

# Instilling defect tolerance in new compounds

Aron Walsh and Alex Zunger

**The properties of semiconducting solids are determined by the imperfections they contain. Established physical phenomena can be converted into practical design principles for optimising 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: conductivity-promoting ('doping') defects and impurities can create free carriers which 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 which 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 that microelectronics, photovoltaics, transparent conductors, light-emitting diodes (LEDs) and 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 are featuring in a leading role. These new materials and the underlying technologies have not benefited as much from the insights gained from condensed matter theory of defects in semiconductors. For example, topological insulators such as  $\text{Bi}_2\text{S}_3$  are hardly insulators because intrinsic defects render them n-type in the bulk, placing the Fermi level inside the bulk conduction band. This fundamental shortcoming of current topological insulators is still not fixed. 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 these new classes of compounds.

## Defect problems requiring doping by design

Building upon a century of developments in empirical and semi-empirical models<sup>1,2</sup>, the modern theory of defects in crystalline solids, based upon first-principles electronic structure techniques, exposes phenomena that can be converted into practical approaches for optimising a broad range of technology-enabling materials. Calculation of defect levels based on Greens functions<sup>3-5</sup> progressed to supercell treatments including a complete description of local structure optimisation, chemical potentials, and charge states<sup>6,7</sup>. 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 Fermi level position determines whether specific band structure features are accessible.

## Realities of point defect behaviour

**1. Defect formation is 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 actuality, however, 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 of the reactants  $\{\mu\}^{6-9}$ . The formation energies  $\Delta H_{D,q}(\mu, E_F)$  of defect type D (e.g. vacancy, 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, i.e. n-type (electron poor, i.e. 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, i.e. p-type (electron-rich, i.e. n-type). Likewise, anion vacancies are difficult (easy) to form under growth conditions that are anion rich (anion poor) and cation vacancies are difficult (easy) to form under growth conditions that are cation rich (cation poor).

These relationships decide if an impurity contemplated by a researcher will in fact agree to substitute a host atom (or be rejected). They determine which of the possible host crystal sites will be substituted; whether the impurity will be ionised and contribute free carriers; if the generated electrons or holes will be eliminated by structural rearrangements; and if charge carriers survive such compensation, will they be localised or delocalised. 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 localisation or compensation).

**2. Unavoidable defects:** According to textbooks, defects cost energy to form, which implies that all solids will be close to 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'<sup>10</sup>. 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<sup>11</sup>. Thus, building defect tolerant materials has intrinsic limits when the defects are unavoidable – encoded in the basic genetics and thermodynamics of the host material.

**3. Natural off-stoichiometry promotes doping:** 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 associated electrical levels. Such compounds can be intrinsically (as-grown) n-type or p-type without any intentional doping. Examples include half-Heusler compounds<sup>12</sup> and quaternary kesterite semiconductors<sup>13</sup>. The good news is that such tendencies are predictable from knowledge of phase equilibria<sup>12,13</sup>.

**4. Compounds have a genetic doping preference (p-type, n-type, both, or neither):** 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 below) ‘dopability’ reflects the nature of the chemical bonding and electronic states in the host<sup>14</sup>. A compound may rearrange its atomic structure in response to added carriers of a given type (electrons or holes)<sup>15</sup>. 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<sup>16–19</sup>. Whilst 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<sup>20</sup>.

**5. Doping limits due to competing phases:** 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; 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 (illustrated in Figure 1) is ZnO:Al, where Al is an effective n-type dopant at low concentrations. 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<sup>20</sup>. Eventually an electrically insulating secondary phases such as ZnAl<sub>2</sub>O<sub>4</sub> form at higher concentrations<sup>21</sup>. The limits of accessible atomic chemical potential space can be taken into account by constructing phase diagrams that account for all competitive phases<sup>22</sup>. 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<sup>23</sup>.

## Physical principles for defect tolerance

**1. Managing defects in a fixed host material:** If a specific host material must be used for independent reasons (e.g. 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 suppress 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 electron carrier concentration and increase the resistivity. The current record-efficiency perovskite solar cells were obtained through efficient management of the chemical potential of iodine during growth to suppress non-radiative recombination channels<sup>24</sup>.

Another concept applicable to a fixed host material involves manipulating the solubility of target dopants. p-type doping is inhibited by "hole killer defects" such as an anion vacancy or cation interstitial, which can be overcome by designing growth conditions that destabilize them: "kill the killer". An example 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<sup>25</sup>. 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<sup>26</sup>, has been extremely successful in doping wide-gap LED semiconductors, and has recently been applied to enhance conductivity in ZnSnN<sub>2</sub><sup>27</sup>.

**2. Design the electronic structure of new host materials:** (a) Choose an antibonding upper valence band, likely to form shallow defects. A longstanding challenge in this field is to identify a universal 'design principle' telling us how to select host materials that displace defect levels from the band gap region (where they easily scatter free carriers) into resonance within the valence or the conduction bands. The defect tolerance idea pioneered by Zhang, Wei, Zunger and Yoshida<sup>28</sup> stated that the presence of an upper valence band that is antibonding and a lower conduction band that is bonding (the reverse of what simple molecular orbital models of solids suggest), signify that dangling bond defects would be repelled quantum-mechanically into the continuum bands, leaving the band gap '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<sup>2+</sup> or Sn<sup>2+</sup>)<sup>29,30</sup> with bonding s orbitals deep inside the valence band (e.g. CsSnBr<sub>3</sub>) or when d-p repulsion leads to a bonding d band below the valence band (e.g. CuInSe<sub>2</sub>).

(b) Choose a large dielectric constant to enhance screening. If charged defects are present in the host material, their influence should be minimised. 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 ionised impurity scattering – depend on the square of the dielectric constant<sup>2</sup>. 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<sub>2</sub>ZnSnS<sub>4</sub>, which is one factor that underpins their lauded defect tolerance<sup>30–32</sup>.

*(c) Choose a low carrier mass to suppress small polarons.* The spatial localisation 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 can act as a simple descriptor of 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 localising in the lattice<sup>33</sup>. For example, metal oxides often feature a high hole effective mass ( $> 1 m_e$ ) due to the localisation of the O 2p orbitals forming the valence band, leading to the formation of small polarons and the absence of effective p-type conductivity<sup>34</sup>.

*(d) Take advantage of 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 ionisation are calculated) and then evaluate carrier density at the measurement temperature  $T_{\text{device}}$ , for example, simulating samples that are quenched to room temperature<sup>12,13,20</sup>. 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<sub>2</sub>CoO<sub>4</sub> can be made Zn-rich in excess of its critical precipitation limit, thus exploring metastable (but kinetically protected) enhanced doping<sup>35</sup>.

*(e) Design 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 more shallow (closer, or even

below the valence band edge); hence, more likely to produce free holes. Some tested examples are discussed in this section (see also Figure 1).

Even if isolated acceptor levels and donor levels reside in the band gap (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” (ODS). An example is when two Cu vacancy acceptors  $2V_{\text{Cu}}^-$  and an In-on-Cu antisite donor  $\text{In}_{\text{Cu}}^{++}$  in  $\text{CuInSe}_2$  form thermodynamically stable structures of  $m(2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^{++})^0$  units interlaced with  $n$  units of  $\text{CuInSe}_2$ , cleaning up the band gap from the levels of the component defects. This gives rise to a series of ODS characterized by  $(n,m)$  and observed experimentally<sup>36</sup>. Bleaching the band gap from adverse effects of individual defects by combining them to form innocuous centres is a 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  $(\text{N}_\text{C}-4\text{Si}_\text{C})^+$  whose donor level is repelled upwards<sup>37</sup>; 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<sup>38,39</sup>. Starting with the N-on-O substitutional acceptor,  $\text{N}_\text{O}^-$  in ZnO, one can use “cluster doping” where a cluster of four isovalent Mg-on-Zn centers  $4\text{Mg}_{\text{Zn}}$  combine with  $\text{N}_\text{O}$  to produce an engineered shallow acceptor level<sup>40</sup>  $(4\text{Mg}_{\text{Zn}}-\text{N}_\text{O})^-$ . To realise 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<sup>41</sup>. The description of out-of-equilibrium systems<sup>35</sup> 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 realisations of electronic structure theory is a major one (this is not the case for defect-free bulk calculations<sup>42</sup>). The need to perform a series of ‘post-DFT corrections’ (to account for band gap errors on defect levels; quasi-particle corrections; finite size effects, etc.)<sup>6,7,43</sup> reduce the transferability and predictive power of these

methods. The development of automated procedures for defect calculations<sup>44,45</sup> and machine learning of results<sup>46</sup>, 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<sup>47</sup> that can capture long-range polarisation effects for charged defects, and describe the wavefunctions of shallow donors and acceptors that can extend over hundreds to thousands of unit cells.

Finally, the ability to design new materials with specific properties is considered a grand challenge in the physical sciences<sup>48–50</sup>. High-throughput screening of materials tends to focus on response functions that are characteristic of the bulk crystal (e.g. structural, mechanical, 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 minimised 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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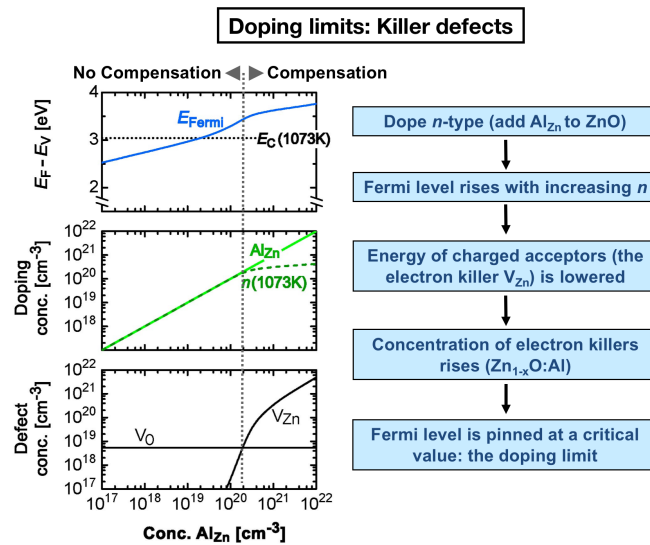
Aron Walsh is at the Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK and the Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea. Alex Zunger is at the University of Colorado, Boulder, Colorado 80309, USA.

email: a.walsh@imperial.ac.uk, alex.zunger@colorado.edu

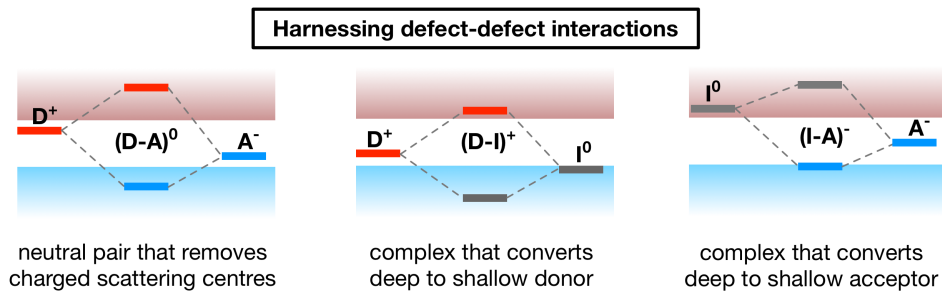
1. Stoneham, A. M. *Theory of Defects in Solids*. (OUP Oxford, 1975).
2. Pantelides, S. T. The Electronic Structure of Impurities and Other Point Defects in Semiconductors. *Rev. Mod. Phys.* **50**, 797 (1978).
3. Koster, G. F. & Slater, J. C. Wave Functions for Impurity Levels. *Phys. Rev.* **95**, 1167 (1954).
4. Baraff, G. A. & Schlüter, M. Self-Consistent Green's-Function Calculation of the Ideal Si Vacancy. *Phys. Rev. Lett.* **41**, 892–895 (1978).
5. Lindefelt, U. & Zunger, A. Quasi Bands in Green's-Function Defect Models. *Phys. Rev. B* **24**, 5913 (1981).
6. Lany, S. & Zunger, A. Assessment of Correction Methods for the Band-Gap Problem and for Finite-Size Effects in Supercell Defect Calculations: Case Studies for ZnO and GaAs. *Phys. Rev. B* **78**, 235104 (2008).
7. Freysoldt, C. *et al.* First-Principles Calculations for Point Defects in Solids. *Rev. Mod. Phys.* **86**, 253 (2014).
8. Zhang, S. B. & Northrup, J. E. Chemical Potential Dependence of Defect Formation Energies in GaAs: Application to Ga Self-Diffusion. *Phys. Rev. Lett.* **67**, 2339 (1991).
9. Wei, S.-H. Overcoming the Doping Bottleneck in Semiconductors. *Comput. Mater. Sci.* **30**, 337–348 (2004).
10. Hart, G. L. W. & Zunger, A. Origins of Nonstoichiometry and Vacancy Ordering in Sc<sub>1-x</sub>□<sub>x</sub>S. *Phys. Rev. Lett.* **87**, 275508 (2001).
11. Wang, N. *et al.* Microscopic Origin of the P-Type Conductivity of the Topological Crystalline Insulator SnTe and the Effect of Pb Alloying. *Phys. Rev. B* **89**, 45142 (2014).

12. Yu, Y. G., Zhang, X. & Zunger, A. Natural off-Stoichiometry Causes Carrier Doping in Half-Heusler Filled Tetrahedral Structures. *Phys. Rev. B* **95**, 85201 (2017).
13. Chen, S., Walsh, A., Gong, X.-G. & Wei, S.-H. Classification of Lattice Defects in the Kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub> and Cu<sub>2</sub>ZnSnSe<sub>4</sub> Earth-Abundant Solar Cell Absorbers. *Adv. Mater.* **25**, 1522–1539 (2013).
14. Zunger, A. Practical Doping Principles. *Appl. Phys. Lett.* **83**, 57–59 (2003).
15. Walukiewicz, W. Intrinsic Limitations to the Doping of Wide-Gap Semiconductors. *Phys. B Condens. Matter* **302–303**, 123 (2001).
16. Walukiewicz, W. Mechanism of Fermi-Level Stabilization in Semiconductors. *Phys. Rev. B* **37**, 4760 (1988).
17. Zhang, S. B., Wei, S.-H. & Zunger, A. A Phenomenological Model for Systematization and Prediction of Doping Limits in II–VI and I–III–V<sub>2</sub> Compounds. *J. Appl. Phys.* **83**, 3192 (1998).
18. Zhang, S. B., Wei, S.-H. & Zunger, A. Microscopic Origin of the Phenomenological Equilibrium ‘Doping Limit Rule’ in N-Type III-V Semiconductors. *Phys. Rev. Lett.* **84**, 1232 (2000).
19. Walsh, A. *et al.* Limits to Doping of Wide Band Gap Semiconductors. *Chem. Mater.* **25**, 2924 (2013).
20. Lany, S. & Zunger, A. Dopability, Intrinsic Conductivity, and Nonstoichiometry of Transparent Conducting Oxides. *Phys. Rev. Lett.* **98**, 45501 (2007).
21. Horwat, D. *et al.* On the Deactivation of the Dopant and Electronic Structure in Reactively Sputtered Transparent Al-Doped ZnO Thin Films. *J. Phys. D: Appl. Phys.* **43**, 132003 (2010).
22. Buckeridge, J., Scanlon, D. O., Walsh, A. & Catlow, C. R. A. Automated Procedure to Determine the Thermodynamic Stability of a Material and the Range of Chemical Potentials Necessary for Its Formation Relative to Competing Phases and Compounds. *Comput. Phys. Commun.* **185**, 330–338 (2014).
23. Mazin, I. I. *et al.* Theoretical Prediction of a Strongly Correlated Dirac Metal. *Nat. Commun.* **5**, 4261 (2014).
24. Yang, W. S. *et al.* Iodide Management in Formamidinium-Lead-Halide-based Perovskite Layers for Efficient Solar Cells. *Science (80-. )*. **356**, (2017).
25. Buckeridge, J. *et al.* Determination of the Nitrogen Vacancy as a Shallow Compensating Center in GaN Doped with Divalent Metals. *Phys. Rev. Lett.* **114**, 16405 (2015).
26. Neumark, G. F. Defects in Wide Band Gap II-VI Crystals. *Mater. Sci. Eng. R Reports* **21**, 1–46 (1997).
27. Fioretti, A. N. *et al.* Effects of Hydrogen on Acceptor Activation in Ternary Nitride Semiconductors. *Adv. Electron. Mater.* **3**, 1600544 (2017).
28. Zhang, S. B., Wei, S.-H., Zunger, A. & Katayama-Yoshida, H. Defect Physics of the CuInSe<sub>2</sub> Chalcopyrite Semiconductor. *Phys. Rev. B* **57**, 9642 (1998).
29. Walsh, A., Payne, D. J., Egdell, R. G. & Watson, G. W. Stereochemistry of Post-Transition Metal Oxides: Revision of the Classical Lone Pair Model. *Chem. Soc. Rev.* **40**, 4455–4463 (2011).
30. Brandt, R. E., Stevanović, V., Ginley, D. S. & Buonassisi, T. Identifying Defect-Tolerant Semiconductors with High Minority-Carrier Lifetimes: Beyond Hybrid Lead Halide Perovskites. *MRS Commun.* **5**, 265 (2015).
31. Walsh, A., Scanlon, D. O., Chen, S., Gong, X. G. & Wei, S.-H. Self-Regulation Mechanism for Charged Point Defects in Hybrid Halide Perovskites. *Angew. Chemie Int. Ed.* **54**, 1791 (2015).
32. Steirer, K. X. *et al.* Defect Tolerance in Methylammonium Lead Triiodide Perovskite. *ACS Energy Lett.* **1**, 360–366 (2016).
33. Fröhlich, H. Electrons in Lattice Fields. *Adv. Phys.* **3**, 325 (1954).
34. Stoneham, A. M. *et al.* Trapping, Self-Trapping and the Polaron Family. *J. Phys. Condens. Matter* **19**, 255208 (2007).
35. Perkins, J. D. *et al.* Inverse Design Approach to Hole Doping in Ternary Oxides: Enhancing P-Type Conductivity in Cobalt Oxide Spinels. *Phys. Rev. B* **84**, 205207 (2011).
36. Zhang, S. B., Wei, S.-H. & Zunger, A. Stabilization of Ternary Compounds via Ordered Arrays of Defect Pairs. *Phys. Rev. Lett.* **78**, 4059 (1997).
37. Segev, D. & Wei, S.-H. Design of Shallow Donor Levels in Diamond by Isovalent-Donor Coupling. *Phys. Rev. Lett.* **91**, 126406 (2003).
38. Sokol, A. A. *et al.* Point Defects in ZnO. *Faraday Discuss.* **134**, 267–282 (2007).
39. Lyons, J. L., Janotti, A. & Van De Walle, C. G. Why Nitrogen Cannot Lead to P-Type Conductivity in ZnO. *Appl. Phys. Lett.* **95**, 252105 (2009).
40. Li, J., Wei, S.-H., Li, S.-S. & Xia, J.-B. Design of Shallow Acceptors in ZnO: First-Principles Band-Structure Calculations. *Phys. Rev. B* **74**, 81201 (2006).
41. Buckeridge, J., Jevdokimovs, D., Catlow, C. R. A. & Sokol, A. A. Nonstoichiometry and Weyl Fermionic Behavior in TaAs. *Phys. Rev. B* **94**, 180101 (2016).
42. Lejaeghere, K. *et al.* Reproducibility in Density Functional Theory Calculations of Solids. *Science (80-. )*. **351**, 3000 (2016).
43. Kumagai, Y. & Oba, F. Electrostatics-Based Finite-Size Correction for First-Principles Point Defect Calculations. *Phys. Rev* **89**, 195205 (2014).
44. Goyal, A., Gorai, P., Peng, H., Lany, S. & Stevanović, V. A Computational Framework for Automation of Point Defect Calculations. *Comput. Mater. Sci.* **130**, 1–9 (2017).
45. Broberg, D. *et al.* PyCDT: A Python Toolkit for Modeling Point Defects in Semiconductors and Insulators. *arXiv* 1611.07481 (2016).
46. Medasani, B. *et al.* Predicting Defect Behavior in B2 Intermetallics by Merging Ab Initio Modeling and Machine Learning. *npj Comput. Mater.* **2**, 1 (2016).
47. Berger, D. *et al.* Embedded-Cluster Calculations in a Numeric Atomic Orbital Density-Functional Theory Framework. *J. Chem. Phys.* **141**, 24105 (2014).
48. Energy, U. D. of. *Materials Genome Initiative for Global Competitiveness*. (2011).
49. Gautier, R. *et al.* Prediction and Accelerated Laboratory Discovery of Previously Unknown 18-Electron ABX Compounds. *Nat. Chem.* **7**, 308–316 (2015).
50. Butler, K. T., Frost, J. M., Skelton, J. M., Svane, K. L. & Walsh, A. Computational Materials Design of Crystalline Solids. *Chem. Soc. Rev.* **45**, 6138–6146 (2016).





**Figure 1** The formation of charge compensating centres (killer defects) 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<sup>20</sup>.



**Figure 2** 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. (left panel) The first approach removes deep levels by forming a charge neutral complex, e.g.  $In_{Cu}^{2+} + 2V_{Cu}^- \rightarrow (In_{Cu} + 2V_{Cu})^0$  in  $CuInSe_2$ .<sup>28</sup> (centre panel) The second approach forms a shallow donor from a deep donor by binding to an isovalent impurity, e.g.  $N_C^+ + 4Si_C^0 \rightarrow (N_C + 4Si_C)^+$  in diamond.<sup>37</sup> (right panel) The third approach converts a deep acceptor to a shallow acceptor by binding to an isovalent impurity, e.g.  $4Mg_{Zn} + N_O^- \rightarrow (4Mg_{Zn} + N_O)^-$  in ZnO.<sup>40</sup>