

## Electronic properties of bulk 3D, 2D Ruddlesden-Popper phases and colloidal quantum dots of halide perovskite semiconductors: recent results

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In the past five years, solution-processed organometallic perovskite based solar cells have emerged as a promising thin-film photovoltaic technology. Presently, the intended optoelectronic applications of this class of materials are in the realm of conventional semiconductors. Meanwhile, in this new family of semiconductors, the spin-orbit coupling is giant and shows up in the conduction band, the band gap is direct with the critical wavevector located at one of the edges of the reference Brillouin zone, and all these distinctive features including lattice strain deserve a specific theoretical framework.<sup>1</sup> Then, the electronic band structure can be modeled using either Density Functional Theory calculations or empirical methods such as the tight-binding model and the multiband **k.p** method provided that accurate descriptions of symmetry properties are proposed.<sup>2</sup> Among others, excitonic effects play a crucial role in ensuring device efficiencies. For instance, in 3D halide-based hybrid perovskites, the strong reduction of the exciton binding energy at room temperature is essential for the operation of photovoltaic devices.<sup>3</sup> The exciton fine structure also plays an important role for the emission properties of colloidal halide perovskite nanostructures.<sup>4</sup> Related 2D Ruddlesden-Popper phases, composed of perovskites layers sandwiched between two layers of large organic cations, have recently demonstrated improved photostability under standard illumination as well as humidity resistance over 2000 hours, affording a conversion efficiency of 12.5 %.<sup>5</sup> In this case, intrinsic quantum<sup>6</sup> and dielectric carrier confinements<sup>7</sup> are afforded by the organic inner barriers, which leads to a stable Wannier exciton at room temperature. However, device efficiencies are essentially related to extremely efficient internal exciton dissociation through edge states in layered 2D Ruddlesden-Popper perovskites, as shown from the investigation of both thin films and small single crystals.<sup>8</sup>

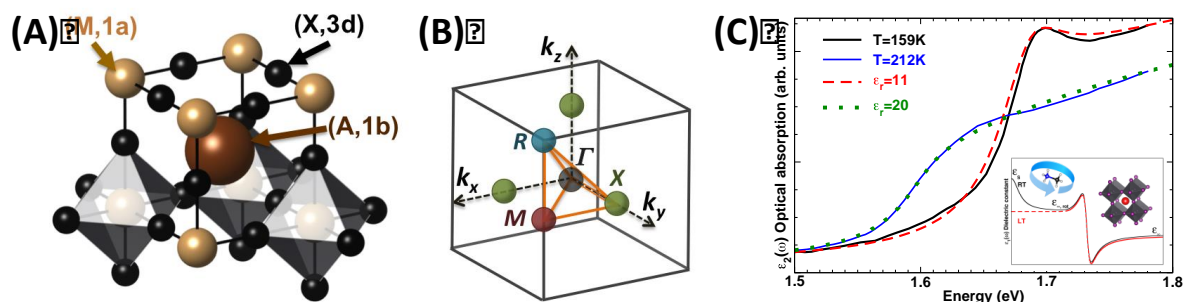


Fig. 1. (A) Real space 3D view of the  $Pm\bar{3}m$  reference cubic crystal structure of metal-halide perovskites of general formulae  $AMX_3$  where A is an inorganic or an organic cation, M a metal and X an halogen. (B) Reciprocal space 3D view showing the first Brillouin Zone (BZ) of the  $Pm\bar{3}m$  space group. Points of high symmetry in the cubic BZ are indicated by conventional letters with  $\Gamma$  denoting the origin of the BZ; X the center of a square face,  $M(1/2,1/2,0)$  a center of a cube edge and  $R(1/2,1/2,1/2)$  a vertex of the cube. (C) Optical absorption spectra of  $CH_3NH_3PbI_3$  highlighting exciton screening. Experimental data recorded at 159 K (black line) and 212 K (blue line) are taken from T. Ishihara, J. of Lum. 1994, 60&61, 269. Theoretical spectra for bound and continuum pair states are computed considering two-particle wave function and effective mass equations for electron and hole.

## References

- <sup>1</sup> J. Even et al, J.Phys. Chem Lett. 2015, J. Phys. Chem. C 2015, M. Kepenekian et al, ACS Nano 2015
- <sup>2</sup> S. Boyer-Richard, J. Phys. Chem. Lett. 2016
- <sup>3</sup> H.H. Fang et al, Adv. Func. Mat. 2015, W. Nie et al, Nature Comm. 2016, H. Diab et al J. Phys. Chem. Lett. 2016, A. Neukirch et al, Nanoletters 2016
- <sup>4</sup> M. Fu et al, Nanoletters 2017
- <sup>5</sup> H. Tsai et al, Nature 2016
- <sup>6</sup> J. Even et al, Phys. Rev. B 2012, ChemPhysChem 2014, L. Pedesseau et al, ACS Nano 2016, C. Stoumpos et al, Chem 2017
- <sup>7</sup> D. Saponi et al, Nanoscale 2016, M. Smith et al, Chem. Sci. 2017
- <sup>8</sup> J. C. Blancon et al, Science 2017

The project leading to this work has received funding from the European Union's Horizon 2020 program, through a FET Open research and innovation action under grant agreement No 687008.