

Electronic properties of 2D hybrid organic/inorganic perovskites for optoelectronic applications

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Two-dimensional layered organic-inorganic perovskite semiconductors exhibit a strong coupling of the exciton in a dielectric cavity. Density functional theory (DFT) is used to study the structural, electronic and vibrational properties of various Hybrid Organic Perovskite (HOP) solids. Careful study of band edge electronic states confirms the 2D character of the electronic and optical (TE) properties. The dielectric confinement associated to the organic layer plays an important role to enhance excitonic binding. More, the optoelectronic properties are essentially associated to a direct transition and three reference Bloch states. A general 3x3 k.p model Hamiltonian is then proposed. It is extended to include spin-orbit coupling effects. A reverse band ordering is predicted by comparison to standard semiconductor compounds. The conduction band edge is indeed related to the vectorial and reducible representation.

Key words: Organic-inorganic perovskite semiconductors, Density functional theory, electronic and optical (TE) properties

I. INTRODUCTION

Hybrid Organic/inorganic Perovskite solids (HOP) have attracted increasing interest over the past decade due to their potential applications. In particular, hybrid nanomaterials are expected to offer a way towards enhanced performances of optoelectronic devices [1]. The versatility of the organic part affords the possibility of fine tuning material's properties. Among them, self-assembled (SAHOP) layered (2D) structures have recently shown enhanced non-linear optical properties in microcavities [2]. Moreover, such compounds have also been suggested as a novel class of materials with improved photo-conversion efficiency, especially for organic/inorganic perovskites based on relatively small organic cations [3, 4]. Recently, DFT calculations have been performed by Even et al [5] on a prototype Single Crystal Hybrid Organic layered Perovskite (SCHOP) and combined with symmetry analysis of the band edge Bloch states. In particular, the ordering of the band edge states is found reversed compared to tetrahedrally bonded conventional semiconductor structures. Moreover, from the computation of

SCHOP Kane's energy parameters, we have explained the underlying mechanism of the optical activity resulting from a subtle interplay between the electronic structure and exciton binding energies. Interestingly, it has also been shown that the spin-orbit coupling (SOC) induces a large splitting of the conduction bands, in comparison to the splitting of the valence bands of conventional semiconductors.

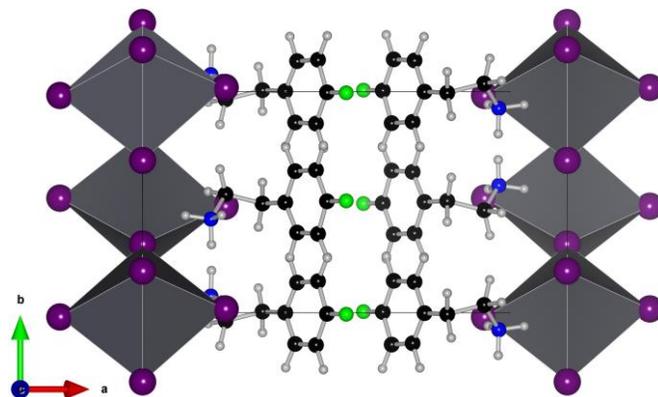


Fig. 1. Crystal structure of the 4F-PEPL.

II. COMPUTATIONAL DETAILS

Total energy DFT calculations are carried out by means of the *ab initio* ABINIT code [6] within the PBE gradient correction for exchange [7]. A plane-wave basis set with an energy cutoff of 950 eV is used to expand the electronic wavefunctions. The reciprocal space integration is performed over a 1x4x4 Monkhorst-Pack grid [8, 9]. The energy is computed from the linear response method [6] and convergence is accurately reached with tolerance on the residual potential which stems from differences between the input and output potentials. The spin-orbit coupling (SOC) interaction is taken into account. Although numerous SAHOP systems with lead-halides have been studied, only a few related crystallographic

structures of SCHOP are known precisely. In fact, growth of monocrystals for X-ray diffraction is difficult because of the lattice disorder and strain induced by the organic molecule that plays a fundamental role in the dielectric confinement. We have performed electronic band-structure calculations with many body corrections within the GW approximation [10, 11] where G is the Green function and W is the screened interaction.

III. RESULTS

We consider the mono-crystalline 4F-PEPI as material model (Fig.1). No electronic energy dispersion occurs along the Γ -X direction (characterizing the stacking axis in real space), which is an inherent consequence of the dielectric mismatch between PbI_4 and the organic sheet. As a result, the density of states close to the band gap exhibits a reduced 2D dimensionality in connection with the observed 2D character of excitons in the SAHOP counterpart [12].

The DFT electronic structure also reveals a direct band-gap character in agreement with the observed luminescence at room temperature [2, 13]. The fundamental transitions with and without SOC are of 1.2 and 2.0 eV respectively, to be compared to the measured value of 2.35eV. The band gap is known to be underestimated in DFT ground state computation. This deficiency can be corrected by including many-body effects (GW self-energy correction for the band gap and Bethe Salpeter equation resolution for the exciton) but such calculations are beyond available computational resources for large systems. Despite this shortcoming, the overall conclusions related to the energy band dispersions and symmetries are reliable and can help to build accurately semi-empirical Hamiltonians (e.g. in k.p theory) where detailed information of Bloch states and selection rules are required. Similar conclusions can be drawn from the electronic band structure of the monoclinic crystal of $[\text{C}_5\text{H}_{11}\text{NH}_3]_2\text{PbI}_4$. It is a representative member of a large SCHOP and SAHOP family with alcane chains in the organic layer [14-17].

At the Γ -point, the ground state transitions without SOC mainly involve three active Bloch levels: a non-degenerate level for the valence-band maximum (VBM) and two nearly degenerate levels for the conduction-band minimum. These two bands belong to the vectorial representation. The third member function of the vectorial representation is splitted by the strong crystal field. A further small degeneracy lifting is associated to the low temperature symmetry breaking and strain into the unit cell. The fundamental transition of SCHOP thus displays a nearly-perfect transverse electric character (TE), further enhanced in SAHOP by orientational disorder introduced by the organic layer [15]. It is similar to conventional zinc-blende quantum wells with D_{2d} point symmetry or anisotropic wurtzite bulk compounds with C_{6v} point symmetry. Symmetry and ordering of the Bloch states are however reversed for SCHOP.

IV. CONCLUSIONS

Based on DFT calculations and symmetry analysis of the Bloch states, the ordering of band edge states and the optical activity including Kane's energy of a prototype SCHOP crystal have been investigated. The significant value of the Kane's energy associated with the large excitonic binding energy reported for the corresponding SAHOP account for the

attractive optical responses evidenced in this class of hybrid materials. Additional insight can be gained from a k.p model starting from symmetry properties of the Bloch states which can efficiently model excitonic and spin-orbit couplings.

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