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Physical properties of 3D and 2D Ruddlesden-Popper halide perovskite semiconductors

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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 deserve a specific theoretical framework.[1] 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.[2] 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.[1,3] 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 %.[4] In this case, intrinsic quantum[5] and dielectric carrier confinements[6] are afforded by the organic inner barriers, which leads to a stable Wannier exciton at room temperature.

References

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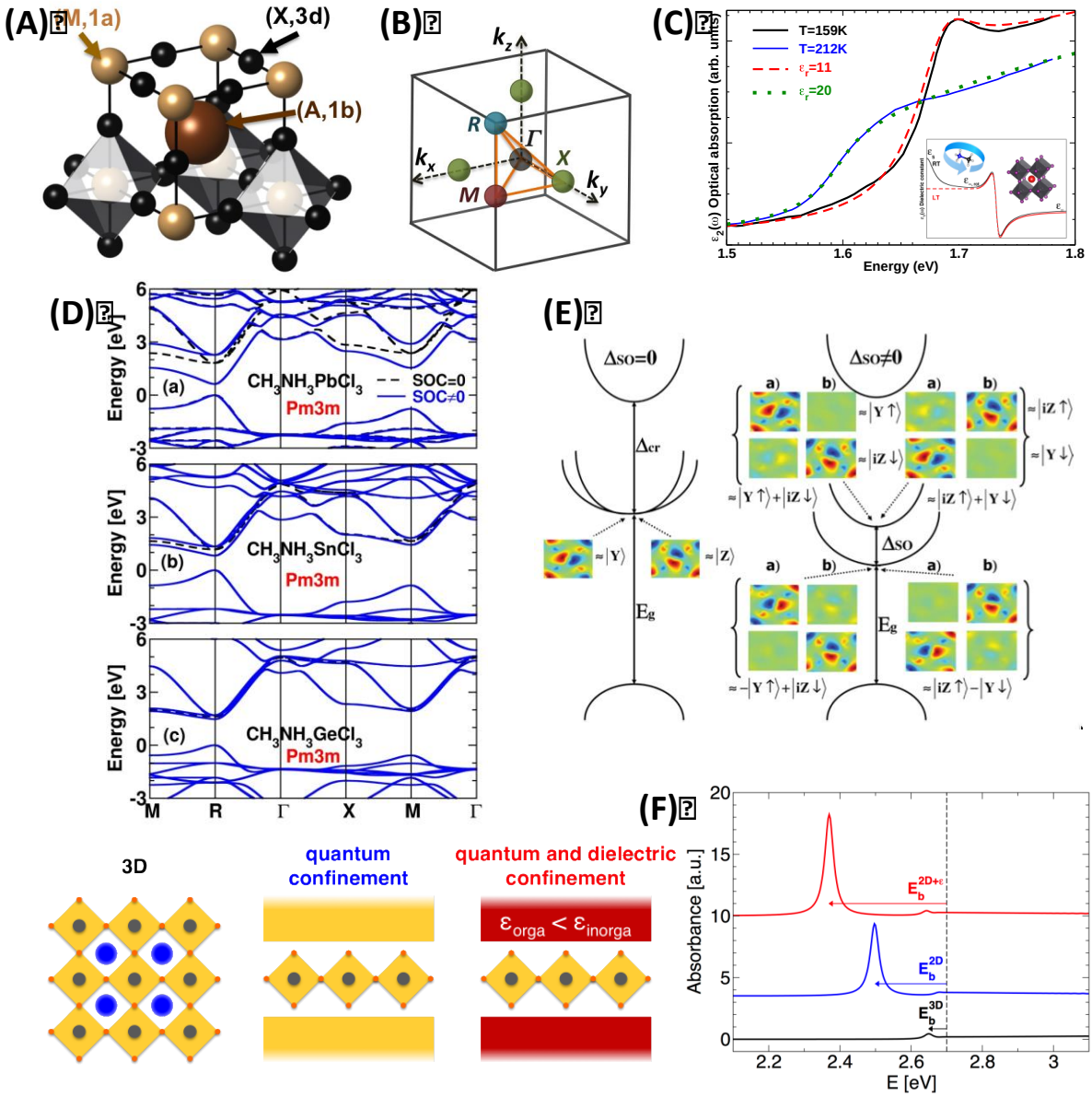

Fig. 1. (A) Real space 3D view of the Pm$\bar{3}$m reference cubic crystal structure of metal-halide perovskites of general formulae AMX_3 where A is an inorganic or an organic cation, M a metal and X an halogen. (B) Reciprocal space 3D view showing the first Brillouin Zone (*BZ*) of the Pm$\bar{3}$m space group. Points of high symmetry in the cubic *BZ* are indicated by conventional letters with *Γ* 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. (D) Electronic band diagrams for the high temperature cubic phases (Pm$\bar{3}$m) of $CH_3NH_3MCl_3$: (a) M=Pb (b) M=Sn and (c) M=Ge, calculated at the LDA level of theory without (black dashed lines) and with (blue straight lines) Spin Orbit Coupling (SOC). (E) Schematic representation the electronic band diagram without (Δ_{SO} = 0) and with ($\Delta_{SO}\neq0$) the SOC interaction. Δ_{cr} represents the anisotropy of the crystal field and E_g the band gap energy. The real (a) and imaginary (b) parts of the complex spinorial components of the CBM1 and CBM2 states are represented for the 2D hybrid perovskite[pFC6 H5 C2 H4 NH3]2 PbI4, with the spin up component plotted on top of the spin down component. (F) Optical absorption computed using a **k·p**/ BSE approach for a model hybrid perovskite considered as a 3D material with ε_∞ = 5.0 (black line), a 2D material with only quantum confinement and ε_∞ = 5.0 (blue line), a 2D material with both quantum and dielectric confinement (red line).