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# First-principles DFT study of charge and anion ordering transitions in molecular conductors

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Accurate first-principles density-functional theory (DFT) calculations have now become possible for systems with large and complex unit cells like many molecular conductors. Although simple tight-binding approaches based on the conducting sublattice have been and will continue to be extremely useful in understanding the basic aspects of the electronic structure of molecular conductors, some features require a more precise evaluation for a comparison with experimental results to be meaningful. A study combining the use of DFT and X-ray diffuse scattering for  $\alpha$ -(BEDT-TTF)<sub>2</sub>KHg(SCN)<sub>4</sub> [1] suggested that the anion sublattice plays a very important role in understanding the charge density wave transition in this system. The modulation in this salt is considerably more involved than those following a standard Peierls mechanism and is triggered by the anion sublattice. Following these findings we have reexamined the nature of the charge and anion ordering transitions in some molecular metals like  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> and several Bechgaard salts. For  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> the calculated charges of the room temperature structure are in good agreement with Raman studies but the variation as a result of the transition is smaller than suggested by the analysis of the X-ray structures. Our analysis [2] suggests again a strong involvement of the anion sublattice in the charge ordering transition coupled with a subtle polarization mechanism involving both the  $\sigma$  and  $\pi$  electrons of the donor as well as the hydrogen bonding at the donor-acceptor interface. The band structure calculated for the system under pressure clearly shows the emergence of a Dirac cone as well as carrier pockets very close to the Fermi level. The anion ordering transitions in several Bechgaard salts are revisited on the basis of these findings with special emphasis on the role of anions [3]. In particular we discuss the low-temperature Fermi surfaces for (TMTSF)<sub>2</sub>X ( $X = \text{ClO}_4$ ,  $\text{NO}_3$  and  $\text{PF}_6$ ), the connection with the superconductivity gap for  $X = \text{ClO}_4$  and show that the transverse component of the SDW for  $X = \text{PF}_6$ ,  $\text{ClO}_4$  and  $\text{NO}_3$  salts are successfully accounted by the nesting vector of these surfaces.

[1] P. Foury-Leylekian, J.-P. Pouget, Y.-J. Lee, R. M. Nieminen, P. Ordejn, E. Canadell, Phys. Rev. B (2010) **82**, 134116.

[2] P. Alemany, J.-P. Pouget, E. Canadell, Phys. Rev. B (2012) **85**, 195118.

[3] P. Alemany, J.-P. Pouget, E. Canadell, manuscripts in preparation.