Frustrated electrons on the triangular lattice in a quasi-two-dimentional Mott insulator, Pd(dmit)$_2$ salts


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A series of molecular crystals, β'-type $\chi$[Pd(dmit)$_2$]$_y$ display a rich variety of electronic and magnetic properties [$X$ is a monovalent cation, Et$_3$Me$_x$Z, where $y = 0, 1, 2$, Me = CH$_3$, Et = C$_2$H$_5$, Z = P, As and Sb, and dmit denotes 1,3-dithiol-2-thione-4,5-dithiolate]. At ambient pressure, most of the β'-Pd(dmit)$_2$ salts are Mott insulators associated with the half-filled band due to the strong dimerization of Pd(dmit)$_2$ molecules. Their magnetic properties at low temperatures depend strongly on the cation; EtMe$_2$Sb salt shows a quantum spin liquid (QSL) state, Et$_3$Me$_2$Sb salt shows a nonmagnetic charge ordering state and others exhibit antiferromagnetic ordering. The antiferromagnetic compounds turn to a superconductor by applying a pressure of less than 1 GPa. In the present study, systematic variation of the electronic structures of β'-X[Pd(dmit)$_2$]$_y$ with different kinds of cations are investigated by first-principles density functional theory calculations. The valence bands are analyzed with a molecular orbital (MO) representation of an isolated dimer, [Pd(dmit)$_2$]$_2$. It has been reported that the rich variety of the spin configurations originates from the anisotropy of the approximately isosceles triangular network formed by the dimers. The spacial anisotropy is evaluated by introducing a frustration parameter, i.e., a ratio of inter-dimer transfer integrals $t'/t$. As the parameter gets close to 1.0, the triangular lattice becomes a regular triangular, and the spin-frustration is maximized. However, extended Hückel tight-binding (EHTB) calculations show that $t'/t$ for EtMe$_2$Sb salt which shows a QSL state is 0.91 but that for Et$_3$Me$_2$Sb salt is 1.01 [1]. In general, results by EHTB method depend on the choice of MOs as the basis which are made to calculate the overlap matrices. For the estimations of $t'/t$, the HOMO of Pd(dmit)$_2$ are used, since it has been understood that the bands crossing the Fermi level are built with the antibonding pair of the HOMO. However, the present first-principles calculations for an isolated dimer reveal that two MOs near the Fermi level are composed of the mixture of both HOMO and LUMO of Pd(dmit)$_2$. To derive the frustration parameter from first-principles calculations, transfer integrals are calculated based on an effective dimer model determined by a numerical fitting to the first-principles band structure near the Fermi level with fragment MO scheme. The obtained $t'/t$ value for EtMe$_2$Sb salt is 0.97, which gets closer to the maximum level of spin-frustration of 1.0. In both calculation methods, the cation dependences of the frustration parameters are in fairly good agreement with each other, and well explain experimentally observed magnetic ground states. We also report noticeable differences, in bandwidth and anisotropy of Fermi surface depending on the type of cations in relation to the frustrations.