First-principles study of a semi-metallic state in single-component molecular conductor \([\text{Pd(dddt)}_2]\) under pressure

Takao Tsumuraya\(^1\), Hiori Kino\(^2\), Tatsuya Shishidou\(^3\), Reizo Kato\(^4\), and Tsuyoshi Miyazaki\(^1\)

\(^1\)National Institute for Materials Science (NIMS), Tsukuba, 305-0044, Japan.
\(^2\)MANA, National Institute for Materials Science (NIMS), Tsukuba, 305-0044, Japan.
\(^3\)AdSM, Hiroshima University, Kagamiyama, Higashi-hiroshima, 739-8530, Japan.
\(^4\)RIKEN, 2-1 Hirosawa, Wako-shi, 351-0198, Japan.

A single-component molecular conductor, \([\text{Pd(dddt)}_2]\) (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) is insulating at ambient pressure, but it becomes a conducting state under a pressure of 12.6 GPa \([1]\). The electrical resistivity was measured by using diamond anvil cell. By performing structural optimization on the basis of the first-principles calculations, we found anisotropic Dirac cones at the Fermi level under a pressure of 8 GPa. The analysis of the electronic structure clarified that, at ambient pressure, the valence band is predominately composed of the highest occupied molecular orbital (HOMO) of an isolated \([\text{Pd(dddt)}_2]\) monomer, while the conduction band mostly consists of the lowest unoccupied molecular orbital (LUMO). These bands become close to each other under pressure, and the Dirac cones appear, where inter-molecular hybridization between the HOMO and LUMO increases. Such multi-orbital nature is essential for the formation of the Dirac cones.

The pair of Dirac points on two-dimensional (2D) plane \((k_x, k_y)\) are located along a high symmetry line in the Brillouin zone, \(\Gamma-Y\) line when \(k_z = 0\) \([\text{Fig. 1(a)}]\). As \(k_z\) (perpendicular to the 2D plane) increases, the contact points move away from the symmetric line \([\text{Fig. 1(b) and (c)}]\), and the two Dirac points merge, where a gap appears above a finite \(k_z\) value \([\text{Fig. 1(d)}]\). We also considered the spin-orbit coupling (SOC) effect in \([\text{Pd(dddt)}_2]\). It is clear that the SOC induces a tiny band gap at the Dirac points.

Simple explanation on the effect of the SOC in this system will be presented.

![Figure: \(k_z\) dependence of three-dimensional band structure without spin-orbit interaction.]

E-mail: TSUMURAYA.Takao@nims.go.jp