Finally, it is interesting to note that the value of m_c* for the magneto-optical transitions from the mid-gap defect level is consistent with previous interband measurements but conflicts with the intraband result found here and in previous intraband work of others.

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Theory of Substitutional Deep Traps in Covalent Semiconductors

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The energies of substitutional deep A_1 impurity levels in zinc-blende semiconductors are predicted and related to the impurities' atomic energies and to host dangling bond (ideal vacancy) energies.

In this Letter we predict which elements of the periodic table are likely to form substitutional A_1-symmetric traps with energy levels deep within the forbidden band gaps of covalently bonded semiconductors; and we provide a conceptual framework for understanding the major chemical trends in deep-trap energies. This simple but general theory (i) provides a satisfactory definition of what constitutes a "deep" trap[1]; (ii) it explains the major chemical trends in deep-trap energies, including their dependences on the host energy bands and the impurities' atomic structures; (iii) it shows why data for deep-trap energies do not define a single smooth function of impurity atomic energy, even though clear trends with atomic energy are apparent; (iv) it explains why impurities whose atomic energies differ by ~ 10 eV produce trap energies differing by only a fraction of an electron volt[2]; (v) it predicts the derivatives of deep-trap energies with respect to host-alloy composition x in alloys such as $GaAs_{1-x}P_x$ and shows why these derivatives depend only weakly on the impurities[3,4]; and (vi) it explains why in alloys the trap energies do not follow the nearby band edges as x varies, but instead are often nearly linear functions of composition.[3-5]

The central assumption of the present work is that the major chemical *trends* in deep-trap energies are determined by the energy bands of the

undisturbed hosts and by the impurities' atomic structures: The response of the host electrons and lattice to the insertion of an impurity is a higher-order correction to the trap energy that, if significant, is presumed to scale monotonically with the trap depth—and therefore does not alter the *relative ordering* of the various trap levels. Ample justification for this atomistic viewpoint is provided by data that exhibit trends when the trap energies are plotted versus atomic energies.[1]

To exploit the "quasiatomic" nature of substitutional defects in tetrahedrally bonded semiconductors, we neglect the long-ranged part of the defect potential and define a deep impurity to be one whose short-ranged *central-cell potential alone is sufficiently strong to bind a state.* We employ a simple Koster-Slater model in an orthogonalized-tight-binding–function basis, with the nearest-neighbor matrix elements of the model host Hamiltonian empirically adjusted to reproduce the principal features of the known band structures. Matrix elements involving second-nearest and more-distant neighbors are neglected. There are five basis functions per ion (two s orbitals, three p orbitals). The nearest-neighbor transfer-matrix elements v are found to scale as the inverse square of the bond length[6] d; thus, for a substitutional defect in an unrelaxed host, the eigenvalue equation for the trap energy E becomes

$$\frac{1}{V_l} = g_{lb}(E) = \int \frac{D_{lb}(E')dE'}{E-E'}. \qquad (1)$$

Here l labels the irreducible representation of the tetrahedral point group, D_{lb} is the central-cell partial density of states, and g_{lb} is the l-symmetric contribution to the diagonal impurity-site matrix element of the Green's function. The site (anion or cation) is labeled by b, and, in the present model, the symmetry is either s-like ($l=A_1$) or p-like ($l=T_2$). The defect potential V_l is the difference between impurity and host central-site matrix elements and may be taken to be proportional to the difference in atomic orbital energies[7] [e.g., for the $l=A_1$ or s-like state of N in GaP, $\epsilon_{2s}(\mathrm{N})-\epsilon_{3s}(\mathrm{P})$]. Details of the calculations[1] and discussion of the relevant literature[8] may be found elsewhere.

The multibranched nature of the solutions of Eq. (1), $E_{lb}(V_l)$, explains why analyses of trends in trap energies have failed to define a single-valued relationship between deep-trap levels and atomic energies.

The solutions of Eq. (1) define an approximately hyperbolic trap-energy function $E_{lb}(V_l)$ whenever $g_{lb}(E)$ vanishes and is an approximately linear function of E. The nearly hyperbolic shape of the trap energy as a function of the atomic energy difference V_l is the key to understanding deep-trap energies. The intersection of each quasihyperbola with the band edges defines attractive and repulsive threshold potentials, one of which the defect potential V_l must exceed if it is to bind a state within the gap. The asymptotes of the hyperbolas are the dangling-bond or ideal vacancy energies $E_{lb}(\pm\infty)$; and the trap energies become "pinned" to these asymptotes, and bounded by them. For example, the theory predicts that in GaP no A_1-symmetric P-substitutional deep electron traps exist below the A_1 Ga dangling-bond energy. The dangling-bond energies are determined by the host and not by any impurity; hence, the pinning of deep-trap energies to the dangling-bond asymptotes implies that the *deep-trap wave functions are predominantly hostlike* rather than impuritylike. This pinning, which has not been adequately recognized in previous deep-level studies, is the reason why large differences in atomic energies influence trap energies only weakly; and it implies that the defect potentials need not be accurately known.

The theory's ability to predict chemical trends is convincingly documented by data for deep levels in alloys such as $GaAs_{1-x}P_x$, where the energy level of a single defect can be systematically altered by changing the host-alloy composition x. In Fig. 1, the predictions of Eq. (1), evaluated in the virtual crystal approximation, are compared with data[4] for the A_1-symmetric N and O traps in $GaAs_{1-x}P_x$, because these data represent the most thorough and extensive study of simple, identifiable deep traps in an alloy host. The theory correctly predicts the changes of the trap energies with alloy composition, dE/dx; this derivative depends very little on the impurity because of pinning: The deep levels are hostlike. The deep-trap energies do not follow nearby band edges as the alloy composition varies; instead, the localized traps couple to distant energy bands and follow the linearly varying dangling-bond energy which has a multiband character. The N trap in GaP was once thought to be a shallow impurity by virtue of its small binding energy (< 0.1 eV); however, its failure to "follow" nearby band edges when perturbed by alloying or pressure indicates that it is, in fact, a deep trap that is accidentally close to the conduction band edge in

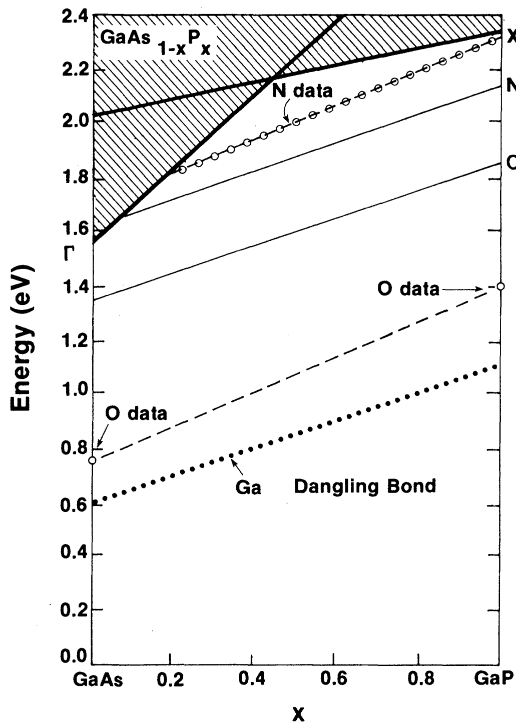

FIG. 1. Comparison of predictions (solid and dotted lines) with data for the N and O A_1-symmetric deep energy levels, as a function of the host $GaAs_{1-x}P_x$ alloy composition x.

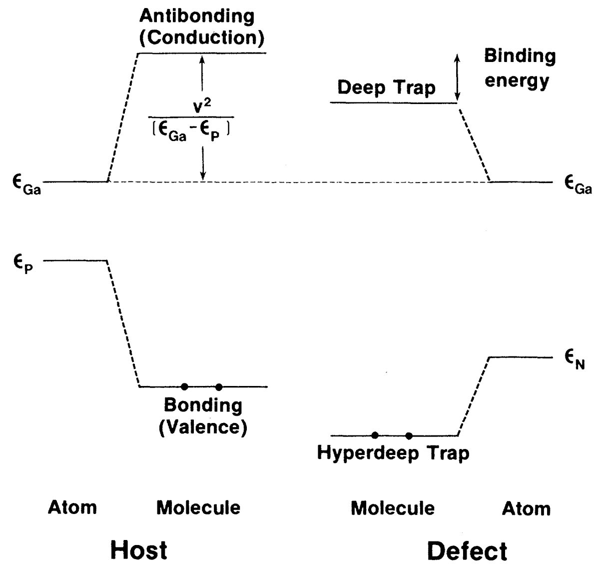

FIG. 2. Two-state model, schematically showing the atomic energy levels of Ga, P, and N, and the corresponding bonding and antibonding levels.

GaP.

The remarkably close agreement between this very simple theory and the data for N supports the interpretation that N is an electron trap: The theory correctly predicts that the N trap should be accidentally shallow in GaP, deep in $GaAs_{0.5}P_{0.5}$, and unbound in GaAs. The success of the theory in predicting dE/dx for oxygen suggests that the impurity is substitutional rather than interstitial, and lends credence to the identification of that trap level in GaAs by showing that it is the same impurity as the one responsible for the oxygen level in GaP. The modest discrepancy between the predicted and measured trap energies for oxygen in GaP is likely caused by the response of the host electrons and lattice to the insertion of the defect.

The essential physical points of this theory are that (i) associated with every deep electron trap within the band gap there is a filled, electrically inactive "hyperdeep" level normally below or within the valence band [this level is predicted by Eq. (1)]; and (ii) the electronic structure of the deep level is largely controlled by its orthogonality to the hyperdeep level. The hyperdeep level is an impuritylike bonding state, and so the *deep level is a hostlike antibonding state.*

To extract this physics from the calculations, we consider a simple, limiting case of a "defect molecule" consisting of an anion-substitutional deep trap and its neighboring cations. We imagine "turning off" the interactions between the defect molecule and the rest of the host, limit our consideration to s-atomic orbitals and A_1 molecular orbitals, and compare the defect molecule with the corresponding host molecule. To be specific, we consider the N anion-substitutional isoelectronic trap in GaP (Fig. 2).

The Ga and P atomic energy levels, ϵ_{Ga} and ϵ_P, are the "parents" of the defect molecule conduction and valence "bands," respectively; these bands are also the bonding and antibonding states resulting from hybridization of the Ga and P by the nearest-neighbor coupling v. The bonding-antibonding splitting causes the Ga-like conduction band to lie, by perturbation theory, $\sim v^2/(\epsilon_{Ga} - \epsilon_P)$ above the Ga atomic or dangling-bond level. When P is converted into N by lowering its atomic energy from ϵ_P to ϵ_N, the splitting is reduced by virtue of the larger energy denominator $\epsilon_{GA} - \epsilon_N$. (The transfer matrix element v is the same for N in the unrelaxed lattice as for P, because we have $v \propto d^{-2}$.) Thus, the GaN antibonding state—the deep trap—lies below the GaP antibonding conduction band and appears "bound" relative to it. Furthermore, the deep-trap level

FIG. 3. Predicted energies (relative to the conduction band edge) of the A_1-symmetric deep impurity levels, as functions of impurity orbital energy. Relevant impurities are listed above the figure in the order of decreasing predicted deep-trap binding energy, from F to Hg. Each quasihyperbola is for a different host. Only the major trends for the deep levels are significant: E.g., for anion traps in GaP, O is very deep, N is borderline deep, S is borderline shallow, and impurities to the right of Se are shallow (unbound by the central-cell potential alone); N is unbound in GaAs, deep in GaP, and very deep in Si. The theory does not purport to order the binding energies of shallow traps (which are all represented as having zero binding energy in this work). Occasional misorderings [e.g., S is actually slightly deeper than N in GaP, by virtue of its long-range Coulomb potential, omitted in Eq. (1); but in $GaAs_{1-x}P_x$ the correct ordering of N and S. is restored] will be discussed in subsequent work. If no quasihyperbola is given for a particular host and site (e.g., anion site of InP), no substitutional impurity at that site is expected to produce a deep trap.

has a Ga-like wave function and an energy that must lie above the Ga dangling-bond energy, no matter how negative the impurity energy ϵ_N might be. This pinning of the deep level to the dangling-bond energy is a consequence of the antibonding nature of the trap and its orthogonality to the bonding hyperdeep trap, which is N-like and becomes more so as the impurity energy ϵ_N deepens. The pinning occurs when all of the hyperdeep state's wave function is on the anion impurity N, so that the ordinary deep trap is completely cationlike or Ga-like.

The predicted A_1-symmetric deep levels for the hosts Si, Ge, GaAs, GaP, GaSb, AlAs, AlP, InAs, InP, ZnSe, and ZnTe, as obtained from Eq. (1), are given in Fig. 3. A detailed comparison of these predictions with data will be presented elsewhere, together with predictions for T_2-symmetric levels.[1] The chemical trends predicted in Fig. 3 should provide a zeroth-order framework for identifying and cataloguing substitutional deep traps in sp^3-bonded semiconductors.

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