the electronic band structure using an \textit{ab initio} band calculation package, and obtain a tight binding model fit to the \textit{ab initio} band structure. Using the model and the Boltzmann’s equation approach, we calculate the temperature dependence of the Seebeck coefficient. We conclude that the peculiar band structure is the origin of the large Seebeck coefficient and the appearance of the maximum value at a certain temperature.

Keywords: \(\tau\)-type organic conductor, quasi-two-dimensional system, thermopower, band structure

1. Introduction

Recently, large thermopower has been experimentally observed in quasi-two-dimensional organic conductors having \(\tau\)-type alignment of the donor molecules, e. g. \(\tau\)-(EDO-S,S,DMEDT-TTF)\(_2\)(AuBr\(_2\))\(_{1+y}\) \((y \leq 0.875)\). \(\)The absolute value of the Seebeck coefficient takes its maximum of about \(|S| \approx 150 \mu\text{V/K} \) around the temperature of \(T \approx 100 \text{ K} \) to \(T \approx 150 \text{ K} \).

A possible link between the large thermopower and the electronic structure is of special interest. In fact, a calculated band structure for \(\tau\)-(EDO-S,S,DMEDT-TTF)\(_2\)(AuBr\(_2\))\(_{1+y}\) using the extended Hückel method \(^2\) has shown presence of a star-shaped Fermi surface and a peculiar band structure with flat portions near the \(\Gamma\) point. Another feature of this material is the variation of the band-filling corresponding to the amount of anions. The anion content of \(y\) corresponds to the electron band filling of \(n = 1.5 - y/2\).

In the present study, we perform an \textit{ab initio} band calculation for \(\tau\)-(EDO-S,S,DMEDT-TTF)\(_2\)(AuBr\(_2\)) using the WIEN2K package,\(^5\) and make a tight binding model fit to the obtained \textit{ab initio} band structure. We calculate the Seebeck coefficient using the Boltzmann’s equation approach and show that the peculiar band structure is the origin of the large Seebeck coefficient.

2. Band structure

We have performed calculations using all-electron full potential linearized augmented plane-wave (LAPW) + local orbitals (lo) method to solve the Kohn-Sham equations using density functional theory (DFT) within the framework of WIEN2K \(^5\). This implements the DFT with different possible approximation for the exchange correlation potentials.
The exchange correlation potential is calculated using the generalized gradient approximation (GGA). The single-particle wave functions in the interstitial region are expanded by plane waves with a cutoff of $R_{\text{MT}}K_{\text{max}} = 3.0$, where $R_{\text{MT}}$ denotes the smallest muffin tin radius and $K_{\text{max}}$ is the maximum value of the $K$ vector in the plane wave expansion. In $\tau$-(EDO-S,S-DMEDT-TTF)$_2$AuBr$_2$, the muffin-tin radii are assumed to be 2.38, 2.11, 1.61, 1.27, 1.18 and 0.64 atomic units (au) for Au, Br, S, O, C and H, respectively. For the value of $K_{\text{max}}$ and the plane wave cutoff energy, $K_{\text{max}} = 4.7$ and the plane wave cutoff energy is 298.8 eV for $\tau$-(EDO-S,S-DMEDT-TTF)$_2$AuBr$_2$. The wave functions in the muffin tin spheres are expanded up to $l_{\text{max}} = 10$, while the charge density are Fourier expanded up to $G_{\text{max}} = 20$. Calculations are performed by using 512 $k$-points in the irreducible Brillouin zone.

The calculated band structure is shown in Figure 3(a). We have made a tight binding model fit to the $ab$ initio band as shown in Figure 3(b), where the transfer energies are determined as $t_1 = 161.61$, $t_2 = -157.29$, $t_3 = -11.44$, $t_4 = 21.26$, and $t_5 = -2.81$ [meV]. As seen in Figure 3(a), there are two band dispersions near the Fermi level, separated by a band gap. The band width is estimated to be 1.28 eV, and the maximum value of the band gap is around 0.13 eV.

3. Boltzmann’s equation approach

Using the Boltzmann’s equation approach, the thermopower is given by

$$ S = \frac{1}{eT}K_0^{-1}K_1, $$

(1)

where $e(<0)$ is the electron charge, $T$ is the temperature, tensors $K_0$ and $K_1$ are given by

$$ K_n = \sum_k \tau(k) v(k) v(k) \left\{ -\frac{\partial f(\varepsilon_k)}{\partial \varepsilon_k} \right\} (\varepsilon_k - \mu)^n, $$

(2)

Here, $\varepsilon(k)$ is the band dispersion, $v(k) = \nabla_{\varepsilon} \varepsilon(k)$ is the group velocity, $\tau(k)$ is the quasiparticle lifetime, $f(\varepsilon)$ is the Fermi distribution function, and $\mu$ is the chemical potential. Hereafter, we simply refer to $(K_n)_{xx}$ as $K_n$, and $S_{xx} = (1/eT)(K_1/K_0)$ for diagonal $K_0$ as $S$. Using $K_0$, conductivity can be given as $\sigma_{xx} = e^2K_0 \equiv \sigma$. Roughly speaking for a constant $\tau$,

$$ K_0 \sim \Sigma'(v_A^2 + v_B^2), \quad K_1 \sim (kB_T)\Sigma'(v_B^2 - v_A^2) $$

(3)

(apart from a constant factor) stand, where $\Sigma'$ is a summation over the states in the range of $|\varepsilon(k) - \mu| \approx kB$, and $v_A$ and $v_B$ are typical velocities for the states above and below $\mu$, respectively. In usual metals, where $v_A \sim v_B$, the positive and negative contributions in $K_1$ nearly cancel out to result in a small $S$. Now, let us consider a band that has a somewhat flat portion at the top (or the bottom), which sharply bends into a highly dispersive portion below (above). We will refer to this band structure as the “pudding mold” type\[3\]. For this type of band with $\mu$ sitting near the bending point, $v_A \gg v_B$ holds for high enough temperature, so that the cancellation in $K_1$ is less effective, resulting in $|K_1| \sim (kB_T)\Sigma'v_A^2$ and $K_0 \sim \Sigma'v_A^2$, and thus large $|S| \sim O(k_B/e) \sim O(100)\mu$V/K. An important point for this type of band is that the large $v_A$ and the large Fermi surface result not only in large $|K_1/K_0|$ but also in large $K_0 \propto \sigma$ as well, being able to give a large power factor $S^2\sigma$. The pudding mold type band scenario well explains the coexistence of large thermopower and metallic conductivity observed in Na$_2$CoO$_2$\[4\].

Now, if we look at the band structure of the $\tau$-type conductor from this viewpoint, the lower band has a nearly flat portion at the top, while the upper band has a nearly flat portion at the bottom. Therefore, the band structure can be considered as “inverted pudding mold type band” on top of a “pudding mold type band”.

4. Thermopower
The absolute value of the calculated $S$ is somewhat smaller than the experimental one [1], the overall tendency of the temperature dependence is well reproduced by the calculation when we adopt $y = 0.875$.

The reason for the appearance of the maximum value of $S$ can be understood as follows. In the low temperature regime, due to the presence of the band gap, only the upper band is effective, which gives a negative Seebeck coefficient. The Seebeck coefficient in this temperature regime can be large (despite the metallic conductivity) because of the inverted pudding mold shape of the upper band. At higher temperatures, the lower band, which gives a positive contribution to $S$, becomes effective, and this suppresses the absolute value, resulting in a maximum value at a certain temperature.

5. Conclusion

We have studied the origin of the large thermopower in the $\tau$-type organic conductor. We have performed an ab initio band calculation by using WIEN2K, and made a tight binding model fit to the ab initio band. Using this tight binding model, we have calculated the Seebeck coefficient which nicely reproduces the experimental results. We conclude that the peculiar band structure consisting of pudding + inverted pudding pudding mold type bands is the origin of the large thermopower as well as the appearance of the maximum value at a certain temperature. A more detailed analysis (such as on the molecule dependence) is now underway [2].

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