Electronic structure and charge ordering in α-(BEDT-TTF)$_2$I$_3$ by DFT calculations

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α-(BEDT-TTF)$_2$I$_3$ is a well-known two-dimensional organic conductor, which exhibits a metal-insulator transition at T_{CO}=135K. It shows a charge ordered state below T_{CO}, as observed by an X-ray diffusion experiment [1]. The charge ordering of this material has also been studied theoretically using model Hamiltonian [2].

We have theoretically investigated electronic structure and charge ordering in α-(BEDT-TTF)$_2$I$_3$ by DFT calculations. The practical calculations were carried out by means of CRYSTAL09 package with basis set of Gaussian type. We used effective core pseudo-potential for iodine and the basis set of 6-31G type for the other atoms.

Figure 1 shows electronic band dispersion of α-(BEDT-TTF)$_2$I$_3$ calculated with the B3LYP functional for crystal structure at 20K [1]. As shown in the figure, the system is an insulator with a band gap of 0.14 eV. Figure 2 shows schematic representation of a donor layer in α-(BEDT-TTF)$_2$I$_3$. Molecular sites are denoted as A-C, respectively. Table 1 summarizes molecular charges ρ estimated by the Mulliken population analysis. As seem in Table 1, the system has a charge ordering of horizontal stripe with the ordering of molecular charge $\rho_A \sim \rho_B > \rho_{A'} \sim \rho_C$, which is in agreement with experimental results.

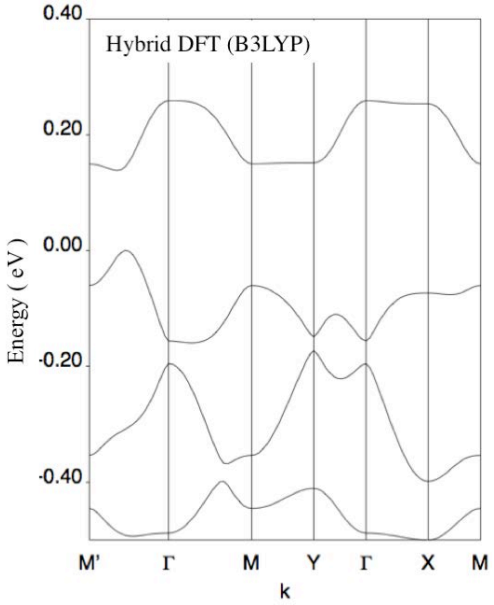

Fig 1. Electronic band dispersion of α-(BEDT-TTF)$_2$I$_3$.

References
[1] T.Kakiuchi et al., J.Phys. Soc. Jpn. **76** (2007) 113702.
[2] Seo, J. Phys. Soc. Jpn. **63** (2000) 805.

Table 1. Molecular charge of α-(BEDT-TTF)$_2$I$_3$ for the crystal structure at 20K.

	ρ_A	$\rho_{A'}$	ρ_B	ρ_C
Pure DFT (BLYP)	0.52	0.37	0.45	0.34
Hybrid DFT (B3LYP)	0.61	0.32	0.51	0.31
Exp. (X-ray) [1]	0.82	0.29	0.73	0.26

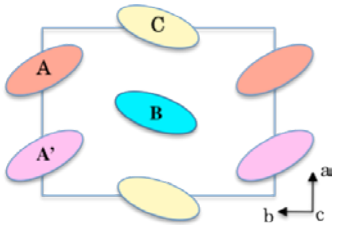

Fig 2. Unit cell structure.