Switching Electronic Properties in a 2D CrI_2/α-In_2Se_3 Heterostructure via Ferroelectric Polarization

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In this work, we explore, by means of first-principles calculations based on density functional theory (DFT), the structural, electronic, and magnetic properties of a CrI_2 monolayer and its interaction with a ferroelectric monolayer of In_2Se_3. We analyse how the strain induced at the interface stabilizes a Néel-type antiferromagnetic configuration, which is absent in the isolated CrI_2 monolayer. We further examine the influence of the In_2Se_3 polarization on magnetism and the interfacial charge transfer. Our results show that when the ferroelectric polarization of the In_2Se_3 is reversed, the band alignment of CrI_2/In_2Se_3 switches from a straddling (type I) to a staggered (type II) configuration, and the band gap changes from an indirect gap (0.89 eV) to a direct gap (0.65 eV). These findings reveal a polarization switchable band alignment mechanism, positioning the CrI_2/In_2Se_3 heterostructure as a promising candidate for optoelectronic applications.

Motivation

- α-In_2Se_3 exhibits robust ferroelectricity at the monolayer limit, offering promising advances in device miniaturization [1].
- Controlling band alignment using electric fields allows the exploration of novel optoelectronic functionalities.
- Magnetoelastic coupling in 2D heterostructures combining ferroelectric (FE) and magnetic monolayers enables the design of controllable electronic devices.

Can the electronic properties of a transition metal dihalide be controlled by switching the polarization of the ferroelectric monolayer?

Computational Details

DFT calculations within the PAW method, as implemented in VASP [2]:

- Generalized gradient approximation (**GGA**) with the Perdew–Burke–Ernzerhof (**PBE**) exchange–correlation functional.
- **DFT+U** approach in Dudarev's approximation was adopted for a better treatment of d-electrons of Cr atoms with U=7 eV
- 500 eV energy cutoff on the plane wave basis.
- Valence electrons: **In** ($4d^{10}\,5s^2\,5p^1$), **Se** ($4s^2\,4p^4$), **Cr** ($3d^5\,4s^1$) y **I** ($5s^2\,5p^5$).
- Structural relaxation: forces on each ion are less than 0.005 eV/Å.
- Grimme's **DFT-D3** scheme for van der Waals interaction and dipolar correction are taken into account.

Pristine CrI_2: strain effects

- CrI_2 is a transition metal dihalide that, in the monolayer form, has a magnetic moment of 4 µB per Cr. Its in-plane lattice constants are **a** = 4.04 Å and **b** = 4.27 Å, with an angle of 118°.

- **(a)** The fundamental structure of CrI_2 exhibits a **Jahn–Teller** distortion that breaks the lattice symmetry, generating four first neighbors at a distance **d1** and two second neighbors at a distance **d2**. The ground magnetic state is FM **(b)**.

- **(d)** A Heisenberg model was constructed considering first and second neighbors interactions (J_1 and J'_1, respectively).

$$H = -\sum_{\langle ij\rangle}(J_1 + J'_1)\hat{s}_i \cdot \hat{s}_j |s|^2 + E_{others}$$

Estructura	J_1 (meV)	J'_1 (meV)
Fundamental	2.52	0.39
Con Strain	2.15	−0.24
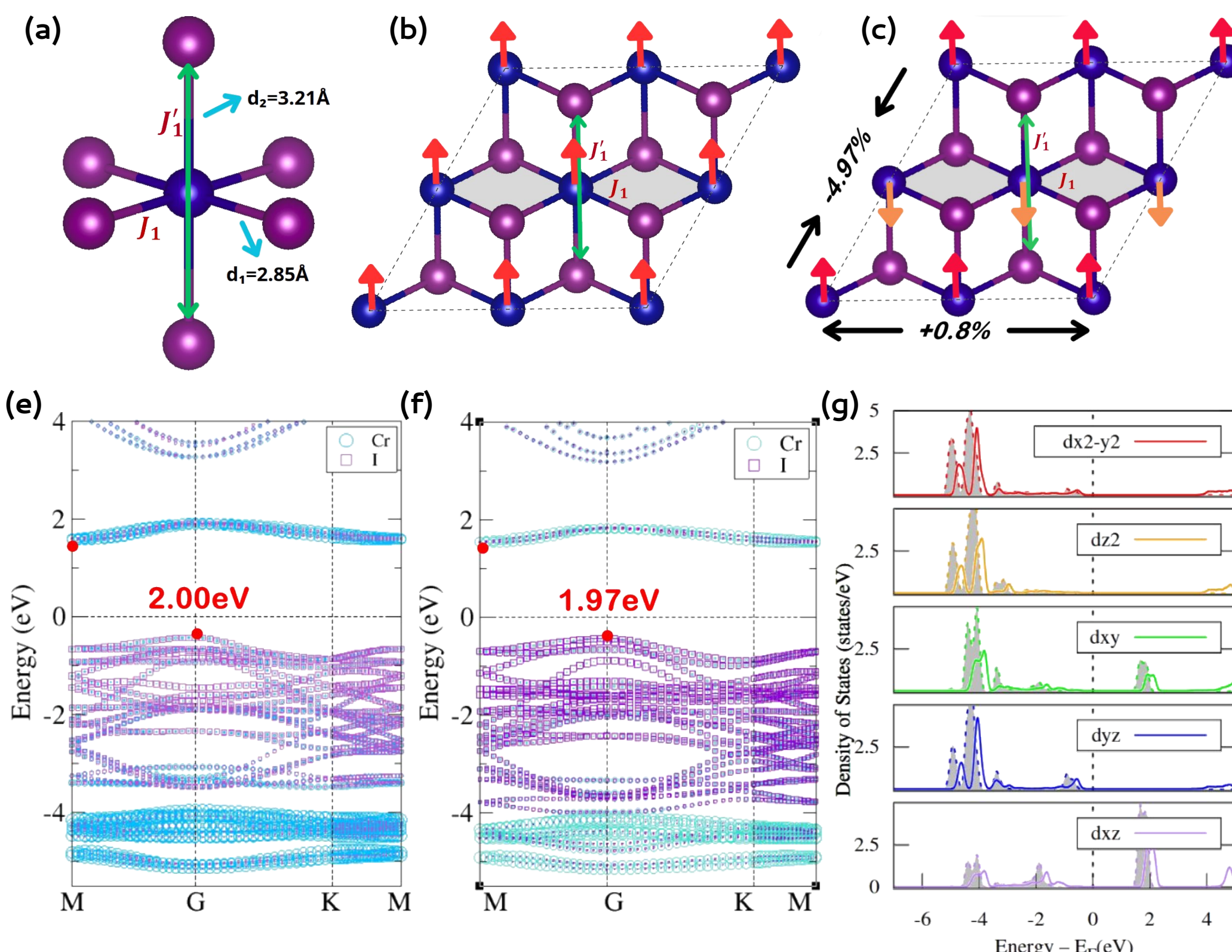
(c) To match the CrI_2 monolayer with In_2Se_3 (lattice parameter a = 4.07 Å), a biaxial strain was applied: **+0.8%** along the a direction (tensile) and **−4.97%** along the b direction (compressive).

Under these conditions, the CrI_2 monolayer transitions to a Néel-type antiferromagnetic (**AFM–Néel**) order[3].

The nearest-neighbor distances after strain are d_1 = 2.85 Å and d_2 = 3.09 Å.
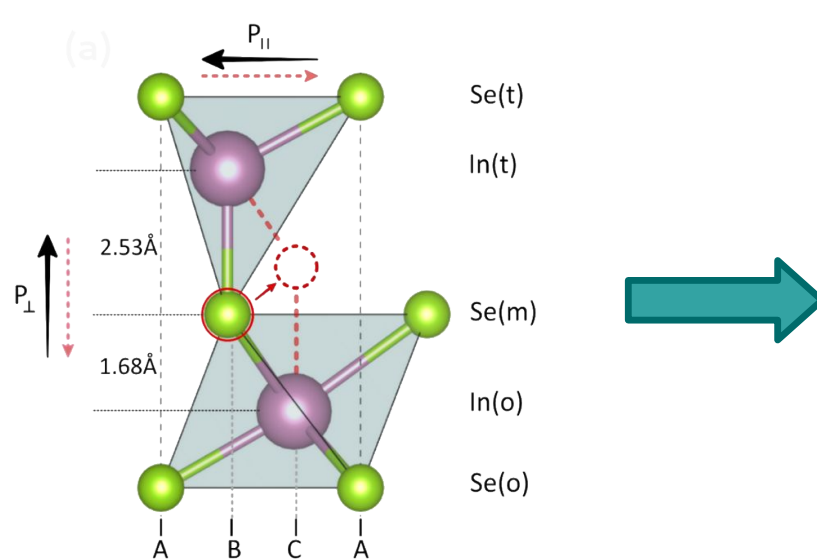
(e) The band structure exhibits an indirect band gap of 2 eV and shows no significant changes when the system is subjected to strain **(f)**.

(g) In the orbital-projected density of states (PDOS) of **Cr**, a general shift of the states can be observed in the strained structure with respect to the pristine one (shaded regions).
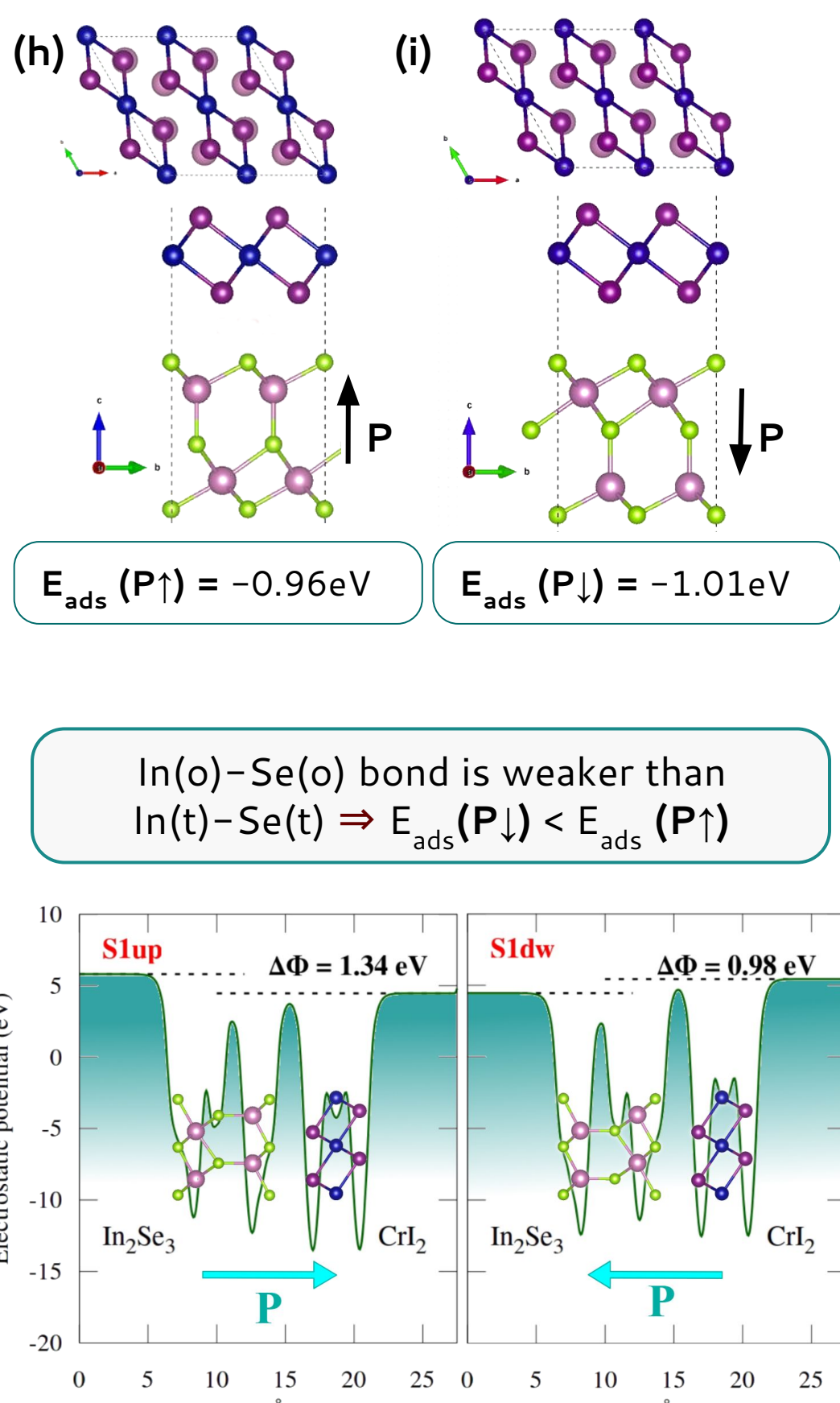
CrI_2/In_2Se_3 Heterostructure

Possible adsorption sites on the surface of In_2Se_3 were studied. the most favorable configuration was found to be the (h), (i) arrangement.

In the α-In_2Se_3 monolayer, surface In atoms adopt tetrahedral coordination (**In(t)**) under P↑ polarization, while they switch to octahedral coordination (In(o)) under P↓ polarization.

| E_{ads} (P↑) = −0.96 eV | E_{ads} (P↓) = −1.01 eV |

In(o)–Se(o) bond is weaker than In(t)–Se(t) $\Rightarrow$ E_{ads}(P↓) < E_{ads}(P↑)

The electrostatic potential of pristine In_2Se_3 is 1.20 eV. In the CrI_2/In_2Se_3 heterostructure, this potential increases (P↑) or decreases (P↓) with the substrate polarization, indicating that the electronic properties of CrI_2 can be tuned by the ferroelectric polarization.
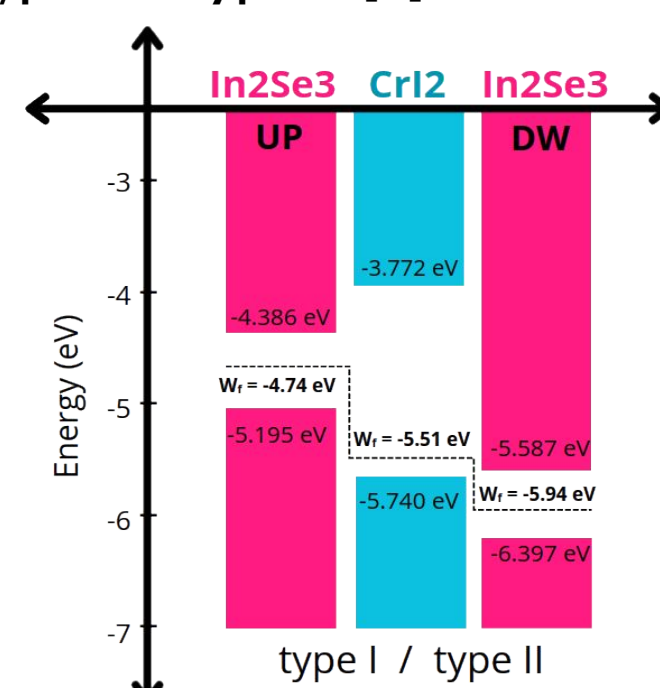
Band alignment in CrI_2/In_2Se_3

The band structure of the CrI_2/In_2Se_3 heterostructure depends on the polarization of In_2Se_3:
When the polarization is reversed from **P↑** to **P↓**, a reduction in the band gap is observed, accompanied by a transition from an indirect to a direct band gap.

This evolution is associated with a change in the band alignment, from ty**pe** I to **type** II [4].

As a consequence, the carriers can shift from being confined within a single material to becoming spatially separated across different layers — a key effect for photocatalysis, charge separation, and the design of 2D optoelectronic devices controllable by electric fields.

This result demonstrates that the electronic properties of the heterostructure can be reversibly modulated.

Bibliography and Acknowledgments
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