Low Temperature Crystal Structures and Band Parameters in β'-($Me_{4-x}Et_xZ$)[$Pd(dmit)_2$]$_2$

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β'-$EtMe_3Sb[Pd(dmit_2)]_2$ ($Pd(dmit)_2$: Figure 1) forms a spin-1/2 isosceles triangular lattice of the dimer unit $[Pd(dmit_2)]_2$, characterized with J = 200-300 K. A quantum spin liquid (QSL) state is realized as a magnetic ground state in the $EtMe_3Sb$ salt. Many experimental and theoretical studies were performed to reveal the nature of QSL realized in the $EtMe_3Sb$ salt [1-3]. The triangular lattice in this system is not a result of crystal symmetry, but of the combination of interdimer transfer integrals, t_S, t_B and t_r, ($t_S \sim t_B = t$, $t_r = t'$ in Figure 2) [1]. The series of β'-$Me_{4-x}Et_xZ$ salts are isostructural with different anisotropy parameters t'/t. The magnetic ground state of these salts can be divided into three types, QSL, anti-ferromagnetic long-range order (AFLO) and charge order (CO). The difference in the ground state is understood by the anisotropy of isosceles triangular lattice. The geometric frustration of the $EtMe_3Sb$ salt, realizing the QSL state, is strong (t'/t = 0.91 at room temperature), but the triangular lattice of the $EtMe_3Sb$ salt is slightly distorted from the regular triangular lattice. The QSL state is reported in several molecular conductors with slightly distorted triangular lattices, including the $EtMe_3Sb$ salt [5-6]. The reason why the QSL is observed in the distorted triangular lattice system in molecular conductors remains an open question. Intermolecular lengths and molecular arrangements of molecular crystals are easily changed with temperature. The values of t_S, t_B and t_r at the temperature where the QSL state is realized should be different from those at room temperature due to the thermal contraction. In order to understand the nature of the QSL state, knowledges of the low temperature crystal structure and electronic structure need to be examined in detail. We determined crystal structures of the $EtMe_3Sb$ salt (QSL), and Me_4Sb, Et_2Me_2As and Me_4As salts (T_N = 12-35K) from room temperature to 5 K. Then we calculated electric structures with tight-binding approximation method and the first-principle DFT method at each temperature based on experimentally obtained crystal structures [7].

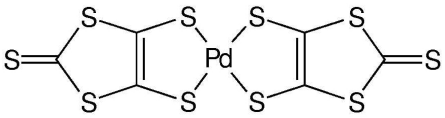

Figure 1. $Pd(dmit)_2$ molecule.

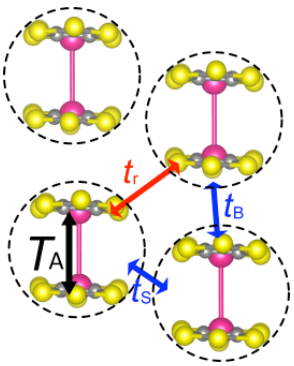

Figure 2. Interdimer transfer integrals.

Figure 3 shows temperature dependence of t_S, t_B and t_r in the $EtMe_3Sb$ salt. They linearly increased with lowering temperature. Since t_S and t_B increased keeping the same ratio and t_r slightly increased, the anisotropy of the triangular lattice was enhanced with lowering temperature. The situation is the same in other salts. At 5 K, the ratio t'/t decreased by 15% compared with the room temperature value in every salt (Fig. 4). The intradimer transfer integral T_A is approximately related to the effective on-site Coulomb energy on the dimer $[Pd(dmit)_2]_2$. Therefore, the ratio T_A/W (W: band width) shows the strength of the correlation effect. With lowering temperature, W increased more rapidly than T_A. The T_A/W was decreased by 10% at 5 K from the room temperature value, that is, the correlation effect decreased with lowering

temperature. Due to the tight dimerization, the intradimer S· · · S distances show smaller changes than the interdimer S· · · S distances. Therefore, the temperature dependence of T_A/W should be the result of the difference between intra- and interdimer thermal contraction. This is common feature of all β'-Pd(dmit)$_2$ salts.

We performed the first-principles DFT calculations. The anisotropy of the Fermi surface is enhanced with lowering temperature, which is very similar to the result of the tight-binding calculation. This temperature dependence is consistent with the enhancement of the anisotropy of triangular lattice. The conducting band is composed of the anti-bonding HOMO and is isolated from other bands at each temperature. This indicates that the dimer model using only HOMO-HOMO interactions can well describe the low-temperature electric structure of the EtMe$_3$Sb salts. The partial density of states (PDOS) for the conduction band indicates that the majority of the conduction band is composed of the p-orbital in S. Although some short S· · · HC contacts exist between cation and Pd(dmit)$_2$ molecule, the contribution of C atoms in the EtMe$_3$Sb cation to the PDOS is less than 0.015 /eV and thus the cation orbitals cannot hybridize to the conduction band. The arch-shaped distortion of the Pd(dmit)$_2$ molecule plays a key role in the cation dependence of the t'/t value. It was revealed that the short S· · · HC contacts controls the arch-shaped distortion, and the resulting steric effects have an impact on the electric structure.

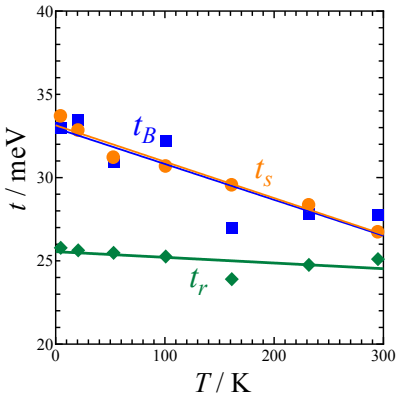

Figure 3. Temperature dependence of inter dimer transfer integrals in the EtMe$_3$Sb salt.

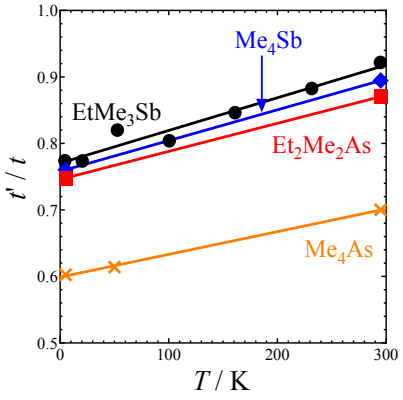

Figure 4. Temperature dependence of t'/t in the EtMe$_3$Sb, Me$_4$Sb, Et$_2$Me$_2$As and Me$_4$As salts.

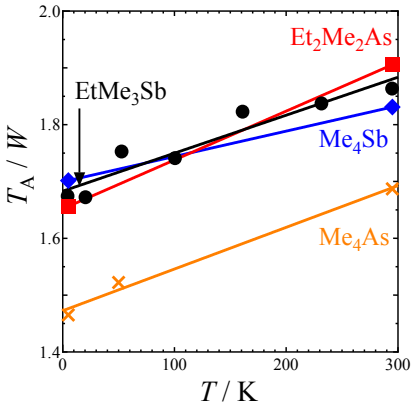

Figure 5. Temperature dependence of T_A/W in the EtMe$_3$Sb, Me$_4$Sb, Et$_2$Me$_2$As and Me$_4$As salts.

References

[1] R. Kato, *Bull. Chem. Soc. Jpn.*, **87**, 355 (2014).

[2] S. Yamashita, T. Yamamoto, Y. Nakazawa, M. Tamura and R. Kato, *Nature Commun.*, **2**, 275 (2011).

[3] M. Yamashita, N. Nakata, Y. Senshu Y, M. Nagata, HM, Yamamoto and R. Kato, T. Shibauchi, Y. Matsuda, *Science*, **328**,1246 (2010).

[4] T. Itou, A. Oyamada, S. Maegawa and R. Kato, *Nature Phys.*, **6**, 673 (2010).

[5] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, G. Saito, *Phys. Rev. Lett.*, **91**, 107001 (2003).

[6] T. Isono, H. Kamo, A. Ueda, K. Takahashi, M. Kimata, H. Tajima, S. Tsuchiya, T. Terashima, S. Uji, H. Mori, *Phys. Rev. Lett.*, **112**, 177201 (2014).

[7] K. Ueda, T. Tsumuraya and R. Kato, *Crystals*, **8**, 138 (2018).