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Intrinsic defects in primary halide perovskites: A first-principles study of the thermodynamic trends

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Defects in halide perovskites play an essential role in determining the efficiency and stability of the optoelectronic devices based on these materials. We present a systematic study of intrinsic point defects in six primary metal halide perovskites, MAPbI3, MAPbBr3, MAPbCl3, FAPbI3, CsPbI3, and MASnI3 (where MA denotes methylammonium and FA denotes formamidinium), based upon density functional theory calculations. Within a single computational scheme, using the SCAN+rVV10 functional, we compare the impact of changing anions and cations on the defect formation energies and the charge state transition levels in the six compounds, and identify the physical origins underlying the observed trends. Dominant defects in the lead iodide compounds are the A+ cation interstitials (A = Cs, MA, FA), charge-compensated by I− interstitials or lead (2−) vacancies. In the lead bromide and lead chloride compounds, halide interstitials are most prominent, and for MAPbCl3, the chlorine vacancy also becomes important. These trends can be explained in terms of the changes in electrostatic interactions and chemical bonding upon replacing cations and anions. Defect physics in MASnI3 is strongly dominated by tin (2−) vacancies, promoted by the easy oxidation of the tin. Intrinsically, all compounds are mildly p doped, except for MASnI3, which is strongly p doped. All acceptor levels created by defects in the six perovskites are shallow. Some defects, halide vacancies and Pb or Sn interstitials in particular, can create deep donor traps. Although such traps might hamper the electronic behavior of MAPbCl3, in bromine- and iodine-based perovskites their equilibrium concentrations are too small to affect the materials’ properties.

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I. INTRODUCTION

Metal halide perovskites are emerging semiconducting materials for optoelectronic applications, with a general composition AMX3, where A = methylammonium (MA), formamidinium (FA), or Cs; M = Pb or Sn; and X = I, Br, or Cl [1–3]. Applications of these materials in photovoltaics have drawn particular attention, as the photovoltaic conversion efficiency of metal halide perovskite solar cells (PSCs) has grown spectacularly from 3.8% in 2009 [4] to 25.5% in 2020 [5]. On the downside, the materials are hampered by long-term instabilities [6–14], leading to severe loss of solar cell efficiency [15–21]. Because of the soft nature of the perovskite crystals, formation of defects is unavoidable during the materials’ growth and device operation, and the materials’ degradation is likely triggered by these defects [18–27].

One of the widely employed strategies for defect management is composition engineering [16,22]. PSCs can achieve a higher efficiency and be more stable through the use of a mixture of cations and/or anions within the perovskite structure [28–32]. By finding the right mix, the formation of defects can be suppressed, and the number of charge-carrier recombination centers can be reduced [1,16,22,30]. However, composition engineering often results in several intertwined changes that also impact the structure of the final perovskite films, leaving its exact function in defect control ambiguous. To achieve a better fundamental understanding, characterizing the precise nature of the defects becomes an important task.

Due to the limitations of experimental techniques in identifying different defect types or in characterizing their microscopic structure [16,26,33–35], the study of defects has greatly benefited from computational modeling based on density functional theory (DFT), in particular for the elementary point defects [36–49]. Many studies have focused on a single perovskite material AMX3 [36–38,40,43–47], or on a set of materials where either the anion X or the cation A or M is varied [39,41,42]. Such studies have been performed using a diversity of structural models and computational methods, specifically DFT functionals, which makes it challenging to compare the results of different studies quantitatively.

Defect levels and thermodynamics can be sensitive to the DFT functional used, for instance [37,50]. In a previous study on point defects in MAPbI3 we have observed that, in order to obtain accurate results for defect properties, it is important to use the same functional for both geometry and electronic structure optimizations in a self-consistent way [50]. Moreover, in the same study we have concluded that including van der Waals (vdW) terms in the functional is essential. These long-range, nonbonding interactions have an opposite effect...
on the formation energies of the two quintessential types of point defects, vacancies and interstitials.

In this work, we calculate and compare defect properties of six primary metal halide perovskites, MAPbI₃, MAPbBr₃, MAPbCl₃, FAPbI₃, CsPbI₃, and MASnI₃, using a single computational technique, in order to systematically study the effect of different compositions on the defect thermodynamics. The changes in the defect formation energies and the charge state transition levels, upon variation of the X anion, A cation, and M cation, are compared and analyzed. The dominant defects in each perovskite are identified and their electronic nature is examined.

II. COMPUTATIONAL APPROACH

A. DFT calculations

DFT calculations are performed with the Vienna Ab Initio Simulation Package (VASP) [51–53], employing the SCAN+rVV10 [54] functional for electronic calculations and geometry optimization. This functional combines the strongly constrained and appropriately normed (SCAN) [55] meta-generalized gradient approximation (meta-GGA) functional with the long-range van der Waals interactions from the revised Vydrova–van Voorhis nonlocal correlation functional (rVV10) [56]. It emerged in a previous study as a reliable functional for calculating defect properties of metal halide perovskites [50].

We omit spin-orbit coupling (SOC), as we have shown that SOC has little effect on the formation energies of defects [50]. Our calculations use a plane-wave kinetic energy cutoff of 500 eV and a Γ-point-only k-point mesh. The energy and force convergence criteria are set to 10⁻⁴ eV and 0.02 eV/Å, respectively. Spin polarization is included in all calculations. Bond orders of covalent bonds and atomic charges are calculated using the density derived electrostatic and chemical (DDEC6) charge partitioning method, as implemented in the CHARGEMOL code [57–59].

B. Structures

For MA- and FA-based perovskites, we choose the tetragonal phase as a starting point, while for the Cs-based perovskites the orthorhombic phase is used [60]. Each of these structures contains four AMX₃ formula units per unit cell. Defective structures are created starting from 2×2×2 supercells, which contain 32 formula units per supercell. The structures of MAPbI₃, CsSnI₃, and FAPbI₃ are taken from Refs. [61–63] and reoptimized with the SCAN+rVV10 functional, including reoptimizing the volume of the unit cell.

We have noticed that, upon introduction of defects, the FA cations in FAPbI₃ in the whole supercell rotate, accompanied by a significant distortion of the PbI₆ octahedral framework. This indicates that the starting structure of FAPbI₃ is not the actual lowest energy state with the SCAN+rVV10 functional. No such elaborate distortions are observed in MAPbI₃ or CsPbI₃. This is possibly due to the inclusion of vdW interactions, which are relatively more important for the large FA ion than for the smaller MA or Cs ions. Note that vdW interactions are missing in the Perdew-Burke-Ernzerhof functional that was used in Ref. [63] to generate the structure of FAPbI₃.

For FA-based perovskites we therefore generate new structures by removing the defects again from the optimized structures, and reoptimize the atomic positions and volume. The structures with the lowest total energies are then selected for the further study of defects. A more detailed description of the procedure and analysis is described in Fig. S1 of the Supplemental Material [64].

Structures for MAPbBr₃, MAPbCl₃, and MASnI₃ are created by substituting I in MAPbI₃ with Br or Cl or substituting Pb with Sn. Similarly, the CsPbI₃ structure is created by substituting Sn in CsSnI₃ with Pb. These structures, including the volume of the unit cell, are then optimized with the SCAN+rVV10 functional.

An interstitial is created by adding to the supercell a cation or an anion in a specific charge state, and then optimizing the atomic positions within the supercell. Likewise, a vacancy is created by removing from the supercell a cation or an anion. In order to find the most preferable site for each defect, different nonequivalent positions in each perovskite are tested using a strategy similar to that in our previous work [50]. Subsequently, the structures with the lowest total energy are selected.

C. Defect formation energy

An important physical property typically used to characterize point defects is the defect formation energy (DFE) [65,66]. The DFE determines which defects are dominantly present under thermodynamic equilibrium conditions. Defects with smaller formation energies are easier to form and are present in higher concentrations. Such defects are then more likely to play a role in the materials’ degradation processes.

The DFE ΔHᵢ is calculated from the expression [65]

$$\Delta H_i(D^q) = E_{\text{tot}}(D^q) - E_{\text{bulk}} - \sum_i n_i \mu_i \leq E_F + E_{\text{VBM}} + \Delta V + E_{\text{corr}}^q,$$

where $D^q$ indicates the type of defect with charge $q$, $E_{\text{tot}}(D^q)$ and $E_{\text{bulk}}$ are the DFT total energies of the defective and pristine supercells, respectively, and $n_i$ and $\mu_i$ specify the number of atoms and chemical potential of species $i$ added to ($n_i > 0$) or removed from ($n_i < 0$) the pristine supercell in order to create the defect. Creating a charge $q$ requires taking electrons from or adding them to a reservoir at a fixed Fermi level, as indicated by the second line in Eq. (1).

The Fermi energy is calculated as $E_F + E_{\text{VBM}}$, with $0 \leq E_F \leq E_g$, the band gap, and $E_{\text{VBM}}$ the energy of the valence band maximum. As it is difficult to determine the latter from a calculation on a defective cell, one establishes $E_{\text{VBM}}$ in the pristine cell, shifted by $\Delta V$, which is calculated by lining up the core level on one same atom in the pristine and the neutral defective cell that is far from the defect [65,67].

$E_{\text{corr}}$ corrects for the electrostatic interaction between a charged point defect and its periodically repeated images. As in Refs. [37,50] we find that the $2 \times 2 \times 2$ tetragonal supercell and the dielectric screening in AMX₃ perovskites are sufficiently large, such that this correction is small and can be neglected. We neglect vibrational contributions to the DFE as
FAPbI₃ are qualitatively similar to (a). As halfway between points A and B, charges are injected in a material, it has to be charge neutral: neutrality condition, which expresses the fact that, if no and electrons of the semiconductor material, CsI₃ or CsI₄ for CsPbI₃ [44, 69] [see Fig. 1(c)]. In the typical small in the present compounds [50, 68]. well as the influence of thermal expansion on it, as these are typically small in the present compounds [50, 68].

Figure 1(a) gives the calculated stability diagram of MAPbI₃, MASN₁₃, and CsPbI₃. The stability diagrams of MAPbBr₃, MAPbCl₃, and FAPbI₃ are qualitatively similar to (a). μᵢ = μᵢᵢᵢ, molecule/2 corresponds to Δμ₁ = 0 in the figures, and μM = μM, bulk defines ΔμM = 0 for M = Pb, Sn. The points A and B define iodine-rich and iodine-poor conditions, respectively. Iodine-medium conditions (point C) are defined as halfway between points A and B.

The intrinsic Fermi level can be determined by the charge neutrality condition, which expresses the fact that, if no charges are injected in a material, it has to be charge neutral:

\[ p - n + \sum_{i} q c(D^i) = 0, \]  

where \( p \) and \( n \) are the intrinsic charge densities of holes and electrons of the semiconductor material, \( c(D^i) \) is the concentration of defect \( D^i \), and the sum is over all types of charged defects. The concentrations can be calculated from Boltzmann statistics:

\[ c(D^i) = c_0(D^i) \exp \left[ -\frac{\Delta H_f(D^i)}{k_B T} \right]. \]  

The intrinsic Fermi level depends on intrinsic conditions, the exact choice of \( \mu_x \) is not so important, because a change in \( \mu_x \) is exactly compensated by a change in intrinsic Fermi level \( E_F^{(i)} \) [50].

In Sec. III it will be shown that this is the case for MAPbI₃, FAPbI₃, and CsPbI₃. However, in MAPbBr₃, MAPbCl₃, and MASN₁₃, the intrinsic Fermi level is relatively close to the valence band maximum (VBM), so the concentration of holes, \( p \), is not negligible compared to the concentration of defects, and both are important for maintaining charge neutrality. The hole concentration can be calculated from the density of states near the VBM [71], which can be modeled assuming parabolic bands, using the effective hole masses at the VBM [72].

Naturally, in view of Eq. (3), defect concentrations are highly temperature dependent. A further temperature dependence might come from the position of \( E_F^{(i)} \) through solving...
Eq. (2) as function of temperature, which would affect the DFEs and the defect concentrations. We have explored the temperature dependence of $E_F^{(0)}$ and the defect concentrations in MAPbI$_3$ in the temperature range 250–350 K. The results are shown in Fig. S3 of the Supplemental Material [64]. The Fermi level is barely affected by the temperature, implying that the defect concentrations simply scale according to the Boltzmann factor, Eq. (3).

D. Charge state transition level

Under operating conditions, charges are injected in the material, shifting the positions of the (quasi-)Fermi levels for electrons and holes. The charge state transition level (CSTL) $\varepsilon(q/q')$ is defined as the Fermi level position where the charge states $q$ and $q'$ of the same type of defect have equal formation energy, $\Delta H_f(D^q) = \Delta H_f(D^{q'})$. As the DFEs have a simple linear dependence on $E_F$, Eq. (1), this condition can be expressed as

$$\varepsilon(q/q') = \frac{\Delta H_f(D^q, E_F = 0) - \Delta H_f(D^{q'}, E_F = 0)}{q' - q}, \quad (4)$$

where $\Delta H_f(D^q, E_F = 0)$ is the DFE calculated at $E_F = 0$.

The CSTLs influence the electronic properties of the semiconducting perovskites. If these levels are deep inside the band gap, they are able to trap charge carriers, and act as nonradiative recombination centers.

DFT functionals are generally designed to produce accurate total (ground state) energies, but not the excitation spectrum, including the band gap. Indeed band gaps calculated with commonly used functionals, such as SCAN+rVV10, are not very accurate. In the present context this means that DFEs are expected to be accurate, as they mainly depend on total energies, Eq. (1). But CSTLs are affected by the DFT band-gap error. To calculate CSTLs accurately requires the correct positions of the band edges, which might be attainable in principle using GW corrections [73], but in practice such calculations are prohibitively expensive for the large supercells required in the present study. Alternative approaches that give reasonable band-gap values, such as the use of certain hybrid functionals, generally perform worse than SCAN in calculating binding or formation energies of solids, which would introduce corresponding errors in calculating DFEs [50].

In the case of the halide perovskites, AMX$_3$, we would argue that the positions of the CSTLs with respect to the band edges are correct in a relative sense. The VBM and conduction band minimum (CBM) have X anion and M cation ion character, respectively, and the positions of the VBM and CBM can be modeled in terms of M cation–X anion bonding and antibonding [60]. M-cation or X-anion interstitials or vacancies involve the same (but frustrated) bonding and antibonding, and have either dominant valence band or conduction band character. For the states resulting from such defects one would thus expect the relative position with respect to the band edges to be given correctly [74]. The A cations in the perovskite are not directly involved in the electronic states around the band gap. Their defects only supply a mild Coulomb potential, which results in shallow traps only.

III. RESULTS AND DISCUSSION

Following the strategy outlined in the previous section, we calculate the defect thermodynamics and electronic properties of the halogen vacancy $V_X$, the metal vacancy $V_M$, and the A-cation vacancy $V_A$ in the perovskites AMX$_3$, and of their corresponding interstitials $X_i$, $M_i$, and $A_i$. All point defects are studied in the neutral, as well as in all physically reasonable charged states. We study the six elementary perovskites MAPbI$_3$, MAPbBr$_3$, MAPbCl$_3$, FAPbI$_3$, CsPbI$_3$, and MA$\text{SnI}_3$, which enables us to test the effect of halide substitution (from the first three compounds in this series), of A-cation substitution (comparing FAPbI$_3$ and CsPbI$_3$ to MAPbI$_3$), and of metal substitution (comparing MA$\text{SnI}_3$ and MAPbI$_3$).

The calculated DFEs and CSTLs are shown in Fig. 2, which will be discussed in more detail below. We will focus on the energies; optimized geometries of the point defects in different charge states are visualized in Fig. S4 of the Supplemental Material [64]. The results shown in Fig. 2 are calculated for halide-medium growth conditions (the points marked C in Fig. 1). For comparison, the DFEs of the AMX$_3$ perovskites at halide-rich and -poor conditions (points A and B in Fig. 1) are shown in Figs. S5–S7 of the Supplemental Material [64].

Figures 2(a)–2(f) show the DFEs, $\Delta H_f(D^q)$, of all vacancies and interstitials as a function of the position of the Fermi level, $E_F$, with respect to the position of the VBM, $E_{\text{VBM}}$. All curves show a linear relation, as $\Delta H_f(D^q) \propto qE_F$, where $q$ is the charge state of the defect [Eq. (1)]. For each defect and $E_F$ the curve of the most stable defect is shown as a solid line. The intrinsic Fermi level, $E_F^{(0)}$, is found by obeying the charge neutrality condition, Eq. (2).

The points in Figs. 2(a)–2(f) where the curves discontinuously change slope are in fact crossing points between two curves belonging to different charge states of the same defect. These points mark the CSTLs, where a defect changes its charge state [Eq. (4)]. The CSTLs are visualized in Figs. 2(g)–2(l) with respect to $E_{\text{VBM}}$ and $E_{\text{VBM}} + E_F$. Note that for ease of comparison the VBMs of different perovskites are aligned to the same position.

Using the results shown in Fig. 2, we will analyze in the following sections the effects on the defect physics of the perovskite AMX$_3$, upon varying the halide (X anion), the A cation, and the metal (M cation). We use MAPbI$_3$ as a point of reference, whose calculated DFEs are shown in Fig. 2(a). Close to intrinsic conditions ($E_F^{(0)} = 0.33$ eV), point defects in MAPbI$_3$ have a preference for a specific charge state, interstitials appear as anions or cations, $I_i^+$, $M_A^+$, and Pb$_i^{2+}$, and vacancies have a charge opposite to their anion or cation interstitial counterparts, $V_i^-$, $V_{MA}^-$, and $V_{Pb}^{3-}$. Defects in other halide perovskites have the same pattern of charges close to intrinsic conditions, as shown in Figs. 2(b)–2(f).

A. Varying the X anion

The DFEs of defects at intrinsic conditions in MAPbI$_3$, MAPbBr$_3$, and MAPbCl$_3$ are compared in Fig. 3(a). A uniform trend is not present; the DFEs of the Pb and the MA
FIG. 2. (a)–(f) Defect formation energies in six $AMX_3$ perovskites calculated at halide-medium conditions, using the SCAN+rVV10 functional: the vertical dashed lines represent the intrinsic Fermi level with respect to the VBM, the solid lines represent the energetically most favorable defects, and the dashed lines other defects. (g)–(l) Charge state transition levels: the most important ones are indicated by colored lines, representing a change of a single unit $\pm e$ starting from one stable charge state of a defect [50]; the bottom and top gray areas represent the valence and conduction bands (calculated with SCAN+rVV10 without SOC), aligned at the VBM.

interstitials increase going from I to Br and to Cl, whereas the DFEs of the Pb and halide vacancies increase going from I to Br, and then decrease again going from Br to Cl, and the DFEs of MA vacancies and halide interstitials are very similar for I, Br, and Cl.

The trend for the Pb and halide vacancies can be explained by two competing factors. The cell volume decreases significantly going from I to Br to Cl, as shown in Fig. 3(b). This increases the electrostatic (Madelung) potential, and makes it energetically more difficult to create a vacancy in the lattice. However, also the chemical bond order of Pb-$X_6$ decreases going from I to Br to Cl, as shown in Fig. 3(c), which should make it easier to create a vacancy. The competition between these two factors gives a nonmonotonic DFE increasing from I to Br, but decreasing from Br to Cl.

The volume effect works opposite for interstitials as compared to vacancies, which is mainly connected to the size of the interstitial. As the cell volume decreases going from I to Br to Cl, it becomes energetically more difficult to insert a large interstitial in the lattice. This is particularly true for the large MA and Pb interstitials, whose DFEs increase going from I to Br to Cl. For the $X$ interstitial, the DFE changes very little, because, as the volume becomes smaller going from I to Br to Cl, so does the interstitial ion.

Among these defects, the variations in DFEs of vacancies $V_{MA}^-$, $V_{X}^-$ and the interstitial $X_i^-$ are relatively moderate, $\lesssim 0.25$ eV. These defects are less sensitive to the volume changes of the perovskite lattice, since the changes they induce in the lattice can be compensated to a certain degree by changes in I-Pb-I angles and the tilting of octahedra, as shown in Figs. S4(c), S4(d), and S4(f) of the Supplemental Material [64]. In contrast, the MA and Pb interstitials induce

FIG. 3. (a) Defect formation energies at intrinsic conditions of MAPbI$_3$, MAPbBr$_3$, and MAPbCl$_3$; (b) volume per formula unit of the pristine perovskite lattices; and (c) Pb-$X_6$ bond orders, where larger values indicate stronger covalent bonds [57–59].
significant changes in the local structure, while the vacancy Pb involves significant breaking of Pb-X bonds (see Figs. S4(a), S4(b), and S4(c) of the Supplemental Material [64]). As a result, their DFEs have a larger variation of up to 0.6 eV upon changing the halogen X in the perovskites.

Due to its consistently small DFE, the halide interstitial $X^-$ is always the most stable negatively charged defect in MAPbX$_3$ under intrinsic conditions. The situation is more varied for the compensating positively charged defects. Whereas for MAPbI$_3$ the dominant positively charged defect is the MA interstitial MA$_i^+$, for MAPbBr$_3$ and MAPbCl$_3$, the negative charge in the halide interstitials is compensated for a large part by holes in the valence band, whereas for MAPbCl$_3$ also the halide vacancy $V_{Cl}^-$ plays a role [Figs. 2(a)–2(c)].

To be specific, the two most stable defects at intrinsic conditions in MAPbI$_3$ are the interstitials MA$_i^+$ and I$_i^-$ with DFEs of 0.47 and 0.48 eV, respectively [Fig. 2(a)], and equilibrium concentrations of $1.37 \times 10^{14}$ and $1.09 \times 10^{14}$ cm$^{-3}$ at room temperature, respectively [Eq. (3)]. A third, but somewhat less prominent, defect is the vacancy $V_{PB}^-$ with a DFE of 0.50 eV, and an equilibrium concentration of $1.44 \times 10^{13}$ cm$^{-3}$. All other defects have a DFE that is more than 0.1 eV larger than that of the two interstitials, leading to an equilibrium concentration that is more than two orders of magnitude smaller.

The dominant defect in MAPbBr$_3$ is Br$_i^-$ with a DFE of 0.49 eV, and an equilibrium concentration at room temperature of $9.03 \times 10^{13}$ cm$^{-3}$. Likewise, in MAPbCl$_3$, $V_{Cl}^-$ and Cl$_i^-$ are the most prominent defects, with DFEs of 0.48 and 0.55 eV, respectively, and concentrations of $1.09 \times 10^{14}$ and $8.54 \times 10^{12}$ cm$^{-3}$, respectively. It is interesting to note that only for MAPbCl$_3$ the dominant defects support the classic picture of Frenkel defects in ionic crystals, as represented by the halide vacancy and interstitial, which is consistent with the fact that the bonding in this material of the three is the most dominantly ionic.

The CSTLs of MAPbI$_3$, MAPbBr$_3$, and MAPbCl$_3$ can be compared in Figs. 2(g)–2(i). Although the SCAN+RVV10 functional is not designed to produce an accurate band gap, it is still possible to make some general statements about the electronic activity of the various defects. Under intrinsic conditions all defects in AMX$_3$ are charged, and positive and negative defects can act as potential traps for electrons and holes.

Starting with MA-related defects, neither the top valence bands nor the bottom conduction bands have any MA character [60], and the main effect of MA$_i^+$ defects is to create a local electrostatic potential that is attractive for electrons or holes, respectively. As electrostatic screening decreases going from the I to the Br to the Cl compound, one might expect this potential to become stronger and the associated defect states to become deeper.

For instance, the CSTLs of MA$_i^+$ have only 0.05 eV below the CBM in MAPbI$_3$, making it a shallow electron trap. In MAPbBr$_3$ and MAPbCl$_3$ the CSTLs of MA$_i^+$ have 0.12 and 0.21 eV below the CBM, respectively. Whereas the latter are not shallow traps anymore, the DFEs of MA$_i^+$ in MAPbBr$_3$ and MAPbCl$_3$ under intrinsic conditions are 0.86 and 1.03 eV, leading to concentrations ($4.28 \times 10^7$ and $7.11 \times 10^4$ cm$^{-3}$) that are negligible. In contrast, in MAPbI$_3$ the interstitial MA$_i^+$ is one of the dominant defects, but there it only forms a shallow trap.

Proceeding with other relatively abundant defects in MAPbI$_3$, I interstitials and Pb vacancies, their CSTLs I$_i^-$ and V$_{PB}$ are close to the VBM. We suggest that the fact that these defects do not form states that are deep inside the band gap has a simple explanation. Hybridization between I and Pb states results in bands where the maximum energy levels have maximum antibonding character. The states at the VBM have maximum antibonding and dominantly I character [60]. Defect states associated with I interstitials and Pb vacancies also have I character. One expects hybridization around a defect to be smaller than in the pristine material, as the bonding geometry around a defect is less than optimal. Defect states then have less than maximum antibonding character, and the associated defect states are not likely to have an energy far above the VBM, even if negatively charging these localized states should push their energy upwards. This reasoning should hold for all AMX$_3$ compounds, and indeed it can be observed in Fig. 2 that $X_i$ and $V_{PB}$ CSTLs remain close to the VBM.

Likewise, the states at the CBM of MAPbI$_3$ have maximum antibonding and dominantly Pb character [60]. Defects with electronic states that have Pb character are I vacancies and Pb interstitials. Following the above reasoning, such defects involve nonoptimal antibonding, which implies that their states are likely to appear below the CBM or, in other words, inside the band gap of the semiconductor. Positively charging these localized states should push their energy even further downwards.

Indeed, defects in MAPbI$_3$ that give less shallow levels are $V_{PB}$, which can act as electron traps with (+0) and (2+/+) transitions of 0.15 and 0.31 eV below the CBM, respectively. However, as the DFEs of these two defects under equilibrium conditions are 0.61 and 0.71 eV, respectively, their equilibrium concentrations of $6.10 \times 10^{11}$ and $3.66 \times 10^{10}$ cm$^{-3}$ are too small to make these defects harmful.

The same is not true for the Pb$_{2i}^+$ and $V_{PB}$ defects in MAPbBr$_3$ and MAPbCl$_3$. As shown in Fig. 4, both these defects become deeper electron traps going from the I to the Br and the Cl compound. This is potentially harmful, because $V_{Cl}^+$ is a dominant defect in MAPbCl$_3$, as discussed above.

In summary, considering both DFEs and CSTLs, there are no detrimental effects in MAPbI$_3$, as relatively abundant defects (MA$_i^+$, I$_i^-$, and Pb$_{2i}^+$) only create shallow traps, and defects with less shallow levels ($V_{PB}$ and Pb$_{2i}^+$) have a negligible concentration under equilibrium conditions, which agrees with the general consensus [36,37]. So does the MAPbBr$_3$. In contrast, $V_{Cl}^+$ is the most abundant defect in MAPbCl$_3$, and has deep levels that can act as electron traps.

### B. Varying the A cation

The DFEs at intrinsic conditions of defects in FAPbI$_3$, MAPbI$_3$, and CsPbI$_3$ are compared in Fig. 5(a). Again, a uniform trend upon changing the A cation in the perovskite lattice is not present, but for four of the six defects, the DFEs increase significantly going from FA to MA, whereas going from MA to Cs the changes are much smaller. Exceptions to
conduction bands, according to Ref. [60]. The colored boxes indicate the relative positions of the valence and conduction bands around the band gap [60]. The ease with which these two interstitials can be introduced reflects the space in the lattice created by its rather large volume [Fig. 5(b)].

The vacancy $V_{\text{Pb}}^{2-}$ is also fairly easy to create in FAPbI$_3$ with a DFE of 0.15 eV. We suggest that this is because this Pb vacancy allows for a local relaxation of the lattice of Pb$_6$ octahedra, which shows a large tilting and distortion in FAPbI$_3$ (see Fig. S1 of the Supplemental Material [64]). A way to visualize this is to look at the changes in Pb-I bond lengths for the I atoms neighboring the Pb vacancy. As shown in Fig. 5(c), compared to MAPbI$_3$ and CsPbI$_3$, a larger shortening of Pb-I bonds occurs in FAPbI$_3$, indicating a stronger local structural relaxation.

In contrast, the DFE of the interstitial Pb$_{\text{i}}^{2+}$ in FAPbI$_3$ is larger than in MAPbI$_3$ and CsPbI$_3$. The Pb interstitial is embedded in the lattice through a fivefold coordination with I atoms of neighboring octahedra (see Fig. S4(b) of the Supplemental Material [64]), which is more difficult to achieve in the already more distorted lattice of FAPbI$_3$. The other exception to the general trend mentioned above is the $V_{\text{I}}^+$ vacancy, which has a similar DFE for all three compounds. We suggest that the local bonding of an I atom in the lattice has become dominant. Specifically, the DFEs of C$i_{\text{a}}^+$ are 0.61 and 0.59 eV, respectively, giving rise to equilibrium concentrations of $8 \times 10^{11}$ and $4 \times 10^{11}$ cm$^{-3}$, respectively. The defect concentration in CsPbI$_3$ is two orders of magnitude lower than that in MAPbI$_3$, indicating better stability of the material with respect to defect formation.

Noticeable is the rather extreme behavior of FAPbI$_3$, where the formation energies of FA$_{\text{i}}^+$ and I$_{\text{i}}^-$ are much smaller than their counterparts in MAPbI$_3$ and CsPbI$_3$, with DFEs of $\sim 0$ eV. The ease with which these two defects can be introduced reflects the space in the lattice created by its rather large volume [Fig. 5(b)].

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Comparing the CSTLs of MAPbI$_3$, FAPbI$_3$, and CsPbI$_3$ [Figs. 2(g), 2(j), and 2(k)], one observes that there is actually little difference between the materials. The analysis of the position and character of the CSTLs as presented in Sec. III A still holds. This makes sense, as the $A$ cation does not directly contribute to the electronic structure of the valence and conduction bands around the band gap [60].

The $A$-cation-related defects, $A_{\text{i}}^{+}$ and $V_{\text{A}}^{-}$, $A =$ MA, FA, Cs, have levels close to the CBM and the VBM, respectively, and the defects with electronic I character, I$_{\text{i}}^-$ and $V_{\text{Pb}}^{2-}$, have levels close to the VBM, all of which represent shallow traps. The defects with electronic Pb character, Pb$_{\text{i}}^{2+}$ and $V_{\text{I}}^{+}$, can create deep traps, but their concentrations under equilibrium conditions are low.
Formation of negatively charged defects in MASnI₃ is encouraged by the relatively low ionization potential of this compound [41,60,75]. Holes to compensate for the negative charge of the defects are then easily formed in the valence band. The high energy of the valence band is ultimately due to the Sn 5s level being relatively high in energy, which correlates with the relative ease with which Sn(II) can be oxidized to Sn(IV) [60]. In contrast, MAPbI₃ has a larger ionization potential, resulting from the Pb 6s level being relatively low in energy, correlating with a more difficult oxidation of Pb(II) to Pb(IV).

At the same time, the DFEs of positively charged defects in MASnI₃ remain large, so that the charge of these defects does not compensate that of the negatively charged defects. Charge neutrality then has to be achieved by the hole charge carriers in the perovskite [see Eq. (2)], which results in MASnI₃ being an intrinsic n-type semiconductor. The DFEs of MASnI₃ are shown in Fig. 6, calculated under the assumption that the Fermi level is pinned at the top of the valence band, i.e., $E_F^{(1)} = 0$. In fact, the vacancy $V_{Sn}^{2−}$ still has a negative formation energy of $−0.21$ eV under these conditions.

A negative formation energy indicates that such defects can be formed spontaneously, which questions the stability of the MASnI₃ phase. Note, however, that the theory outlined in Sec. II C assumes the dilute limit of defect concentration, where defects have no mutual interaction. So, whereas negative DFEs can be an indication of an unstable phase, they are by themselves not a proof. In any case, they indicate that MASnI₃ is a degenerate p-type semiconductor.

In order to avoid an excessive amount of Sn vacancies, the growth conditions of the MASnI₃ perovskite can be tuned to iodine-poor conditions, for instance by increasing the relative amount of SnI₂ in the precursors [76]. At iodine-poor conditions, the formation of $V_{Sn}^{2−}$ defects can be significantly suppressed, with a DFE raised to $0.26$ eV [Fig. 6(a)]. However, also under these conditions MASnI₃ remains an intrinsic p-type semiconductor (see Fig. S7(c) of the Supplemental Material [64]).

The DFEs of MAPbI₃ are actually the same under I-medium and I-poor conditions, which stems from an exact compensation between the effect of a change in the iodine chemical potential and that of a change in the intrinsic Fermi level [50] (compare Figs. S5(b) and S5(c) of the Supplemental Material [64]). This compensation mechanism is operative as long as the intrinsic Fermi level stays sufficiently far from the band edges, and charge neutrality is determined by the balance between charged defects only. This compensation does not work anymore if an appreciable concentration of intrinsic charge carriers markedly influences the charge balance, as is the case for MASnI₃. Comparing the DFEs of MAPbI₃ and MASnI₃ under I-poor conditions, which are most physical for MASnI₃, we observe that there is only a moderate difference. The DFEs of $V_{Pb}^{+}$, $I^{−}$, and $M^{2+}$ differ by $\lesssim 0.1$ eV between the two compounds.

In Secs. III A and III B changes in equilibrium volume of the different perovskites have been involved to explain the trends in DFEs. As the equilibrium volume of MASnI₃ is only 2% smaller than that of MAPbI₃ (see Table S2 of the Supplemental Material [64]), volume effects are small.

The DFEs of $V_{MA}^{−}$ and $MA^{+}$ in MASnI₃ are $\sim 0.25$ eV lower than in MAPbI₃. It can be explained by the fact that the interaction of the MA cations with the SnI framework in MASnI₃ is weaker than with the PbI framework in MAPbI₃, which facilitates the formation of MA vacancies in the former, and impedes the formation of MA interstitials. The Sn-I bond is slightly more covalent than the Pb-I, as demonstrated by the larger bond order and the smaller charge on the Sn versus the Pb ions [Fig. 6(b)]. The charges on the I ions in the SnI framework are then also smaller than in the PbI framework; thus their Coulomb interaction with the MA cations is somewhat weaker.

The DFE of $V_{Sn}^{2−}$ in MASnI₃ is $\sim 0.25$ eV lower than $V_{Pb}^{2−}$ in MAPbI₃. As discussed above, the ease with which Sn vacancies are formed is facilitated by the special chemistry of Sn. The 2− charge on $V_{Sn}$ in MASnI₃ is more localized than that of $V_{Pb}$ in MAPbI₃. The charge on the Sn atoms in a shell surrounding the Sn vacancy [see Fig. 6(c)] is in total reduced by 0.16e, whereas for Pb atoms the reduction is 0.27e.

![Figure 6](image-url)


Sn more easily retains its positive charge, or, put differently, it is more easily oxidized.

The positions of the CSTLs with respect to the band edges in MASnI$_3$ are similar to those in MAPbI$_3$. Defects with I character, such as I interstitials and Sn vacancies, give only shallow states just above the VBM, for which we suggest an explanation similar to that given in Sec. III A. One concludes that, although Sn vacancies can be relatively abundant, they do not give rise to trap states for holes. Defects with Sn character, such as Sn interstitials and I vacancies, give states below the CBM, where in particular the Sn$_{(2+/-)}$ level forms a deep trap for electrons. However, Sn interstitials are rare under equilibrium conditions, so their electronic effect is minimal. The MA-related defects have no important electronic consequences, either because they only give shallow levels (MA$_i$) or because their concentration is low ($V_{\text{MA}}$).

In summary, the defect chemistry of MASnI$_3$ is rather special, resulting in a very high equilibrium concentration $1.45 \times 10^{16}$ cm$^{-3}$ of $V_{\text{Sn}}^{2-}$ defects (at I-poor conditions). The charge in these vacancies is compensated mainly by holes in the valence band, making this material a degenerate intrinsic $n$-type semiconductor. In contrast to the significant change in defect concentrations, upon changing the $M$ cation from Pb to Sn, the CSTLs show no qualitative changes. Defects that are abundant under equilibrium conditions only display shallow acceptor levels, and defects that can act as electron traps appear only at low concentrations.

### IV. SUMMARY AND CONCLUSIONS

We have conducted a systematic investigation of the defect formation energies (DFEs) and charge state transition levels (CSTLs) of the intrinsic point defects, vacancies, and interstitials in six primary metal halide perovskites, MAPbI$_3$, MAPbBr$_3$, MAPbCl$_3$, FAPbI$_3$, CsPbI$_3$, and MASnI$_3$. The accurate and efficient SCAN+rVV10 functional is employed in all DFT calculations, and all structures are optimized self-consistently. Using MAPbI$_3$ as reference material, we have analyzed the impact of changing anions and cations on the DFEs and CSTLs and identified the underlying physical origins of the observed trends.

The dominant defects and major sources of deep traps under equilibrium conditions are summarized in Table I. The formation energies and concentrations of defects are summarized in Table II. Noticeable is the important role played by halide interstitials in all compounds, except in CsPbI$_3$ and MASnI$_3$, and the absence of halide vacancies, except in MAPbCl$_3$. Van der Waals interactions give a significant contribution to these results by increasing the bonding strength between ions, making it easier to insert an interstitial [50], and are thus important to include. Metal cation vacancies are important in MAPbI$_3$, CsPbI$_3$, and MASnI$_3$, but metal interstitials in appreciable concentrations are absent in all compounds. Likewise, A-cation interstitials are important in the iodide compounds (FAPbI$_3$, MAPbI$_3$, CsPbI$_3$), whereas A-cation vacancies do not occur in significant concentrations.

The changes in the DFEs upon replacing the halide anion in MAPbX$_3$, from X = I to Br to Cl, can be explained from a competition between two factors. First, the lattice volume decreases, which increases the electrostatic (Madelung) potential in the lattice. Such increased electrostatic potential

<table>
<thead>
<tr>
<th>Perovskites</th>
<th>Dominant defects</th>
<th>Major source of deep traps</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI$_3$</td>
<td>MA$^+$, I$<em>{-}$, $V</em>{\text{Pb}}^{2-}$</td>
<td>None</td>
</tr>
<tr>
<td>MAPbBr$_3$</td>
<td>Br$^{-}$</td>
<td>None</td>
</tr>
<tr>
<td>MAPbCl$_3$</td>
<td>V$_{\text{Cl}}^{+}$, Cl$^{-}$</td>
<td>$V_{\text{Cl}}^{+}$</td>
</tr>
<tr>
<td>FAPbI$_3$</td>
<td>FA$^{+}$, I$_{-}$</td>
<td>None</td>
</tr>
<tr>
<td>CsPbI$_3$</td>
<td>Cs$^{+}$, $V_{\text{Pb}}^{2-}$</td>
<td>None</td>
</tr>
<tr>
<td>MASnI$_3$</td>
<td>$V_{\text{Sn}}^{2-}$</td>
<td>None</td>
</tr>
</tbody>
</table>

### TABLE II. Formation energies $\Delta H_f$ (eV) and concentrations $c$ (cm$^{-3}$) at $T = 300$ K of charged defects in six perovskites calculated using the SCAN+rVV10 functional. The results of MASnI$_3$ are calculated based upon I-poor conditions, while those of the other perovskites are calculated based on halide-medium conditions. Formation energies and concentrations of the dominant defects in each perovskite are underlined.

<table>
<thead>
<tr>
<th>Perovskites</th>
<th>$V_{\text{A}}^{-}$</th>
<th>$V_{\text{M}}^{2-}$</th>
<th>$V_{\text{X}}^{+}$</th>
<th>$A_{\text{i}}^{-}$</th>
<th>$M_{\text{i}}^{2+}$</th>
<th>$X_{\text{i}}^{-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI$_3$</td>
<td>0.81</td>
<td>0.50</td>
<td>0.61</td>
<td>0.47</td>
<td>0.71</td>
<td>0.48</td>
</tr>
<tr>
<td>MAPbBr$_3$</td>
<td>0.86</td>
<td>1.00</td>
<td>0.80</td>
<td>0.96</td>
<td>0.83</td>
<td>0.49</td>
</tr>
<tr>
<td>MAPbCl$_3$</td>
<td>0.86</td>
<td>0.84</td>
<td>0.55</td>
<td>1.07</td>
<td>1.14</td>
<td>0.48</td>
</tr>
<tr>
<td>FAPbI$_3$</td>
<td>0.48</td>
<td>0.15</td>
<td>0.72</td>
<td>0.00</td>
<td>0.93</td>
<td>0.00</td>
</tr>
<tr>
<td>CsPbI$_3$</td>
<td>0.73</td>
<td>0.59</td>
<td>0.68</td>
<td>0.61</td>
<td>0.76</td>
<td>0.71</td>
</tr>
<tr>
<td>MASnI$_3$</td>
<td>0.58</td>
<td>0.26</td>
<td>0.68</td>
<td>0.72</td>
<td>0.81</td>
<td>0.40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Perovskites</th>
<th>Defect formation energy $\Delta H_f$ (eV)</th>
<th>Defect concentration $c$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI$_3$</td>
<td>$8.68 \times 10^7$</td>
<td>$6.10 \times 10^{11}$</td>
</tr>
<tr>
<td>MAPbBr$_3$</td>
<td>$1.51 \times 10^7$</td>
<td>$5.23 \times 10^{8}$</td>
</tr>
<tr>
<td>MAPbCl$_3$</td>
<td>$2.28 \times 10^7$</td>
<td>$5.52 \times 10^{10}$</td>
</tr>
<tr>
<td>CsPbI$_3$</td>
<td>$2.00 \times 10^6$</td>
<td>$4.18 \times 10^{10}$</td>
</tr>
<tr>
<td>MASnI$_3$</td>
<td>$6.62 \times 10^{11}$</td>
<td>$1.06 \times 10^{10}$</td>
</tr>
</tbody>
</table>
makes it easier to create (charged) interstitials, and more difficult to create vacancies. Second, the Pb-X bond order decreases from I to Br to Cl, which has the opposite effect.

By varying the A cation in A\text{PbI}_3, from A = FA to MA to Cs, one observes a general increase in the DFEs, which can be explained by a similar volume effect as changing the halogens. A smaller volume increases the Madelung potential, making it more difficult to create vacancies. In this case, a smaller volume also makes it more difficult to create an interstitial, as the lattice becomes more compact. In contrast to the case discussed in the previous paragraph, the chemical bonding is not much affected by A-cation substitution when comparing Cs and MA. However, defects are easily created in FAPbI$_3$, where its large lattice volume allows for an easy creation of interstitials, and a large relaxation in the presence of vacancies.

Comparing MAPbI$_3$ and MASnI$_3$, Sn vacancies are much easier to form than Pb vacancies, so much, that V$_{\text{Sn}}^{2-}$ is the only dominant defect in MASnI$_3$, which can only be charge compensated by holes in the valence band, making this compound an intrinsic p-type semiconductor.

In these substitutions of anions and cations, the majority of CSTLs remain shallow, and move along with band edges. A-cation vacancies and interstitials do not interfere with the basic electronic structure of the perovskites. They only modify the local Coulomb potential slightly and hence form only shallow traps for holes and electrons. Defects that might catch holes, $X^{-}$ and $V_{\text{Pb}}^{2-}$, only create shallow levels around the VBM. The VBM has $X$ character originating from maximally antibonding $M$-$X$ states $[60]$. The two mentioned defects also create states with $X$ character, but with less antibonding character, and thus with a relatively low energy, even if negative charging pushes the defect levels upwards.

In contrast, defects that might catch electrons, $M_{\text{Pb}}^{2+}$ and $V_{\text{X}}^{+}$, can create deep traps. The CBM has $M$ character originating from antibonding $M$-$X$ states $[60]$. The two defects create states with $M$ character, but with less antibonding character, and thus with an energy below the CBM, which can become even lower upon the positive charging. The CSTLs generated by Pb interstitials and halide vacancies upon varying the X anion from I to Br and to Cl can be classified as deep traps. Although these trap states are harmful electronically, the equilibrium concentrations of these defects in MAPbI$_3$ and MAPbBr$_3$ are negligible. However, in MAPbCl$_3$, the concentration of Cl vacancies is higher, so that they are potentially harmful to the electronic properties.

**ACKNOWLEDGMENTS**

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