Frustrated Mott System on the Quasi-Triangular Lattice, Pd(dmit)$_2$ Salts; A First-Principles Study

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Electron correlation and spin frustration on the triangular lattice have attracted much attention recently. A series of molecular crystals, $\beta'$-type $X$[Pd(dmit)$_2$]$_2$ display a rich variety of electronic and magnetic properties [$X$ is a monovalent cation, Et$_y$Me$_{4-y}$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 $\beta'$-Pd(dmit)$_2$ salts are Mott insulators associated with a half-filling band coming from the strong dimerization of Pd(dmit)$_2$ molecules. Their magnetic properties depend strongly on the choice of cation; EtMe$_3$Sb salt shows a quantum spin liquid (QSL) state, Et$_2$Me$_2$P salt has a valence bond solid state, Et$_2$Me$_2$Sb salt shows a non-magnetic charge ordering state and others exhibit antiferromagnetic ordering. Previous studies based on extended Hückel tight-binding calculations concluded that the rich variety of the spin configurations arises from the anisotropy of the triangular networks of the dimers, [Pd(dmit)$_2$]$_2$, in terms of a frustration parameter, i.e., the ratio of inter-dimer transfer integrals $t'/t$ (as defined in Figure). In the present study, to understand the relation between intrinsic magnetic properties and electronic structures, we performed first-principles density-functional theory calculations for $\beta'$-$X$[Pd(dmit)$_2$]$_2$ with different kinds of cations, and found noticeable differences in band width and anisotropy of Fermi surface. Furthermore, frustration parameters are derived from an effective dimer model determined by a numerical fitting to the first-principles band structures near the Fermi level. The differences in the band widths and Fermi surfaces have a tendency which is related to $t'/t$. We also found that $t'/t$ for EtMe$_3$Sb salt, which shows a QSL state, is 0.97, close to the maximum level of spin frustration.

![Image of a graph showing the relation between band width (W) and frustration parameter ($t'/t$). Open circles indicate $t'/t$ value calculated by Hückel method based on HOMO of Pd(dmit)$_2$; Solid circles indicate $t'/t$ value obtained by a numerical fitting to the first principles bands.]

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