

## Supplementary Information for

# Defect tolerance in CsPbI<sub>3</sub>: Reconstruction of potential energy landscape and band degeneracy in spin-orbit coupling

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### **Validity of automatic band edge alignment for HSE and HSE+SOC calculations**

In pseudopotential plane-wave methods, the reference of all eigenvalues is taken to be the average electrostatic potential, which is determined by the charge density  $\rho(r)$  of the unit cell. The change in  $\rho(r)$  due to the addition of SOC is small. We checked this by using PBE functional. We performed PBE+SOC calculation to generate the  $\rho(r)$  of the unit cell and then use this  $\rho(r)$  to calculate the eigenvalues using non-self-consistent PBE calculation. It was found that the change in the positions of VBM and CBM compared with self-consistent PBE calculation is only 0.03 and 0.07 eV, respectively. The change in band gap is only 0.04 eV. These small uncertainty in the alignment by adding the SOC will not affect our discussion in this work. However, it should be noted that the automatic alignment used above is only applicable when the unit cell parameters are all the same. Otherwise, the change in lattice constants can alter the reference energy more significantly and renders the alignment less accurate.

## Evaluation of the shift of the CBM and defect level by spin-orbit coupling

The spin-orbit coupling (SOC) Hamiltonian reads

$$H_{SOC} = \hat{\lambda} \mathbf{l} \cdot \mathbf{s} = \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{\partial V(r)}{\partial r} \mathbf{l} \cdot \mathbf{s} \quad (\text{S1})$$

where  $\mathbf{l}$  ( $\mathbf{s}$ ) is the orbital angular momentum (spin angular momentum) operator.

For  $p$  orbital, there are six states with the orbital electronic angular momentum  $m = 1,$

$0, -1$  and the two possible spin states  $m_s = \pm 1/2$ , which are labeled as  $p_1, \bar{p}_1, p_0, \bar{p}_0,$

$p_{-1}$  and  $\bar{p}_{-1}$ , respectively. For an isolated atom with  $p$  orbitals, the matrix of the SOC

Hamiltonian is calculated in this six-state basis as

$$H_{SOC} = \frac{\lambda}{2} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & \sqrt{2} & 0 & 0 & 0 \\ 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{2} & 0 \\ 0 & 0 & 0 & \sqrt{2} & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{2} \end{pmatrix} \quad (\text{S2})$$

where  $\lambda$  is the SOC constant. Then by diagonalization of Eq. (S2), we have two

eigenvalues as  $-\lambda$  and  $0.5\lambda$ . Thus, the CBM shift is  $-\lambda$  and the total split of CB is

$1.5\lambda$ . According to Eq. (S2),  $\delta E^{(1)} = \langle p_z | H_{SOC} | p_z \rangle = 0$ . Note that this result will not

change if  $|p_x\rangle$  or  $|p_y\rangle$  is used for  $|p_z\rangle$ . The matrix element  $\langle p_z | \lambda \mathbf{l} \cdot \mathbf{s} | p_i \rangle$  in the

main text of Eq. (3) can be obtained from Eq. (S2).

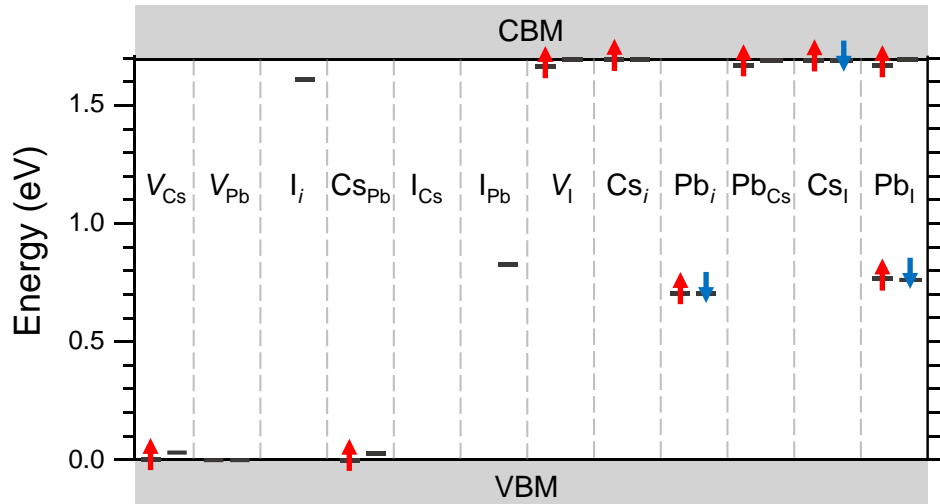


Figure S1 The Kohn-Sham levels of intrinsic defects with neutral charge in CsPbI<sub>3</sub> calculated by HSE+SOC. The arrows denote directions of the magnetic moment of the occupied states along the  $z$  direction. Note that no in-gap state appears for I<sub>Cs</sub>.

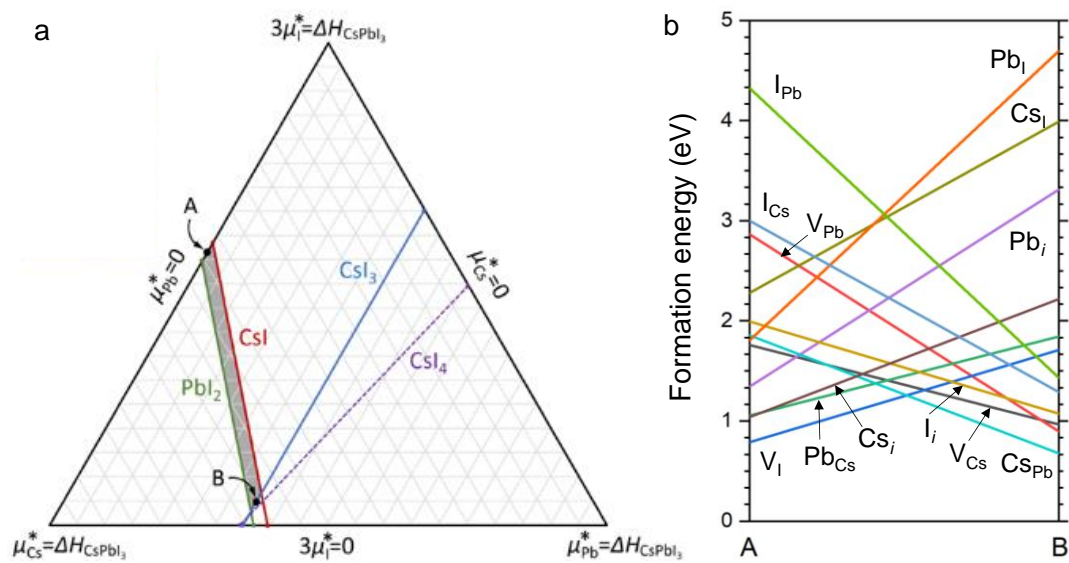


Figure S2. (a) Atomic potential space spanned by  $\mu_{\text{Cs}}$ ,  $\mu_{\text{Pb}}$ , and  $\mu_{\text{I}}$ . Point A and B denote the I-poor and I-rich conditions, respectively. (b) Formation energy of intrinsic neutral defects in  $\text{CsPbI}_3$  at varying conditions between I-poor (A) and I-rich (B).

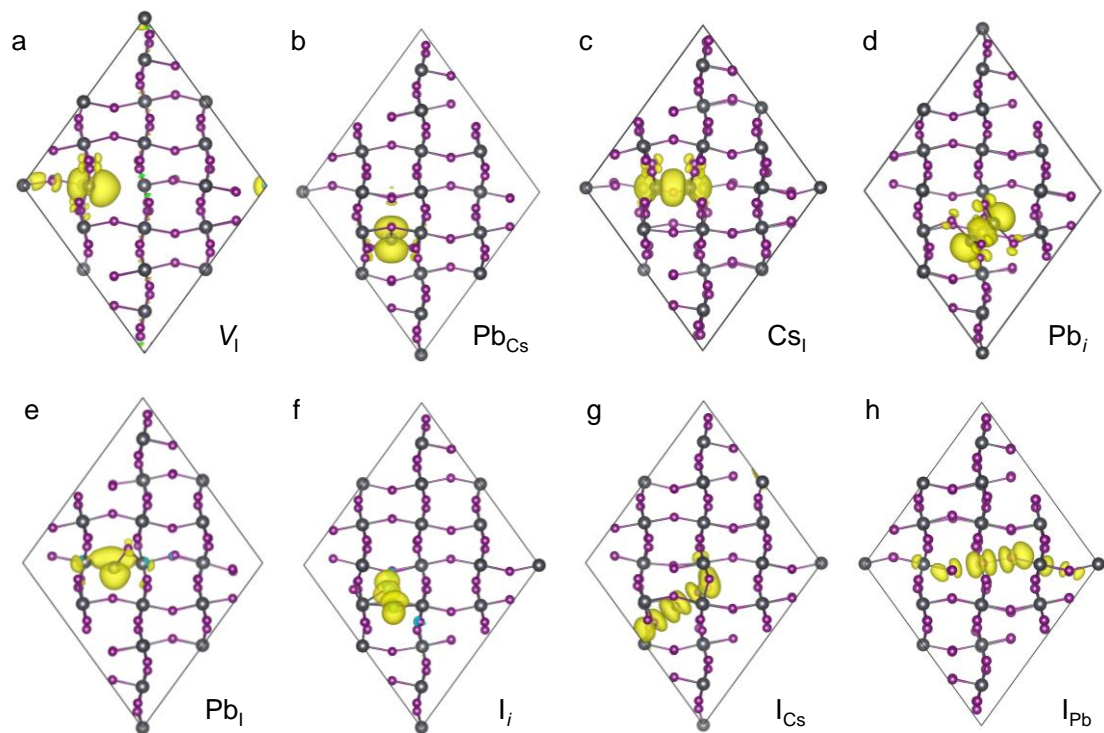


Figure S3 Charge density of the localized defect levels for intrinsic defects in CsPbI<sub>3</sub> calculated by HSE without SOC.

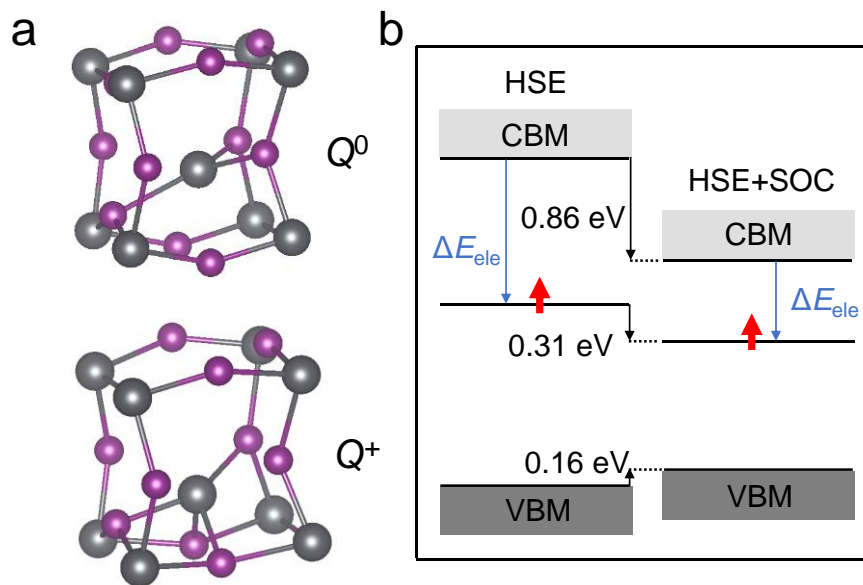


Figure S4. (a) Stable structures of the antisite defect  $\text{PbCs}^0$  without (upper, denoted as  $Q^0$ ) and with SOC (lower, denoted as  $Q^+$ ). (b) Comparison of the CBM, VBM and defect Kohn-Sham level without and with SOC, both of which were calculated based on the  $Q^0$  structure. The electronic energy gain by forming the structural distortion of  $Q^0$  relative to  $Q^+$  was also compared.

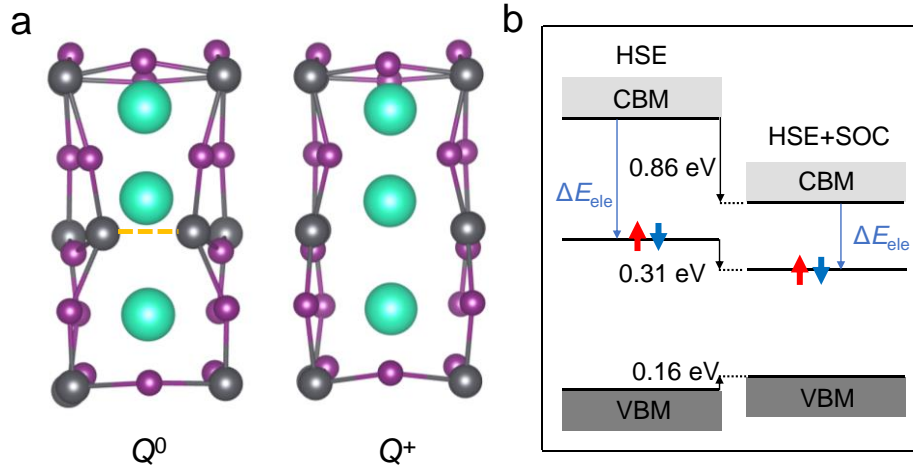


Figure S5. Stable structures of the antisite defect  $\text{CsI}^0$  without (left, denoted as  $Q^0$ ) and with SOC (right, denoted as  $Q^+$ ). (b) Comparison of the CBM, VBM and defect Kohn-Sham level without and with SOC, both of which were calculated based on the  $Q^0$  structure. The electronic energy gain by forming the structural distortion of  $Q^0$  relative to  $Q^+$  was also compared.



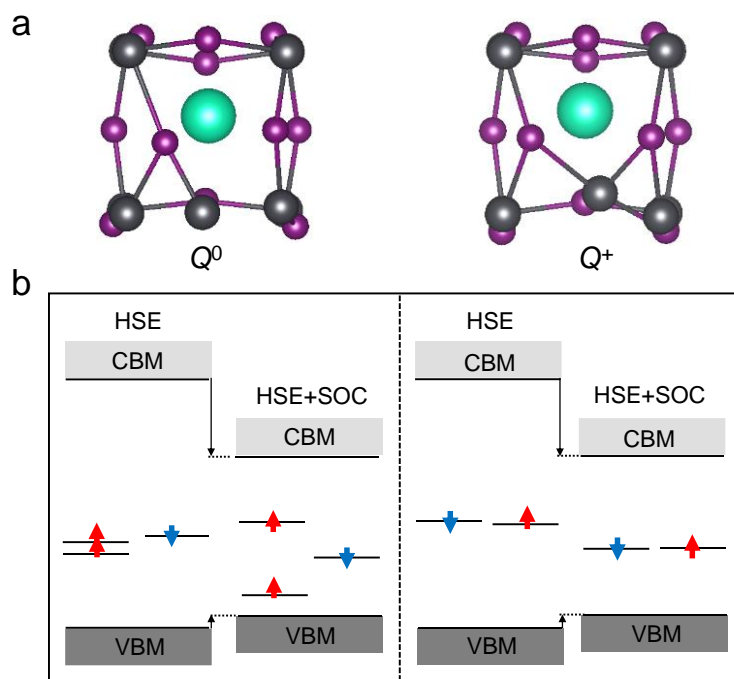


Figure S6. Stable structures of the antisite defect  $\text{Pb}_I^0$  without (left, denoted by  $Q^0$ ) and with SOC (right, denoted by  $Q^+$ ). (b) Left: Comparison of the CBM, VBM and defect Kohn-Sham level without and with SOC, both of which were calculated based on the  $Q^0$  structure. Right: Similar to Left but based on the  $Q^+$  structure.

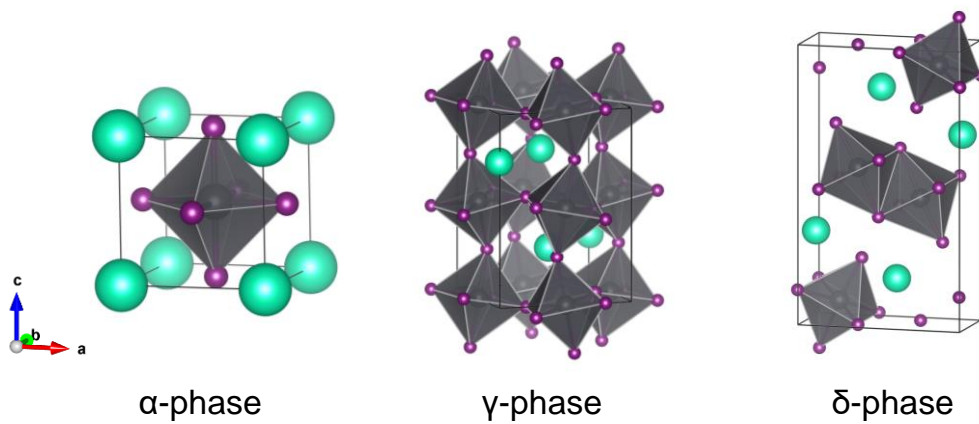


Figure S7. Structures of different phases of CsPbI<sub>3</sub>.

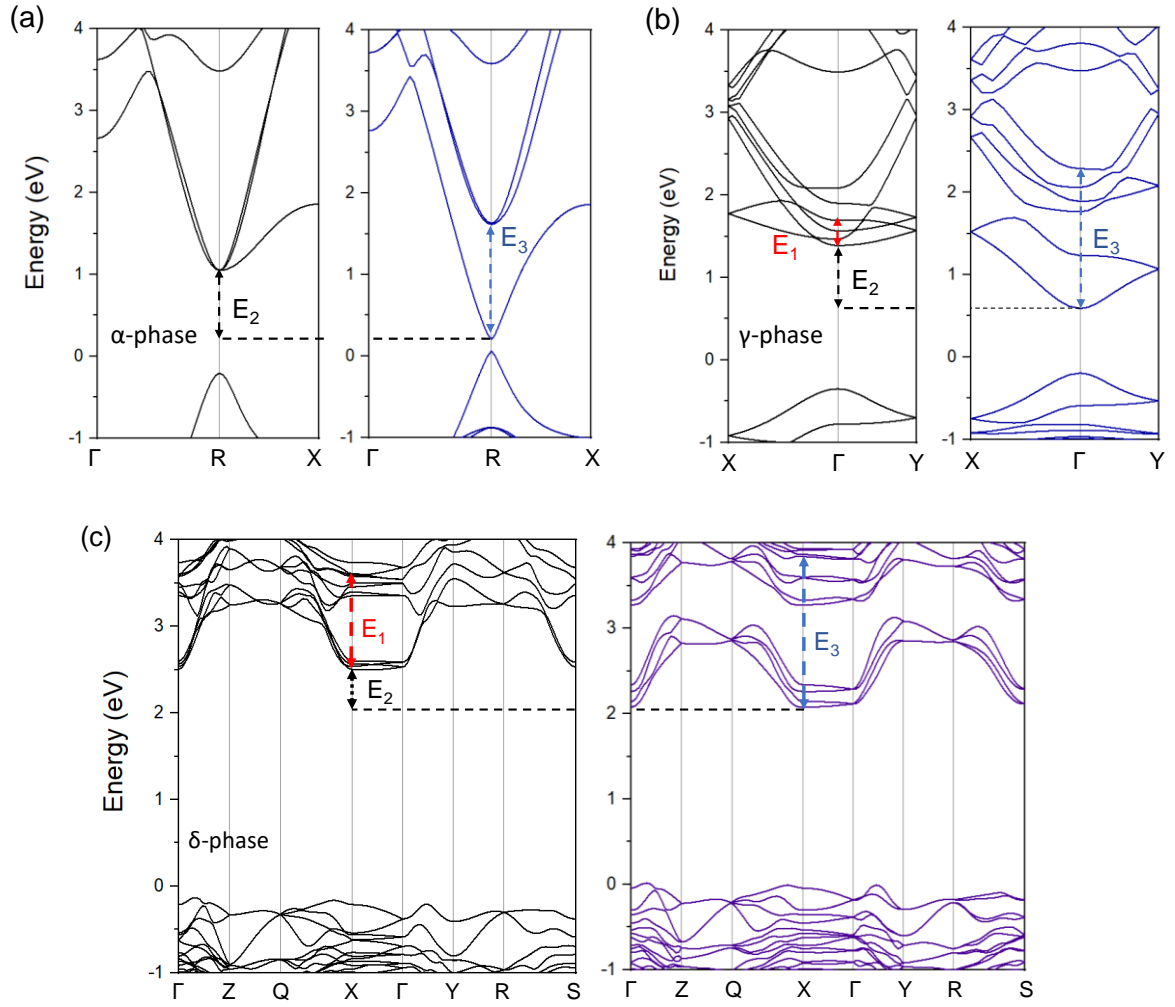


Figure S8. Band structures of  $\alpha$ - (a),  $\gamma$ - (b) and  $\delta$ - (c) phases  $\text{CsPbI}_3$ . The left (right) one in each figure is the result calculated without (with) SOC. The label  $E_1$  denotes the initial splitting of CBM originated from the low-symmetry structures,  $E_2$  denotes the shift of CBM by SOC and  $E_3$  denotes the total splitting of CBM after inclusion of SOC. Then the CBM splitting induced by SOC is calculated as  $E_3 - E_1$ .