commentary

# Instilling defect tolerance in new compounds

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The properties of semiconducting solids are determined by the imperfections they contain. Established physical phenomena can be converted into practical design principles for optimizing defects and doping in a broad range of technology-enabling materials.

Impurities and defects in solids dictate their physical properties. Such imperfections come in a few fundamental flavours: doping (conductivity-promoting) defects and impurities can create free carriers that enable electronics; 'killer defects' (deep, charged recombination centres), on the other hand, quench transport; and charge scattering defects reduce mobility. Materials that cannot be doped (most wide-gap insulators) or that have vanishing free carrier mobility at room temperature (many Mott insulators) are not useful for many electronic and optoelectronic technologies. Owing to the strong historical interaction between the theory of defects and doping of semiconductor-based technologies — be they microelectronics, photovoltaics, transparent conductors, light-emitting diodes (LEDs), or, more recently, spintronics — a lot has been understood about the physics and properties of defects in inorganic semiconductors.

New technologies are focusing attention on less explored classes of compounds — such as halide perovskites, metal–organic frameworks, two-dimensional materials, and topological insulators — where defects feature in a leading role. For example, topological insulators such as $Bi_2S_3$ are hardly insulators because intrinsic defects render them n-type in the bulk, placing the Fermi level inside the bulk conduction band. Also, halide perovskite solar cells have not been effectively doped and thus have not benefited from all-perovskite p–n junctions (instead interfaces with hole- or electron-selective transporting layers have been imported from organic devices). This Commentary points to lessons learned from theoretical understanding of defect physics in semiconductors that could be leveraged in new classes of compounds.

## Doping by design

Building on a century of developments in empirical and semi-empirical models[1,2], the modern theory of defects in crystalline solids, based on first-principles electronic structure techniques, exposes phenomena that can be converted into practical approaches for optimizing a broad range of technology-enabling materials. Calculation of defect levels based on Greens functions[3–5] progressed to supercell treatments including a complete description of local structure optimization, chemical potentials and charge states[6,7]. There are many routes available to instilling defect tolerance in new compounds, and the specific approach can be adapted to the target material and device. For applications that are limited by electrical conductivity and mobility, including transparent conductors and thermoelectric devices, an optimal material would combine high carrier concentrations with weak carrier scattering. For light conversion in solar cells and LEDs, non-radiative recombination channels must be removed at all costs. In the new generation of 'quantum materials' (such as topological conductors, Weyl conductors and high-$T_C$ superconductors), control of the carrier concentrations is key, as the position of the Fermi level determines whether specific band structure features are accessible.

## Realities of point defect behaviour

All solids in equilibrium contain intrinsic defects. A compound may also contain unintentional chemical impurities and extrinsic dopants. The behaviour of such point defects is governed by several factors.

**Defect formation as a function of dual parameters.** Many recent theoretical studies on defects and doping in semiconductors consider a band structure representation where impurity atoms replace host atoms in a high-concentration limit, forming a new stoichiometric compound. In reality, the rules that control defects in crystals arise from the relationship between the concentration of point defects and their formation energy, which depends on the parametric Fermi level ($E_F$) and the external conditions that control the chemical potentials ($\mu$) of the reactants[6–9]. The formation energies $\Delta H_{D,q}(\mu,E_F)$ of defect type D (for example, vacancy or interstitial) in charge state $q$ (donors when $q > 0$; acceptors when $q < 0$) are not material constants but depend on the growth environment.

Electron-producing donor defects such as anion vacancies are difficult (easy) to form in a semiconductor that is already electron-rich (electron-poor) — that is, n-type (p-type). In contrast, hole-producing acceptor defects such as cation vacancies are difficult (easy) to form in a semiconductor that is already electron-poor (electron-rich). Likewise, anion vacancies are difficult (easy) to form under growth conditions that are anion-rich (anion-poor), and the opposite holds for cation vacancies.

These relationships decide if an impurity contemplated by a researcher will either successfully substitute a host atom or be rejected. They determine which of the possible host crystal sites will be substituted; whether the impurity will be ionized and contribute free carriers; if the generated electrons or holes will be eliminated by structural rearrangements; and, if charge carriers survive such compensation, whether they will be localized or delocalized. Such physical processes were initially ignored in calculations that confused chemical substitution (hypothetical replacement of a host atom by an impurity) with doping (substitution that is thermodynamically protected and releases free carriers that survive carrier localization or compensation).

**Unavoidable defects.** Defects cost energy to form, which implies that all solids will be nearly defect-free at low temperatures. Nevertheless, in many materials defects are omnipresent. In some host solids the natural ground state involves an ordered set of vacancies, as in pure ScS — a naturally occurring, low-entropy 'ordered-vacancy compound'[10]. In other systems, the chemical bonding is so weak that manipulating the dependence of the defect-formation energy on chemical potential and Fermi level can lead to spontaneous defect formation. This is the case for Te-rich SnTe, which has natural Sn vacancies[11]. Thus, building defect-tolerant materials has intrinsic limits when the defects are unavoidable — encoded in the basic genetics and thermodynamics of the host material.

**Doping by natural off-stoichiometry.** In fact, as-grown materials already manifest a defect or doping selectivity. While we are conditioned to accept the Daltonian view of fixed, integer stoichiometry in compounds, the equilibrium that exists between a target compound (say, a ternary ABX phase where A and B are cations) and its competing phases (say, AX and BX) may shift the compound to become naturally A-deficient or B-deficient. This can be achieved through a combination of vacancies, interstitials and anti-sites, each with their own electrical levels. Such compounds can be intrinsically (as-grown) n-type or p-type without any intentional doping. Examples include half-Heusler compounds[12] and quaternary kesterite semiconductors[13]. The good news is that such tendencies are predictable from knowledge of phase equilibria[12,13].

**Genetic doping preferences.** It was once thought that a sufficiently talented crystal grower could entice any material to be doped at will and thus place the Fermi level at a target position. While there is certainly some room for manipulations (see examples later), 'dopability' reflects the nature of the chemical bonding and electronic states in the host[14]. A compound may rearrange its atomic structure in response to added carriers of a given type (electrons or holes)[15]. Such Le Chatellier-type structural rearrangements ('self-regulating response') create intrinsic killer defects that precisely negate the type of free carrier being introduced by external doping. The Fermi level where such compensation is complete is the 'pinning energy' for holes or electrons. The success of doping lies on the position of these pinning energies with respect to the valence and conduction band edges of the host material[16–19]. While this is not easy to anticipate for a new composition or structure, all relevant quantities are accessible from modern first-principles calculations, as in predicting that NiO is naturally p-type under standard growth conditions, while ZnO is naturally n-type[20].

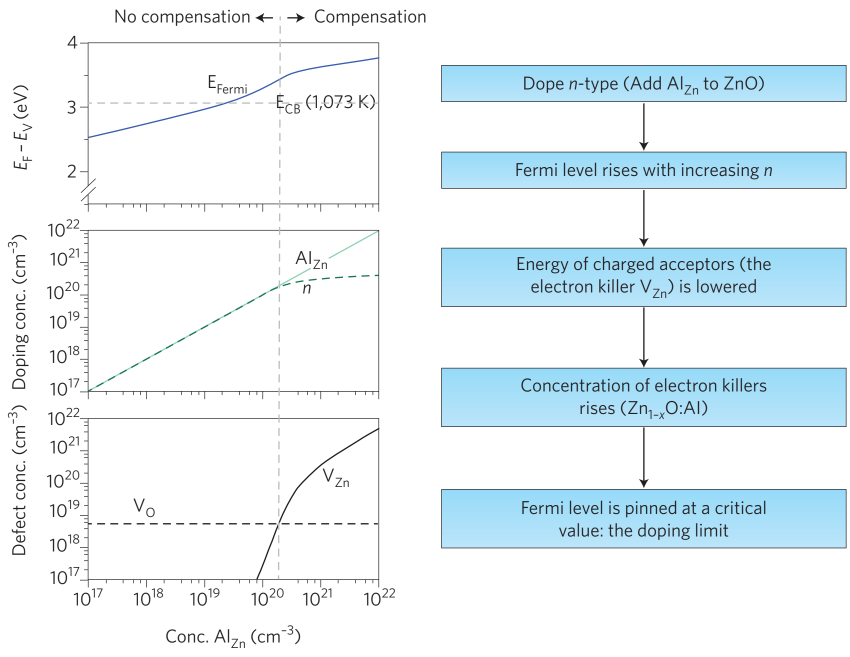


**Figure 1 |** Killer defects. The formation of charge-compensating centres can limit the ability to dope a semiconducting material with holes (p-type) or electrons (n-type). An example is shown for the case of electron doping of ZnO by substituting Zn(II) by Al(III), where $V_{Zn}^{2-}$ acts as a killer defect[20].

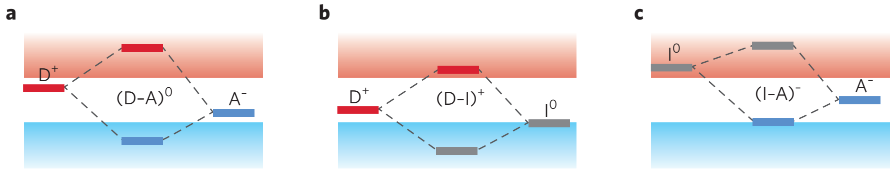
**Doping limits.** The ability to increase the concentration of a dopant to an arbitrary amount, thereby placing the Fermi level at the position likely to produce interesting physics (say, at a Dirac point, to produce specific band degeneracy, formation of spin-liquid or a high density of states) would be highly desirable. However, there are thermodynamic limits above which certain competing phases will form and nullify the effects of doping. One example is ZnO:Al, where Al is an effective n-type dopant at low concentrations (Fig. 1). When the Al dopant concentration exceeds a certain limit, the sample becomes strongly n-type and then the energy to form the acceptor Zn vacancy (an electron killer) is reduced, eventually becoming exothermic. At this point the intentional n-type doping by Al stops because of spontaneous compensation by negatively charged defects[20]. Eventually, electrically insulating secondary phases such as $ZnAl_2O_4$ form at higher concentrations[21]. The limits of accessible atomic chemical-potential space can be taken into account by constructing phase diagrams that account for all competitive phases[22]. While this is now a standard approach in theoretical studies of point defects, it is sometimes overlooked, which may lead to unphysical predictions such as the accessible Fermi level range in kagome spin liquids[23].

## Principles for defect tolerance

By considering the underlying chemical bonding and physical properties, it is possible to influence the defect behaviour of materials to realize their full potential.

**Fixed host materials.** If a specific host material must be used for independent reasons (for example, GaN–InN for LEDs, or diamond for quantum information technology) and this material has 'bad defects', one can manipulate them by using our understanding of how the formation energy can be altered by changing the chemical potential of the reactants during growth. The simplest route to defect tolerance is to avoid them. The equilibrium concentration of a point defect varies exponentially with its formation energy, which provides a route to supress detrimental defects. For example, increasing the partial pressure of oxygen gas during the high temperature anneal of a metal oxide will reduce the concentration (increase the formation energy) of oxygen vacancies in the bulk. For n-type materials such as ZnO, this will decrease the carrier concentration and increase the electrical resistivity. The record-efficiency perovskite solar cells were obtained through efficient management of the chemical potential of iodine during growth to supress non-radiative recombination channels[24].

Another concept applicable to a fixed host material involves manipulating the solubility of target dopants. Hole killer defects, such as an anion vacancy or cation interstitial, inhibit



Neutral pair that removes charged scattering centres

Complex that converts deep to shallow donor

Complex that converts deep to shallow accepter

**Figure 2 |** Defect tolerance. Three approaches to achieving defect tolerance in semiconducting materials that exploits defect–defect interactions. Shown are the defect levels of acceptors ($A^-$), donors ($D^+$) and isovalent impurities (I) with respect to the valence band and conduction band of a host material. **a**, The first approach removes deep levels by forming a charge-neutral complex — for example, $In_{Cu}{}^{2+} + 2V_{Cu}{}^- \rightarrow (In_{Cu} + 2V_{Cu})^0$ in $CuInSe_2$ (ref. 28). **b**, The second approach forms a shallow donor from a deep donor by binding to an isovalent impurity — for example, $N_C{}^+ + 4Si_C{}^0 \rightarrow (N_C + 4Si_C)^+$ in diamond[37]. **c**, The third approach converts a deep acceptor to a shallow acceptor by binding to an isovalent impurity — for example, $4Mg_{Zn} + N_O{}^- \rightarrow (4Mg_{Zn} + N_O)^-$ in ZnO (ref. 40).

p-type doping, which can be overcome by designing growth conditions that destabilize them — that is, kill the killer. An example of this is the use of hydrogen during Mg doping of GaN: without H, excessive p-type Mg doping will lead to the spontaneous formation of nitrogen vacancies once the Fermi level moves sufficiently towards the valence band maximum[25]. But since H acts as a donor, it limits the change in Fermi level (carrier concentration), thus defeating the formation of the compensating defect. Subsequently, H can be annealed out. This general idea, expressed early on by G. F. Neumark[26], has been extremely successful in doping wide-gap LED semiconductors, and has recently been applied to enhance conductivity in $ZnSnN_2$ (ref. 27).

**New host materials.** In some cases, we have the flexibility to design a new compound, where the chemical composition and crystal structure can be engineered with defect tolerance in mind.

*Formation of shallow defects*. A longstanding challenge is to identify a universal design principle that tells us how to select host materials that displace defect levels from the bandgap region (where they easily scatter carriers) into resonance within the valence or the conduction bands. The original defect tolerance concept[28] stated that the presence of an antibonding upper valence band and a bonding lower conduction band (the reverse of what simple molecular orbital models of solids suggest) signifies that dangling bond defects would be repelled quantum-mechanically into the continuum bands, leaving the bandgap clean and allowing for the formation of shallow defects. While factors determining the depth of a defect level are more complex, the general principles often hold for compounds having lone-pair elements (such as $Pb^{2+}$ or $Sn^{2+}$)[29,30] with bonding *s* orbitals deep inside the valence band (for example, $CsSnBr_3$), or when *d*–*p* repulsion leads to a bonding *d* band below the valence band (for example, $CuInSe_2$).

*Enhancing screening*. If charged defects are present in the host material, their influence should be minimized. The dielectric constant reflects the ability of a material to screen an electrostatic perturbation. Many properties critical to semiconductor physics — including the binding energy of excitons, the depth of shallow defect levels, and the rate of ionized impurity scattering — depend on the dielectric constant[2]. Thus, for a given defect population, the compound with the most effective screening will show the greatest tolerance. The dielectric constants found in halide perovskite semiconductors are roughly three times larger than for other thin-film photovoltaic materials such as CdTe and $Cu_2ZnSnS_4$, which is one factor that underpins their lauded defect tolerance[30–32].

*Low carrier mass***.** The spatial localization of electron and hole wavefunctions at defect sites should be avoided as they slow the transport of charge carriers and are associated with thermal energy losses. The effective mass of electrons and holes — related to the energy dispersion of the band structure — plays a special role in semiconductor physics and acts as a descriptor for more complex physical properties. A small mass favours free charge carriers and can support high carrier mobility and electrical conductivity. The effective mass is also a critical factor in avoiding the formation of small polarons: there is a competition between the kinetic energy of a free carrier and the potential energy gain by localizing in the lattice[33]. For example, metal oxides often feature a high hole effective mass ($>m_e$) due to the localization of the O 2*p* orbitals forming the valence band, leading to the formation of small polarons and the absence of p-type conductivity[34].

*Kinetics and temperature control*. Whereas the underlying engine of modern defect calculations is density functional theory (DFT), this does not imply that the theory is carried out at an unrealistic temperature ($T = 0$ K) or strictly at thermodynamic equilibrium. In fact, first-principles defect theory allows one to compute defect incorporation at growth temperature $T_g$ (where dopant solubility and ionization are calculated) and then evaluate carrier density at the measurement temperature $T_{device}$, for example, simulating samples that are quenched to room temperature[12,13,20]. Furthermore, while the incorporation of impurities is generally constrained by the thermodynamic condition that prevents precipitation of a secondary phase rich in the impurity atom (if the chemical potential exceeds the critical value), it is entirely possible to relax this thermodynamic constraint in a calculation and allow oversaturation. For example, $Zn_2CoO_4$ can be made Zn-rich in excess of its critical precipitation limit, thus exploring metastable (but kinetically protected) enhanced doping[35].

*Benign defect complexes*. Defect levels that are energetically too far from the respective band edges (deep levels) may not give up their excess electrons or holes, so effective carrier production (doping) is defeated. Sometimes this limitation can be overcome by adding even more defects into the mix. In quantum mechanics, a two-level system subjected to a coupling potential will mutually repel. If the upper level is a deep donor, pushing it to even higher energy via such repulsion will render the donor shallower (closer, or even above the conduction band edge); hence, more likely to produce free electrons. Analogously, if the lower level is a deep acceptor, pushing it to even lower energies via such a level repulsion will render the acceptor shallower (closer to or even below the valence band edge); hence, more likely to produce free holes. Some tested examples are discussed in this section (see also Fig. 2).

Even if isolated acceptor levels and donor levels reside in the bandgap (and thus form carrier-scattering charged defects), under some circumstances they can combine to form a neutral aggregate so stable that its periodic repetition in the lattice would create ordered defect structures. An example is when two Cu vacancy acceptors $2V_{Cu}{}^-$ and an In-on-Cu antisite donor $In_{Cu}{}^{++}$ in $CuInSe_2$ form thermodynamically stable structures of $m(2V^-{}_{Cu}+In^{2+}{}_{Cu})^0$ units interlaced with *n* units of $CuInSe_2$, cleaning up the band gap from the levels of the component defects. This gives rise to a series of ordered defect structures characterized by (*n*,*m*) and observed experimentally[36]. Bleaching the bandgap from adverse effects of individual defects by combining them to form innocuous centres is an as yet unexplored strategy for many new materials.

A second example of how well-designed energy-level repulsion created by defect complexes can greatly improve the properties of individual defects is when a donor level $D^+$ is too deep to produce free electrons (such as N-on-C in diamond), but adding to the mix a charge-neutral isovalent impurity I (such as Si-on-C in diamond) produces a complex $(N_C\text{-}4Si_C)^+$ whose donor level is repelled upwards[37]; hence, the manipulated donor is now shallow.

One could also design a shallow acceptor from a deep acceptor. It has been well established that an isolated N substitution in ZnO results in a deep acceptor level above the valence band[38,39]. Starting with the N-on-O substitutional acceptor, $N_O^-$ in ZnO, one can use cluster doping where a cluster of four isovalent Mg-on-Zn centres $4Mg_{Zn}$ combine with $N_O$ to produce an engineered shallow acceptor level[40] $(4Mg_{Zn}\text{-}N_O)^-$. To realize such a prediction, the loss in configurational entropy due to the cluster formation should be offset by the gain in enthalpy; or a strategy based on designer chemical precursors could be used to access metastable dopant configurations.

## Challenges and opportunities

At this stage, several issues remain open when applying defect theory to novel systems, from fundamental physical to computational challenges, as well as the design of materials with tailored properties. Doping of quantum materials is currently an issue, where many-body interactions and topological constraints alter our current understanding of defect processes. It was recently shown for TaAs that Weyl fermion formation is possible only over a narrow range of stoichiometry (Ta deficiency) and temperature[41]. The description of out-of-equilibrium systems[35] is also important where kinetic factors leading to defect formation, stability and transport should be accounted for. For semiconductors processed from solution and annealed at relatively low temperatures, such as the hybrid perovskites, the defect concentrations may not be governed by equilibrium thermodynamics.

When it comes to computational challenges, the inability to match defect calculations performed by different realizations of electronic structure theory is a major one (this is not the case for defect-free bulk calculations[42]). The need to perform a series of post-DFT corrections (to account for bandgap errors on defect levels, quasiparticle corrections, finite size effects and so on)[6,7,43] reduce the transferability and predictive power of these methods. The development of automated procedures for defect calculations[44,45] and machine learning of results[46] has the potential to overcome these limitations in the future. There is also a need to further develop procedures beyond a supercell approach (periodic boundary conditions) to accurately describe dilute defects, including embedded crystal techniques[47] that can capture long-range polarization effects for charged defects, and describe the wavefunctions of shallow defects that can extend over thousands of unit cells.

Finally, the ability to design new materials with specific properties is a grand challenge in the physical sciences[48–50]. High-throughput screening of materials tends to focus on response functions that are characteristic of the bulk crystal (for example, structural, mechanical and optical properties). Control of lattice defects, which govern the concentrations, stability and transport of electrons and holes in semiconductors, will be a critical factor for practical device applications. As discussed above, some defects can be avoided by changing processing conditions, while the effects of others can be minimized by tailoring the electronic structure, dielectric response and defect–defect interactions.

In summary, applications of any material to optical, transport or topological architectures is largely predicated on the control of defects and doping that either supply or destroy free carriers. The rapid development of new classes of materials faces the same critical need for manipulating and design of the defects and doping in such samples. The fruitful interaction between the condensed-matter theory of defects and technology in the fields of well-studied classes of materials (such as semiconductors and metal oxides) offers an opportunity for effectively leveraging this knowledge without need for rediscovery. ❐

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## References

1. Stoneham, A. M. *Theory of Defects in Solids* (Oxford Univ. Press, 1975).
2. Pantelides, S. T. *Rev. Mod. Phys.* **50,** 797–858 (1978).
3. Koster, G. F. & Slater, J. C. *Phys. Rev.* **95,** 1167–1176 (1954).
4. Baraff, G. A. & Schlüter, M. *Phys. Rev. Lett.* **41,** 892–895 (1978).
5. Lindefelt, U. & Zunger, A. *Phys. Rev. B* **24,** 5913–5931 (1981).
6. Lany, S. & Zunger, A. *Phys. Rev. B* **78,** 235104 (2008).
7. Freysoldt, C. *et al. Rev. Mod. Phys.* **86,** 253–305 (2014).
8. Zhang, S. B. & Northrup, J. E. *Phys. Rev. Lett.* **67,** 2339–2342 (1991).
9. Wei, S.-H. *Comput. Mater. Sci.* **30,** 337–348 (2004).
10. Hart, G. L. W. & Zunger, A. *Phys. Rev. Lett.* **87,** 275508 (2001).
11. Wang, N. *et al. Phys. Rev. B* **89,** 045142 (2014).
12. Yu, Y. G., Zhang, X. & Zunger, A. *Phys. Rev. B* **95,** 085201 (2017).
13. Chen, S., Walsh, A., Gong, X.-G. & Wei, S.-H. *Adv. Mater.* **25,** 1522–1539 (2013).
14. Zunger, A. *Appl. Phys. Lett.* **83,** 57–59 (2003).
15. Walukiewicz, W. *Physica B* **302–303,** 123–134 (2001).
16. Walukiewicz, W. *Phys. Rev. B* **37,** 4760–4763 (1988).
17. Zhang, S. B., Wei, S.-H. & Zunger, A. *J. Appl. Phys.* **83,** 3192–3196 (1998).
18. Zhang, S. B., Wei, S.-H. & Zunger, A. *Phys. Rev. Lett.* **84,** 1232–1235 (2000).
19. Walsh, A. *et al. Chem. Mater.* **25,** 2924–2926 (2013).
20. Lany, S. & Zunger, A. *Phys. Rev. Lett.* **98,** 045501 (2007).
21. Horwat, D. *et al. J. Phys. D: Appl. Phys.* **43,** 132003 (2010).
22. Buckeridge, J., Scanlon, D. O., Walsh, A. & Catlow, C. R. A. *Comput. Phys. Commun.* **185,** 330–338 (2014).
23. Mazin, I. I. *et al. Nat. Commun.* **5,** 4261 (2014).
24. Yang, W. S. *et al. Science* **356,** 1376–1379 (2017).
25. Buckeridge, J. *et al. Phys. Rev. Lett.* **114,** 016405 (2015).
26. Neumark, G. F. *Mat. Sci. Eng. R* **21,** 1–46 (1997).
27. Fioretti, A. N. *et al. Adv. Electron. Mater.* **3,** 1600544 (2017).
28. Zhang, S. B., Wei, S.-H., Zunger, A. & Katayama-Yoshida, H. *Phys. Rev. B* **57,** 9642–9656 (1998).
29. Walsh, A., Payne, D. J., Egdell, R. G. & Watson, G. W. *Chem. Soc. Rev.* **40,** 4455–4463 (2011).
30. Brandt, R. E., Stevanović, V., Ginley, D. S. & Buonassisi, T. *MRS Commun.* **5,** 265–275 (2015).
31. Walsh, A., Scanlon, D. O., Chen, S., Gong, X. G. & Wei, S.-H. *Angew. Chemie Int. Ed.* **54,** 1791–1794 (2015).
32. Steirer, K. X. *et al. ACS Energy Lett.* **1,** 360–366 (2016).
33. Fröhlich, H. *Adv. Phys.* **3,** 325–361 (1954).
34. Stoneham, A. M. *et al. J. Phys. Condens. Matter* **19,** 255208 (2007).
35. Perkins, J. D. *et al. Phys. Rev. B* **84,** 205207 (2011).
36. Zhang, S. B., Wei, S.-H. & Zunger, A. *Phys. Rev. Lett.* **78,** 4059–4062 (1997).
37. Segev, D. & Wei, S.-H. *Phys. Rev. Lett.* **91,** 126406 (2003).
38. Sokol, A. A. *et al. Faraday Discuss.* **134,** 267–282 (2007).
39. Lyons, J. L., Janotti, A. & Van de Walle, C. G. *Appl. Phys. Lett.* **95,** 252105 (2009).
40. Li, J., Wei, S.-H., Li, S.-S. & Xia, J.-B. *Phys. Rev. B* **74,** 081201 (2006).
41. Buckeridge, J., Jevdokimovs, D., Catlow, C. R. A. & Sokol, A. A. *Phys. Rev. B* **94,** 180101 (2016).
42. Lejaeghere, K. *et al. Science* **351,** aad3000 (2016).
43. Kumagai, Y. & Oba, F. *Phys. Rev. B* **89,** 195205 (2014).
44. Goyal, A., Gorai, P., Peng, H., Lany, S. & Stevanović, V. *Comput. Mater. Sci.* **130,** 1–9 (2017).
45. Broberg, D. *et al.* Preprint at http://arxiv.org/abs/1611.07481 (2016).
46. Medasani, B. *et al. npj Comput. Mater.* **2,** 1 (2016).
47. Berger, D. *et al. J. Chem. Phys.* **141,** 024105 (2014).
48. *Materials Genome Initiative for Global Competitiveness* (National Science and Technology Council, 2011).
49. Gautier, R. *et al. Nat. Chem.* **7,** 308–316 (2015).
50. Butler, K. T., Frost, J. M., Skelton, J. M., Svane, K. L. & Walsh, A. *Chem. Soc. Rev.* **45,** 6138–6146 (2016).

## Acknowledgements

A.W. acknowledges support from the Royal Society, the EPSRC (grant no. EP/K016288/1) and the EU Horizon2020 Framework (STARCELL, grant no. 720907). A.Z. is supported by the US Department of Energy, Office of Science, Basic Energy Science, MSE Division under grant no. DE-FG02-13ER46959, and by EERE Sun Shot initiative under DE-EE0007366.