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# Electron and hole stability in GaN and ZnO

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## Abstract
We assess the thermodynamic doping limits of GaN and ZnO on the basis of point defect calculations performed using the embedded cluster approach and employing a hybrid non-local density functional for the quantum mechanical region. Within this approach we have calculated a staggered (type-II) valence band alignment between the two materials, with the N 2p states contributing to the lower ionization potential of GaN. With respect to the stability of free electron and hole carriers, redox reactions resulting in charge compensation by ionic defects are found to be largely endothermic (unfavourable) for electrons and exothermic (favourable) for holes, which is consistent with the efficacy of electron conduction in these materials. Approaches for overcoming these fundamental thermodynamic limits are discussed.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

ZnO and GaN are wide bandgap semiconducting materials that have become staples of the optoelectronics industry owing to their bandgaps of approximately 3.5 eV, which are suitable for blue light emission [1, 2]. Both materials crystallize in the hexagonal close-packed wurtzite crystal structure, and are heteropolar owing to the large electronegativity of O and N compared to the metals Zn and Ga [3]. An important factor for the commercial applications of these materials is the extent to which their electronic structure can be modified and controlled by doping, which has been the subject of much experimental [1, 2, 4–8] and theoretical [9–22] interest to date. Both materials tend to be of n-type, with electron carrier concentrations for the nominally pure materials of the order of $10^{16}$–$10^{19}$ cm$^{-3}$ [23].

We have recently presented an approach to address the problem of treating hole or electron defect equilibria in semiconducting and insulating materials using a computational method based on an embedded quantum mechanical cluster model, in which we calculate the energies associated with the fundamental defect reactions controlling hole, electron and defect concentrations [11]. Our approach allows us to

assess directly whether doping will lead to the introduction of electronic or defect states; here we apply the method to the case of ZnO and GaN.

We report that both materials respond to electrons and holes in a similar fashion: point defect compensation to annihilate free holes present in the bulk lattice is energetically favourable, while the materials can tolerate the presence of excess electrons. These predictions agree with the large background n-type carrier concentrations and the difficultly in achieving p-type behaviour in the bulk materials. Approaches to overcome the thermodynamic limitations to doping are discussed.

## 2. The embedded cluster approach

Assessment of the reaction energies involving the creation and annihilation of point defects will allow us to predict whether hole or electron doping is favourable with respect to ionic defect formation. The standard approach, which has been applied in recent years to modelling defect formation in semiconducting materials such as ZnO [12–14, 16, 17, 22, 24] and GaN [19, 25, 26], is density functional theory (DFT) employing a plane-wave basis set under periodic boundary

conditions [27]. For the treatment of point defects, a supercell is created and typically the calculated thermodynamic quantities need to be converged with respect to supercell size; this is a particular problem for defects in non-zero charge states, where the electrostatic errors arising from interacting images are long-ranged and polarization effects require careful handling [28, 29].

Instead we adopt the hybrid QM/MM (quantum mechanical/molecular mechanical) embedded cluster approach, which has its conceptual origins in the classical Mott–Littleton method [30] that was developed to treat charged defect centres in dielectric materials. Analogous methods have been applied successfully to a wide range of defect-related problems in ionic and semi-covalent materials, as incorporated into the codes ICECAP [31], GUESS [32], AIMP [33], QMPOT [34] and EPE [35]. Our approach is implemented into the ChemShell package [36, 37], which interfaces between a QM code (GAMESS-UK[3]) and a classical mechanical code (GULP [39]); the technical details have been presented elsewhere [18, 36, 37]. This approach avoids artificial interactions between periodic images, while providing a proper dielectric and elastic response to point defect formation using a Born shell model [40] potential (individual parametrizations have been reported for ZnO [18, 21, 41] and GaN [20]). Another advantage of this approach is that the vacuum level is accessible, which facilitates the calculation of ionization reactions with an absolute energy reference.

In the QM/MM approach implemented in ChemShell, which builds upon the original ICECAP [31] development, screening of charged defects is treated explicitly in the inner region (typically of radius 15 Å), while the outer region is polarized through long-range electrostatic forces that extend to infinity. The latter term is calculated by Jost's formula:

$$E_{\text{Polarization}} = -\frac{Q^2}{2R}\left(1 - \frac{1}{\varepsilon}\right)$$

where $Q$ is the charge of the defect, $R$ is the radius of the inner region and $\varepsilon$ is the dielectric constant of the material (taken as an isotropic average of the dielectric tensor), which may be the static or high frequency constant, depending on whether a vertical or adiabatic process is being considered. In our approach, $\varepsilon$ is available from the underlying periodic MM calculation of the perfect bulk material.

Crucial to the success of DFT to describe the QM region is the choice of exchange and correlation functional to describe QM effects. For a quantitative description of the electronic states of insulators, in particular for the correct description of localized defect levels, we employ the hybrid non-local B97-1 (for ZnO) and B97-2 (for GaN) functionals [42, 43], which improve upon commonly used local or semi-local exchange and correlation functionals. The B97 class of functional has been shown to reproduce accurately thermochemical data, while providing a good description of electronic properties, including ionization potentials, as well as reaction barriers [42, 43].

For the inner QM region of ZnO, the triple-zeta valence with polarization (TZVP) basis set [44] was employed, with a large-core pseudopotential for the cations [45]. For GaN, an optimized version of the SBKJC small-core pseudopotential and basis set [46] was used for Ga, while a modified Def2-TZVP basis set [47] was used for N. For the present computational set-up, the calculated valence bandwidths of ZnO (3.3 eV) and GaN (6.1 eV) compare reasonably well with the experimental values of 5.3 eV [2] and 7 eV [48], respectively. For ZnO, the upper valence band features are very well reproduced [49], but the large-core Zn pseudopotential removes the states to higher binding energy. The full computational set-up used for the calculation of the point defects in both ZnO [18, 20, 21] and GaN [50] is presented elsewhere; the focus in this study is on the comparison and implications of these results.

## 3. Natural valence band offset

The alignment of valence bands between semiconductors is a problem for electronic structure techniques employing periodic boundary conditions due to the absence of an unambiguous energy reference: the absolute energy of an electron is generally not a calculable bulk quantity [51][4]. Instead, relative energies should be calculated. One approach is to align deep-lying core states (or a planar averaged electrostatic potential) from both sides of a material heterojunction (e.g. ZnO|ZnS) that is constructed along a non-polar crystallographic direction [52–54]. The effect of strain arising from the heterojunction must also be taken into account to extrapolate these values to the 'natural' offset of the true bulk materials [55]. Such an approach has limitations both when the structures of the two materials are different (e.g. the cubic spinel and tetragonal rutile crystal structures) or when there is a valence mismatch (e.g. between II–VI and III–V materials) as interface-dependent dipoles cannot be avoided; ZnO and GaN fall into the latter category. In the embedded cluster approach, the problem of band alignment is inherently avoided, as a common energy reference can be used for all calculations, as set by the mean electrostatic potential of the perfect material, which is in turn determined by the Ewald summation within the MM model representation. Moreover, following Ewald's convention, we can compare directly electrostatic energies and defect levels of different materials or the same material under different external conditions.

Experimental measurements based on x-ray photoelectron spectroscopy have determined an offset of 0.8 eV for a (0001) heterojunction of GaN and ZnO (with GaN lying higher than ZnO) [56]. Huda *et al* calculated a valence band offset of 0.7 eV [57] on the basis of DFT calculations (at the level of GGA + $U$) and a range of possible heterostructure models. The results from our calculations are shown in figure 1: ionization potentials of 7.7 eV (ZnO) and 6.9 eV (GaN), with respect to the vacuum level, result in a natural band offset of 0.8 eV. The value is therefore consistent both with experiment and a previous computational estimation. Taking the known experimental bandgaps, the bottom of the conduction band of

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[3] GAMESS-UK is a package of *ab initio* programs. See [38].

[4] Only if a unit cell with zero lower multipoles can be defined can the electrostatic potential then converge absolutely and the bulk energy of an electron is calculable.
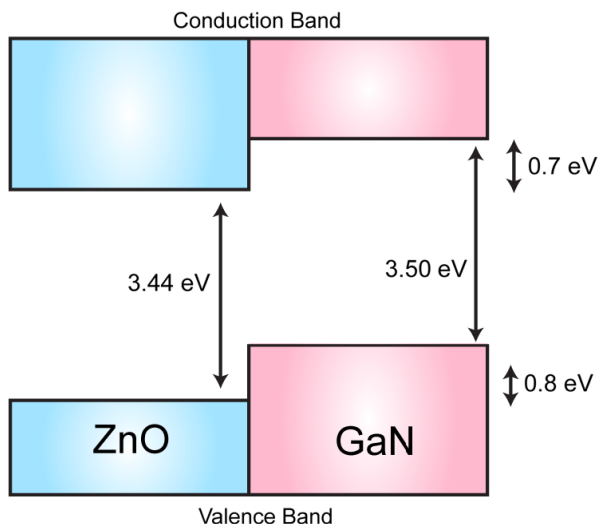
**Figure 1.** The natural valence band offset between wurtzite-structured ZnO and GaN, as calculated from the QM/MM method (86- and 72-atom QM clusters, embedded with an excess of 5000 polarizable MM ions and terminating in a dielectric continuum, with an extra layer of remote point charges providing a correct Madelung field on the active region) with reference to the vacuum level. The bandgap values are taken from experiment [23].



**Figure 2.** An illustration of the general process whereby a positively charged hole carrier is charge-compensated by the formation of a positively charged oxygen vacancy defect. There exists a subtle balance between the energetic cost of neutral defect formation, the ionization energy of the defect and the magnitude of the electronic bandgap. For wide bandgap materials, ionic disorder will typically be preferred over electronic disorder.

ZnO is therefore lower in energy than in GaN by approximately 0.7 eV.

The smaller ionization potential of GaN and larger electron affinity of ZnO would suggest an increased preference for holes (GaN) and electrons (ZnO) based purely on electrostatic grounds. Furthermore, the staggered 'type-II' [58] band offset should facilitate the separation or recombination of charge carriers at the material interface, which could be of benefit for photovoltaic or light emission applications.

## 4. Ionic versus electronic disorder

Modification of the concentrations of electronic species (holes or electrons) in semiconducting materials may be achieved by changes in stoichiometry or by the introduction of aliovalent dopants [59, 60]. For example, doubly charged cation dopants (e.g. $Mg^{2+}$) substituting at a cation site in a trivalent nitride, such as GaN, have an effective negative charge and may be charge-compensated by the formation of a hole; while doping with a divalent anion dopant (e.g. $O^{2-}$) at the nitrogen site gives a species with an effective positive charge leading to electron compensation. It should be remembered that the alternative compensation by point defects can also occur. For the case of GaN, dopants with an effective negative charge may be compensated by nitrogen vacancies or gallium interstitials and those with an effective positive charge by gallium vacancies or nitrogen interstitials. The underlying process is illustrated in figure 2.

The relative concentrations of these defects are determined by solid-state thermodynamics [61, 62], as we have recently shown in the case of ZnO [11]. Here, we have formulated the redox reactions whereby electronic species are exchanged with point defect compensation for both ZnO and GaN (see table 1).
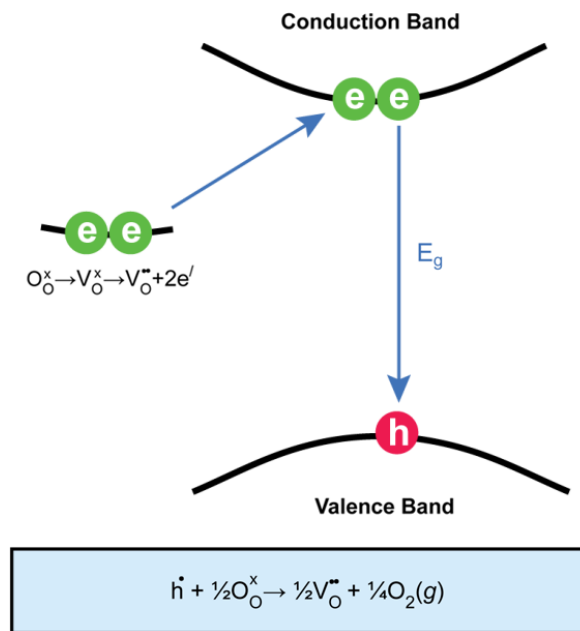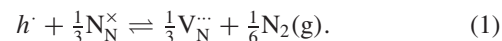
Let us take, for example, p-doping of GaN: an electron hole is converted to nitrogen vacancy compensation by the redox reaction

$$h^{\cdot} + \tfrac{1}{3}N_N^{\times} \rightleftharpoons \tfrac{1}{3}V_N^{\cdots} + \tfrac{1}{6}N_2(g). \tag{1}$$

The 'reactants' of reaction (1) are an electron hole in the bulk lattice ($h^{\cdot}$) and an $N^{3-}$ ion at the perfect lattice site ($\tfrac{1}{3}N_N^{\times}$), while the 'products' are a triply ionized nitrogen vacancy ($\tfrac{1}{3}V_N^{\cdots}$) and the gaseous nitrogen released from the lattice ($\tfrac{1}{6}N_2(g)$). The energy of this reaction can be determined directly from the calculated ionization potential of GaN, the formation energy of an ionized nitrogen vacancy, and the total energy of a nitrogen molecule. If the energy of such a reaction is appreciably negative (exothermic), then holes will be thermodynamically unstable with respect to vacancies under normal growth conditions. Equivalent processes can occur for the compensation of electrons; all of the processes considered are listed in table 1. The compensation reaction will generally favour defects in higher charge states; however, transient charge states are not considered, i.e. hole traps resonant in the valence band or electron traps resonant within the conduction band.

Remarkably, all reactions involving the replacement of electrons by point defects are large and positive: compensation by cation vacancies or anion interstitials is not expected to occur to any significant concentration (see table 1(b)). The corresponding electroneutrality condition for positively charged donor centres ($D^{\cdot}$) is $[D^{\cdot}] \approx [e']$ (where square brackets are used to denote the concentration of the respective species), which is consistent with the known efficacy of

**Table 1.** Calculated reaction energies ($\Delta E_\mathrm{f}$) for defect processes in ZnO and GaN, in which electron and hole carriers are charge-compensated by ionic defects. Negative values refer to exothermic reactions (most hole compensation processes), while positive values refer to endothermic reactions (all electron compensation processes). The defect reactions are formulated using the standard Kröger–Vink notation, where a superscript prime refers to an extra negative charge, while a dot refers to an extra positive charge and a cross to a neutral species.

| | ZnO defect reactions | $\Delta E_\mathrm{f}$ (eV) | GaN defect reactions | $\Delta E_\mathrm{f}$ (eV) |
|---|---|---|---|---|
| **(a) Hole carriers** | | | | |
| Anion-rich | $h^\cdot + \frac{1}{2}O_O^\times \rightleftharpoons \frac{1}{2}V_O^{\cdot\cdot} + \frac{1}{4}O_2(g)$ | $-0.74$ | $h^\cdot + \frac{1}{3}N_N^\times \rightleftharpoons \frac{1}{3}V_N^{\cdot\cdot\cdot} + \frac{1}{6}N_2(g)$ | $-0.77$ |
| | $h^\cdot + \frac{1}{2}ZnO(s) \rightleftharpoons \frac{1}{2}Zn_i^{\cdot\cdot} + \frac{1}{4}O_2(g)$ | $-0.50$ | $h^\cdot + \frac{1}{3}GaN(s) \rightleftharpoons \frac{1}{3}Ga_i^{\cdot\cdot\cdot} + \frac{1}{6}N_2(g)$ | $-0.11$ |
| | $h^\cdot + Zn_{Zn}^\times + \frac{1}{2}O_2(g) \rightleftharpoons V_{Zn}^\cdot + ZnO(s)$ | $1.64$ | $V_{Ga}^\cdot$ electronically unstable | |
| Cation-rich | $h^\cdot + \frac{1}{2}O_O^\times + \frac{1}{2}Zn(s) \rightleftharpoons \frac{1}{2}V_O^{\cdot\cdot} + \frac{1}{2}ZnO(s)$ | $-2.59$ | $h^\cdot + \frac{1}{3}N_N^\times + \frac{1}{3}Ga(s) \rightleftharpoons \frac{1}{3}V_N^{\cdot\cdot\cdot} + \frac{1}{3}GaN(s)$ | $-1.18$ |
| | $h^\cdot + \frac{1}{2}Zn(s) \rightleftharpoons \frac{1}{2}Zn_i^{\cdot\cdot}$ | $-2.35$ | $h^\cdot + \frac{1}{3}Ga(s) \rightleftharpoons \frac{1}{3}Ga_i^{\cdot\cdot\cdot}$ | $-0.52$ |
| | $h^\cdot + Zn_{Zn}^\times \rightleftharpoons V_{Zn}^\cdot + Zn(s)$ | $5.34$ | $V_{Ga}^\cdot$ electronically unstable | |
| **(b) Electron carriers** | | | | |
| Anion-rich | $e' + \frac{1}{4}O_2(g) \rightleftharpoons \frac{1}{2}O_i''$ | $1.73$ | $e' + \frac{1}{2}N_2(g) \rightleftharpoons N_i'$ | $4.66$ |
| | $e' + \frac{1}{2}Zn_{Zn}^\times + \frac{1}{4}O_2(g) \rightleftharpoons \frac{1}{2}V_{Zn}'' + \frac{1}{2}ZnO(s)$ | $0.75$ | $e' + \frac{1}{3}Ga_{Ga}^\times + \frac{1}{6}N_2(g) \rightleftharpoons \frac{1}{3}V_{Ga}''' + \frac{1}{3}GaN(s)$ | $1.39$ |
| | $V_O'$ electronically unstable | | $e' + N_N^\times \rightleftharpoons V_N' + \frac{1}{2}N_2(g)$ | $4.65$ |
| Cation-rich | $e' + \frac{1}{2}Zn_{Zn}^\times \rightleftharpoons \frac{1}{2}V_{Zn}'' + \frac{1}{2}Zn(s)$ | $2.60$ | $e' + \frac{1}{3}Ga_{Ga}^\times \rightleftharpoons \frac{1}{3}V_{Ga}''' + \frac{1}{3}Ga(s)$ | $1.79$ |
| | $e' + \frac{1}{2}ZnO(s) \rightleftharpoons \frac{1}{2}O_i'' + \frac{1}{2}Zn(s)$ | $3.58$ | $e' + GaN(s) \rightleftharpoons N_i' + Ga(s)$ | $5.88$ |
| | $V_O'$ electronically unstable | | $e' + N_N^\times + Ga(s) \rightleftharpoons V_N' + GaN(s)$ | $3.42$ |

electron conduction in these materials, and the range of growth techniques and environments, with which n-type materials can be grown. The absolute values for the reactions are much larger in GaN. In particular, the formation of a compensating zinc vacancy under oxygen-rich conditions costs only 0.75 eV for ZnO, while a compensating gallium vacancy costs 1.39 eV under nitrogen-rich conditions. For ZnO, the energy of the forward reaction is reduced by the large formation enthalpy of ZnO ($\Delta H_\mathrm{f}^\circ = -350.5$ kJ mol$^{-1}$) [63], while that of GaN is substantially lower ($\Delta H_\mathrm{f}^\circ = -110.5$ kJ mol$^{-1}$) [63].

In contrast to electron compensation, most reactions involving the replacement of holes by point defects are negative under both anion- and cation-rich environments: holes are unstable with respect to the formation of anion vacancies and cation interstitials (see table 1(a)). Under anion-rich conditions (those typical for material growth), the corresponding electroneutrality conditions with respect to negatively charged acceptor species (A') are $2[A'] \approx [V_O^{\cdot\cdot}]$ for ZnO and $3[A'] \approx [V_N^{\cdot\cdot\cdot}]$ for GaN. The most exothermic reaction occurs for the formation of compensating anion vacancies under cation-rich conditions. For ZnO this value is highly negative ($-2.59$ eV), while for GaN it is less negative ($-1.18$ eV). Again this trend can be related to the formation enthalpy of the material, where the production of ZnO can favour the electron hole to point defect compensation reaction.

Considering alternative defect charge states, we have included the positively charged zinc vacancy for ZnO in table 1(a), which is electronically stable, but which is found not to be competitive for hole compensation and, in fact, results in the only endothermic reaction. For GaN, the positively charged gallium vacancy is not electronically stable (the spin quadruplet state lies resonant in the valence band). While the negatively charged oxygen vacancy is unstable for ZnO, the nitrogen vacancy in GaN can accept a surplus electron (resulting in spin-pairing of the initial doublet state) [64];

the energy for electron compensation is high at 4.65 eV (see table 1(b)) under anion-rich conditions due to the weak trapping of electrons by neutral vacancies, but is lower in energy than forming a nitrogen interstitial species.

## 5. Overcoming thermodynamic limits

While fundamental thermodynamics drives against the formation of holes in both ZnO and GaN, this factor may of course be overcome by means of kinetics: for the redox reactions to proceed, ion exchange must occur with an environment. Exchange will be limited by the transport of the charged defects through the lattice and at the material surface, which is feasible at high temperatures, but at low temperatures the defects can be effectively 'frozen in'. For example, for ZnO, the migration barriers for charged zinc and oxygen vacancies have been calculated as 1.4 eV and 1.7 eV, respectively [17]. Other barriers to compensation that may exist during device fabrication include capping layers, the formation of stable heterostructures or nanoengineering [65]. The equilibrium constants for the compensation reactions could, in principle, be tuned using hydrostatic or epitaxial strain, which can change the valence and conduction band position for oxide materials [52, 54, 66, 67].

For ZnO, the observation of true p-type conductivity with delocalized hole states remains controversial: initial reports of p-type conduction in ZnO [68–70] and a theoretical proposal of the co-doping approach [71] have been followed by a rapidly growing number of studies [72–74]. Our calculations suggest that p-type behaviour will not be present for a material in thermal equilibrium, irrespective of the dopant, unless the material is doped above a certain threshold that it no longer behaves structurally/electronically as bulk ZnO. One recent possible example is the case of Li-doped ZnO, which is long known to create localized hole states deep in

the bandgap [5]; however, Yi *et al* succeeded in alloying ZnO with up to 16 at.% Li by pulsed-laser deposition and reported a transition to p-type conductivity above 4% [75], but the microscopic structure of the conductive material remains poorly characterized, including the homogeneity of the alloyed phase and the ratio of interstitial to substitutional lithium in the wurtzite lattice. Both independent confirmation of their results and structural clarification are still required.

For GaN, the longstanding difficulty in obtaining p-type material was overcome in 1989 by the activation of Mg-doped GaN samples by low-energy electron beam irradiation [76]; however, even after such treatment, the hole concentrations achieved are low and the acceptor levels are deep (hundreds of millielectronvolts above the valence band). Furthermore, the process requires dopant concentrations in the $10^{19}$ cm$^{-3}$ range, of which less than one per cent are ionized electron acceptors [77]. Self-compensation of Mg dopant by intrinsic defects has been proposed on the basis of electrical measurements performed as a function of dopant concentration [78]; at higher concentrations, Mg clustering has been observed [79]. The nature of the p-type conductivity is therefore not conventional for GaN compared to other semiconducting materials.

Our study has suggested that the principal barrier to achieving p-type behaviour in wide bandgap materials is ionic compensation. We have only considered the role of native defects; however, for specific dopants, self-compensation will also exclude the stabilization of hole carriers, e.g. $[\text{Li}'_{\text{Zn}}]/[\text{Li}^{\bullet}_i]$ in ZnO or $[\text{Mg}'_{\text{Ga}}]/[\text{Mg}^{\bullet\bullet}_i]$ in GaN, with the relative concentrations determined by the thermodynamics of defect formation. The two successful examples of doping in ZnO and GaN discussed above require extremely high doping levels that will substantially modify the host structural and electronic properties including the Madelung field, and the position of the conduction and valence bands; these effects will result in a change to the equilibrium between ionic and electronic defects in the system. We suggest that the proposed framework can be used in the future design of functional electronic materials.

## 6. Conclusions

The results from our calculations have demonstrated that electron carriers are stable species in ZnO and GaN, while hole carriers can be quenched by the formation of charge-compensating ionic defects. We have not commented upon the origin of the carriers (i.e. deep or shallow donors or acceptors), but simply the fate of free carriers present in the bulk lattice under conditions of thermodynamic equilibrium.

Future work should be concerned with improving this approach to go beyond the $T = 0$ K approximation (where the free energies—including both enthalpic and entropic contributions—become relevant) and to account for specific growth conditions (where quantitative concentrations can be calculated, e.g. under a given set of elemental chemical potentials). A complete theoretical framework for assessing the doping limits of materials would enable a large scale screening of both known and hypothetical materials for a range

of electronics applications. As stated by A M Stoneham in the conclusion to his 1975 book *Theory of Defects in Solids*: 'In principle, all these difficulties can be overcome by currently available methods. It remains to be seen whether this will be done'.

## Acknowledgments

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