First-principles study on structural and electronic properties of Pd(dmit)$_2$ salts under high pressure

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A series of two-dimensional layered organic compounds $\beta'$-type (Cation)[Pd(dmit)$_2$]$_2$ (Cation= Me$_{4-x}$Et$_x$A, x = 0, 1, 2, A= P, As, Sb); Me=CH$_3$, Et=C$_2$H$_5$, dmit = 1,3-dithiol-2-thione-4,5-dithiolate) exhibit a variety of electric and magnetic properties such as pressure induced superconductivity, valence bond solid state and quantum spin liquid state. Most of $\beta'$-Pd(dmit)$_2$ compounds are Mott insulators at ambient pressure associated with a relatively narrow and half-filled conduction band. Previous theoretical and experimental studies for these compounds share the following common features; 1) Pd(dmit)$_2$ unit is strongly dimerized with one negative charge [Pd(dmit)$_2$]$^{2-}$. [1, 2] Bands crossing the Fermi level are mainly composed of the antibonding pair of HOMO in the Pd(dmit)$_2$ molecules. The half-filled bands originate from the strongly dimerized nature of the Pd(dmit)$_2$ molecules. 2) The band width of the anti-bonding HOMO band represents an anisotropy of the two-dimensional quasi triangular networks in terms of the Pd(dmit)$_2$ dimers. The anisotropy of triangular lattices is slightly different from one to another Pd(dmit)$_2$ salt depending on the type of the counter cation. Therefore, pressure effects on electric properties of $\beta'$-type Pd(dmit)$_2$ salts with many kinds of cations have been extensively investigated, and a rich variety of electric properties are reported. For example, Me$_4$Sb and Et$_2$Me$_2$P salts exhibit pressure-induced superconductivity around 1GPa, but these salts shows non-metallic behavior again under higher-pressure. [3] On the other hand, Me$_4$P and Me$_4$As salts have never exhibited a metallic behavior under hydrostatic pressure up to 8GPa. Quite recently, the four-probe electrical resistivity for Me$_4$P and Et$_2$Me$_2$P salts has been measured up to 20GPa by using a diamond anvil cell. [4] The results clearly show that a metallic state appears at greater than 10GPa and 13.6GPa, respectively. It is also noted that these new metallic behaviors disappear when higher-pressure is applied. In the present study, electronic structures of Me$_4$P and Et$_2$Me$_2$P salts at extremely high pressures are investigated using first-principles calculations based on the density functional theory. Structural optimizations for lattice parameters and internal coordinates under hydrostatic pressure up to 20GPa are performed theoretically using the ultra-soft pseudo-potential method with the generalized gradient approximation. We focused on how the crystal structures are changed at high pressures, and demonstrate that many bands overlap with the antibonding HOMO bands near the Fermi level. The possible origins of the phase transitions will be also discussed.