Microscopic Origin of the Phenomenological Equilibrium “Doping Limit Rule” in *n*-Type III-V Semiconductors

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The highest equilibrium free-carrier doping concentration possible in a given material is limited by the “pinning energy” which shows a remarkable universal alignment in each class of semiconductors. Our first-principles total energy calculations reveal that equilibrium -type doping is ultimately limited by the spontaneous formation of *close-shell acceptor defects:* the (−)-charged cation vacancy in AlN, GaN, InP, and GaAs and the (1−)-charged *DX* center in AlAs, AlP, and GaP. This explains the alignment of the pinning energies and predicts the maximum equilibrium doping levels in different materials.

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Semiconductor-based high technology owes its existence, in large, to the fact that these materials can be doped, i.e., produce free charge carriers. Indeed, failure to dope a class of materials is often the single most important bottleneck for advancing semiconductor-based electronic or optoelectronic technology. Recent examples of difficult-to-dope systems include -type doping of wide-gap II-VI compounds [1] and nitrides [2], -type doping of diamond [3], and -type doping of transparent oxides [4]. In addition to these cases one notices that even if certain materials can be doped, there is a maximum equilibrium doping limit that cannot be exceeded. This maximum dopability is vanishingly low for certain “undopable” systems (-ZnO, -ZnS, -ZnTe), and is finite for others. For example, GaP can be doped -type only up to 10^{1} cm^{-} [5], while GaAs can be doped even to a level of 10 ^{0} cm^{-} [6]. A recent discovery provides a certain insight into the nature of this “doping limit” [7–10]: it showed that the failure to dope is related not merely to the existence of a large band gap, but to the position of the valence band maximum (VBM) with respect to a phenomenological “ -like pinning energy” $^{(\ )}_{\mathrm{p}}$, and the position of the conduction band minimum (CBM) with respect to the “ -like pinning energy” $^{(\ )}_{\mathrm{p}}$. Remarkably, in a given material class the values of $^{(\ )}_{\mathrm{p}}$ and separately $^{(\ )}_{\mathrm{p}}$ tend to line up, on an “absolute” energy scale obtained by aligning the VBM’s of different materials according to their respective band offsets [11]. This is illustrated by the dashed lines in Fig. 1 for III-V compounds (see also Ref. [10] for II-VI and I-III-VI compounds). The emerging phenomenological “equilibrium doping limit” rules are as follows: (a) A material for which $^{(\ )}_{\mathrm{p}} \ll$ $_{\mathrm{M}}$ cannot be doped -type. (b) A material for which $^{(\ )}_{\mathrm{p}} \gg$ $_{\mathrm{V\ M}}$ cannot be doped -type. This remarkable rule permits one to guess rather accurately if a material can be doped or not at equilibrium (and roughly by how much), merely by positioning its band edge energies on a diagram such as Fig. 1. However, the origin of this generally successful rule remains unclear.

In this paper we investigate, using first-principles total energy calculations, the microscopic origin of the -type pinning close-shell structures, such as the *triply* charged cation vacancy or the *singly* charged *DX* center. In these *close-shell*

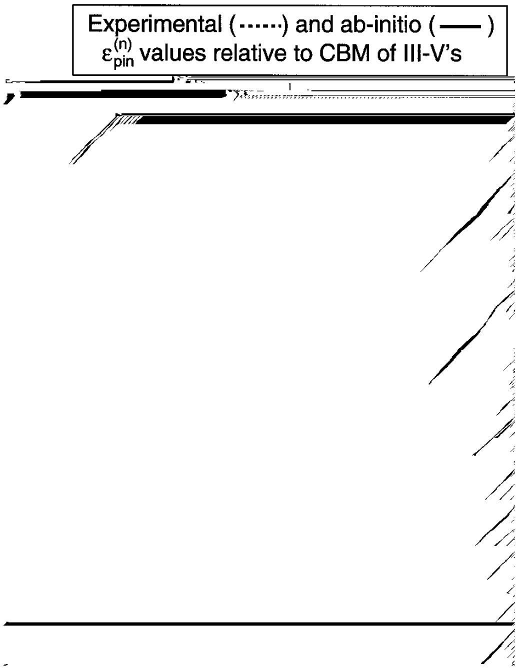

FIG. 1. LDA-corrected (solid lines) vs the experimental (dashed lines) -type pinning energies in seven III-V compounds. (a) Cation vacancies. (b) *DX* centers. The shaded region denotes the conduction bands with band alignments taken from Ref. [11]. The energy zero is the VBM of GaAs.

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defects, the energy required to form defect gap levels is approximately canceled by the energy needed to fully occupy them. This cancellation results in approximate material independence of $_{p}^{(\ )}$, hence in the alignment of $_{p}^{(\ )}$ across different materials. Our first-principles calculated $_{p}^{(\ )}$ are in good agreement with those obtained from the phenomenological model (Fig. 1), and can thus be used to predict the ultimate equilibrium doping limits in other materials, given their band offsets with materials in Fig. 1.

The formation enthalpy of a defect α (either native or foreign) of charge is

$\Delta H^{(}$,0a5 TD ( )Tj)Tj /F6 1 Tf 075.8tc23 0 Tf5a20the885 ( )Tj /F3 1 T 5,. 11 -1.643.8(hence)-346.2(i 0 355 (0 5 TD ((Tj)Tj /F6 1 Tf 075.8tc23 0 Tf5a2h

The LDA values of $^{($

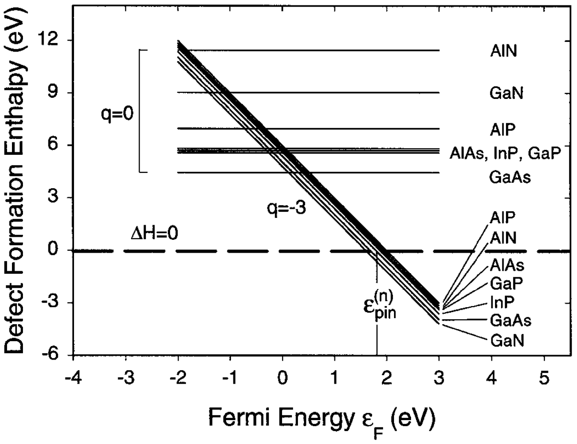

FIG. 3. Cation vacancy formation enthalpies for = 0 and −, respectively, as a function of the Fermi energy on an absolute energy scale in seven III-V compounds. The zero of the Fermi energy $_F$ is set at the VBM of GaAs.

nitrides, one may consider Si as a potential dopant provided that Si produces a shallow $(+/0)$ level, because the Si-derived *DX* center is unstable. The lack of Si-derived *DX* stability has been interpreted [20] in terms of a too small lattice spacing of the nitrides. On the other hand, one should avoid oxygen as an dopant at least in AlN [23] because the oxygen-derived *DX* center is stable. The calculated $(+/-)$ transition energy for the oxygen is, however, too high so $^{(\;)}_{\rm p}$ in AlN is still given by the Al vacancy in Table I.

We may understand (ii) above via a qualitative model where one separates the total energy of a system into a sum of its occupied eigenvalues plus the rest (= electron-electron double counting plus the ion-ion term): $E \quad = \Sigma \quad + F$. A bulk zincblende semiconductor has 6 electrons in its VBM. When a *neutral* cation vacancy forms, the VBM-derived defect level is occupied by $\quad - N$ electrons, where N is the cation valence (= in III-V and 2 in II-VI compounds). Thus, using Eq. (2)

$$\Delta E(V_N{}^{=0}) = (\quad - N) \quad - \quad {}_{\rm V\;M} + F(V_N) - F(\text{host}), \tag{10}$$

and, from Eq. (1) with $\quad = 1$ and $\quad = E_{\rm a}$,

$$\Delta H(V_N{}^{=0}) = (\quad - N) \quad - \quad {}_{\rm V\;M} + F(V_N) - F(\text{host}) + E_{\rm a} \,. \tag{11}$$

For a charge cation vacancy, $\Delta H(V_N) = \Delta H(V_N{}^{=0}) - \quad + \quad _F$, thus

$$\Delta H(V_N) = [\;(\quad - \quad {}_{\rm V\;M}) + F(V_N) - F(\text{host}) + E_{\rm a} \;] - (\quad + N) \quad + \quad _F\,. \tag{12}$$

Depending on and N, the enthalpy $\Delta H(V_N)$ can vary