



Thermal stabilization of defect charge states and finite-temperature charge transition levels



Tobias Hainer , Ethan Berger, Esmée Berger, Olof Hildeberg, Paul Erhart & Julia Wiktor

Point defects introduce localized electronic states that critically affect carrier trapping, recombination, and transport in functional materials. The associated charge transition level (CTLs) can depend on temperature, requiring accurate treatment of vibrational free energy contributions. In this work, we use machine-learned interatomic potentials to efficiently compute temperature-dependent (CTLs) for vacancies in MgO, LiF, and CsSnBr₃. Using thermodynamic integration, we quantify free energy differences between charge states and calculate the vibrational entropy contributions at finite temperatures. We find that temperature significantly affects the (CTLs) across all three materials, with substantial energy level shifts in MgO and LiF over the investigated temperature ranges. Most notably, in CsSnBr₃ a neutral charge state becomes thermodynamically stable above 40K, introducing a Fermi-level window absent at 0K. We show that the widely used static, zero-kelvin defect formalism can miss both quantitative (CTL) shifts and the qualitative emergence of new stable charge states.

Defects play a crucial role in determining the physical properties of materials, influencing mechanical, electronic, and thermal behavior^{1–5}. In particular, in functional applications such as photovoltaics they can both critically enhance and degrade the performance of solar energy devices^{2,6,7}. Under realistic operating conditions, defects are unavoidable, making it essential to understand their impact on material behavior. In non-metals, charged defects can form and interact strongly with their environment through long-range Coulomb forces, influencing electronic and ionic processes. A key property of such defects is the charge transition level (CTL), which determines the thermodynamically favorable charge state for a given Fermi level. These (CTLs) are strongly influenced by the local chemical environment and therefore can be sensitive to temperature⁸. Accurate predictions of (CTLs) are essential for understanding defect-related properties, underscoring the need for detailed studies of their behavior including finite-temperature effects.

These defect-related properties have mainly been modeled using density functional theory (DFT), an accurate but computationally expensive method that becomes prohibitive for larger systems and/or is limiting when thermal effects are important. Many studies have mapped out (CTLs) at zero kelvin for a wide range of materials^{9–14}. While this allows a static characterization of defects, capturing behavior at finite temperatures remains a significant challenge. At finite temperatures, contributions from spin, electronic, vibrational and orientational entropy play a role in the free energy formulations^{15,16}. Among these, vibrational entropy typically has the largest impact and must be accounted for to accurately predict defect

formation energies at finite temperatures. Incorporating this temperature dependence is therefore essential for reliable predictions above zero kelvin.

Finite-temperature effects have been explored within the (quasi-)harmonic approximation but also using molecular dynamics approaches^{16–20}, as well as through analyses of defect-induced volume changes and band-edge fluctuations²¹. These studies show that temperature induces only modest variations in defect formation free energies. However, a comprehensive understanding of the temperature dependence of (CTLs) is still emerging.

Here, we demonstrate a finite-temperature framework for defect (CTLs) by combining (DFT)-trained neuroevolution potential (NEP) models with thermodynamic integration (TI) directly between charge states to quantify the temperature dependence of (CTLs), as well as to determine the temperature dependence of optical transitions associated with vacancies in MgO, LiF, and CsSnBr₃. Building on the recent work on defect line shapes¹⁸, for each material, a (NEP) model was trained on (DFT) reference data encompassing defect configurations across the relevant charge states. To explicitly represent the vacancy, the atoms neighboring the defect site were decorated with alternative atomic labels, enabling the potential to distinguish local environments associated with different charge states¹⁸. Two distinct (TI) paths were employed to accurately capture the temperature-induced changes in the (CTLs): the Frenkel-Ladd path²² and a direct integration path connecting machine-learned potential (MLIP) labeled to represent different charge states. Compared to previous finite temperature studies of defect free energies and (CTLs), our work provides a practical and general workflow for obtaining finite temperature (CTLs) based on (MLIP),

decomposes vibrational and band-edge (valence band maximum (VBM)) contributions across three representative material classes and demonstrates the finite temperature emergence of a neutral defect charge state in CsSnBr_3 that is unstable at 0K.

Results

Charge transition levels and optical transition energies

The performance of the trained (NEP) models is shown in Fig. 1. All models achieve R^2 scores close to 1 and low root mean square error (RMSE) scores. Phonon dispersions were calculated to benchmark the (NEP) models against (DFT). For MgO and LiF, two force constant expansion models were trained using HIPHIVE²³ for each material, one on (NEP) data and one on (DFT) data, from which phonon dispersions were obtained via Phonopy. For CsSnBr_3 , phonon dispersions were obtained directly from Phonopy using both (NEP) and (DFT) force data. Loss during training, parity plots and phonon dispersion comparisons can be seen in Figs. S1–S9.

Using (TI) with our (MLIP), we first obtained the free energy of the charge states and pristine cells by integrating along the Frenkel–Ladd path. The defect formation energies were then evaluated using Eq. (1), including the (VBM) and correction terms.

These calculations enabled the construction of defect formation energy diagrams as a function of Fermi energy at various temperatures, as shown in Fig. 2a–c. In these plots, only the thermodynamically most stable charge state is shown at each Fermi energy. The positions of the (VBM) and conduction band minimum (CBM) are marked by solid vertical lines, with colors corresponding to their respective temperatures. While we train our (nep) models on data generated with semilocal functionals, we adjust the band edges in the formation energy plots for a more direct comparison with experimental data. It has been shown that (CTL) of localized defects are found at similar absolute energies at different levels of theory²⁴. Therefore, we only adjust the positions of the (VBM) and (CBM) in the plots. The shifts are taken from comparisons between calculations performed at the PBEsol level of theory for MgO and LiF, and at the r2SCAN+rVV10 level for CsSnBr_3 , against hybrid-functional calculations using the PBE0(α) method. In the case of CsSnBr_3 , we additionally incorporate the shifts from including the spin-orbit coupling. For MgO and LiF, the values of the exact-exchange fraction ($\alpha = 0.34$ and $\alpha = 0.50$, respectively) are taken from ref. 25, where

they were determined using Koopmans' theorem applied to the hydrogen probe and the $\text{H}^+/0$ level. For CsSnBr_3 we use $\alpha = 0.26$, following ref. 26, where the bromine vacancy was used as a probe.

From the formation energy diagrams, the (CTLs) at the temperatures where (TI) was performed were extracted, shown as the $\times$ -markers in Fig. 2d–f. Note that the shifts of (CTLs) in these plots are reported relative to the temperature dependent (VBM), shifts of all (VBM) and (CBM) can be seen in Fig. S16–S21. Because the Frenkel–Ladd path requires extensive sampling to achieve convergence, the full temperature dependence of the (CTLs) was obtained using a direct (TI) path between (MLIPs) representing different charge states, also shown in Fig. 2d–f. The two (TI) approaches yield closely agreeing results at all temperatures, while the direct path is substantially more computationally efficient. This enhanced efficiency is evident from the faster convergence shown in the SI (Fig. S10 and Fig. S11). This likely arises from the smaller energy differences along the (TI) path between charge states compared with those encountered along the Frenkel–Ladd path. Moreover, evaluating the free energy difference between charge states via the Frenkel–Ladd route requires two separate (TI) calculations, one for each charge state. In contrast, the direct charge-state path requires only a single (TI) calculation to obtain the (CTL). Thus, the direct path both halves the minimum number of required (TI) runs and converges substantially faster than the Frenkel–Ladd path.

Optical transition energies ($E_{\text{opt}}(q'/q)$ for transition from q to q') were calculated both at zero kelvin, using configurational coordinate diagrams (Fig. 3a–c), and at finite temperatures, using molecular dynamics (MD) simulations (Fig. 3d–f). These transitions are reported relative to the temperature dependent (VBM) and move similarly to the associated (CTLs). This is in agreement with previous results showing that the optical transition levels fluctuate similarly to the (CTL) in CsPbBr_3 ¹⁷. The configuration coordinate diagram represents the potential energy surface (PES) as the structure transforms between different defect geometries, where the energy differences between charge states at their minima correspond to emission or absorption processes. These diagrams were constructed by interpolating between the relaxed geometries of different charge states while the (MLIP) predicted the energy along the transformation path. These represent the zero-kelvin optical transitions, as they are derived from relaxed geometries. At finite temperatures starting at 10 K, (MD) trajectories of defect-containing

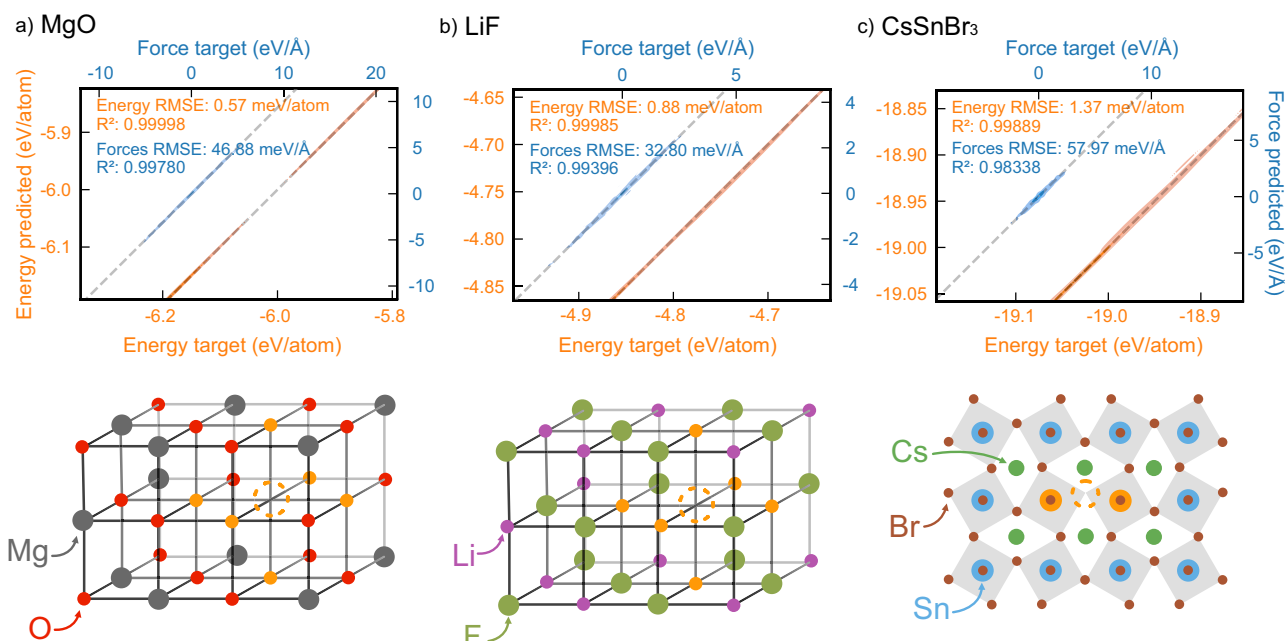


Fig. 1 | Machine-learned interatomic potential and illustrations of marked structures. **a** The MgO model performance. Six closest Mg atoms to the oxygen vacancy are marked. **b** The LiF model performance. Six closest Li atoms to the

fluorine vacancy are marked. **c** The CsSnBr_3 model performance. Two closest Sn atoms to the bromine vacancy are marked.

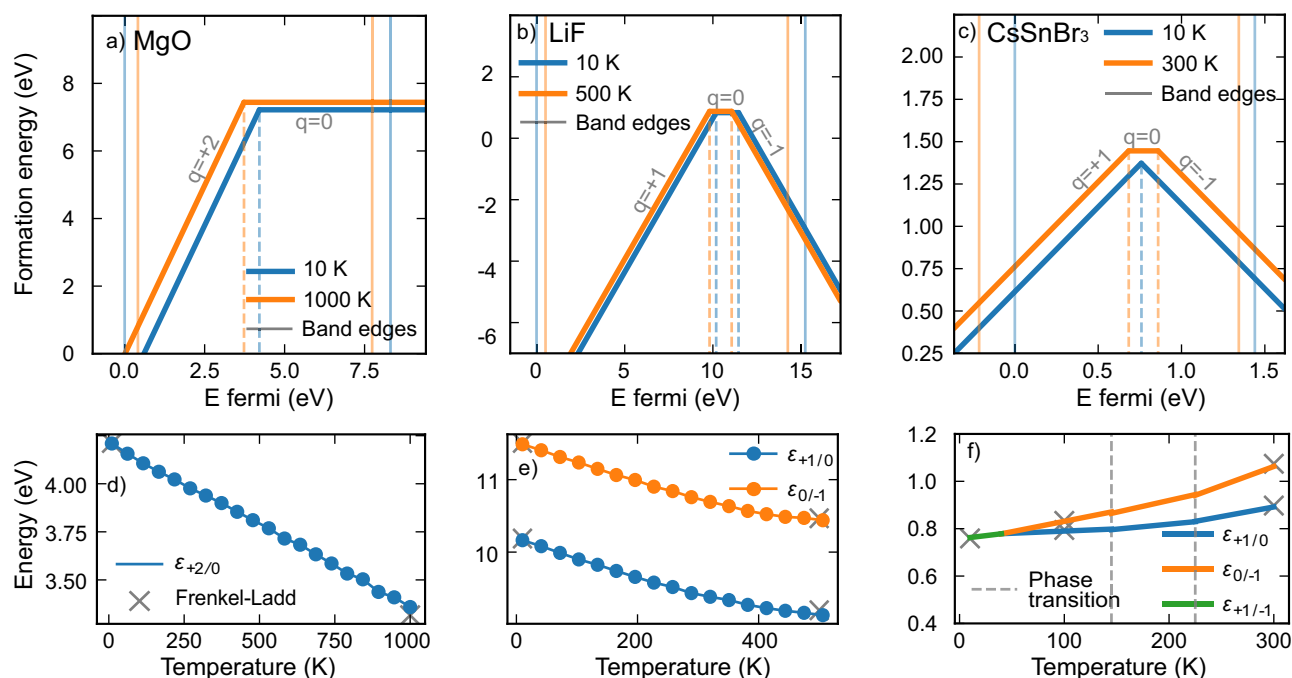


Fig. 2 | Temperature-dependent (CTLs) for MgO, LiF, and CsSnBr₃ with regard to (VBM) position. Dashed lines represent the positions of the (CTLs) and solid vertical lines indicate (VBM) and (CBM) positions, colored according to the temperature they represent. **a, d** The $\epsilon_{+2/0}$ level in MgO shifts by approximately -850 meV over a temperature range of 1000 K. **b, e** In LiF, the $\epsilon_{+1/0}$ and $\epsilon_{0/-1}$ levels

shift by about -1080 meV and -1110 meV, respectively, over 500 K. **c, f** The (CTLs) exhibited a shift of roughly 120 meV, 320 meV and 220 meV over the 300 K for the transitions between $+1/0$, $0/-1$ and $+1/-1$ respectively. Notably, a region where the neutral charge state is thermodynamically favorable is introduced around 40 K.

cells were generated in charge state q , while the energies were simultaneously evaluated for charge state q' . The energy differences between these states correspond to the optical transition energies between states q and q' , reflecting electronic excitations or absorption occurring on timescales too short for atomic relaxation. The temperature-dependent optical transition levels are shown in Fig. 3d–f. The shaded regions represent the widths of the sampled emission and absorption distributions. For each temperature, the mean values and distribution widths were extracted from individual NPT ensemble simulation runs with durations ranging from 0.2 ns to 5 ns.

To account for quantum effects, Phonopy^{27,28} was used to compute the vibrational free energy correction for thermodynamic properties and energy corrections for optical transition energies, employing both classical and quantum statistics for all structures. We corrected the formation free energies and optical transition energies by accounting for the temperature-dependent difference between the quantum and classical cases. This correction is particularly important at low temperatures, where high-frequency modes remain thermally inactive yet still contribute through zero-point motion. The magnitude of the quantum corrections was small overall (see Figs. S22–S24), though its relative impact varied across materials. For MgO and LiF, the absolute corrections were largest, yet their effect on the (CTLs) and optical transition energies was minor, as the relevant energy scales in these materials are large in comparison. For CsSnBr₃, the absolute corrections were smaller, but carried greater relative significance given the comparatively modest magnitude of the energy shifts. The most notable consequence was a shift in the stabilization temperature of the neutral charge state from 60 K to 40 K. Unless otherwise stated, all results presented include quantum corrections.

Throughout all simulations, no defect diffusion was observed, a critical requirement, as the neighbor-marking approach relies on the defect remaining stationary.

MgO

Oxygen vacancies in MgO with charge states $+2$ and 0 were investigated, resulting in one (CTL). This (ctl) exhibits a clear temperature dependence

(Fig. 2a, d) that is driven by both vibrational entropy and a shift in (VBM). The direct path between charge states yielded a (CTL) ($\epsilon_{+2/0}$) shift of $-0.850 \text{ meV K}^{-1}$.

Five independent models were trained on different splits of the reference database, resulting in an ensemble that reproduces the temperature dependence of $\epsilon_{+2/0}$ across the full range studied. The full model agrees well with the ensemble of model splits at every temperature, and the spread between splits remains far smaller than the shift itself (Fig. S27).

Over the temperature range studied, the (vbm) increases by approximately 414 meV, see Fig. S16 for details. This shift contributes to roughly half of the (CTL) movement. Excluding this shift from the total free energy change, the vibrational contribution from the path between different charge states averages $-0.436 \text{ meV K}^{-1}$.

For MgO, the optical transitions between the neutral and $+2$ charge states were considered. From the configurational coordinate diagram (Fig. 3a) these transitions appear as the energy difference between the states in their respectively relaxed geometries. We note that these zero kelvin vertical transitions are in reasonably good agreement with previous work done within the G_0W_0 approximation and the Bethe-Salpeter approach²⁹. Furthermore, the temperature dependence of these optical transitions and their fluctuation (Fig. 3d) reveals a decrease in transition energies, which aligns well with the observed change in the (CTL). In this figure, the shaded area indicates the standard deviation of the sampled optical transition energies, showing that these distributions widen with increased temperature. This increase in distribution width is similar for both charge states.

LiF

For LiF, fluorine vacancies with charge state -1 , 0 or $+1$ were investigated, leading to two (CTLs) as all states have a region of stability. Both (CTLs) exhibit a shift with temperature (Fig. 2b, e). The shifts in (CTLs) from the direct integration are $-2.160 \text{ meV K}^{-1}$ and $-2.220 \text{ meV K}^{-1}$ for the $+1/0$ and $0/-1$ transitions, respectively.

As for MgO, five independent models were trained on different splits of the reference database, resulting in an ensemble in which both levels follow

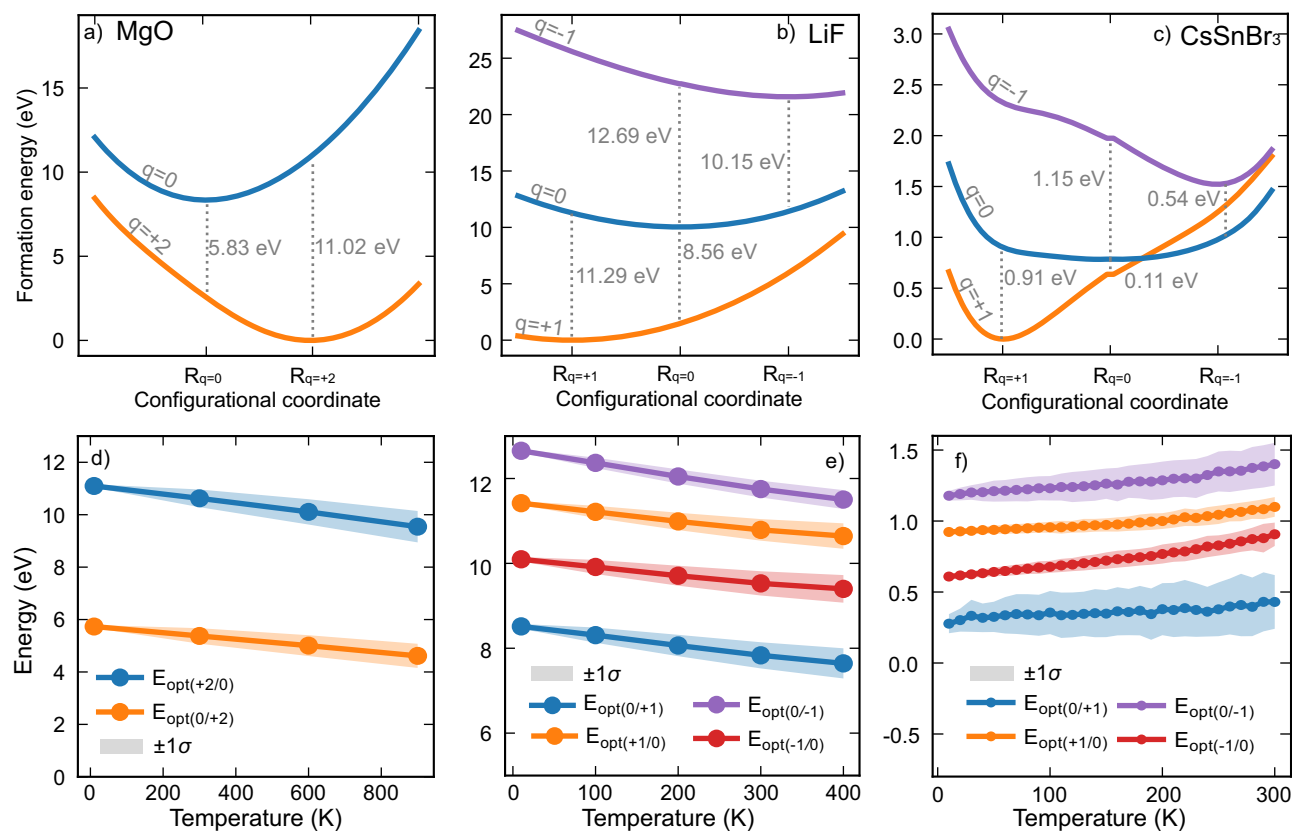


Fig. 3 | Configurational coordinate diagrams and temperature-dependent optical transitions for MgO, LiF, and CsSnBr₃. a–c The energy difference in the relaxed geometry of each charge state defines the corresponding emission or absorption energy. The specific emission and absorption energies are shown as insets in the

figures. d–f Emission and absorption energies during (MD) simulations at different temperatures. The shaded area represents the standard deviations of the sampled emission and absorption distributions.

the full model closely and the slopes are consistent (Fig. S28). The spread between splits is small compared to the shifts of the (CTLs).

The shift in (VBM) over 500K was around 605meV (see Fig. S18). Excluding this from the (CTLs) movement, the shifts become -0.950meVK^{-1} and -1.010meVK^{-1} for the $+1/0$ and $0/-1$ transitions, respectively. This is a substantial shift, even when excluding the (VBM) contribution, underscoring the importance of including vibrational entropy.

For LiF, the optical transitions between the neutral and $+1/-1$ charge states were considered (Fig. 3b, e). As in the case of MgO, the temperature dependence of these optical transitions and their fluctuations (Fig. 3e) show a slight decrease in transition energies with increasing temperature, which aligns well with the observed change in the (CTL). Furthermore, the distribution widths of different transitions are on the same scale.

CsSnBr₃

For CsSnBr₃, bromine vacancies with charge state $-1, 0$ or $+1$ were investigated. In both the orthorhombic and tetragonal phases there are non-degenerate vacancy sites. The difference in (CTL) positions between these are about 0.025eV at zero kelvin and they all converge to the same values in the cubic phase as they become degenerate. In this section, we report findings from the defect site that yields the lowest formation energy in the zero kelvin limit. At absolute zero, only the negative and positive charge states are thermodynamically stable. However, at temperatures above approximately 40K, a region in which the neutral charge state becomes thermodynamically favored emerges (Fig. 2c). The onset temperature is sensitive to the model training, since it is obtained as the intersection of two levels with similar slopes, so that a small uncertainty in the levels themselves translates into a large uncertainty in the crossing point. As for MgO and LiF, five models were trained on independent splits of the dataset, and these reproduce the (CTL) shifts of the full model (Fig. S29). Across the ensemble

of splits, the neutral charge state becomes stable at 46(31)K, where the uncertainty is the standard deviation across the five models and no quantum corrections are applied (Fig. S30). Every model places the onset between 14K and 82K, so the emergence of the neutral state well below room temperature is robust even though its precise onset is not. Due to the soft dynamics of this material, independent (TI) simulations fluctuated a lot in comparison to both LiF and MgO, requiring more sampling to reach convergence. For this reason, linear fits of the movement of the (CTLs) were performed. Additionally, two phase transitions are observed across the temperature range considered, an orthorhombic to tetragonal transition at 140K and a tetragonal to cubic transition at 225K. The linear fits were performed for each phase, showing minor changes in (CTL) slope at these transitions (Fig. 2f). Thus, structural phase transitions do not introduce discontinuous (CTL) shifts for this defect. The (CTLs) exhibited shifts of 0.400meVK^{-1} , 1.065meVK^{-1} , and 0.733meVK^{-1} for the transitions between $+1/0$, $0/-1$, and $+1/-1$, respectively.

The (VBM) shift (-214meV between 0 and 300 K, see Fig. S20) accounts for a substantial part of the (CTL) motion, but the sign and magnitude of the residual vibrational contribution differ between transitions, leading to the stabilization of the neutral state. Excluding the (VBM) shift, the (CTL) moves by -0.313meVK^{-1} , 0.353meVK^{-1} , and 0.020meVK^{-1} for the transitions between $+1/0$, $0/-1$, and $+1/-1$, respectively. This highlights that the vibrational entropy is the effect stabilizing the neutral charge state at higher temperatures in CsSnBr₃. These results show that, for CsSnBr₃, the (CTL) moves slightly and has a substantial contribution from the change in the (VBM). This small movement in the (CTLs) due to vibrational entropy over this temperature range aligns well with previous results for halide perovskites¹⁹. However, the results also show the importance of including finite temperature effects as the neutral charge state emerges as thermodynamically stable for some Fermi energies

only above 40K. This is also consistent with the (DFT) results, where only a single (CTL) is obtained at 0K, see Fig. S31.

For CsSnBr₃, the optical transitions between the neutral and $+1/-1$ charge states were considered (Fig. 3c). The optical transitions and their fluctuations (Fig. 3f) exhibit an increase in transition energies. This is consistent with the (CTLs) of CsSnBr₃ and also with previous studies showing that the optical transitions shifts together with (CTLs) in CsPbBr₃¹⁷. Furthermore, the vertical energy distributions associated with transitions from the neutral to the charged states are substantially broader than for all other transitions. This is reflected by the flat energy landscape of the neutral charge state in comparison with both the negative and positive charge state (Fig. 3c). When calculating absorption or emission events from the neutral charge state during (MD), the system naturally exhibits larger structural fluctuations, as the flat energy landscape allows it to move in and out of geometries corresponding to the energy minima of the negative and positive charge states.

The minor discrepancy in optical transition energies when comparing the relaxed geometry (Fig. 3c) to the low-temperature MD runs (Fig. 3f) likely arises from the disparity in system sizes, 60 versus 2560 atoms. Additionally, the two methods of structural optimization, static relaxation versus MD at 10K, naturally lead to subtle variations in the final atomic configurations.

Comparison

The temperature dependence of the (CTLs) across the investigated materials reveals distinct trends governed by the combination of vibrational entropy and (VBM) shifts.

For all materials investigated, substantial temperature dependence of the (CTLs) was identified. In MgO, the (CTL) movement is due to a near-equal shift in (VBM) and vibrational entropy. For LiF, contributions from vibrational entropy alone accounts for significant movements in (CTL) positions, which gets amplified when including the (VBM) movement. This emphasizes that lattice vibrations can drive significant (CTL) shifts and shows that these effects are of importance when modeling defect energetics. For CsSnBr₃, the temperature-induced movements of the (CTLs) are moderate and influenced mainly by (VBM) shifts. Effects such as these have been measured experimentally, for instance in GaSe where the difference between two (CTL), from Ga vacancies, increases from 0.17 eV to 0.38 eV over a range of 290.5 eV³⁰. This corresponds to a change of roughly 0.722 meV K⁻¹, which is on the same order of magnitude as our results. Temperature shifts in the optical transition energies (Fig. 3d–f) have also been reported in previous experimental³¹ and theoretical studies¹⁸.

Furthermore, the most interesting observation related to the (CTLs) in CsSnBr₃ is the change that takes place at 40 K, where the neutral charge state becomes stable at some Fermi energies. The width of this stability range grows as temperature increases and at 300 K the neutral charge state is the most stable one across a substantial part of the band gap. This stabilization is driven by the flat potential energy surface of the neutral charge state, see the $q = 0$ line in Fig. 3c, which allows a larger volume of configuration space to become accessible already at low temperatures, leading to a faster increase in entropy compared to the positive and negative charge states. More generally, whenever a charge state that is unstable at 0K and exhibits a flatter (PES) than the competing stable charge states, finite-temperature entropic contributions can drive its stabilization. Perovskites are natural candidates for such behavior, as their soft lattices allow the local structure around a defect to respond strongly to changes in charge state, so that competing charge states can differ substantially in the curvature of their energy landscapes. A systematic investigation of defect (CTL) across this material class is therefore likely to reveal further charge states that are absent from the zero-kelvin picture.

Our results highlight two points: The inclusion of finite-temperature effects is of importance due to the potential temperature dependence of (CTLs) and due to the possible introduction of new thermodynamically favorable charge states.

Discussion

To conclude, we have quantified the temperature dependence of (CTLs) and optical transition energies for vacancies in MgO, LiF and CsSnBr₃ by employing (MLIPs).

The direct (TI) path between charge states achieves high computational efficiency because the free energy differences along this path are small, in contrast to the much larger changes usually encountered in the Frenkel-Ladd path to an Einstein crystal. As a result, less sampling is required to obtain accurate estimates of the vibrational free energy differences.

The results show that temperature can shift (CTLs) by hundreds of meV, with the cause of these shifts differing between materials. Notably, in CsSnBr₃ we find the emergence of a thermodynamically stable neutral charge state only above 40K. This shows that even if (CTLs) only vary slightly due to vibrational entropy contribution, this could have a significant impact by introducing entirely new thermodynamically stable charge states. Finite temperature shifts in (CTLs) and the emergence of new charge states as reported here are directly relevant for predicting doping limits and non-radiative recombination in wide-gap functional materials.

Together, these findings demonstrate that finite-temperature effects are essential for reliable predictions of defect energetics. We show that the widely used static formalism of defect modeling fails to capture details that are important under operating conditions for these materials.

Methods

Defect formation free energy and CTLs

The defect formation free energy for a defect X in charge state q is given by Eq. (1).

$$G^f[X^q](T, \mu_e) = G_{\text{tot}}[X^q](T) - G_{\text{tot}}[\text{bulk}](T) - \sum_i n_i \mu_i + q(E_{\text{VBM}}(T) + \mu_e) + E_{\text{corr}}(q). \quad (1)$$

Here, $G_{\text{tot}}[X^q]$ and $G_{\text{tot}}[\text{bulk}]$ denote the Gibbs free energies of the defect-containing and pristine supercells, respectively. Note that we compute Helmholtz free energies, F , rather than Gibbs free energies, G . This is justified by the PV term being negligible at low pressures for these formation free energies¹⁶. The term $\sum_i n_i \mu_i$ accounts for the chemical potential contributions associated with adding or removing atoms of type i . Since the (CTL) does not depend on the chemical potentials, all μ_i are treated as constants throughout this study. The term $q(E_{\text{VBM}} + \mu_e)$ represents the energy required to add or remove q electrons referenced to the (VBM). The temperature dependence of the (VBM) was obtained from (MD) snapshots via deep core level alignment, with further details given in the SI (Fig. S15). E_{corr} is the correction term for finite-size effects, which in the present work is charge dependent and evaluated using the Freysoldt, Neugebauer and Van de Walle (FNV) correction scheme^{32,33}. The values for ionic chemical potentials, temperature-dependent (VBM) shifts, and (FNV) corrections are reported in the SI.

(CTLs) determine the thermodynamically favorable charge state of a defect at a given Fermi level. The (CTL) between charge states q and q' , denoted as $\epsilon_{q/q'}$, is calculated from the difference in the defect formation free energies,

$$\epsilon_{q/q'} = \frac{F^f[X^q; \mu_e = 0] - F^f[X^{q'}; \mu_e = 0]}{q' - q}. \quad (2)$$

MLIP for charged defects

To obtain well-converged (TI) results, we require an efficient way to perform (MD) simulations. For this purpose, (NEP) models^{34,35} were trained for MgO, LiF, and CsSnBr₃, with reference data generated using (DFT) as implemented in the Vienna Ab initio Simulation Package^{36,37}. The PBEsol exchange-correlation functional³⁸ was employed for MgO and LiF, while the r2SCAN+rVV10 functional^{39,40} was used for CsSnBr₃. All calculations employed the projector-augmented wave method with a plane-wave energy

cutoff of 520 eV. Brillouin zone sampling used Γ -centered grids with a spacing of $0.27\text{\AA}^{-1}$ for LiF and MgO, and $0.15\text{\AA}^{-1}$ for CsSnBr₃.

To benchmark the choice of exchange-correlation functional for CsSnBr₃, predicted energies from r2SCAN+rVV10 were compared against r2SCAN+rVV10+SOC and r2SCAN0+rVV10 across all defect geometries with the different charge states. Defect geometries were obtained by relaxing 159-atom supercells using the (NEP) model. The results show good agreement between functionals, with all key features preserved, justifying the use of r2SCAN+rVV10 alone for training data generation without resorting to hybrid functionals. See Fig S25 for this comparison.

Training utilized the GPUMD³⁴ and CALORINE packages⁴¹. The initial datasets comprised both pristine and defective structures, generated by rattling ideal structures. An iterative training procedure was employed after the first generation of models, based on running (MD) with previous generation models to pick out structures for training of the new generation. Snapshots were selected at random, with the exception of structures taken from trajectories in which the energy or temperature diverged, which were included so that the models were explicitly trained on the configurations at which the previous generation had failed. The structures included were furthermore filtered on forces to prevent extreme configurations from skewing the dataset. The cutoff for this filter was set to $30\text{eV}\text{\AA}^{-1}$ for all materials. This procedure was repeated until the energy and force (RMSE) were sufficiently low and the models remained stable during (MD). The final energy and force (RMSEs) were 0.6meVatom^{-1} and $46.8\text{eV}\text{\AA}^{-1}$ for MgO, 0.9meVatom^{-1} and $32.8\text{eV}\text{\AA}^{-1}$ for LiF, and 1.4meVatom^{-1} and 58.0meVatom^{-1} for CsSnBr₃, comparable to previously reported (NEP) models⁴². All (NEP) models used a radial and angular cutoff of $8\text{\AA}$ and $4\text{\AA}$, respectively. Both three and four-body terms were included for the angular descriptors. Furthermore, all (NEP) models used one hidden layer consisting of 30 neurons. For MgO, we included O vacancies with charge states 0 and +2; for LiF, F vacancies with charge states −1, 0, and +1; and for CsSnBr₃, Br vacancies with charge states −1, 0, and +1. In all training configurations, atoms neighboring a vacancy were labeled according to the charge state of that vacancy¹⁸. For MgO and LiF, the six Mg or Li atoms surrounding an O or F vacancy, respectively, were labeled, as illustrated in Fig. 1. In CsSnBr₃, the two Sn atoms closest to the defect were labeled. These labels encode the charge state of the associated vacancy.

Thermodynamic integration

To obtain free energy differences between charge states, including anharmonic contributions, we performed both Frenkel-Ladd (TI) and (TI) directly between charge states. The non-equilibrium (TI) approach evaluates the irreversible work, W_{irr} , performed during the switching process between two Hamiltonians (H_i and H_f) through,

$$W_{\text{irr}}^{\lambda_i \rightarrow \lambda_f} = \int_0^{t_s} [H_f(t) - H_i(t)] \frac{d\lambda}{dt} dt, \quad (3)$$

where λ is switched from λ_i to λ_f over the switching time t_s . The coupling Hamiltonian used was $H(\lambda) = (1 - \lambda)H_i + \lambda H_f$. The switching function used along all (ti) paths was $\lambda = (70.0s^4 - 315.0s^3 + 540.0s^2 - 420.0s + 126.0)s^5$, where $s = t/t_s$ with t being the current elapsed time along the switching path. The free energy difference is then obtained via,

$$\Delta F = \frac{1}{2} \left\langle W_{\text{irr}}^{\lambda_i \rightarrow \lambda_f} \right\rangle - \frac{1}{2} \left\langle W_{\text{irr}}^{\lambda_f \rightarrow \lambda_i} \right\rangle, \quad (4)$$

where the average is taken over many independent switching trajectories. In the following, one TI run refers to a forward switch $\lambda_i \rightarrow \lambda_f$ followed by a reverse switch $\lambda_f \rightarrow \lambda_i$, each of duration t_s , so that ΔF in Eq. (4) is obtained from a single such pair.

The Frenkel-Ladd path²², which connects the system described by the (NEP) model to a reference Einstein crystal with analytically known free energy, was used to calculate the free energy of both a pristine and defect cell. The formation energy was then obtained from Eq. (1). This approach

yielded the absolute free energy of each structure at the target temperature, enabling accurate determination of defect formation free energies. These formation energies for different charge states were subsequently used in Eq. (2) to calculate the (CTLs).

Atoms neighboring the defect are assigned a distinct species label to encode the charge state of the vacancy, an approach that has proven effective in previous work^{18,43}. In the (NEP) models, the marked neighbors of a vacancy are treated as distinct atomic species rather than as an inert tag on an existing species. Each charge state has its own labeled neighbor species, so the number of chemical species exceeds the number of chemical elements: four types for MgO (Mg, O, and labeled Mg for $q = 0, +2$), five for LiF (Li, F and labeled Li for $q = -1, 0, +1$), and six for CsSnBr₃ (Cs, Sn, Br, and labeled Sn for $q = -1, 0, +1$). As for any species in a (NEP) model, each labeled species carries its own trainable parameters. To perform (TI) directly between charge states, a second copy of the trained model is created in which the labeled species corresponding to charge states q_1 and q_2 are interchanged. Applied to the same atomic configuration, the two models therefore interpret the marked atoms as neighbors to a vacancy of charge state q_1 and q_2 , respectively. Both use the same trained parameter set, and the interchange affects only the marked atoms: any atom with only unmarked neighboring atoms within the descriptor cutoff has an identical descriptor and identical parameters under both models, so its site energy is unchanged and the energetics of the supercell away from the defect cancel exactly between them. This method is illustrated in Fig. S26. Performing (TI) along a path between these two potentials then directly yields the free energy difference between charge states,

$$\Delta F = F_{\text{tot}}[X^{q_1}] - F_{\text{tot}}[X^{q_2}]. \quad (5)$$

This is one part of what is required to evaluate the (CTL) between charge states q_1 and q_2 , given in Eq. (2). Evaluating Eq. (2), the bulk free energy $F_{\text{tot}}[\text{bulk}]$ and the chemical potential term $\sum_i n_i \mu_i$ cancel exactly, leaving

$$e_{q_1/q_2} = \frac{\Delta F + (q_1 - q_2)E_{\text{VBM}} + [E_{\text{corr}}(q_1) - E_{\text{corr}}(q_2)]}{q_2 - q_1}. \quad (6)$$

For both MgO and LiF, structures of 13824 atoms were used during all simulations, while for CsSnBr₃ 2560 atoms were used. The convergence tests of these can be seen in Figs. S12–S14. The lower number of atoms in CsSnBr₃ was due to the fact that these simulations needed more independent runs to reach convergence. An exception to the number of atoms applies to Fig. 3a–c, where smaller cells were used to enable direct comparison with (DFT) in the functional benchmarking, see Fig. S25.

For the Frenkel-Ladd (TI) path, reference structures for each temperature were obtained as time-averaged configurations from 150ps (MD) runs in the NPT ensemble with stochastic cell rescaling⁴⁴, averaging over the final 75ps. Runs were then initialized by running (MD) with the NVT ensemble using the Langevin method⁴⁵, after which the Frenkel-Ladd (TI) was performed. 30 independent runs were performed for each temperature for MgO and LiF, and 60 independent runs were performed for each temperature for CsSnBr₃. For the direct (TI) path, runs were initialized by equilibrating the cells at each temperature in the NPT ensemble using stochastic cell rescaling. Equilibration times ranged from 4 ps to 20 ps, according to how quickly the cell volume converged. After this, a direct (TI) run was performed. One equilibration followed by direct (TI) was performed per temperature for MgO and LiF. For CsSnBr₃, this procedure was repeated 5 times at each temperature, each repetition consisting of an independent equilibration followed by a (TI) run. The direct (TI) simulations were performed with 50,000 time steps during the switch between Hamiltonians, as justified by the benchmark in the SI. With the time step of 1fs employed during all runs, this corresponds to 50 ps in switching time. During the direct (TI) path, the NVT ensemble using the Langevin method was used. Temperature was controlled with a relaxation time of 0.1 ps in both the NVT and NPT simulations, and the barostat in the NPT simulations used a relaxation time of 0.2 ps.

Uncertainty estimation

To assess the sensitivity of the (CTLs) to the model training, five additional (NEP) models per material were trained on independent random 80/20 training/test splits of the same reference database, with all hyperparameters fixed and only the partitioning and random seed varied. Direct (TI) was performed for each model at every temperature, giving an ensemble estimate of the model-induced uncertainty in the (CTLs) and hence in the underlying free energy differences. Results are reported as the ensemble mean and standard deviation and are compared with the model used throughout the main text in Figs. S27–S30.

Data availability

All NEP models, as well as the DFT databases used to train these models, are available on Zenodo at <https://doi.org/10.5281/zenodo.17939378>.

Received: 13 January 2026; Accepted: 1 October 2026;

Published online: 23 October 2026

References

- Lubomirsky, I. Mechanical properties and defect chemistry. *Solid State Ion.* **177**, 1639–1642 (2006).
- Pantelides, S. T. The electronic structure of impurities and other point defects in semiconductors. *Rev. Mod. Phys.* **50**, 797–858, <https://doi.org/10.1103/RevModPhys.50.797> (1978).
- Skrypnik, Y. V. & Loktev, V. M. Electrical conductivity in graphene with point defects. *Phys. Rev. B* **82**, 085436, <https://doi.org/10.1103/PhysRevB.82.085436> (2010).
- Gorai, P., Famprikis, T., Singh, B., Stevanović, V. & Canepa, P. Devil is in the defects: electronic conductivity in solid electrolytes. *Chem. Mater.* **33**, 7484–7498 (2021).
- Qu, Z., Sparks, T. D., Pan, W. & Clarke, D. R. Thermal conductivity of the gadolinium calcium silicate apatites: effect of different point defect types. *Acta Materialia* **59**, 3841–3850 (2011).
- Ball, J. M. & Petrozza, A. Defects in perovskite-halides and their effects in solar cells. *Nat. Energy* **1**, 1–13 (2016).
- Park, J. S., Kim, S., Xie, Z. & Walsh, A. Point defect engineering in thin-film solar cells. *Nat. Rev. Mater.* **3**, 194–210 (2018).
- Greene-Diniz, G., Kuhn, K. J., Hurley, P. K. & Greer, J. C. First principles modeling of defects in the $\text{Al}_2\text{O}_3/\text{In}_{0.53}\text{Ga}_{0.47}$ as system. *J. Appl. Phys.* **121**, 075703, <https://doi.org/10.1063/1.4975033> (2017).
- Meggiolaro, D. & De Angelis, F. First-principles modeling of defects in lead halide perovskites: best practices and open issues. *ACS Energy Lett.* **3**, 2206–2222, <https://doi.org/10.1021/acsenergylett.8b01212> (2018).
- Du, M.-H. Density functional calculations of native defects in $\text{CH}_3\text{NH}_3\text{PbI}_3$: effects of spin-orbit coupling and self-interaction error. *J. Phys. Chem. Lett.* **6**, 1461–1466, <https://doi.org/10.1021/acs.jpcclett.5b00199> (2015).
- Liang, Y. et al. First-principles investigation of intrinsic point defects in perovskite CsSnBr_3 . *Phys. Rev. Mater.* **5**, 035405, <https://doi.org/10.1103/PhysRevMaterials.5.035405> (2021).
- Linderälv, C., Lindman, A. & Erhart, P. A unifying perspective on oxygen vacancies in wide band gap oxides. *J. Phys. Chem. Lett.* **9**, 222–228 (2018).
- Freysoldt, C. et al. First-principles calculations for point defects in solids. *Rev. Mod. Phys.* **86**, 253–305, <https://doi.org/10.1103/RevModPhys.86.253> (2014).
- Alkauskas, A., Broqvist, P. & Pasquarello, A. Defect levels through hybrid density functionals: Insights and applications. *Phys. Status Solidi (b)* **248**, 775–789, <https://doi.org/10.1002/pssb.201046195> (2011).
- Mishin, Y., Sørensen, M. R. & Voter, A. F. Calculation of point-defect entropy in metals. *Philos. Mag. A* **81**, 2591–2612, <https://doi.org/10.1080/01418610108216657> (2001).
- Mosquera-Lois, I., Kavanagh, S. R., Klarbring, J., Tolborg, K. & Walsh, A. Imperfections are not 0 K: free energy of point defects in crystals. *Chem. Soc. Rev.* **52**, 5812–5826, <https://doi.org/10.1039/D3CS00432E> (2023).
- Cohen, A. V., Egger, D. A., Rappe, A. M. & Kronik, L. Breakdown of the static picture of defect energetics in halide perovskites: the case of the Br vacancy in CsPbBr_3 . *J. Phys. Chem. Lett.* **10**, 4490–4498 (2019).
- Linderälv, C., Österbacka, N., Wiktor, J. & Erhart, P. Optical line shapes of color centers in solids from classical autocorrelation functions. *npj Computational Mater.* **11**, 101, <https://doi.org/10.1038/s41524-025-01565-x> (2025).
- Mosquera-Lois, I. & Walsh, A. Dynamic Vacancy Levels in CsPbCl_3 Obey Equilibrium Defect Thermodynamics. *PRX Energy* **4**, 043008, <https://doi.org/10.1103/dxmb-8s96> (2025).
- Mosquera-Lois, I., Klarbring, J. & Walsh, A. Point defect formation at finite temperatures with machine learning force fields. *Chem. Sci.* **16**, 8878–8888, <https://doi.org/10.1039/D4SC08582E> (2025).
- Qiao, S. et al. Temperature effect on charge-state transition levels of defects in semiconductors. *Phys. Rev. B* **105**, 115201, <https://doi.org/10.1103/PhysRevB.105.115201> (2022).
- Addula, R. K. R., Veeram, S. K. & and, S. N. P. Review of the Frenkel-ladd technique for computing free energies of crystalline solids. *Mol. Simul.* **47**, 824–830, <https://doi.org/10.1080/08927022.2020.1775221> (2021).
- Eriksson, F., Fransson, E. & Erhart, P. The hiphive package for the extraction of high-order force constants by machine learning. *Adv. Theory Simul.* **2**, 1800184 (2019).
- Chen, W. & Pasquarello, A. Correspondence of defect energy levels in hybrid density functional theory and many-body perturbation theory. *Phys. Rev. B-Condens. Matter Mater. Phys.* **88**, 115104 (2013).
- Miceli, G., Chen, W., Reshetnyak, I. & Pasquarello, A. Nonempirical hybrid functionals for band gaps and polaronic distortions in solids. *Phys. Rev. B* **97**, 121112 (2018).
- Bischoff, T., Wiktor, J., Chen, W. & Pasquarello, A. Nonempirical hybrid functionals for band gaps of inorganic metal-halide perovskites. *Phys. Rev. Mater.* **3**, 123802 (2019).
- Togo, A., Chaput, L., Tadano, T. & Tanaka, I. Implementation strategies in phonopy and phono3py. *J. Phys. Condens. Matter* **35**, 353001 (2023).
- Togo, A. First-principles phonon calculations with phonopy and phono3py. *J. Phys. Soc. Jpn.* **92**, 012001 (2023).
- Rinke, P. et al. First-principles optical spectra for *f* centers in MgO . *Phys. Rev. Lett.* **108**, 126404, <https://doi.org/10.1103/PhysRevLett.108.126404> (2012).
- Redkin, R. A. et al. Temperature-dependent optical absorption and dIIs study of as-grown and electron-irradiated gas crystals. *Crystals* **15** (2025).
- Nam, K. B., Li, J., Lin, J. Y. & Jiang, H. X. Optical properties of aln and gan in elevated temperatures. *Appl. Phys. Lett.* **85**, 3489–3491, <https://doi.org/10.1063/1.1806545> (2004).
- Freysoldt, C., Neugebauer, J. & Van de Walle, C. G. Fully ab initio finite-size corrections for charged-defect supercell calculations. *Phys. Rev. Lett.* **102**, 016402, <https://doi.org/10.1103/PhysRevLett.102.016402> (2009).
- Freysoldt, C., Neugebauer, J. & Van de Walle, C. G. Electrostatic interactions between charged defects in supercells. *Phys. status solidi (b)* **248**, 1067–1076, <https://doi.org/10.1002/pssb.201046289> (2011).
- Fan, Z. et al. GPUMD: A package for constructing accurate machine-learned potentials and performing highly efficient atomistic simulations. *J. Chem. Phys.* **157**, 114801 (2022).
- Song, K. et al. General-purpose machine-learned potential for 16 elemental metals and their alloys. *Nat. Commun.* **15**, 10208 (2024).
- Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).

37. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Mater. Sci.* **6**, 15–50 (1996).
38. Perdew, J. P. et al. Restoring the density-gradient expansion for exchange in solids and surfaces. *Phys. Rev. Lett.* **100**, 136406, <https://doi.org/10.1103/PhysRevLett.100.136406> (2008).
39. Sabatini, R., Gorni, T. & de Gironcoli, S. Nonlocal van der Waals density functional made simple and efficient. *Phys. Rev. B* **87**, 041108, <https://doi.org/10.1103/PhysRevB.87.041108> (2013).
40. Furness, J. W., Kaplan, A. D., Ning, J., Perdew, J. P. & Sun, J. Accurate and Numerically Efficient r^2 SCAN Meta-Generalized Gradient Approximation. *J. Phys. Chem. Lett.* **11**, 8208–8215 (2020).
41. Lindgren, E. et al. calorine: A Python package for constructing and sampling neuroevolution potential models. *J. Open Source Softw.* **9**, 6264 (2024).
42. Fan, Z. et al. qnep: A highly efficient neuroevolution potential with dynamic charges for large-scale atomistic simulations. *J. Chem. Theory Comput.* **22**, 4787–4801, <https://doi.org/10.1021/acs.jctc.6c00146> (2026).
43. Berger, E., Hainer, T., Möslinger, T., Erhart, P. & Wiktor, J. Stability of polarons and oxygen vacancies in BiVO_4 revealed by machine-learning-driven simulations. *PRX Energy* **5**, 033004, <https://doi.org/10.1103/xwxv-6s55> (2026).
44. Bernetti, M. & Bussi, G. Pressure control using stochastic cell rescaling. *J. Chem. Phys.* **153**, 114107, <https://doi.org/10.1063/5.0020514> (2020).
45. Bussi, G. & Parrinello, M. Accurate sampling using Langevin dynamics. *Phys. Rev. E* **75**, 056707, <https://doi.org/10.1103/PhysRevE.75.056707> (2007).

Acknowledgements

We thank Sofia Cellini for useful comments.

Author contributions

T.H. trained all models, carried out the free energy and optical transition calculations, contributed to the study design, and wrote the first draft of the manuscript. Ethan B. took part in developing the free energy calculation workflow. Esmée B. performed the DFT calculations for the initial MgO dataset. O.H supported in creating training data and training initial models for CsSnBr_3 . P.E developed the basis for the free energy analysis and provided input during project conception. J.W led the project conception and design, supervised the project, and performed the band alignment calculations. All authors contributed to writing and/or reviewing the manuscript.

Funding

We acknowledge funding from the Swedish Strategic Research Foundation through a Future Research Leader programme (FFL21-0129), the Swedish

Energy Agency (grant No. 45410-1), the Swedish Research Council (2018-06482, 2019-03993, and 2020-04935), the European Research Council (ERC Starting Grant No. 101162195), and the Knut and Alice Wallenberg Foundation (Nos. 2023.0032 and 2024.0042). The computations were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS) at C3SE, PDC, and NSC, partially funded by the Swedish Research Council through grant agreement no. 2022-06725.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41524-026-02369-3>.

Correspondence and requests for materials should be addressed to Tobias Hainer or Julia Wiktor.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2026

This Article in Press is shared early to give you faster access to new research. It is citable and carries a permanent DOI. The final edited version will replace it automatically.

Thermal Stabilization of Defect Charge States and Finite-Temperature Charge Transition Levels

Tobias Hainer, Ethan Berger, Esmée Berger, Olof Hildeberg, Paul Erhart, and Julia Wiktor*

Department of Physics, Chalmers University of Technology, SE-41296, Gothenburg, Sweden

* julia.wiktor@chalmers.se

Contents

Supplementary Note 1: Machine-learned potentials	3
S1. Loss function during training of machine-learned interatomic potential (MLIP) for MgO	3
S3. Parity plot for energies, forces, virials and stresses in MgO	3
S3. MgO phonon dispersion from both NEP and DFT calculations	4
S4. Loss function during training of MLIP for LiF	4
S6. Parity plot for energies, forces, virials and stresses in LiF	5
S6. LiF phonon dispersion from both NEP and DFT calculations	5
S7. Loss function during training of MLIP for CsSnBr ₃	6
S8. Parity plot for energies, forces, virials and stresses in CsSnBr ₃	6
S9. CsSnBr ₃ phonon dispersion from both NEP and DFT calculations	7
Supplementary Note 2: Comparison of thermodynamic integration paths	7
S10. Results and standard error for the energy difference between charge states 0 and +2 in MgO at 10 K	8
S11. Results and standard error for the energy difference between charge states 0 and +2 in MgO at 1000 K	8
Supplementary Note 3: Convergence with cell size	8
S12. TI results as a function of cell size in MgO at 50 K	9
S13. TI results as a function of cell size in MgO at 1000 K	9
S14. TI results as a function of cell size in CsSnBr ₃ at 100 K	10
Supplementary Note 4: Chemical potential, corrections, and VBM shifts	10
S15. Gaussian fits to density of states (DOS) in MgO. Dashed red curve is the Gaussian fit to deep levels and dashed vertical line is the VBM position	11
S16. VBM movement for MgO	12
S17. CBM movement for MgO	12
S18. VBM movement for LiF	13
S19. CBM movement for LiF	13
S20. VBM movement for CsSnBr ₃	14
S21. CBM movement for CsSnBr ₃	15
Supplementary Note 5: Quantum corrections	15
S22. Quantum corrections for MgO	15
S23. Quantum corrections for LiF	16
S24. Quantum corrections for CsSnBr ₃	16
Supplementary Note 6: Functional influence on energy	16
S25. Energies in the various relaxed defect geometries for different functionals	17
Supplementary Note 7: Direct integration between charge states	17
S26. Illustration of the labeling procedure used for the direct integration between charge states	17

Supplementary Note 8: Performance of different model splits	17
S27. Temperature dependence of the CTL in MgO for independent NEP model splits	18
S28. Temperature dependence of the CTLs in LiF for independent NEP model splits	19
S29. Temperature dependence of the CTLs in CsSnBr ₃ for independent NEP model splits	19
S30. Onset temperature for the stability of the neutral charge state in CsSnBr ₃ across model splits . .	20
Supplementary Note 9: DFT prediction of zero kelvin CTLs	20
S31. Energies are obtained from DFT, on DFT-relaxed structures	21

Supplementary Note 1: Machine-learned potentials

Here, the losses during training are presented for all models as well as the parity plots showing the performance for energies, forces, virials, and stresses. Also, the phonon dispersions for the models are included.

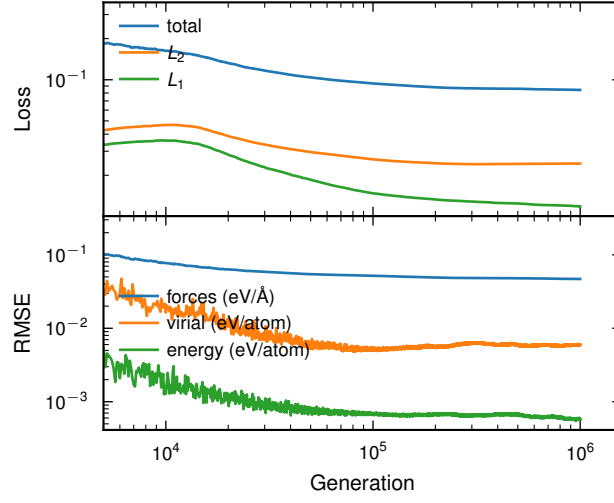


Fig. S1: Loss function during training of MLIP for MgO. The evolution of the total loss, along with the L_1 and L_2 norms are shown in the top plot. The bottom plot shows the RMSE of forces, virials and energies.

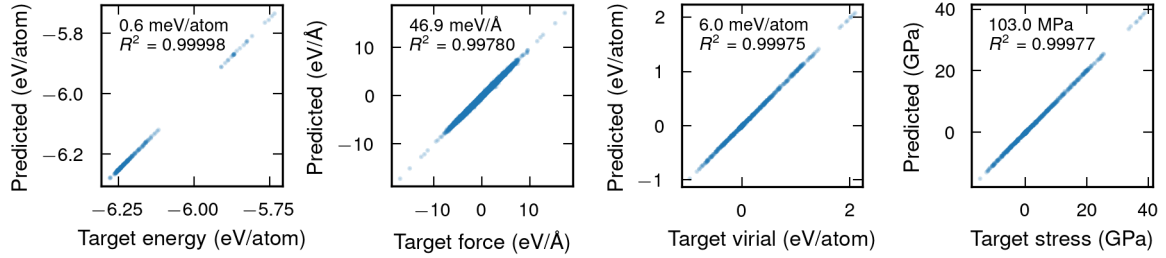


Fig. S2: Parity plot for energies, forces, virials and stresses in MgO. The inset values indicate RMSE and R^2 score. The plots are based on all data available.

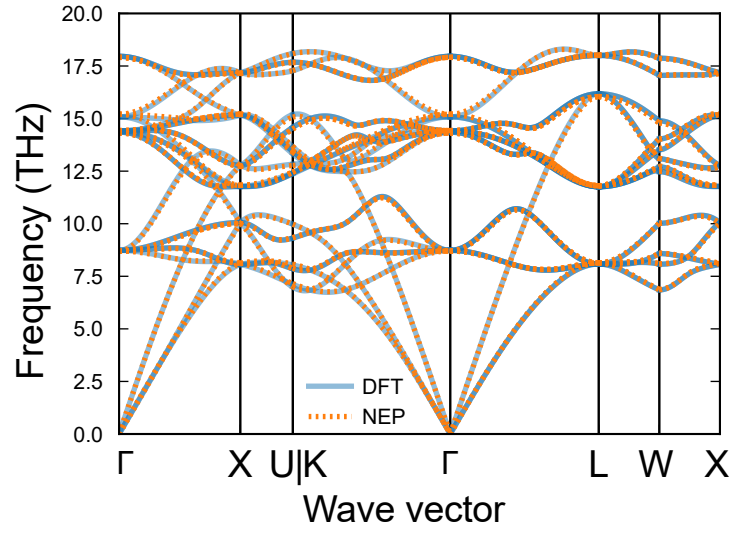


Fig. S3: MgO phonon dispersion from both NEP and DFT calculations. The comparisons shows close agreement between the MLIP and reference data.

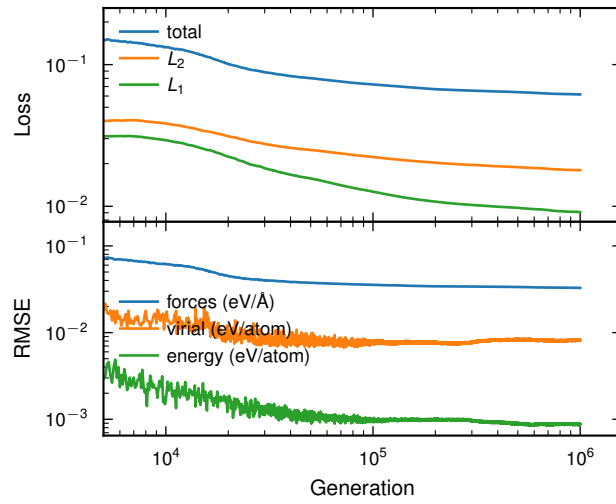


Fig. S4: Loss function during training of MLIP for LiF. The evolution of the total loss, along with the L_1 and L_2 norms are shown in the top plot. The bottom plot shows the RMSE of forces, virials and energies.

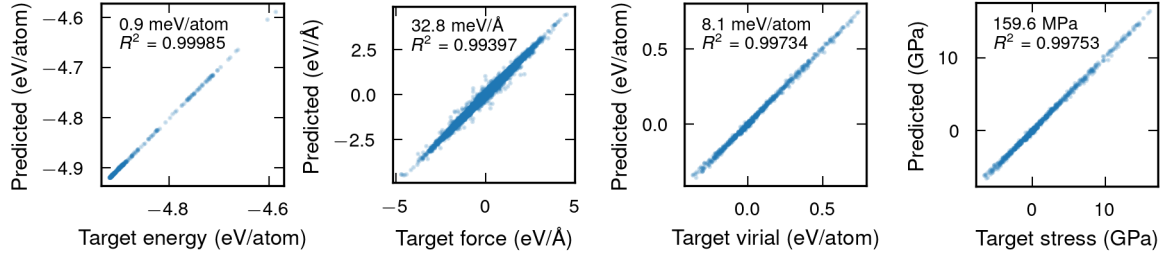


Fig. S5: Parity plot for energies, forces, virials and stresses in LiF. The inset values indicate RMSE and R^2 score. The plots are based on all data available.

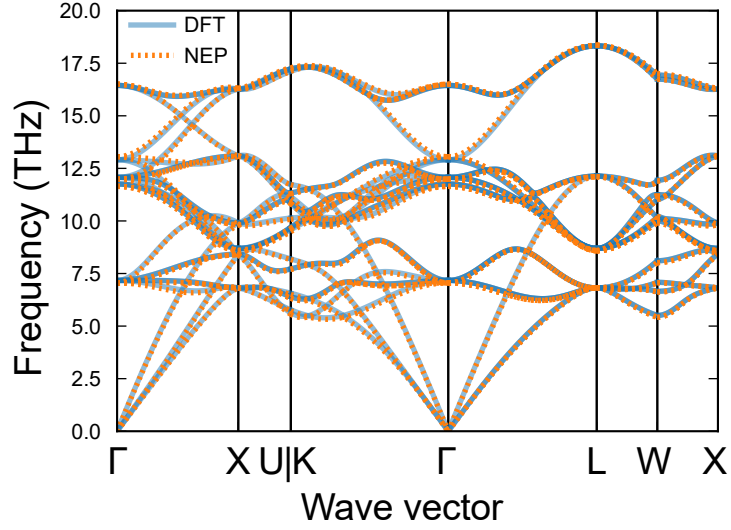


Fig. S6: LiF phonon dispersion from both NEP and DFT calculations. The comparisons shows close agreement between the MLIP and reference data.

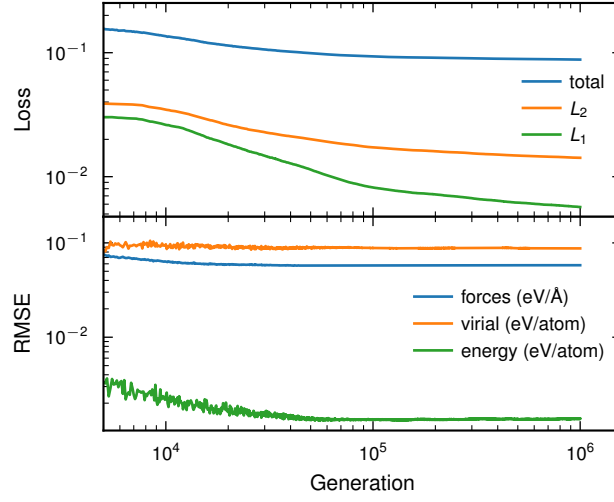


Fig. S7: Loss function during training of MLIP for CsSnBr_3 . The evolution of the total loss, along with the L_1 and L_2 norms are shown in the top plot. The bottom plot shows the RMSE of forces, virials and energies.

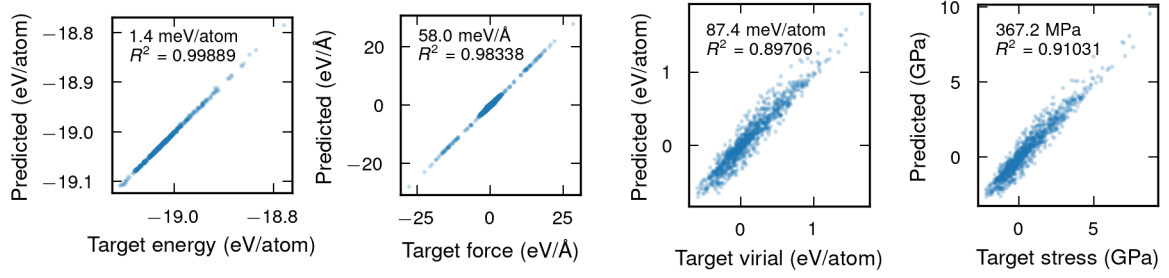


Fig. S8: Parity plot for energies, forces, virials and stresses in CsSnBr_3 . The inset values indicate RMSE and R^2 score. The plots are based on all data available.

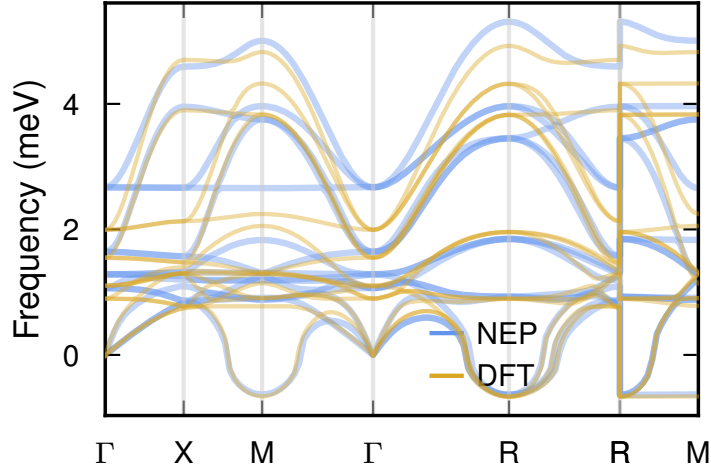


Fig. S9: CsSnBr₃ phonon dispersion from both NEP and DFT calculations. The MLIP captures key features from the reference data, especially around the M- and R-mode.

Supplementary Note 2: Comparison of thermodynamic integration paths

To illustrate the computational efficiency of the direct integration path, a benchmark of this method in comparison with the Frenkel-Ladd path was made for the free energy difference between the charge states 0 and +2 for an oxygen vacancy in MgO at 50 K. From Figure S10 and Figure S11 it is clear that the direct path converges faster than the Frenkel-Ladd method, with its standard error for 3 runs outperforming the Frenkel-Ladd path for 30 runs for all numbers of steps. Note that the energies reported here are not corrected with regard to valence band maximum (VBM) and the FNV scheme, but instead are the raw data obtained from the methods.

Based on this benchmark, a minimum of 30 Frenkel-Ladd runs were performed for each temperature, each with at least 50 000 steps. For the direct integration, at least 50 000 steps were performed for each temperature. The timestep used throughout this work was 1 fs.

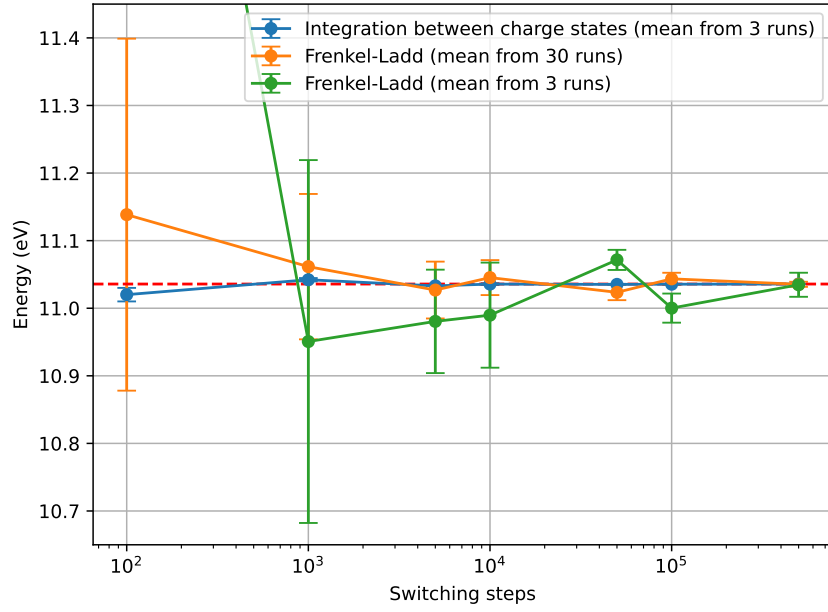


Fig. S10: Results and standard error for the energy difference between charge states 0 and +2 in MgO at 10 K. Three cases were considered, direct integration between charge states averaged over 3 runs, and the Frenkel-Ladd path averaged over 3 and 30 runs. Convergence with number of steps is clearly much quicker for the direct integration method, as it essentially converges already after 1000 steps.

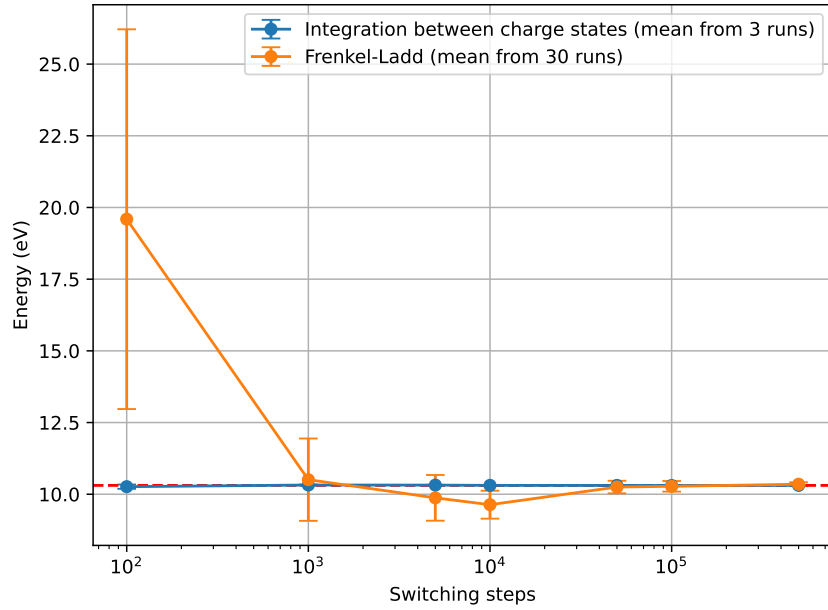


Fig. S11: Results and standard error for the energy difference between charge states 0 and +2 in MgO at 1000 K. Three cases were considered, direct integration between charge states averaged over 3 runs, and the Frenkel-Ladd path averaged over 30 runs.

Supplementary Note 3: Convergence with cell size

For MgO and LiF, simulations were performed in supercells of 13824 atoms. This was converged with regards to the number of atoms, as highlighted by Figure S12 and Figure S13 which shows the MgO convergence of TI runs.

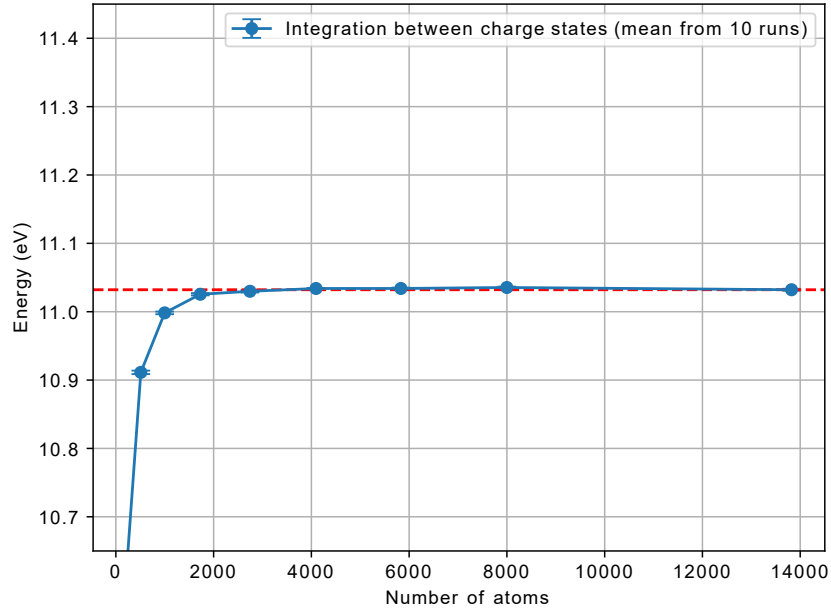


Fig. S12: TI results as a function of cell size in MgO at 50 K. The convergence check shows that the cell size is well converged already around 2000 atoms.

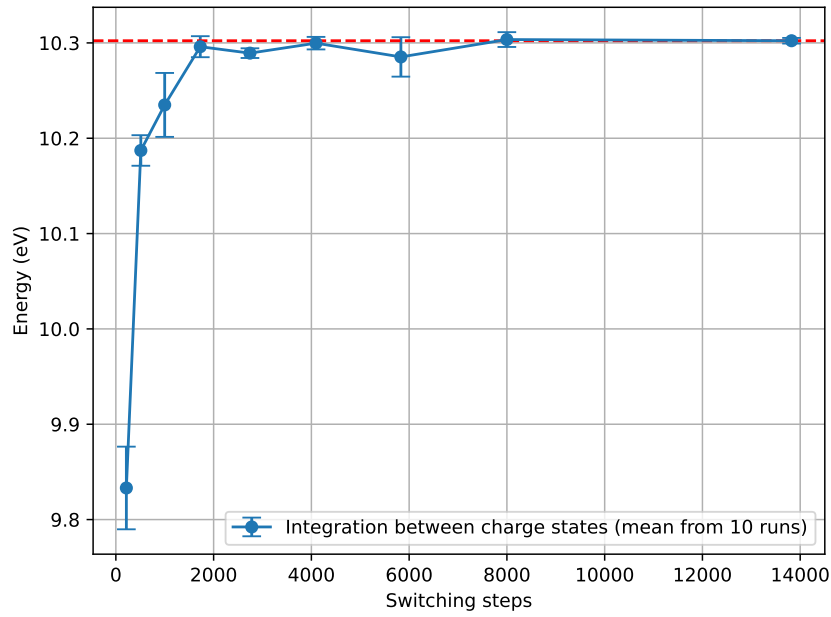


Fig. S13: TI results as a function of cell size in MgO at 1000 K. The convergence check shows that the cell size is well converged already around 2000 atoms.

The simulations of CsSnBr_3 used cells with 2560 atoms. The smaller cell size stemmed from the need to average over more independent runs to obtain converged TI results. 2560 atoms were deemed well converged, see Figure S14.

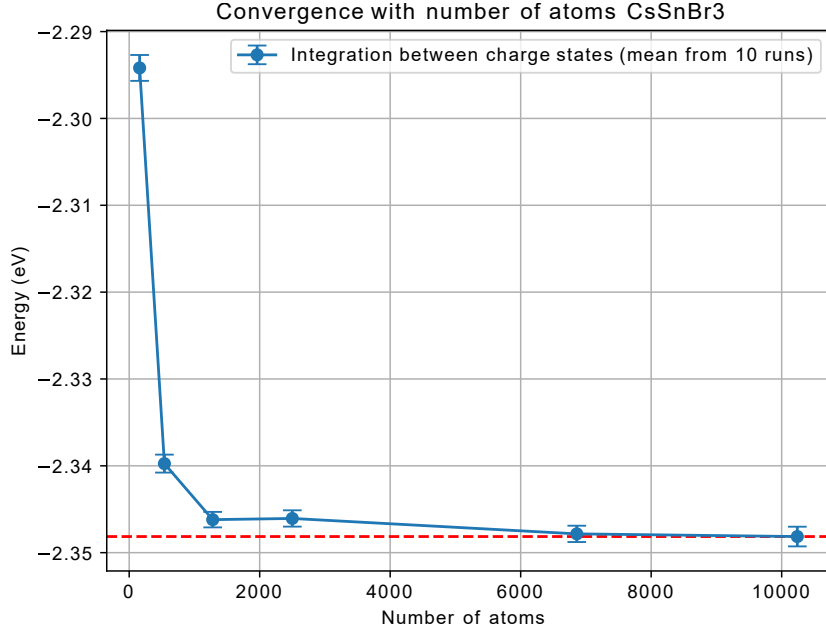


Fig. S14: TI results as a function of cell size in CsSnBr₃ at 100 K. The convergence check shows that the cell size is well converged already around 2000 atoms.

Supplementary Note 4: Chemical potential, corrections, and VBM shifts

The chemical potentials were obtained from density functional theory (DFT) calculations of appropriate reference phases, chosen such that their energy differences yield the chemical potential of each defect species. The specific reference phases used for each material are detailed in the corresponding subsections below.

Finite-size corrections for charged supercells were evaluated using the FNV scheme. All corrections were computed at 0 K and subsequently assumed to be temperature independent throughout this work.

The temperature dependence of the VBM was calculated using deep core states as reference levels. Snapshots from molecular dynamics (MD) simulations at finite temperatures were extracted, and DFT calculations were performed to obtain the electronic DOS for each snapshot. A Gaussian fit was performed to deep levels for the electronic DOS of snapshots obtained from MD heating runs. The distance between the mean of this fit and the VBM was then calculated to track the VBM shift. This method is illustrated for one snapshot in Figure S15. The same method was used to track the conduction band maximum (CBM) movement.

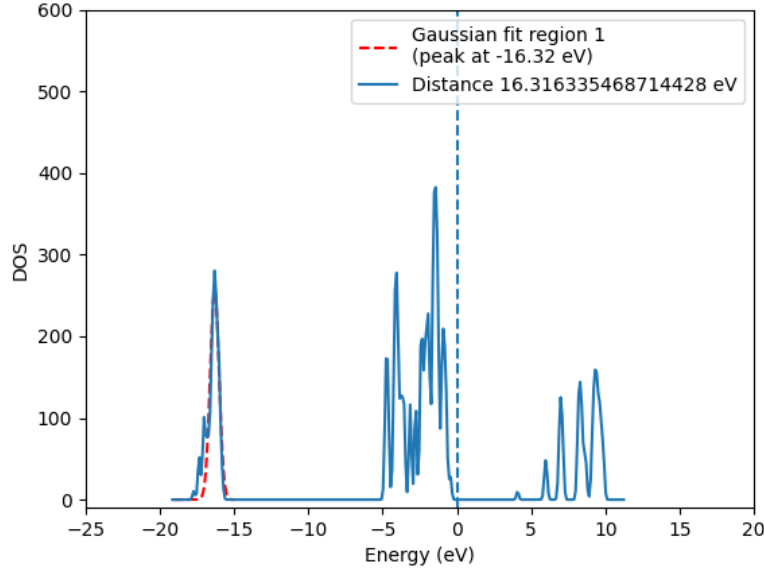


Fig. S15: Gaussian fits to DOS in MgO. Dashed red curve is the Gaussian fit to deep levels and dashed vertical line is the VBM position .

MgO

The oxygen chemical potential was evaluated at the Mg-rich limit. Under this condition, the host stability constraint $\Delta\mu_{\text{Mg}} + \Delta\mu_{\text{O}} = \Delta H_f(\text{MgO})$ reduces to $\Delta\mu_{\text{O}} = \Delta H_f(\text{MgO})$. Expanding the formation enthalpy and adding back the elemental oxygen reference $\mu_{\text{O}}^0 = E(\text{O}_2)/2$ causes the two oxygen reference terms to cancel exactly. The final chemical potential is therefore obtained directly from two DFT total energies,

$$\mu_{\text{O}} = E(\text{MgO}) - \mu_{\text{Mg}}^0, \quad (\text{S1})$$

where $\mu_{\text{Mg}}^0 = E(\text{Mg bulk})/N_{\text{Mg}}$ is the energy per atom of bulk Mg metal. The ionic chemical potential of O was found to be -4.45 eV in the Mg-rich environment.

For MgO, the FNV scheme yields a correction of 722 meV for the $+2$ charge state. The VBM shift as a function of temperature and fit of this data can be seen in Figure S16. The CBM as a function of temperature can be seen in Figure S17.

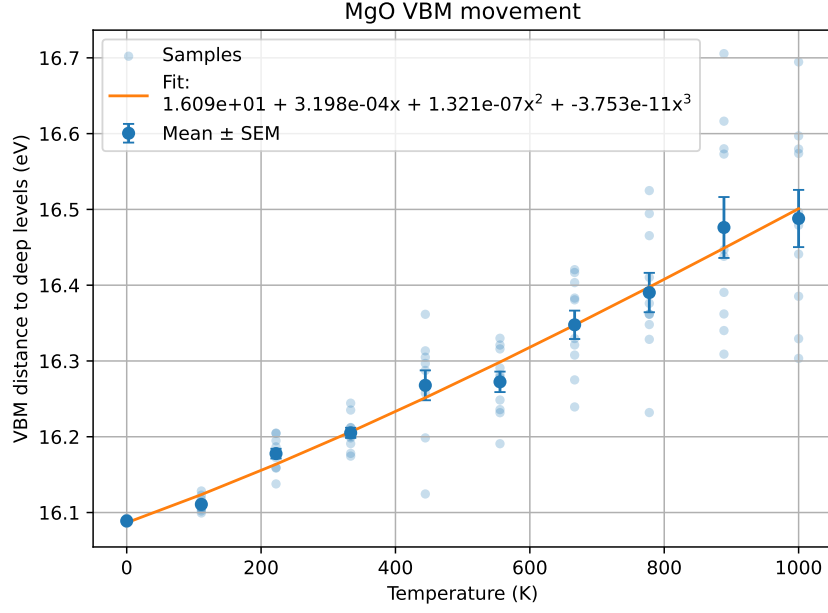


Fig. S16: VBM movement for MgO. A polynomial of degree 3 was fit to the data which is used in all calculations.

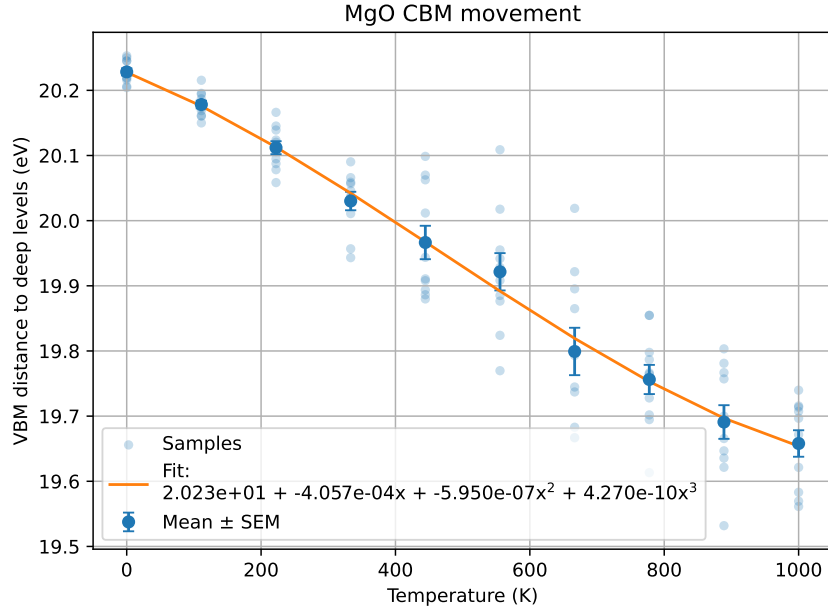


Fig. S17: CBM movement for MgO. A polynomial of degree 3 was fit to the data which is used in all calculations.

LiF

The fluorine chemical potential was evaluated at the Li-rich limit, where Li is in equilibrium with bulk Li metal and $\Delta\mu_{\text{Li}} = 0$. Under this condition, the host stability constraint $\Delta\mu_{\text{Li}} + \Delta\mu_{\text{F}} = \Delta H_f(\text{LiF})$ reduces to $\Delta\mu_{\text{F}} = \Delta H_f(\text{LiF})$. Expanding the formation enthalpy and adding back the elemental fluorine reference $\mu_{\text{F}}^0 = E(\text{F}_2)/2$ causes the two fluorine reference terms to cancel exactly. The final chemical potential is therefore obtained directly from two DFT total energies,

$$\mu_{\text{F}} = E(\text{LiF}) - \mu_{\text{Li}}^0, \quad (\text{S2})$$

where $\mu_{\text{Li}}^0 = E(\text{Li bulk})/N_{\text{Li}}$ is the energy per atom of bulk Li metal. The ionic chemical potential of Li was found to be -7.903 eV in the Li-rich environment.

For LiF, the calculated FNV corrections amount to 541 meV for the $+1$ charge state and 0.465 eV for the -1 charge state. The VBM shift as a function of temperature and fit of this data can be seen in Figure S18. The CBM as a function of temperature can be seen in Figure S19.

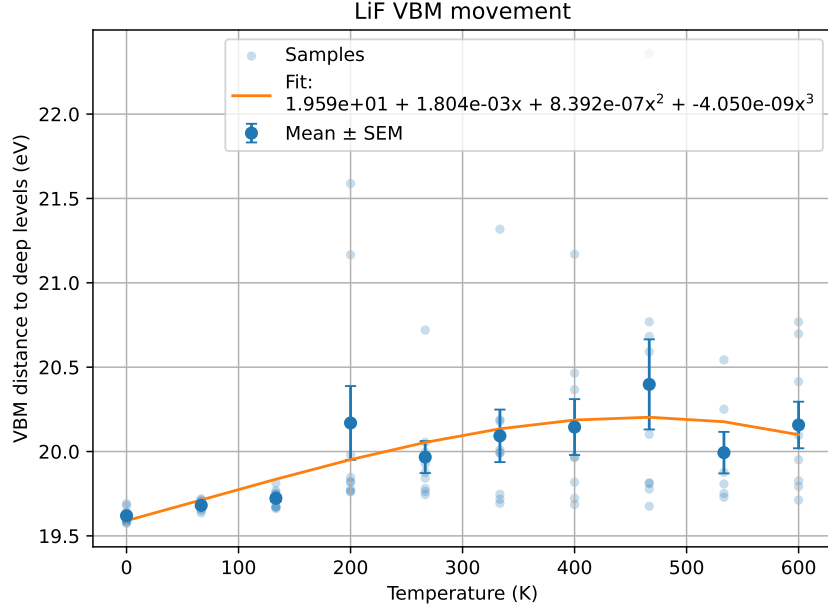


Fig. S18: VBM movement for LiF. A polynomial of degree 3 was fit to the data which is used in all calculations.

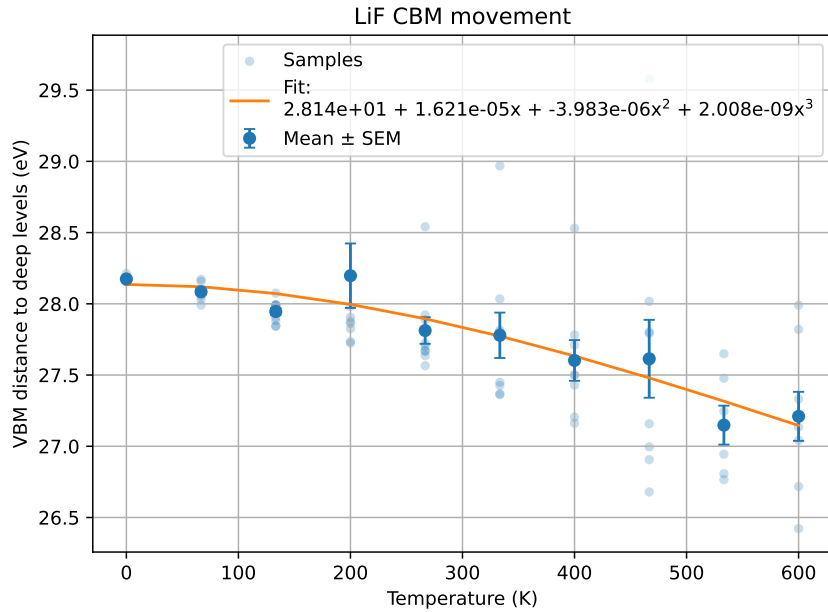


Fig. S19: CBM movement for LiF. A polynomial of degree 3 was fit to the data which is used in all calculations.

CsSnBr₃

The bromine chemical potential was evaluated at the Sn-rich limit, where Sn is in equilibrium with bulk Sn and $\Delta\mu_{\text{Sn}} = 0$, with the CsBr competing phase boundary active. The host stability constraint $\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Sn}} +$

$3\Delta\mu_{\text{Br}} = \Delta H_f(\text{CsSnBr}_3)$ and the active CsBr boundary $\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Br}} = \Delta H_f(\text{CsBr})$ together eliminate $\Delta\mu_{\text{Cs}}$ upon subtraction. Expanding both formation enthalpies, the elemental cesium reference cancels completely since Cs appears in both phases, while the elemental bromine reference cancels after adding back $\mu_{\text{Br}}^0 = E(\text{Br}_2)/2$ to obtain the absolute potential. The elemental tin reference μ_{Sn}^0 does not cancel, since Sn appears only in CsSnBr_3 and not in CsBr.

The final chemical potential is therefore obtained directly from three DFT total energies,

$$\mu_{\text{Br}} = \frac{1}{2} \left[E(\text{CsSnBr}_3) - E(\text{CsBr}) - \mu_{\text{Sn}}^0 \right], \quad (\text{S3})$$

where $\mu_{\text{Sn}}^0 = E(\text{Sn})/N_{\text{Sn}}$ is the energy per atom of bulk Sn. The ionic chemical potential of Br was found to be $\mu_{\text{Br}} = -14.471$ eV evaluated in the Sn-rich environment.

In the case of CsSnBr_3 , the +1 and -1 charge states require corrections of 172 meV and 113 meV, respectively. The VBM shift as a function of temperature and fit of this data can be seen in Figure S20. The CBM as a function of temperature can be seen in Figure S21.

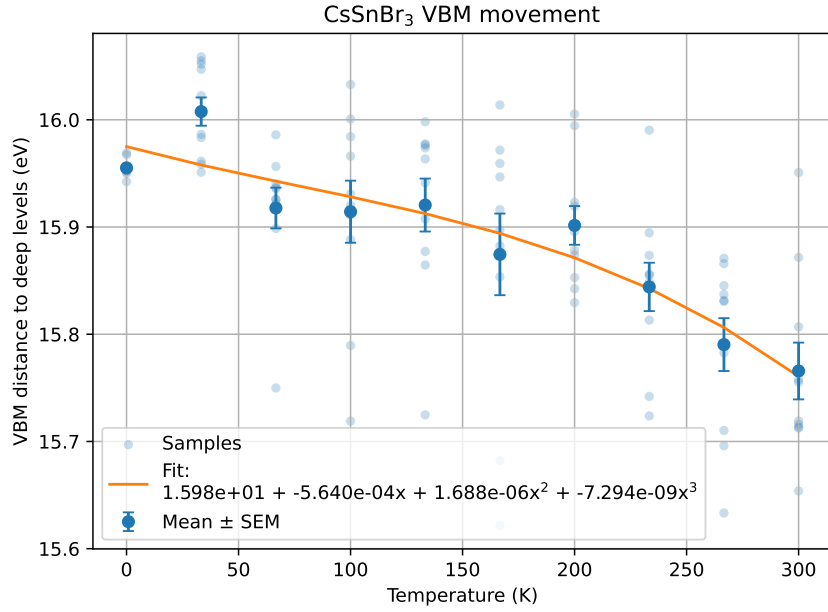


Fig. S20: VBM movement for CsSnBr_3 . A polynomial of degree 3 was fit to the data which is used in all calculations.

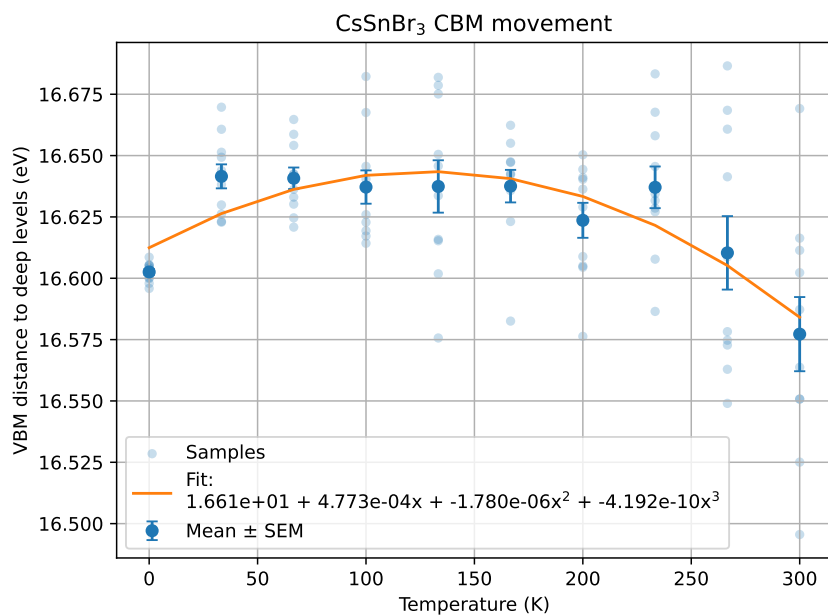


Fig. S21: CBM movement for CsSnBr₃. A polynomial of degree 3 was fit to the data which is used in all calculations.

Supplementary Note 5: Quantum corrections

Quantum corrections were calculated using Phonopy [1, 2]. The vibrational free energy using both classical and quantum statistics for all defective and pristine structures. Below follows the results for the free energy differences between different structures for all materials.

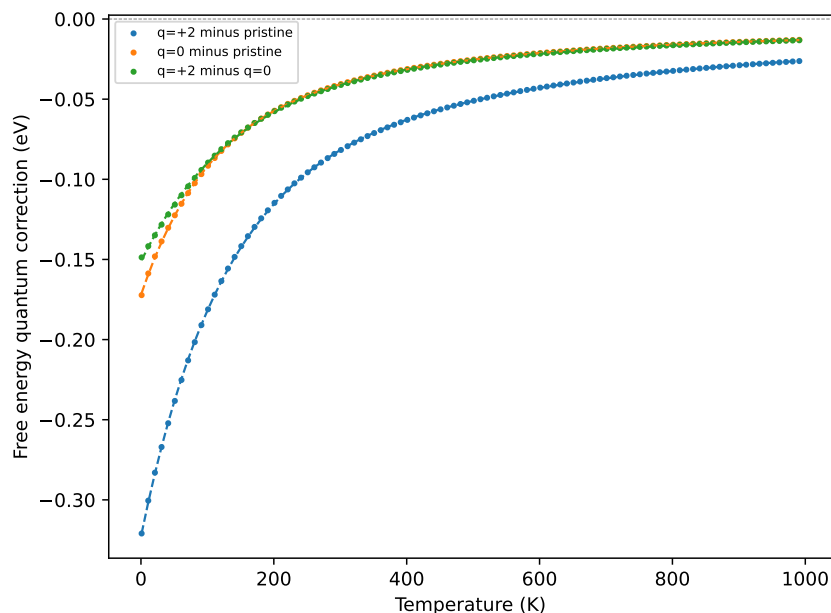


Fig. S22: Quantum corrections for MgO. This plot gives the value used to correct for quantum effects when comparing energies between charge states.

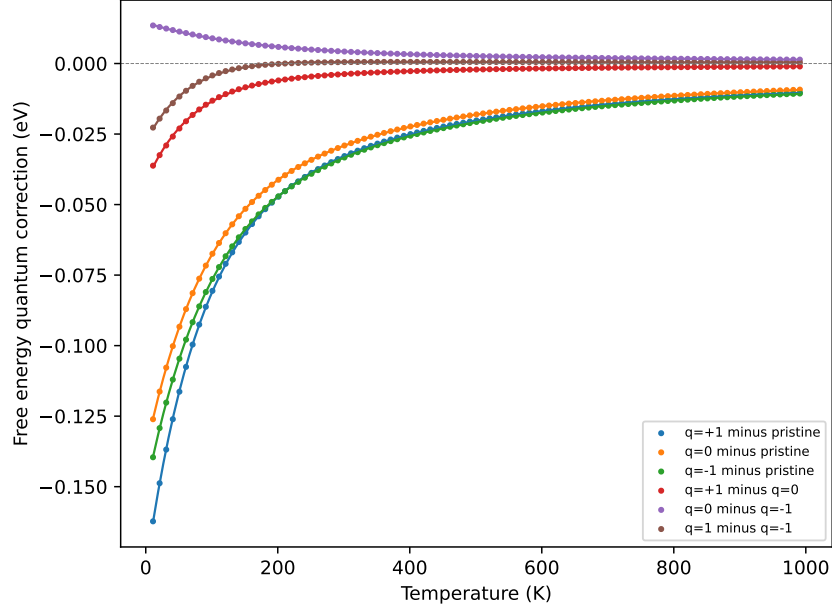


Fig. S23: Quantum corrections for LiF. This plot gives the value used to correct for quantum effects when comparing energies between charge states.

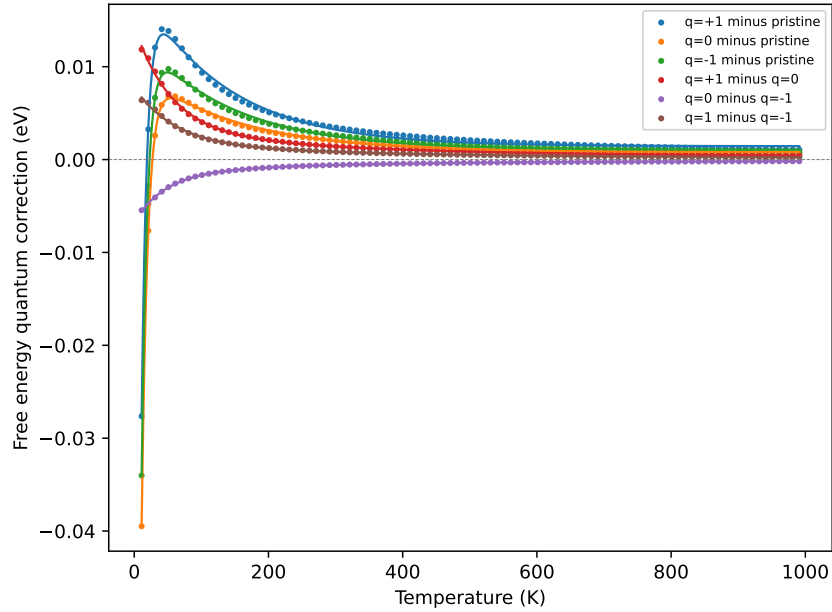


Fig. S24: Quantum corrections for CsSnBr₃. This plot gives the value used to correct for quantum effects when comparing energies between charge states.

Supplementary Note 6: Functional influence on energy

To assess the sensitivity of the defect dynamics to the choice of exchange-correlation functional, we computed energies for the relaxed defect geometries using r2SCAN+rVV10, r2SCAN+rVV10+SOC, and r2SCAN0+rVV10. The results are shown in Figure S25, where each relaxed geometry is taken from 159 atom structures relaxed with the NEP model. Notably, the neutral charge state retains its flat PES regardless of the functional employed. The two non-zero charge states likewise exhibit consistent behavior across all three functionals. Taken together, these results demonstrate that our choice of functional is robust, and that the differences between functionals are insufficient to justify the added computational cost of hybrid calculations in the training set.

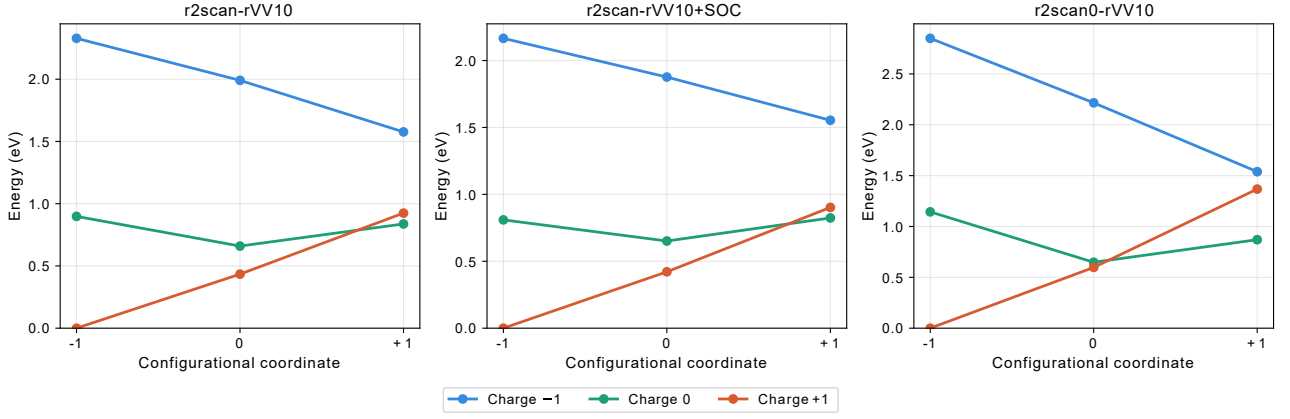


Fig. S25: Energies in the various relaxed defect geometries for different functionals . The consistent flattening of the neutral charge state PES across r2SCAN+rVV10, r2SCAN+rVV10+SOC, and r2SCAN0+rVV10 confirms that the chosen functional is sufficient to capture the key physics, no hybrid functional is required.

Supplementary Note 7: Direct integration between charge states

The method of marking neighbors based on defect charge state is illustrated in Figure S26. Performing TI between these models with different labels directly yields the free energy difference between charge states.

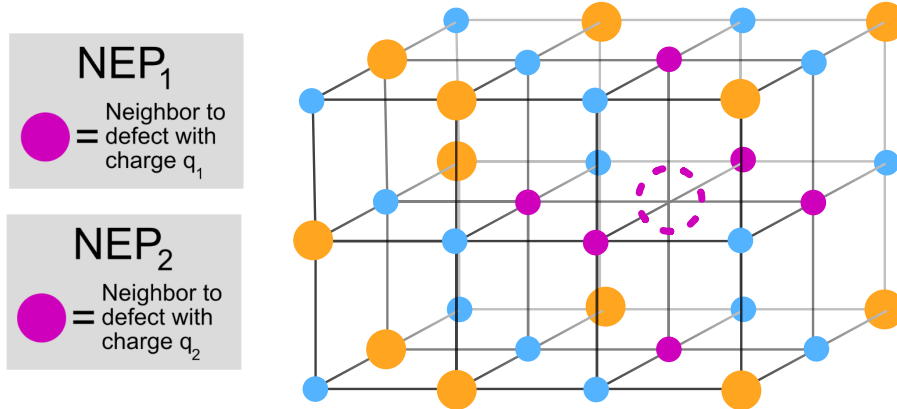


Fig. S26: Illustration of the labeling procedure used for the direct integration between charge states. The two NEP models, NEP_1 and NEP_2 , are constructed so that the neighboring atoms are related to vacancies with charge state q_1 and q_2 , respectively.

Supplementary Note 8: Performance of different model splits

The CTLs reported in the main text were obtained with a single NEP model per material, trained on the full reference database. To assess how sensitive the results are, we trained five additional models per material on different training/test splits of the same database, keeping all hyperparameters fixed and varying only the partitioning and the random seed. The training/test splits were divided in random 80/20 portions. The temperature dependence of the CTLs, which is directly linked to the free energies, was obtained for every model, resulting in an uncertainty estimate of the models. In the following, *full* refers to the model used in the main text and *splits* to this ensemble. Note that no quantum corrections are applied in the following section.

For MgO (Figure S27) the splits reproduces the $\varepsilon_{+2/0}$ behavior of the full model across the entire temperature range. The slope is similar between the splits and the full model, and the STD for the splits grows with temperature, which is expected.

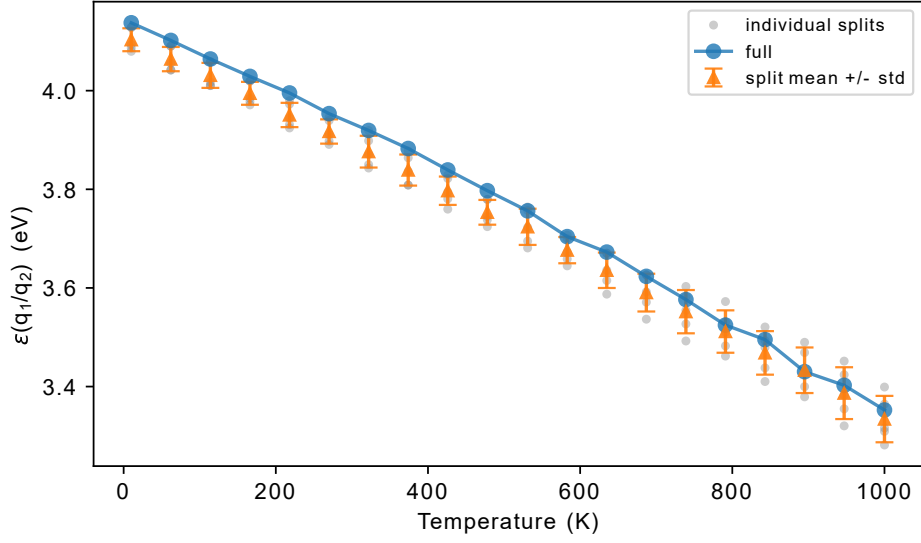


Fig. S27: Temperature dependence of the CTL in MgO for independent NEP model splits. The $\varepsilon_{+2/0}$ level of the oxygen vacancy relative to the temperature-dependent VBM, obtained from direct TI between charge states using NEP models trained on 5 different training/validation splits of the same reference database. The spread between splits provides an estimate of the uncertainty associated with the model training.

For LiF (Figure S28) both the $\varepsilon_{+1/0}$ and the $\varepsilon_{0/-1}$ level follow the full model closely, and the full model is always within one STD of the splits. The slopes extracted from the splits are also consistent.

The more complex potential energy surface of CsSnBr_3 made it harder to train stable models. We therefore trained more than five models in total and kept the five splits shown in Figure S29, removing outliers. Since the number of TI simulations scales with the number of splits and the number of temperatures, and that several independent TI runs are necessary to obtain good statistics for CsSnBr_3 , the trajectories used here were shorter than those of the production runs reported in the main text (2 ps compared with 50 ps). The full model and the split agrees well with each other. The separation between the two levels widens with temperature for every split, which is the feature responsible for the emergence of the neutral charge state.

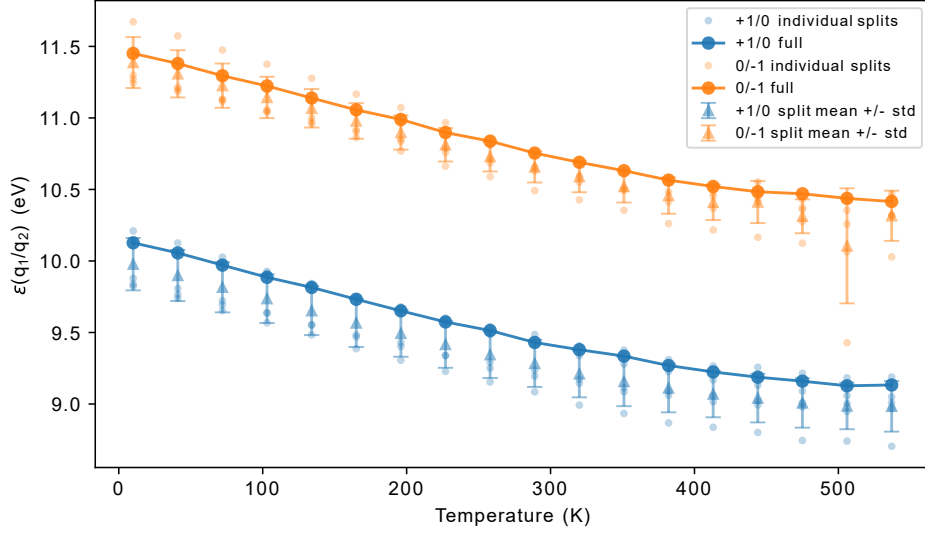


Fig. S28: Temperature dependence of the CTLs in LiF for independent NEP model splits. The $\varepsilon_{+1/0}$ and $\varepsilon_{0/-1}$ levels of the fluorine vacancy relative to the temperature-dependent VBM, obtained from direct TI between charge states for NEP models trained on different training/validation splits. All splits reproduce the same slopes within the split-to-split scatter.

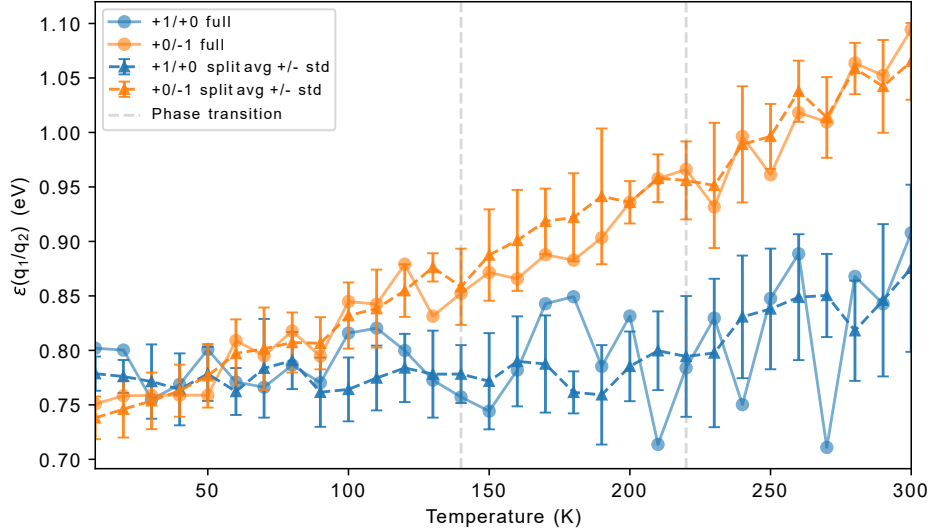


Fig. S29: Temperature dependence of the CTLs in CsSnBr₃ for independent NEP model splits. The $\varepsilon_{+1/0}$, $\varepsilon_{0/-1}$ and $\varepsilon_{+1/-1}$ levels of the bromine vacancy relative to the temperature-dependent VBM for NEP models trained on different training/validation splits. These runs for CsSnBr₃ used fewer simulation steps than for the production runs in the main article (2 ps compared with 50 ps). This is well motivated by the convergence check in Figure S11, and only shifted the full-model prediction for the neutral charge state as stable by 5.4 K.

The onset of the neutral charge state stability is summarized in Figure S30 for the different splits, which shows the temperature at which $\varepsilon_{+1/0}$ and $\varepsilon_{0/-1}$ cross for each model. These crossings were calculated by doing linear fits of the CTLs in the temperature range 0 to 140 K and noting the temperature at which the $\varepsilon_{+1/0}$ and $\varepsilon_{0/-1}$ crosses. The full model gives 54.6 K and the split ensemble (46 ± 31) K, note here that no quantum corrections are applied. The comparatively large spread is expected: the crossing temperature is obtained from the intersection of two levels with similar slopes, so a small uncertainty in the levels themselves translates into

a large uncertainty in the intersection point. The important observation is that every split places the crossing between 14 and 82 K, i.e. far below room temperature, so the emergence of a thermodynamically stable neutral bromine vacancy well below ambient conditions is a robust feature of the models and not an artifact of one particular training run.

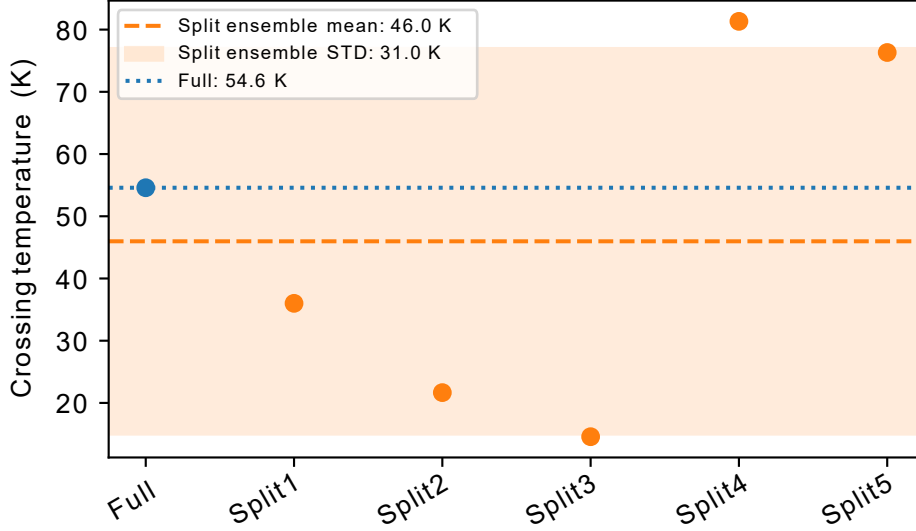


Fig. S30: Onset temperature for the stability of the neutral charge state in CsSnBr_3 across model splits. Temperature at which the $\varepsilon_{+1/0}$ and $\varepsilon_{0/-1}$ levels cross, i.e. above which the neutral bromine vacancy becomes thermodynamically stable in a window of Fermi energies, extracted for each NEP model split. The emergence of the neutral charge state is reproduced by all splits, with the onset temperature varying by only a few tens of kelvin.

Supplementary Note 9: DFT prediction of zero kelvin CTLs

To verify that our finite-temperature framework reduces to the expected static limit, we computed the defect formation energies directly from DFT using the same settings as used in training data generation. The resulting formation energies are shown in Figure S31. Only a single CTL is obtained, as the neutral charge state does not become thermodynamically stable for any position of the Fermi level. This is the same behavior as the low-temperature limit of our NEP-based free energies, which likewise show a single CTL in the zero kelvin limit.

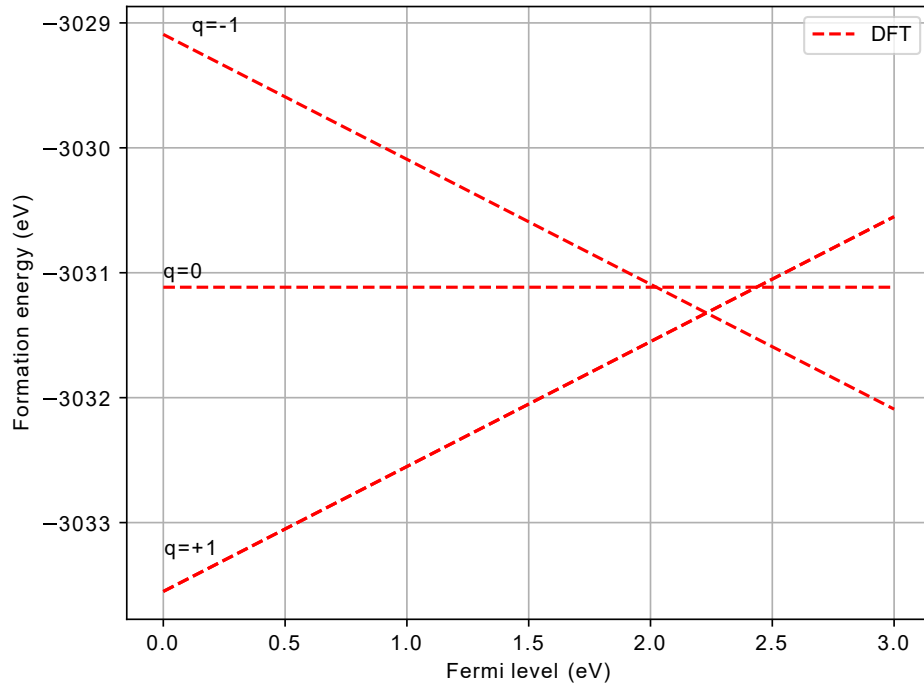


Fig. S31: Energies are obtained from DFT, on DFT-relaxed structures. This therefore correspond to the zero-kelvin formation free energies predicted by DFT, in agreement with the low-temperature limit of our NEP model.

- [1] Atsushi Togo. First-principles phonon calculations with phonopy and phono3py. *J. Phys. Soc. Jpn.*, 92(1):012001, 2023. doi: 10.7566/JPSJ.92.012001.
- [2] Atsushi Togo, Laurent Chaput, Terumasa Tadano, and Isao Tanaka. Implementation strategies in phonopy and phono3py. *J. Phys. Condens. Matter*, 35(35):353001, 2023. doi: 10.1088/1361-648X/acd831.