Compound Defects in Halide Perovskites: A First-Principles Study of CsPbI₃

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ABSTRACT: Lattice defects affect the long-term stability of halide perovskite solar cells. Whereas simple point defects, i.e., atomic interstitials and vacancies, have been studied in great detail, here we focus on compound defects that are more likely to form under crystal growth conditions, such as compound vacancies or interstitials, and antisites. We identify the most prominent defects in the archetype inorganic perovskite CsPbI₂ₓ through first-principles density functional theory (DFT) calculations. We find that under equilibrium conditions at room temperature, the antisite of Pb substituting Cs forms in a concentration comparable to those of the most prominent point defects, whereas the other compound defects are negligible. However, under nonequilibrium thermal and operating conditions, other complexes also become as important as the point defects. Those are the Cs substituting Pb antisite, and, to a lesser extent, the compound vacancies of PbI₂ or CsPbI₃ units, and the I substituting Cs antisite. These compound defects only lead to shallow or inactive charge carrier traps, which testifies to the electronic stability of the halide perovskites. Under operating conditions with a quasi-Fermi level very close to the valence band, deeper traps can develop.

INTRODUCTION

On the basis of their outstanding efficiency (25.7% to date)¹ and relative ease of fabrication, halide perovskite solar cells seem to be poised for large scale applications. The primary obstacle blocking their present commercialization is their relative rapid degradation under operating conditions.²⁻⁵ On a microscopic level, lattice defects in the perovskite materials initiate the degradation process, as they facilitate migration of ions,⁶⁻¹⁰ chemical reactions,¹¹,¹² phase transitions,¹３,¹⁷ and phase segregation.¹⁴ Because of the experimental difficulties in characterizing defect structures microscopically, much of our current understanding of lattice defects in halide perovskites stems from results obtained from electronic structure calculations based on density functional theory (DFT). Following common semiconductor practice,¹⁵,¹⁶ elementary defects consisting of single atomic interstitials, vacancies, or antisites have been at the center of interest.¹⁷⁻²¹ In a previous work,²² we have studied vacancy and interstitial point defects in six primary Pb- and Sn-based halide perovskites with different cations (Cs, MA, FA) and anions (I, Br, Cl), within a single computational framework.²³ One prevalent conclusion from most of these computational studies is that in these materials the point defects with the highest concentrations under equilibrium growth conditions, only introduce shallow traps.

Defects in halide perovskites with a more complex structure have also been considered.²³⁻²⁶ Conceptually, such complex defects can be thought of as resulting from a recombination of simple atomic point defects (vacancies or interstitials) to, for instance, PbI₂ or MAI compound vacancies in MAPbI₃.²⁴⁻²⁶ Within this line of thought also antisites can be interpreted as compound defects, resulting from a recombination of an interstitial and a vacancy of different species. For instance, in CsPbI₃, cation antisites result from a recombination of a Cs vacancy (interstitial) and a Pb interstitial (vacancy).²⁰ Some compound defects have been predicted to form shallow defects only,²⁰,²³ whereas others have the potential to form deep traps.

The formation energy of compound defects is typically much higher than that of simple point defects, which implies that under normal equilibrium conditions (room temperature, atmospheric pressure) the concentration of compound defects, including antisites, is negligible.¹⁵⁻¹⁸ In fact, assuming that a perovskite is formed under equilibrium conditions at room temperature, then often even the concentration of point defects is quite low.²² However, many crystal growth conditions are highly nonequilibrium (involving a high temperature annealing step, for instance), and defects can be formed during growth in appreciable concentrations. In molecular dynamics simulations that use a reactive force field,¹⁰,²⁸ applied to halide perovskites containing an appreciable amount of point defects, one often observes...
recombination of the latter to compound defects. From positron annihilation lifetime spectroscopy, assisted by DFT calculations, there is evidence of charge carrier trapping at compound vacancy defects in MAPbI₃.²⁶

In this paper, we study compound defects, vacancies, interstitials, and antisites, in the archetype inorganic perovskite CsPbI₃, by means of first-principles DFT calculations. Already this simplest of the halide perovskite compounds exhibits a wide variety of possible compound defects. Mapping out their relative likelihood of formation provides information potentially applicable to the whole class of halide perovskite compounds. Not only do we calculate the equilibrium concentrations of compound defects, but through explicitly considering the possible recombination reactions of elementary point defects, we also assess their concentrations under nonequilibrium conditions. The effect of these compound defects on the electronic properties is examined, in particular their potential to form deep traps.

**COMPUTATIONAL METHODS**

**DFT Calculations.** Density functional theory (DFT) calculations are performed with the Vienna Ab-Initio Simulation Package (VASP),²⁹–³¹ employing the SCAN+rVV10³² functional for electronic calculations and geometry optimization. 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. The SCAN functional has a superior overall performance concerning binding/formation energies over a wide range of materials and bonding configurations; for a summary, see ref 23 and references therein. In addition, as discussed in ref 23, inclusion of van der Waals interactions is important for obtaining accurate energies in lead iodide perovskites. As the SCAN functional is numerically somewhat more demanding than more traditional density functionals, we have performed additional convergence tests of defect formation energies (DFEs) with respect to increasing the kinetic energy cutoff for the plane wave basis set. The results, as shown in the Supporting Information, Figure S1, demonstrate that the DFEs calculated with the present cutoff are converged to within 0.01 eV. Spin–orbit coupling is omitted, as it has little effect on the formation energies of the most prominent defects.³³ Spin polarization is included in all calculations.

The SCAN+rVV10 functional has a similar band gap problem as more conventional semilocal functionals, which makes it more difficult to establish the energies of defect levels with respect to the band edges.¹⁶,³⁴ Hybrid functionals, fitted to reproduce the experimental band gap, may reduce this problem, and improve the description of certain classes of defect levels.¹⁹,³⁵,³⁶Benchmarking this semiempirical approach by comparison to results obtained by beyond-DFT/Hartree–Fock techniques, such as GW,³⁷ suffers from the fact that those results critically depend on the technical details of such calculations.³⁸ More importantly in the present context, hybrid functionals can worsen the description of the thermochromstry.¹⁶ As the latter is a key concern in this paper, we have chosen not to use a hybrid functional. Note moreover that, under thermodynamic conditions, i.e., at thermal equilibrium, the position of the Fermi level is determined by the charge neutrality condition, to be discussed below, and under that condition the defect formation energies do not depend upon the band gap, or explicitly, not on the positions of the band edges.²³,³⁷

As in our previous work,²² point defects or compound defects are created in a 2 × 2 × 2 orthorhombic supercell of CsPbI₃, which contains 32 formula units. The lattice volume and ionic positions of the pristine supercell are fully relaxed. Within the supercell, atomic positions of defective structures are optimized. As compound defects are typically larger than simple point defects, we have performed additional tests regarding the size of the supercell, see Supporting Information, Table S1, and have concluded that the 2 × 2 × 2 supercell is sufficiently large.

**Defect Formation Energy.** Under equilibrium conditions, the concentrations of lattice defects can be obtained from Boltzmann statistics

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

where \(D^q\) indicates the type of defect, either a simple interstitial or vacancy point defect, or a compound interstitial or vacancy, or an antisite defect, with charge \(q\); \(c\) is the defect concentration, and \(c_0\) is the density of possible sites for that particular defect (including orientational degrees of freedom if the defect is not spherically symmetric), where usually \(c \ll c_0\).

Under equilibrium conditions, \(E_f\) and \(E_v\) are the DFT total energies of the defective and pristine supercells, respectively, and \(n_i\) and \(\mu_i\) are the number of atoms and chemical potential of atomic species \(k\) added to \((n_i > 0)\) or removed from \((n_i < 0)\) the pristine supercell in order to create the defect. We use the chemical potentials \(\mu_i\): \(k = \text{Cs}, \text{Pb}, \text{I}\), as determined for I-medium conditions in our previous work.²²

Creating a charge \(q\) requires taking electrons from or adding them to a reservoir at a fixed Fermi level. The latter is calculated as \(E_F + E_{\text{VBM}}\) with \(0 \leq E_F \leq E_v\) 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 an atom in the pristine and the neutral defective cell that is far from the defect.¹⁵,³⁹ As shown in ref 19, the typical supercell used in calculations and the dielectric screening in lead iodide perovskites are sufficiently large, so the electrostatic interaction between a charged defect and its periodically repeated images can be neglected, consistent with our previous work.²²,²³ In addition, we neglect vibrational contributions to the DFEs, and
the effect of thermal expansion on the DFEs, as these are typically small in the present compounds.

Recombination Reaction. We model the recombination of point defects $A_1, \ldots, A_m$ to a compound defect $B$ as a chemical reaction

$$\alpha_1 A_1 + \alpha_2 A_2 + \cdots + \alpha_m A_m \rightarrow \beta B$$

(4)

Reaction equilibrium is defined by

$$\sum_{i=1}^m \alpha_i \mu_i = \beta \mu_B$$

(5)

with $\mu_i$ and $\mu_B$ the chemical potentials of species $A_i$ and $B$, given by

$$\mu_i = \Delta H_f(A_i^0) + k_B T \ln \frac{c_i}{c_{0,i}}$$

(6)

$$\mu_B = \Delta H_f(B^0) + k_B T \ln \frac{c_B}{c_{0,B}}$$

(7)

where $\Delta H_f(D^0)$, $D^0 = A_i^0, B^0$ are the DFEs according to eq 3. $c_i = c(A_i^0), c_B = c(B^0)$ are concentrations, and $c_{0,i} = c_i(A_i^0)$, $c_{0,B} = c_B(B^0)$ are the densities of possible sites (see Table S2 of the Supporting Information for details). Note that we do not assume that charge is conserved in reaction 4. The electron reservoir with Fermi energy $E_F$ can supply electrons or holes, which is accounted for in the DFEs. Equations 5–7 give the law of mass action

$$\frac{c_B}{c_{0,B} - c_B} \prod_{i=1}^m \left( \frac{c_{0,i} - c_i}{c_i} \right)^{\alpha_i} = \exp \left[ -\frac{\Delta H_f}{k_B T} \right]$$

(8)

$\Delta H_f = \beta \Delta H_f(B^0) - \sum_{i=1}^m \alpha_i \Delta H_f(A_i^0)$

(9)

where $\Delta H_f$ is the reaction energy of reaction 4.

If all (simple and compound) defects are in equilibrium with reservoirs at chemical potentials $\mu_i$, eq 3, then their concentrations are given by eq 1, and trivially obey the law of mass action, eq 8. Typically, however, point defects and compound defects are initially created as concentrations $c_i^{(0)}$ and $c_B^{(0)}$, respectively, in a crystal growth process, after which the crystals are extracted and kept at room temperature. The defects then remain, but they can recombine according to eq 4. Not only does this include the possible formation of compound interstitials or vacancies, but also the formation of antisites through the recombination of an interstitial and a vacancy.

As the recombination reaction, eq 4, conserves the total number of atoms of each species, one has

$$c_i + \frac{\alpha_i}{\beta} c_B = c_i^{(0)} + \frac{\alpha_i}{\beta} c_B^{(0)}$$

(10)

Given the initial concentrations $c_i^{(0)}$ and $c_B^{(0)}$, the law of mass action, eq 8, then allows for determining the actual concentrations of the compound defect $c_B$ and of the point defects $c_i$.

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 3, this condition can be expressed as

$$\Delta H_f = \beta \Delta H_f(B^0) - \sum_{i=1}^m \alpha_i \Delta H_f(A_i^0)$$

(9)
\[
\varepsilon(q/q') = \frac{\Delta H_f(D^q, E_F = 0) - \Delta H_f(D^{q'}, E_F = 0)}{q' - q}
\]

(11)

where \(\Delta H_f(D^q, E_F = 0)\) is the DFE calculated at \(E_F = 0\). The CSTLs are important for the electronic properties; if these levels are deep inside the band gap, then they can trap charge carriers and act as nonradiative recombination centers.

Being based on total energies, the CSTLs calculated with SCAN+VV10 should be fairly reliable. The positions of the band edges calculated with SCAN+VV10 suffer from the DFT band gap error. However, we would argue that the positions of the CSTLs with respect to the band edges are correct, because the defects’ electronic states have a character similar to either the valence band or the conduction band. For a more detailed discussion, see ref 22.

**RESULTS AND DISCUSSION**

We consider different possible compound complexes, which are selected as follows. For antisite defects, we use the notation \(A_B\) to indicate that atom \(A\) substitutes atom \(B\) in the lattice. All six antisites are included in our selection, i.e., the cation–cation antisites CsPb\(_2\) and PbCs, and the cation–anion antisites Cs\(_2\)I, Pb\(_2\)I, and I\(_2\). In addition, we consider the compound antisite [2CsI]\(_2\). Of the compound interstitials and vacancies, we focus on those that correspond to formula units of the precursor materials PbI\(_2\) and CsI, and of the perovskite CsPbI\(_3\). Finally, as suggested in ref 42, we investigate the Pb\(_2\)CsPb\(_2\) complex, which basically is an exchange in the lattice between two neighboring Cs and Pb cations.

**Equilibrium Conditions.** Formation of compound defects in semiconductors is often driven by the attractive electrostatic interaction between defects with opposite charge states.\(^{15,16}\) Possible compound vacancies in CsPbI\(_3\), resulting from recombination of the point vacancies \(V_{\text{Cs}}\), \(V_{\text{Pb}}\), and \(V_I\), are then \(V_{\text{Cs}I}\), \(V_{\text{Pb}I}\), and \(V_{[\text{CsPbI}]}\), where the neutral state indeed turns out to be the most stable charge state under intrinsic conditions. Optimized structures of these defects are shown in Figure 1(a−c).

Following the same reasoning, we find the neutral compound interstitial defects [CsI], and [PbI]\(_2\), shown in Figure 1(d,e) through recombination of the point interstitials Cs\(_{\text{i}}^+\), Pb\(_{\text{i}}^+\), and I\(_{\text{i}}^-\). For larger potential compound interstitials, such as [CsPbI]\(_2\), we found that the lattice becomes too distorted and the DFE becomes very large.

Formation energies of the compound vacancies and interstitials, calculated according to eq 3, are shown in Figure 2.(a,b). Taking into account of all point defects and compound defects, the intrinsic Fermi level, \(E_F^{(i)}\), calculated with the charge neutrality condition, eq 2, is 0.58 eV with respect to the VBM. At this condition Cs\(_{\text{i}}^+\) and Pb\(_{\text{i}}^2^-\) are the dominant atomic point defects, and the antisite PbCs\(_{\text{i}}^+\), to be discussed below, is the most dominant compound defect. The compound vacancy and interstitial defects listed above, are then all stable in the neutral state. A list of the DFEs and concentrations, calculated at the intrinsic Fermi level, of these compound defects is given in Table 1.

A compound vacancy defect creates a considerable hole in the lattice, see Figure 1(a–c), and its DFE is correspondingly high. The vacancy \(V_{\text{Pb}I}\) is relatively easiest to form, with a DFE of 1.12 eV, followed by \(V_{\text{Cs}I}\) and \(V_{[\text{CsPbI}]}\) whose DFEs are 1.35 and 1.81 eV, respectively. All of these numbers are \(\geq 0.5\) eV higher than the DFEs of the simple point defects Cs\(_{\text{i}}^+\) and Pb\(_{\text{i}}^2^-\), which means that concentration of compound vacancy defects is negligible at room temperature under equilibrium conditions (Table 1).

Compound interstitial defects, [CsI], and [PbI]\(_2\), can be accommodated in the CsPbI\(_3\) lattice by a distortion or tilting of the Pb–I octahedra, see Figure 1(d,e), albeit at a considerable energy penalty, with DFEs of 1.48 and 1.87 eV, respectively. We conclude that compound interstitial defects also have negligible concentrations at room temperature under equilibrium conditions; see Table 1.

Turning to antisite defects, as there are two different cations in CsPbI\(_3\), antisites can be formed among cations, i.e., by a cation of one type occupying a position of a cation of the other type, PbCs (Pb substitutes Cs) or CsPb\(_2\) see Figure 1(f–g). We stick to the nomenclature of antisites, but note that replacing one cation by another can lead to a notable local distortion of the lattice, such that the substituting ion is significantly displaced from the lattice position of the original ion. Pb ions are nominally \(2^+\), and Cs ions are \(1^+\), so it is not surprising to find the most stable charge states of these antisites as Cs\(_{\text{i}}^+\) and CsPb\(_{\text{i}}^-\). The DFE of PbCs\(_{\text{i}}^+\) is comparable to that of the simple point defects Cs\(_{\text{i}}^+\) and Pb\(_{\text{i}}^2^-\), see Figure 2(c) and Table 1, which means that this antisite occurs relatively frequently under equilibrium conditions. The CsPb\(_{\text{i}}^-\) antisite defect has a DFE that is \(\sim 0.25\) eV larger than that of PbCs\(_{\text{i}}^+\), making it less favorable.

In principle it is possible that a Pb vacancy, Pb\(_{\text{i}}^2^-\), captures two Cs\(_i^+\) ions to form the [2CsI]\(_{\text{i}}^-\) antisite, see Figure 1(h). Somewhat surprisingly, the most stable charge state at the intrinsic Fermi level of this antisite is [2CsI]\(_{\text{i}}^-\). Its DFE is, however, \(\geq 1\) eV larger than that of the CsPb\(_{\text{i}}^-\) antisite, demonstrating that it is difficult to plant two Cs ions in one Pb lattice position; see Figure 1(g,h).

A second possible type of antisite results from placing an anion on a cation position, or vice versa. There are four possibilities, see Figure 1(i–l). Again we maintain the nomenclature of antisites, but note that the replacing anion or cation typically does not occupy a lattice site. For instance,
in the I\textsubscript{Cs} antisite, the I ion does not replace the Cs ion at its lattice position (Figure 1(k)). Instead, it forms a Pb\textsubscript{0}−I−Pb bridge bond nearby, which is a typical bonding configuration for I interstitials.\textsuperscript{25} In this sense, an antisite is actually a bonding configuration between a vacancy and an interstitial.

The most stable charge states of these antisites can be guessed from summing the charges of the point defects that can recombine to these antisites. For instance, Cs\textsubscript{+}\textsuperscript{−} and Pb\textsubscript{+}\textsuperscript{2+} antisites originate from recombining Cs\textsubscript{+}\textsuperscript{−}, respectively Pb\textsubscript{+}\textsuperscript{2+} interstitials with V\textsubscript{I}\textsuperscript{−} vacancies, whereas the I\textsubscript{Cs}\textsuperscript{2−} antisite results from recombining an I\textsubscript{−}\textsuperscript{0} interstitial with a V\textsubscript{Cs}\textsuperscript{−} vacancy. I\textsubscript{Cs}\textsuperscript{2−} is an exception to this rule; it might be a recombination between an I\textsubscript{−}\textsuperscript{0} interstitial and a Pb\textsubscript{+}\textsuperscript{2−} vacancy. In general, cation−anion antisites lead to unusually high charge states for the defects inserted into the CsPbI\textsubscript{3} lattice, Figure 1(i−l). This might in part explain their large DFEs, where all cation−anion antisite defects have a DFE that is at least 0.5 eV larger than that of simple point defects; Figure 2 and Table 1.

Finally, an exchange of two neighboring Cs and Pb cations leads to a defect that can be marked as Cs\textsubscript{0}Pb\textsubscript{0}Cs\textsubscript{0}. It can be thought of as formation of a compound defect between the cation−cation antisites Cs\textsubscript{0}Pb\textsubscript{0} and Pb\textsubscript{0}Cs\textsubscript{0}. Consistent with that, the most stable charge state of Cs\textsubscript{0}Pb\textsubscript{0}Cs\textsubscript{0} is the neutral state. Although in principle this compound defect is a simple exchange of a pair of Cs and Pb cations, its optimized structure involves a significant local distortion of the perovskite lattice, Figure 1(m). The Cs\textsubscript{0}Pb\textsubscript{0}Cs\textsubscript{0} compound defect has a moderate DFE of 1.02 eV, Table 1, which is however significantly larger than that of the individual cation−cation antisites, implying that its concentration under equilibrium conditions is low.

\begin{table}
\centering
\begin{tabular}{llllll}
\hline
\textbf{defects} & \textbf{ΔH} (eV) & \textbf{c\textsubscript{equilibrium}} (cm\textsuperscript{-3}) & \textbf{reaction} & \textbf{ΔH} (eV) & \textbf{c\textsubscript{nonequilibrium}} (cm\textsuperscript{-3}) \\
\hline
V\textsubscript{Cs}\textsuperscript{0} & 1.35 & 2.81 \times 10\textsuperscript{-1} & V\textsubscript{Cs}\textsuperscript{−} + V\textsubscript{I}\textsuperscript{+} & −0.06 & 7.75 \times 10\textsuperscript{4} \\
V\textsubscript{Pb}\textsuperscript{0} & 1.12 & 7.23 \times 10\textsuperscript{2} & V\textsubscript{Pb}\textsuperscript{−} + 2V\textsubscript{I}\textsuperscript{+} & −0.83 & 5.26 \times 10\textsuperscript{14} \\
V\textsubscript{CsPb}\textsuperscript{0} & 1.81 & 1.73 \times 10\textsuperscript{−9} & V\textsubscript{Cs}\textsuperscript{−} + V\textsubscript{Pb}\textsuperscript{−} + 3V\textsubscript{I}\textsuperscript{+} & −1.54 & 5.10 \times 10\textsuperscript{13} \\
\hline
\multicolumn{2}{l}{\textbf{Interstitials}} & \multicolumn{2}{l}{} & \multicolumn{2}{l}{} \\
[CsI]\textsuperscript{0} & 1.48 & 1.51 \times 10\textsuperscript{−3} & Cs\textsuperscript{+} + I\textsuperscript{−} & 0.16 & 1.41 \times 10\textsuperscript{4} \\
[PbI\textsubscript{2}\textsuperscript{3+}] & 1.87 & 1.09 \times 10\textsuperscript{−9} & Pb\textsuperscript{2+} + 2I\textsuperscript{−} & −0.30 & 3.24 \times 10\textsuperscript{13} \\
\textbf{Antisites (Cation−Cation)} & \textbf{Antisites (Cation−Anion)} & \textbf{Cation Pair Exchange} & \textbf{Cation Pair Exchange} & \textbf{Cation Pair Exchange} & \textbf{Cation Pair Exchange} \\
\hline
Pb\textsubscript{Cs}\textsuperscript{+} & 0.56 & 1.71 \times 10\textsuperscript{12} & Pb\textsuperscript{2+} + V\textsubscript{Cs}\textsuperscript{−} & −0.93 & 9.44 \times 10\textsuperscript{15} \\
Cs\textsubscript{Pb}\textsuperscript{−} & 0.81 & 1.09 \times 10\textsuperscript{8} & Cs\textsuperscript{+} + V\textsubscript{Pb}\textsuperscript{−} & −0.39 & 3.88 \times 10\textsuperscript{15} \\
[2Cs\textsubscript{Pb}]\textsuperscript{+} & 1.83 & 7.72 \times 10\textsuperscript{−10} & 2Cs\textsuperscript{+} + V\textsubscript{Pb}\textsuperscript{−} + e\textsuperscript{−} & 0.01 & 1.51 \times 10\textsuperscript{13} \\
\hline
I\textsubscript{Pb}\textsuperscript{2−} & 2.51 & 2.90 \times 10\textsuperscript{−21} & I\textsuperscript{−} + V\textsubscript{Pb}\textsuperscript{−} + e\textsuperscript{−} & 1.24 & 1.12 \times 10\textsuperscript{−12} \\
Pb\textsuperscript{1+} & 1.72 & 1.58 \times 10\textsuperscript{−7} & Pb\textsuperscript{2+} + V\textsuperscript{I}\textsuperscript{+} & 0.25 & 9.82 \times 10\textsuperscript{2} \\
I\textsubscript{Cs}\textsuperscript{2−} & 1.10 & 3.50 \times 10\textsuperscript{3} & I\textsuperscript{−} + V\textsubscript{Cs}\textsuperscript{−} & −0.31 & 1.10 \times 10\textsuperscript{13} \\
Cs\textsuperscript{Pb}\textsuperscript{+} & 1.40 & 4.39 \times 10\textsuperscript{−2} & Cs\textsuperscript{+} + V\textsuperscript{I}\textsuperscript{+} & 0.08 & 3.28 \times 10\textsuperscript{7} \\
\hline
Cs\textsubscript{0}Pb\textsubscript{0}Cs\textsubscript{0} & 1.02 & 2.74 \times 10\textsuperscript{4} & Cs\textsubscript{0} + Pb\textsubscript{0}Cs\textsubscript{0} & −0.35 & 1.14 \times 10\textsuperscript{4} \\
\hline
\end{tabular}
\caption{Formation Energies (ΔH) and Concentrations of Compound Defects under Equilibrium Conditions (c\textsubscript{equilibrium}, T = 300 K); Recombination Reactions and Reaction Energies (ΔH\textsubscript{r}) and Concentrations of Compound Defects under Nonequilibrium Conditions (c\textsubscript{nonequilibrium}, for all at the Intrinsic Fermi Level\textsuperscript{a}}
\end{table}

\textsuperscript{a}The specific nonequilibrium conditions are defined by defect formation at an elevated temperature equilibrium at T = 500 K, followed by allowing for recombination through isolation at T = 300 K.

In summary, under equilibrium conditions at room temperature, only the formation of cation(Cs)−cation(Pb) antisites is prominent, with Pb\textsubscript{Cs}\textsuperscript{+} presenting a comparable concentration to those of the dominant point defects Cs\textsubscript{+} and V\textsubscript{Pb}\textsuperscript{−}, and Cs\textsubscript{Pb} is formed to a lesser extent. Other compound defects, antisites, compound vacancies or interstitials, are not favorable due to their large DFEs.

**Non equilibrium Conditions.** Defect concentrations can change drastically under nonequilibrium conditions. Highly nonequilibrium conditions typically occur during the growth of the perovskite crystals. The resulting concentration of defects can then not be simply deduced from the equilibrium relation (eq 1). The types and concentrations of defects that occur of course depend on the exact growth conditions. To estimate the potential role played by compound defects, we explore the following model.

It starts from the assumption that initially defects are created at an elevated temperature, which could reflect an annealing step during the growth process, for instance, with concentrations that can be estimated from eq 1. The crystal is then brought to room temperature, where the point defects and compound defects present are allowed to recombine or dissociate, according to eq 8, under the constraints of conservation of the total number of atoms in the defects, eq 10.

A key parameter determining the recombination reaction is the reaction energy (eq 9). Table 1 shows the reaction energies, calculated at the intrinsic Fermi level, of the recombination reactions that lead to the compound defects, and Figure 3(a) shows the reaction energies as a function of the Fermi level. For a recombination reaction to lead to an appreciable concentration of a compound defect, its reaction energy needs to be significantly negative.
A third relatively prominent defect is the compound vacancy $V_{\text{CsPb}^0}$ with a concentration of $5.26 \times 10^{14} \text{ cm}^{-3}$. The compound vacancy $V_{\text{CsPb}}^0$ and the anion–cation antisite $I_{\text{Cs}}^{2-}$ occur at lower concentrations of $5.10 \times 10^{13}$ and $1.10 \times 10^{13} \text{ cm}^{-3}$, respectively, whereas the concentrations of the other compound defects are much smaller (under intrinsic Fermi level conditions).

In summary, whereas at equilibrium conditions compound defects are unlikely to form at room temperature, creation of point defects at elevated temperatures and subsequent annealing leads to recombination of point defects, and a prominent appearance of cation–cation antisites $\text{Pb}\text{Cs}^+$ and $\text{CsPb}^-$. Less important, though still present in appreciable quantities, are the compound vacancies $V_{\text{CsPb}}^0$ and $V_{\text{CsPbI}}^0$ and the anion–cation antisite $I_{\text{Cs}}^{2-}$.

**Shifting the Fermi Level.** Nonequilibrium conditions of a different type occur when operating perovskite solar cells. Electrons and holes are produced by light absorption, creating quasi-Fermi levels for electrons and holes that are closer to the band edges than the intrinsic Fermi level. The DFEs, eq 3, and therefore the defect concentrations, eq 1, are affected by the position of the Fermi level, depending on the charge states of the defects.

As can be observed in Figure 2(a,b), the compound vacancies and interstitials maintain their neutral states (and their DFEs) over a large range of Fermi level positions. Only if the Fermi level is close to the conduction band minimum (CBM) does $V_{\text{Cs}}$ become negatively charged, and if the Fermi level is close to the valence band maximum (VBM), then $[\text{Cs}]$, and $[\text{Pb}]$, become positively charged.

The cation–cation antisite $[\text{2Cs}]_{\text{Pb}}^+$, which is positively charged at the intrinsic Fermi level (Figure 2(c)), becomes neutral upon raising the Fermi level and becomes negatively charged for a Fermi level close to the CBM. The other cation–cation antisites behave similar to simple (charged) point defects, with $\text{Pb}\text{Cs}^+$ decreasing its DFE upon lowering the Fermi level, and $\text{CsPb}^-$ decreasing its DFE upon raising the Fermi level.

The DFEs of the highly charged cation–anion antisites of course depend strongly on the position of the Fermi level (Figure 2(d)). The $I_{\text{Cs}}^{2-}$ and $\text{PbI}^3^+$ antisites become favorable for Fermi level positions close to the VBM, and the $I_{\text{Cs}}^{2-}$ and $\text{PbI}^3^+$ become more important for Fermi levels close to the CBM.

At the intrinsic Fermi level, or indeed for a Fermi level positioned anywhere in the midgap region, we find that the most stable charge state of a compound defect is simply the sum of the charges of the point defects involved in the recombination reaction, eq 4:

$$\alpha q_i + \ldots + \alpha n^m = \beta q_h$$  \hspace{1cm} (12)

As long as this holds, the reaction energy does not depend on the exact position of the Fermi level and is constant, see eqs 3 and 9, which can be observed in Figures 3(a) and S4. Consequently, for a Fermi level in this range, the concentrations of the compound defects do not depend upon the exact position of the Fermi level; see Figure 3(b).
Figure 4. Charge state transition levels of compound defects in CsPbI$_3$. The levels representing a change of a single ±e are indicated by colored lines. The bottom and top gray areas represent the valence and conduction bands (calculated with the SCAN+rVV10 functional without spin–orbit coupling). The two horizontal dashed lines are 10 k$_B$T ($T = 300$ K) above the VBM and below the CBM, respectively.

conservation (eq 12) does not necessarily hold, as it becomes energetically more advantageous to accept holes or electrons from the valence or conduction bands by one or more of the defects involved in the reaction. Figure 3(a) shows that, as a result of this, reaction energies can change significantly if the Fermi level comes closer to the band edges. As an example, the reaction energy of [2Cs]$_{[2]}$ decreases if the Fermi level either is close to the VBM or close to the CBM, where this compound defect becomes positively ([2Cs]$^{+}$) or respectively negatively ([2Cs]$^{-2}$) charged.

Most remarkable in Figure 3(a) is the strong decrease of the reaction energy of the cation–anion antisite Pb$_i$, if the Fermi level moves upward from 1.01 eV. At the intrinsic Fermi level, this compound defect is highly charged (Pb$_i^{3+}$, Figure 2(d)), but upon raising the Fermi level, it becomes energetically advantageous to capture one or more electrons from the conduction band and lower its reaction energy. Further noticeable is the strong increase of the reaction energies of the compound vacancies V$_{[Pb]_{[1]}}$ and V$_{[CsPbI]_{[3]}}$ for Fermi levels close to the CBM, and for the antisite I$_{[C]}$ and compound interstitial [Pb$_{[1]}$], for a Fermi level close to the VBM. A detailed description of the reaction and defect formation energies of each compound defect is given in Figure S4 of the Supporting Information.

These changes of the reaction energies upon moving the Fermi level closer to the band edges, have consequences for the defect concentrations (Figure 3(b)). The cation–cation antisites Pb$_{[C]}$ and Cs$_{[P]}$ remain the dominant defect, but for a Fermi level close to the CBM ($E_F > 1.6$ eV), the concentration of the compound vacancies V$_{[Pb]_{[1]}}$ and V$_{[CsPbI]_{[3]}}$, which are third and fourth most important defects at midgap Fermi level positions, become negligible. The cation–anion antisite Pb$_i$ becomes the third most important defect for $E_F > 1.3$ eV. For a Fermi level closer to the VBM not much happens, unless for the rather extreme case $E_F < 0.1$ eV, where the antisite [2Cs]$_{[2]}$ begins to appear in non-negligible concentrations, while the anion–cation antisite I$_{[C]}$ concentration becomes negligible.

**Charge State Transition Levels.** Based on Figure 2 and eq 11, and accepting the caveats presented by DFT functionals, the CSTLs of compound defects are determined. The results for all defects considered in this paper, are shown in Figure 4. The most prominent compound defect, the cation–cation antisite Pb$_{[C]}$, leads to double shallow donor levels, whereas the antisite Cs$_{[P]}$ only leads to a shallow acceptor level. The compound vacancies V$_{[Pb]_{[1]}}$ and V$_{[CsPbI]_{[3]}}$ have both a shallow donor as well as a shallow acceptor level. The anion–cation antisite I$_{[C]}$ has no levels inside the band gap.

At the intrinsic Fermi level, or indeed if the Fermi level is well inside the band gap, these are all compound defects that can occur in appreciable quantities; see Figure 3(b). If the Fermi level is close to the CBM, then the concentration of Pb$_i$ antisites increases. Although this antisite introduces two deep levels inside the band gap, both of these levels involve a change in charge state of two electrons, i.e., 3+/-1 and +/-. These levels are likely to be much less active than donor or acceptor levels associated with a change of one in charge state, as the probability of trapping two electrons simultaneously is very low. If the Fermi level becomes extremely close to the VBM, then the concentration of [2Cs]$_{[2]}$ becomes somewhat higher. As its CSTL (+/-) is well inside the band gap, this compound defect forms a deep trap, which can act as a recombination center.

Besides the defects discussed in the previous two paragraphs, all other defects occur in such negligible quantities, so that their electronic impact is negligible. In fact, the only compound defect considered in this paper that forms a series of deep trap levels, which is the anion–cation antisite I$_{[Pb]}$ (Figure 3(b)), has a very large positive reaction energy (Table 1), so it does not form under practical conditions.

In summary, the relatively abundant compound defects either form shallow donor or acceptor levels ([Pb$_{[C]}$, Cs$_{[P]}$, V$_{[Pb]_{[1]}}$, V$_{[CsPbI]_{[3]}}$ and I$_{[C]}$) or electronically not very active levels (Pb$_i$). Only under relatively extreme conditions, with a Fermi level very close to the VBM, the compound defect [2Cs]$_{[2]}$ can form, which has a deep trap level.

**CONCLUSIONS**

To conclude, we have studied the formation of compound defects in the archetype inorganic halide perovskite CsPbI$_3$ by means of DFT calculations using the accurate and efficient SCAN+rVV10 functional. Considering compound vacancies, V$_{[C]}$, [Pb$_{[1]}$] and V$_{[CsPbI]_{[3]}}$ compound interstitials [Cs$_{[1]}$] and V$_{[CsPbI]_{[3]}}$, cation–cation antisites Pb$_{[C]}$, Cs$_{[P]}$, and [2Cs]$_{[2]}$, anion–cation antisites I$_{[C]}$, I$_{[Pb]}$, Cs$_{[P]}$, and Pb$_i$, and cation pair...
exchange Cs$_{2}$Pb$_{2}$, we evaluate their formation under equilibrium conditions and under conditions that reflect their formation as recombination reactions of simple point defects.

Although the energies of several of these recombination reactions are favorable, under equilibrium conditions at room temperature, only the formation of the antisite where Pb substitutes Cs is prominent, and the concentrations of point defects are too small to give any appreciable amount of other compound defects. However, under nonequilibrium conditions, mimicked by a high temperature annealing step, several types of compound defects can be formed in significant concentrations. Most prominent are the cation–cation antisites Pb$_{Cs}^{+}$ and Cs$_{Pb}^{-}$, with concentrations comparable to those of the dominant point defects Cs$_{i}^{+}$ and Pb$_{i}^{2-}$. Smaller amounts of the compound vacancies V$_{[PbI]_{0}}^{0}$ and V$_{[CsPbI]_{0}}^{0}$ and the anion–cation antisite I$_{Cs}^{2-}$ can be observed, whereas the concentrations of other defects are negligible.

The formation energies and concentrations of compound defects in other halide perovskites will of course be different from those in CsPbI. The same properties of point defects in hybrid organic–inorganic halide perovskites show clear trends upon changing the halide ions or the cations, and at least the Pb-based materials show qualitatively a similar behavior. It is therefore reasonable to assume that compound defects in these materials also show qualitatively similar properties to those in CsPbI.

Under solar cell operating conditions the (quasi) Fermi level can shift to the proximity of the VBM and CBM, which promotes the formation of certain compound defects, and suppresses that of others. If the Fermi level is close to the CBM, then the formation of V$_{[PbI]_{0}}^{0}$ and V$_{[CsPbI]_{0}}^{0}$ is suppressed and that of the cation–anion antisite Pb$_{i}^{-}$ is promoted, whereas if the Fermi level is close to the VBM, then the formation of I$_{Cs}^{2-}$ is suppressed and that of [2Cs]$_{Pb}^{+}$ is promoted. The other defects are less affected by a change in Fermi level.

The antisites and compound vacancies that can occur in appreciable concentrations (Pb$_{Cs}^{-}$, Cs$_{Pb}^{+}$, I$_{Cs}^{-}$, V$_{[PbI]_{0}}^{0}$, and V$_{[CsPbI]_{0}}^{0}$) tend to create shallow trap levels only. The antisite Pb$_{i}$ creates several deep levels, which are, however, not very active electronically, as their charge state transition involves the arrival of two electrons simultaneously. The compound defect [2Cs]$_{Pb}$ leads to a deep trap level. However, as discussed above, this defect is only slightly likely to form if the Fermi level is very close to the VBM. These results illustrate the exemplary electronic tolerance of halide perovskites toward the presence of defects.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c06789.

List of convergence tests of the energy cutoff and size of supercell; number of possible defect sites and counting rule for each compound defect; concentration of compound defects at 300 K; temperature dependence of concentrations of point defects; table of concentrations of point defects; detailed comparison of reaction energies and formation energies of each compound defect (PDF)

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**Notes**

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