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Simultaneous control of ionic and electronic conductivity in materials: Thallium bromide case study

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(Dated:)

Materials that combine tailored electronic and ionic transport properties are fiercely pursued for applications such as catalysis, hydrogen storage, battery cathodes and solid electrolytes, among others. Since these properties are intertwined, optimizing one often results in degrading the other. Therefore, achieving simultaneous control of ionic and electronic conductivity in materials is currently one of the great challenges in solid state ionics. In this letter, we propose a method to limit ionic current without impacting the electronic properties of a general class of materials, based on co-doping with oppositely charged ions. We describe a set of analyses, based on parameter-free quantum mechanical simulations, to assess the efficacy of the approach and determine optimal dopants. For illustration, we discuss the case of thallium bromide, a wide band gap ionic crystal whose promising use as a room-temperature radiation detector has been hampered by ionic migration. We find that acceptors and donors bind strongly with the charged vacancies that mediate ionic transport, forming neutral complexes that render them immobile. Analysis of carrier recombination and scattering by the complexes allows the identification of specific dopants that do not degrade electronic transport in the crystal.

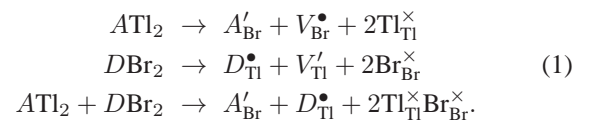
PACS numbers:

Long after solid-state electronics had been mastered, triggering one of the most important technological revolutions in history, the discovery of fast ion conductors (FICs) in the 1960s made possible the development of whole new classes of devices. FICs found application in energy storage and conversion with the creation of lithium ion batteries and fuel cells with solid electrolytes, as well as gas sensors based on zirconia, which are present in virtually every automobile produced worldwide [1]. Since response times for gas sensors or better charge/discharge rates in solid electrolyte batteries depend on the ionic current, the ability to enhance it is highly desirable. This can be achieved by the incorporation of supervalent elements into the host material [1–3]. The charge imbalance introduced by dopants in ionic materials is usually compensated by the formation of oppositely charged vacancies, which result in an increase of ionic current. This is the case for Ti-doped NaAlH_4 used for hydrogen storage [4], Zr-doped CeO_2 used for catalysis or gas sensors [2], transition metal-doped LiFePO_4 used for ion battery cathode [3], to mention some. However, manipulating the ionic conductivity of FICs often affects their electronic properties, which one might want to independently control. For example, in solid electrolytes for batteries or fuel cells the electronic conduction must be suppressed. On the other hand, it must be kept at metallic levels for electrodes or logic switches [5, 6]. The opposite also occurs when dopants meant to improve the electronic properties of a material impair the optimal ionic conductivity [7]. The inability to coordinate ideal ionic and electronic properties is a great challenge that precludes the effective implementation of several materials in technological applications.

In this letter, we tackle the general problem of how to reduce the ionic current in materials without impacting their electronic properties. This is desirable for a wide class of mixed conductors to be employed in transistors, diodes and LEDs, among other applications. We illustrate our approach with thallium bromide (TlBr), a promising material for high-performance room-temperature γ - and X-ray detection [8, 9].

Its exceptional performance, however, invariably degrades after operation times that vary from hours to several weeks [10]. This phenomenon, known as polarization, is associated with an undesirable ionic current in the crystal when electrically biased, leading to the accumulation of charged ions at the electrical contacts of the device. Several ways to circumvent this problem have been attempted, including ultrapurification [11], operation at low temperatures [12], using Tl contacts [13], employing surface treatments [14], engineered device geometry [15, 16], and making larger crystals [17]. None of these techniques, however, solve the polarization problem indefinitely.

Since the mechanism for ionic migration is mediated by electrically charged vacancies [48], we propose a new approach for reducing ionic current through the introduction of supervalent dopants that form neutral pairs with them. Strongly bound, neutral vacancy–dopant pairs are less mobile than the vacancies alone, as experimentally demonstrated for many singly doped (one element) ionic crystals at low temperatures [1, 18, 19]. At room temperature and above, materials doped with supervalent ions show higher ionic current relative to the pristine ones, as discussed above, because the presence of supervalent ions induces the formation of an equal number of new vacancies, which increase the ionic conductivity. Therefore, to achieve a reduction of the ionic current it is necessary to avoid the formation of new vacancies. This is possible by simultaneously co-doping with ions of excess negative (A) and positive (D) charge relative to the host ions (Br^- and Tl^+ , respectively), as indicated by the following defect reactions written in Kröger-Vink notation:



To demonstrate the approach and assess the results, we used quantum mechanical simulations to model the electronic

properties of pristine and doped TlBr (CsCl structure). Calculations were based on density functional theory using both the generalized gradient approximation (GGA-PBE) and a hybrid exchange-correlation functional (HSE06) [49]. With GGA-PBE, we obtained a direct band gap of 1.98 eV (at point X of the Brillouin zone) and a lattice parameter of 4.06 Å for the pristine material, compared to experimental values of 3.01 eV (direct gap) and 3.97 Å, respectively (at 4.7 K [20]). The HSE06 functional yielded improved results of 2.67 eV and 4.04 Å. Inclusion of spin-orbit coupling shifted the conduction band minimum to point R in both approaches, resulting in an indirect gap of 1.50 eV (PBE) and 2.22 eV (HSE06). Some experimental results account for an indirect band gap of about 2.7 eV for this material, but the transition from the valence band maximum at X to the conduction band minimum at R is phonon forbidden [21]. As pointed out in [22], the excellent electronic properties of TlBr for radiation detectors stem from the very shallow nature of Tl and Br vacancies, whose formation energies cross near the middle of the band gap and pin the Fermi level there, as shown in Fig. S1 in the Supplemental Material [23]. The pinning of the Fermi level near mid-gap keeps the free carrier concentration low in the intrinsic material, contributing to the low noise and high energy resolution observed in measured radiation spectra. For a detailed discussion of these effects in radiation detectors, see [24]. Also, the low formation energy of vacancies at the point of Fermi level pinning, 0.4 eV with PBE and 0.46 eV with HSE06, which is a common feature of ionic materials, makes it favorable to compensate extrinsic dopants by the mechanism described in Reactions (1) rather than generating free carriers at the band edges.

We modeled Pb, Te, Se and S dopants in TlBr with $3 \times 3 \times 3$, $4 \times 4 \times 4$, and $5 \times 5 \times 5$ cubic supercells (54, 128, and 250 atoms, respectively). We found that the chalcogens mostly originate either neutral interstitials or negatively charged defects incorporated on Br sites, whereas Pb is positively charged and incorporates on Tl sites. All the dopants were tested on both atomic sites, as well as four nonequivalent interstitial sites. The most favorable configuration was then tested in association with the oppositely charged vacancy, at distances from the 1st to 3rd nearest neighbor. Figure 1 shows the PBE formation energies and charge states of the Pb- and Se-associated defects as a function of the Fermi level. Similar figures for S and Te are available online [23] (Fig. S2). The formation energies were calculated in the standard way [25]:

$$\Delta E_f = E_d - (E_p - n\mu_x) + q(\mu_e + E_{\text{VBM}}), \quad (2)$$

where E_d and E_p are the total energies of the defective and the pristine supercells, respectively, n is the number of atoms of element x removed from the supercell and added to a reservoir whose chemical potential is μ_x , and q is the amount of charge exchanged from a reservoir with electron chemical potential μ_e , which we reference to the energy of the valence band maximum, E_{VBM} . Spurious periodic electrostatic interactions for supercells with charged defects were corrected using Makov-Payne scheme [26] [50]. We neglect in Eq. (2)

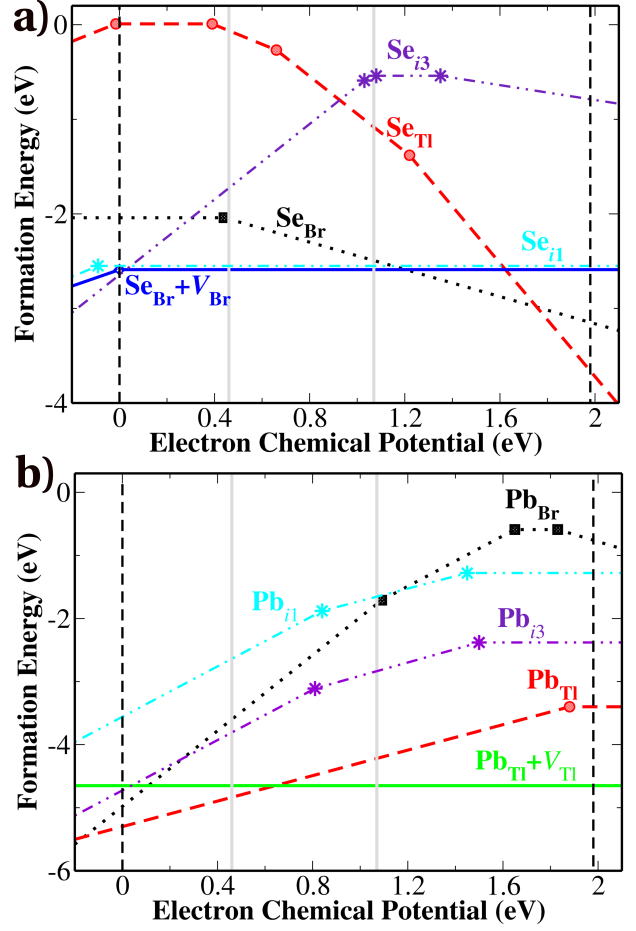


FIG. 1: (color online) Formation energies of Pb (a) and Se (b) defects in TlBr. The lowest energy configuration was tested in association with the oppositely charged vacancy. The slopes of the lines give the charge state of the defects via Eq. (2). The black vertical dashed lines indicate the calculated positions of the band edges in pristine TlBr, and the vertical gray lines bound the region of the Fermi level in which the formation energies of the vacancies are positive (see Fig. S1 in the Supplemental Material [23]). The chemical potentials of Tl and Br were set for stoichiometric conditions.

terms involving the chemical potentials of extrinsic elements because it suffices to know the relative formation energies of different defects associated with each dopant for our purposes. The formation enthalpy of TlBr was evaluated from $\Delta H_f = \mu_{\text{TlBr}} - \mu_{\text{Tl}}^B - \mu_{\text{Br}}^B$, where the superscript B denotes bulk phase. We obtained 1.69 eV with PBE and 1.86 eV with HSE06, both in good agreement with experiment at 1.79 eV [27]. The chemical potential for Tl and Br ions in the stoichiometric regime is given by $\mu_{\text{Tl(Br)}} = \mu_{\text{Tl(Br)}}^B + \Delta H_f/2$ [24, 28]. Results using PBE and HSE06 on $3 \times 3 \times 3$ supercells were in very close agreement for the positions of the charge state transitions relative to the VBM, as shown in Table I in supplemental information [23]. For a discussion on the root of the agreement between PBE and HSE06 results as observed for TlBr, we refer the reader to Ref [29]. Therefore, we can confidently use the PBE results from the larger supercells, which

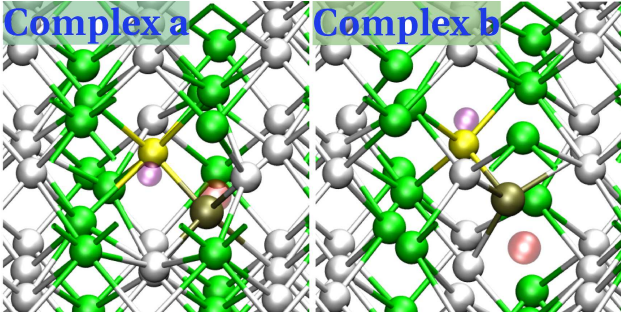


FIG. 2: (color online) Supercells of the TlBr crystal (green spheres = Tl; white spheres = Br) with defect complexes consisting of a donor dopant, Pb_{Tl} (ocher sphere), an acceptor dopant S_{Br} or Se_{Br} (yellow sphere). Vacancies V_{Br} are indicated by translucent purple sphere and V_{Tl} by translucent red sphere. In configuration *a*, the vacancies are nearest neighbors to both dopants, whereas in configuration *b* they are nearest neighbors only to the oppositely charged dopant.

are better converged with respect to finite-size effects. Inclusion of spin-orbit coupling for the transition levels of both Pb and Se doped material did not change the results either.

In Fig. 1 we show that $\text{Pb}_{\text{Tl}}^{\bullet}$ and Se_{Br}' form neutral complexes with V_{Tl}' and V_{Br}^{\bullet} , respectively, indicated by the flat lines. Although neutral Se_i are low formation energy defects, our calculations show that in the vicinity of V_{Br}^{\bullet} they spontaneously collapse into substitutional defects. The binding energy of a defect complex is given by [30]:

$$\Delta E_{\text{bind}} = E_{\text{complex}} - \sum_i E_{d,i}, \quad (3)$$

where E_{complex} is the formation energy of the defect complex and $E_{d,i}$ are the formation energies of each individual defect comprising the complex. Negative values indicate binding complexes. Table I shows the binding energies of several complexes of interest for intrinsic, Pb and Se doped TlBr [51]. Results for complexes involving Pb in association with S or Te are available in Table II in the Supplemental Material [23]. To estimate residual finite size errors, we compare the results for the three supercells. Schottky pairs in HSE06 calculations bind with an energy of -0.56 eV, again showing the reliability of our PBE results, at -0.54 eV. For additional validation, we calculated the binding energy of Ca_{Tl} with V_{Tl} as -0.4 and -0.34 eV with PBE for the $4 \times 4 \times 4$ and the $5 \times 5 \times 5$ supercells, respectively, in striking agreement with the experimental estimation of -0.36 eV [18].

In Fig. 2, we show two main possibilities for the vacancies to bind to the dopant pairs: each vacancy “bonded” to both of the dopants (configuration *a*) or each vacancy “bonded” only to the dopant that has opposite charge to it (configuration *b*). The former is more strongly bound by ~ 0.3 eV than the latter, as indicated in Table I. Moreover, these dopants–vacancies complexes bind much more strongly than the Schottky pairs alone (see Table I). Further, complex *a* is 0.6 eV more binding than the sum of pairs involving only a single vacancy and the oppositely charged dopant and more importantly, 0.5 eV

TABLE I: Binding energies of acceptor-donor complexes, involving or not the intrinsic vacancies. We used both the $4 \times 4 \times 4$ and the $5 \times 5 \times 5$ supercells. Configurations *a* and *b* for the dopant-pair–vacancy-pair complex are shown in Fig. 2. All values were obtained with Eq. (3) including Makov-Payne corrections.

Complex	Sites	E_{bind} (eV)	
		$4 \times 4 \times 4$	$5 \times 5 \times 5$
$V_{\text{Tl}}' + V_{\text{Br}}^{\bullet}$ (Schottky pair)	2 nd NN	-0.44	-0.36
$\text{Se}_{\text{Br}}' + V_{\text{Br}}^{\bullet}$	2 nd NN	-0.54	-0.39
$\text{Pb}_{\text{Tl}}^{\bullet} + V_{\text{Tl}}'$	1 st NN	-0.41	-0.37
$\text{Pb}_{\text{Tl}}^{\bullet} + \text{Se}_{\text{Br}}'$	1 st NN	-0.83	-0.73
$V_{\text{Tl}}' + \text{Pb}_{\text{Tl}}^{\bullet} + \text{Se}_{\text{Br}}' + V_{\text{Br}}^{\bullet}$	config. a	-1.46	-1.29
	config. b	-1.18	-0.93

more binding than the sum of an isolated Schottky pair plus an isolated pair of dopants. If the latter was the most favorable case, the dopants wouldn’t reduce vacancy mobility relative to the intrinsic material. The ionic conductivity of the material varies exponentially with the inverse of the activation barrier, or enthalpy, plus the binding energy given in Table I (see [1]). Therefore, the formation of complexes *a* and *b* shown in Fig. 2 will reduce the mobility of ions much more dramatically than the mere association of Schottky pairs would in pure TlBr.

The remaining question is whether this suppression of ionic current and consequent stabilization of TlBr comes at the expense of its favorable electronic properties. We can generally characterize the electronic properties in terms of the carrier mobilities, μ , and lifetimes of excitations, τ . For the purpose of TlBr as a radiation detector, we require maximizing μ and τ . For TlBr, τ for electrons is very large, on the order of 10^{-2} s [9]. The main source of degradation of τ would be Shockley-Reed-Hall recombination centers. Because the recombination rate increases exponentially with the difference in energy between an electron or hole trap state and the respective band edge, defects that introduce states near the middle of the band gap are most detrimental. We see in Fig. 1 that only very low concentration (high formation energy) Pb-related defects introduce deep levels, indicated by kinks in the formation energy curves. On Tl sites, Pb impurities are very shallow donors. Se_{Br} shows a $-1/0$ acceptor transition as the material becomes more hole-rich (decreasing μ_e) at $E_{\text{VBM}} + 0.44$ eV. However, this transition occurs outside the allowed region of μ_e between the vertical gray lines in Fig. 1. We confirmed this result using the HSE06 functional, extrapolating to the larger supercell sizes, as shown in Table I in supplemental information [23]. Thus, the trap level would always be filled and not affect carrier lifetimes. S_{Br} shows a $-1/0$ acceptor transition even farther in the region of inaccessible Fermi level by more the 0.1 eV by both PBE and HSE06 calculations. Te_{Br} , however, exhibits an acceptor transition deep in the gap (0.16 eV inside the allowed Fermi level range by PBE, 0.4 eV by HSE06). Therefore, Te dopants are detrimental to carrier lifetimes, but S, Se, and Pb are not.

The main carrier scattering mechanism in TlBr at room temperature is expected to be caused by lattice vibrations,

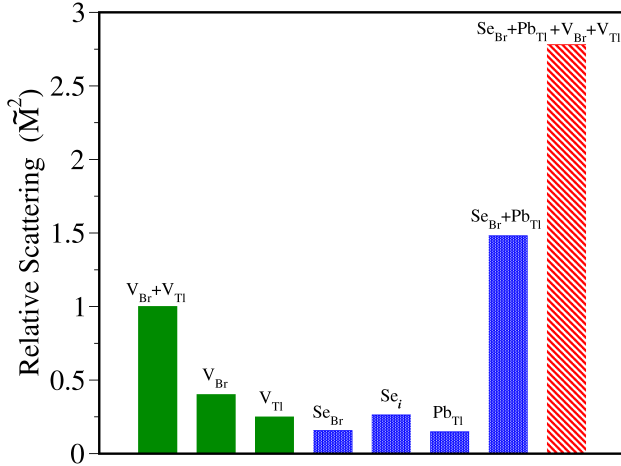


FIG. 3: (color online) Relative carrier scattering strengths of different intrinsic and extrinsic defects and defect complexes in TlBr as given by Eq. (6). The values are normalized to that for the Schottky pair.

since the Debye temperature is only ~ 160 K [31]. The acoustic phonon limit to the mobility can be approximated by [32]:

$$\mu = \frac{2\sqrt{2}\pi}{3} \frac{e\hbar^4 c_\ell}{m^{5/2} (k_B)^{3/2} D_A^2} T^{-3/2}, \quad (4)$$

where e and \hbar are, respectively, the electron charge and the reduced Planck's constant, c_ℓ is the longitudinal elastic constant (3.76×10^{10} N/m² at room temperature for TlBr [33]), m is the effective mass of the carrier of interest (we obtained $m_e = 0.51m_0$ and $m_h = 0.98m_0$, in good agreement with experimental data, $m_e^{\text{expt}} = 0.55m_0$ and $m_h^{\text{expt}} = 0.82m_0$ [34]); k_B is Boltzmann's constant, T is the lattice temperature and D_A is the deformation potential. We computed D_A as described in [35], obtaining -25.67 eV for electrons and -28.14 eV for holes. Using Eq. (4), we calculated the phonon-limited mobility at 300 K as ~ 19 cm²/V for electrons and ~ 3 cm²/V for holes, in excellent agreement with that measured for high quality material [31]. This agreement indicates that phonon scattering dominates the carrier mobility in TlBr and therefore doping the material should not affect electronic transport unless the defect complexes discussed above are orders of magnitude stronger scattering centers than the intrinsic defects, since these dopants should be present in concentrations commensurate to concentration of vacancies, which is around 10^{15} cm⁻³ for a highly pure crystal [11, 19].

The carrier scattering strength of a defect can be estimated using Fermi's golden rule, which gives the scattering rate between two electronic states $\Psi_f(k')$ and $\Psi_i(k)$, with energies ε_f and ε_i , to first order as

$$W_{ij} = \frac{2\pi}{\hbar} |\langle \Psi_f(k') | V_{\text{pert}} | \Psi_i(k) \rangle|^2 \delta(\varepsilon_f - \varepsilon_i), \quad (5)$$

where the perturbation potential $V_{\text{pert}}(\mathbf{r}) = V_d(\mathbf{r}) - V_0(\mathbf{r})$ is the difference between the total self-consistent potential in the defect cell, $V_d(\mathbf{r})$, and the ideal cell, $V_0(\mathbf{r})$. In principle,

Eq. (5) must be integrated over a significant number of pairs of states and k -points in the Brillouin zone to get the total scattering rate. However, a qualitative measure of the average scattering rate can be obtained from V_{pert} alone via [36]

$$\tilde{M}^2 = \left(\int d\mathbf{r} |\nabla V_{\text{pert}}| \right)^2. \quad (6)$$

In Fig. 3 we show the calculated “relative scattering rates,” \tilde{M}^2 , for the different individual defects as well as the complexes of interest for TlBr. We find that the complexes involving dopants and the two types of vacancies are less than three times stronger scattering centers than Schottky pairs. The fact that scattering by dopant complexes is within an order of magnitude of the intrinsic defect scattering, which is overwhelmed by phonon scattering in undoped TlBr, we conclude that co-doping at levels sufficient to bind a large fraction of vacancies would not degrade carrier mobility relative to the pristine material.

In summary, we have described a new approach to limit or control ionic conductivity in a general class of materials without impacting their electronic properties. The approach consists of doping the material with ions supervalent to the host material so that the dopants form neutral complexes with charged vacancies that mediate ionic transport. To prevent the generation of new vacancies that balance the excess charge introduced by the dopants, simultaneous co-doping with donors and acceptors is required. The binding energy of the complexes formed between the dopants and the vacancies must be large compared to that of intrinsic Schottky or Frenkel pairs. To assess the impact of doping on electronic transport in the material, the strength of the carrier scattering of the dopant complexes must be compared with that of intrinsic defects and phonons. Also, the dopants should not introduce deep levels that enhance recombination of carriers, if maximum lifetime is desired. The method can be adapted in a straightforward manner to prospect ideal dopants to enhance ionic mobility and reduce electronic one in solid electrolytes, for example, or to increase both conductivities for ion battery electrodes or logic switches, as discussed in the introduction. Using state of the art quantum mechanical calculations, we analyzed TlBr as a case study since it is an ionic material with excellent electronic properties that degrade over time due to charge build-up from ionic migration. Our results indicate that co-doping TlBr with Pb and Se or S satisfy all the required criteria. Tellurium, however, is ruled out as a favorable co-dopant to Pb because it introduces a deep trap state. We showed that the dopant complexes that form do not significantly affect carrier scattering and mobility. Results using the PBE and HSE06 functionals compared favorably.

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- [48] Even in materials with Frenkel defects, the presence of vacancies facilitates ionic motion because of the emptier lattice.
- [49] We used density functional theory [37, 38] with the generalized gradient approximation as implemented by Perdew, Burke, and Ernzerhof [39] to treat the exchange-correlation term. Core electrons were treated with the projector augmented-wave method [40, 41] as implemented in the VASP code [42, 43]. A plane-wave basis set with a cutoff of 320 eV was used, except for calculations involving S and Ca, where 380 eV was used consistently for all systems involved. For Brillouin zone sampling, we used the tetrahedron method with a Monkhorst-Pack mesh of $5 \times 5 \times 5$ and $4 \times 4 \times 4$ k -points for the smaller and larger supercell, respectively. The atomic coordinates were relaxed until all residual forces were below 0.01 eV/Å. For validation, some calculations were repeated using the HSE06 hybrid functional [44, 45], which mixes 25% screened Hartree-Fock exact exchange with the PBE functional. All HSE06 calculations used a $3 \times 3 \times 3$ supercell with a $4 \times 4 \times 4$ mesh for sampling the Brillouin zone and a k -point reduction factor of 2 for the Hartree-Fock kernel [46].
- [50] There are more recent methods [47] to treat the issue of spurious electrostatic interactions in periodic systems, but they should only differ significantly from Makov-Payne for higher charge states in small supercells. Given the tests we made with different sizes of supercells, such discrepancies are not significant enough to challenge our conclusions.
- [51] The very low binding energy of Schottky pairs reported in [22] (0.03 eV) is probably a result of using a small supercell and neglecting Makov-Payne corrections. For a $3 \times 3 \times 3$ cell we obtained $E_{\text{bind}} = -0.05$ eV without correcting for spurious electrostatic interaction and about -0.54 eV when including the correction.