

Theory of core excitons

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The major chemical trends in the binding energies of intrinsic and extrinsic core excitons are predicted for zinc-blende semiconductors using an empirical tight-binding theory and localized empirical core-hole potentials. A transition from a shallow Wannier exciton to a deep Frenkel exciton is predicted for an exciton at a core-exciton absorption edge, depending on the chemical structure of the excited atom and the localization of the core hole. The theory is applied successfully to the bound and resonant Ga 3*d* core excitons in GaP, GaAs, and GaSb.

I. INTRODUCTION

Since the early days of core-exciton spectroscopy experimenters have suggested that core excitons are markedly different from ordinary Wannier valence excitons,¹ sometimes producing dramatically peaked spectra characteristic of considerably more localized and more strongly bound exciton states (hundreds of meV binding energies vs a few meV). These experimental claims have proven most disturbing in the case of semiconductors whose valence excitons are well described by effective-mass theory.^{2,3} Attempts to attribute the large core-exciton binding energies to dynamical many-body effects have generally failed.³ In this paper we propose an explanation of core-exciton energies based on the idea that the static, central-cell part of the final-state interaction experienced by the exciton's electron can be strong enough to produce a small radius Frenkel exciton.² Thus, because of the localized core hole, the core exciton is a local-

ized antibonding state which is completely distinct from the ordinary Wannier excitons. This antibonding Frenkel exciton is, to our knowledge, a new kind of exciton. It has neither the atomiclike character of ordinary Frenkel excitons nor the virtually 100% hostlike character of Wannier excitons. Instead, it is an antibonding state that samples the local environment of the core hole. As we shall show, in the Frenkel limit the apparent exciton binding energy is determined by one-electron bands distant from the fundamental band gap, is sometimes much larger than the effective-mass value, and can even be negative.

We first define a core exciton to be an electron-hole pair excited state in which the core hole is sufficiently massive that it remains trapped on the same excited atom throughout the lifetime of the exciton. A Frenkel exciton is one in which the electron is localized in or near the same unit cell as the hole, and a Wannier exciton is one in which the electron is not localized in the vicinity of the

hole. Thus, to a good approximation, a core Frenkel exciton has both its electron and its hole in a single unit cell. An impurity core exciton, as distinguished from an intrinsic core exciton, has its hole attached to an impurity atom rather than to a host atom.

II. OPTICAL ALCHEMY APPROXIMATION

A core exciton is different from a valence exciton in that the hole is localized deep within an atomic core and is almost incapable of hopping from one atomic site to another, either by virtue of the small overlap of core wave functions centered on different sites or because of the lack of resonance between the core (impurity) level and the host. In the optical alchemy approximation,⁴ which has been used extensively for calculating core-exciton spectra, the creation of a core exciton at a site is equivalent to the transmutation of the excited atom into an atom whose atomic number is increased by one—because a deep hole plus an electron is little different from a proton plus an electron, provided the hole occupies a smaller radius orbit than the electrons in the chemical bonds.⁵ This optical transmutation does not occur for ordinary valence excitons because the valence hole lies in an outer atomic shell, ordinarily is not self-trapped, and quickly delocalizes to other sites. Hence, a core exciton differs from a valence exciton in the central cell of the hole; and the electron of the core exciton experiences the additional strong potential of the optically transmuted core.

An immediate consequence of these optical alchemy ideas is that the transmuted central-cell “impurity” generates either an extended Wannier exciton or a localized Frenkel core exciton, just as an ordinary impurity in a semiconductor produces either shallow or deep trap states within the forbidden band gap. Indeed, an intrinsic Frenkel core exciton is to be expected in any material that supports a deep level within the band gap for the donor adjacent to the host in the Periodic Table, provided lattice relaxation about the donor is unimportant. Likewise, an impurity exciton is expected to be of the localized Frenkel type if the element corresponding to the impurity’s optical transmutant forms a deep impurity level in the host.

A central notion of this paper is that a covalent material can naturally support both a Wannier

valence exciton at the fundamental band gap and a Frenkel core exciton at the primary core absorption edge. The traditional theories of core excitons in semiconductors have most often predicted that core excitons and valence excitons are simultaneously Wannier type. Deviations from this rule have often been attributed to dynamical effects which, until the recent work of Quattropani *et al.*,³ were thought to be significant. The present work shows that Frenkel core excitons can appear in covalent materials (with Wannier valence excitons) as a result of the static central-cell electron-hole interaction.

III. THEORY

The definition of a Frenkel core exciton is essentially the same as the theoretical definition of a deep impurity level^{6,7}—one whose impurity central-cell potential is sufficiently strong to bind an electron. Thus, recognizing that effective-mass binding energies are much smaller than core binding energies, we neglect the long-ranged Coulombic electron-hole interaction $-e^2/\epsilon r$, which is the same for shallow extended Wannier and for deep localized Frenkel excitons, and we concentrate on the change of electronic structure in the vicinity of the hole. Thus, the theory treats only the short-ranged, central-cell part of the Coulombic electron-hole interaction. Unlike the theory of deep impurities, the theory of Frenkel core excitons in many cases need not consider lattice relaxation around the hole because absorption and emission occur without lattice relaxation. The Franck-Condon principle guarantees that the lattice remains stationary during absorption and emission, and rapid Auger processes in many cases annihilate all the core holes and terminate the emission before the lattice relaxes. (Experiments are normally performed using core levels whose Auger widths are larger than typical Wannier exciton binding energies but comparable with or smaller than Frenkel binding energies.) Thus, in the present work we neglect lattice relaxation and assume either that it is negligible or that it does not alter the chemical trends in the Frenkel exciton energies.

Since the relevant part of the impurity potential of a core hole is localized in one unit cell, one-band effective-mass theory breaks down and the localized hole couples to states in distant energy bands. The minimum number of bands necessary to correctly treat this coupling in a III-V semicon-

ductor is eight, because the sp^3 bonding requires four orbitals per atom. (We use two s states per atom and hence have a ten-band sp^3s^* theory⁸ which is capable of producing either a direct or an indirect band gap.) A Koster-Slater model is appropriate to handle the localized perturbation, and the eigenvalue equation for the electron energy E of bound or resonance states⁷ is (see Appendix A)

$$\frac{1}{V_l} = \int_{-\infty}^{\infty} \frac{D_l(E')dE'}{E - E'} \quad (1)$$

Here l labels the irreducible representations of the point group of the host and D_l is the central-cell partial density of host electronic states.⁶ The potential of the core hole experienced by the electron in the central cell is V_l . In order to simplify the discussion that follows, we restrict our attention to excitons in tetrahedrally bonded sp^3 diamond-structure or zinc-blende-structure semiconductors; hence, we have $l = A_1$ (s -like) or T_2 (p -like) for the tetrahedral group T_d . Of course the physical ideas of the present work can be applied to excitons in other crystal structures. The present theory is formally identical to the theory of deep substitutional impurity levels.^{6,7} In evaluating Eq. (1) it is important to treat the "defect" and the host equally, which we do by using empirical nearest-neighbor tight-binding theory.

By fitting many band structures it is found that differences of on-site matrix elements of the host potential are proportional⁵⁻⁷ to corresponding differences of the energies of atomic levels with the same angular momentum, whereas the anion-cation transfer matrix elements V for all the sp^3 -bonded semiconductors are approximately inversely proportional to the square of the bond length d : $V \propto d^{-2}$. The fact that the transfer matrix elements are functions of d alone⁵ implies that they do not change during the optical transition because the lattice does not relax and the bond length is unaltered; thus, the final-state interaction is diagonal in an orthogonalized tight-binding basis, and the eigenvalue equations, Eq. (1), are scalar. The solutions E to the eigenvalue equations are given as functions of the corrected⁹ atomic energies of the transmutant impurities in Figs. 1-4. There are different solutions depending on whether the core hole is attached to an anion or a cation and whether the excited-state electron is s -like (A_1) or p -like (T_2). Since the calculation is identical to that for the theory of deep impurities^{6,7} we do not discuss its details here, but instead we include a summary of the theory in Appendix A.

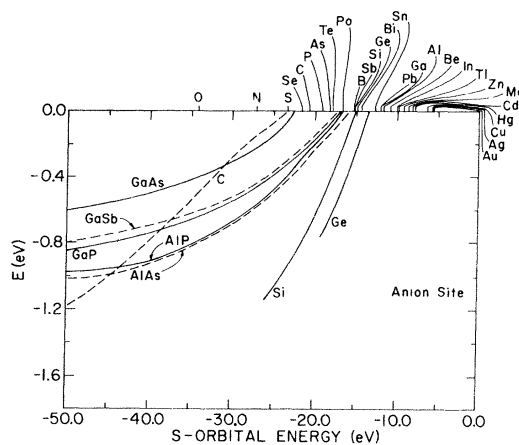


FIG. 1. Predicted primary-gap core-exciton energies for A_1 -symmetric states of an electron orbiting a massive core hole on the anion site. The zero of energy is the primary band gap, whether the material is a direct-gap or an indirect-gap semiconductor. Hence, the energies of this figure are the negative of the exciton binding energies relative to the primary gap. If a finite binding energy is not predicted, the exciton is expected to be of the Wannier type with a small effective-mass binding energy. Each impurity is listed at its optical transmutant's energy. For example, in GaAs the only anion-substitutional impurities which are predicted to produce Frenkel excitons are O, N, and S with binding energies of 0.4, 0.2, and 0.1 eV, respectively. All the other impurities, including Ga (the intrinsic host atom), are predicted to produce Wannier excitons at the primary gap. (In the present work the long-ranged Coulomb interaction is omitted; hence, all Wannier excitons have zero binding energy.) Excitonic resonances above the band gap are not shown.

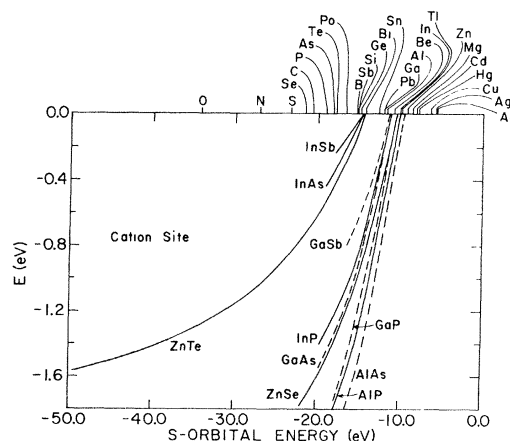


FIG. 2. Predicted core-exciton energies relative to the primary core-exciton gap for A_1 -symmetric states at the cation site.

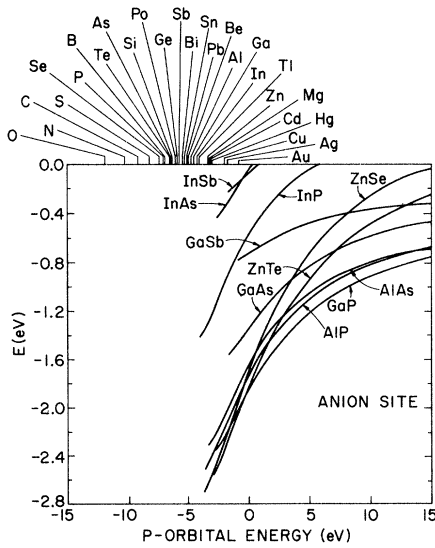


FIG. 3. Predicted core-exciton energies relative to the primary core-exciton gap for T_2 -symmetric states at the anion site.

IV. QUALITATIVE PHYSICS

The essential *qualitative* physics of the model can be illustrated schematically for GaP. We examine the orbitals populated by dipole transitions from the Ga 3p level and the P 2s core— T_2 -symmetric (*p*-like) molecular orbitals. In the ground state the atomic Ga and P levels split into bonding and antibonding levels of the molecule GaP; in the solid these molecular levels broaden into the filled valence and empty conduction bands (Fig. 5). Ex-

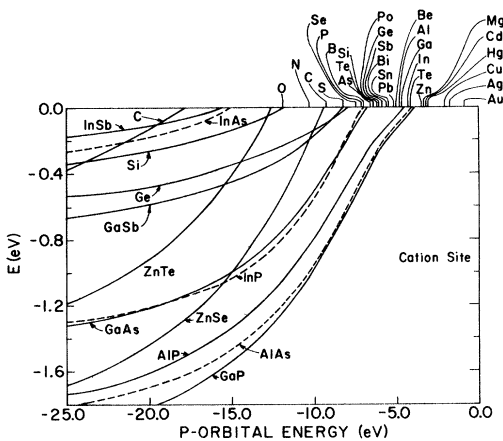


FIG. 4. Predicted core-exciton energies relative to the primary band gap for T_2 -symmetric states at the cation site.

citation of the Ga core transmutes it into $Ga^*=Ge$ and places the optical electron into the Ga^*P antibonding state. The Ga^*P level lies below the conduction-band edge by the binding energy $|E_B|$, primarily because the atomic energy of Ga^* is several electron volts below the unexcited atomic Ga level. Hence, the Ga^*P antibonding level is a localized state within the gap and produces a Frenkel exciton below the conduction-band edge. In contrast, excitation of the P core produces $P^*=S$ and the GaP^* antibonding level resonates with the conduction band. As a result this antibonding level hybridizes with the conduction-band states and the optical electron occupying it becomes somewhat delocalized. The model displayed in Fig. 5 contains the central-cell part of the electron-hole interaction only, and the state created by exciting the P core is not bound to the core hole but instead is an unbound resonance state in the conduction band. Inclusion of the long-ranged Coulombic electron-hole interaction, $-e^2/\epsilon r$, leads to binding of the electron to the hole and a Wannier bound-exciton state at the primary core absorption edge. (We term the lowest energy core to conduction-band transition the “primary” core absorption edge. In contrast with the fundamental absorption edge at the optical band gap, the primary core absorption edge occurs in the x-ray spectrum at several tens of electron volts.)

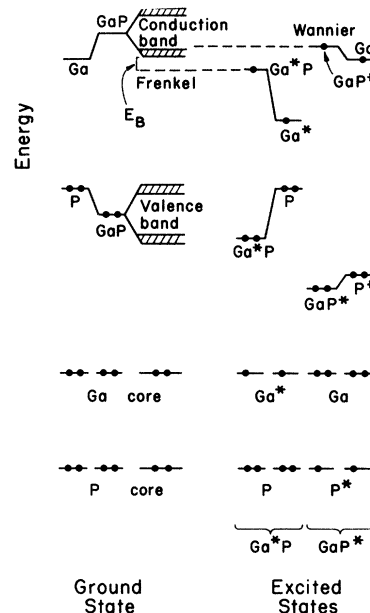


FIG. 5. Schematic energy-level diagram. The scale of energy is compressed and distorted.

The above schematic discussion of the physics can be useful for visualizing the essential qualitative physics of the transition from Frenkel to Wannier exciton behavior, but one should not lose sight of the fact that a correct understanding involves both s and p orbitals on each atomic site and requires a detailed calculation such as that leading to Figs. 1–4.

Figures 1–4 represent the predictions of the energies of core Frenkel excitons relative to the primary band gap on the basis of the empirical tight-binding model. A negative energy means that the central-cell potential of the hole binds an electron in a state within the gap, producing a localized Frenkel exciton. If no binding energy is predicted then the Frenkel exciton is a resonance above the band edge with an apparent negative binding energy. In this case the core exciton in the gap at the primary edge is predicted to be a Wannier exciton with a binding energy nearly equal to the effective-mass-theory value, but differing by a small central-cell correction. (In the present model the Wannier excitons have zero binding energy because the long-ranged electron-hole interaction is omitted in order to simplify the treatment of the dominant central-cell potential.) The calculations have been performed for all of the following zinc-blende hosts: Si, Ge, C, GaAs, GaP, GaSb, AlAs, AlP, InAs, InP, InSb, ZnSe, and ZnTe; if a curve for one of these hosts is missing from a figure then the theory predicts that the bound extrinsic and intrinsic core excitons of that site and symmetry are Wannier-type. Thus, we have predicted the transition from Wannier to Frenkel core-exciton behavior at the primary absorption edge for each of the above hosts, and we have predicted the Frenkel exciton binding energies and their site and symmetry dependences. (Recall that Wannier exciton energies are virtually site independent but that observed core-exciton energies are strongly site dependent.¹⁰)

The reliability of the predictions remains to be tested experimentally. The estimated uncertainty in the predictions based on the empirical tight-binding model is >0.1 eV, but larger errors by perhaps a factor of 2 or more in the absolute exciton energies are possible. The model itself does not allow for the response of the host to the core hole and has not been iterated to self-consistency. Thus, the primary utility of the theory is to *order* the impurity Frenkel exciton binding energies and to *estimate* the impurities for which the Frenkel-to-Wannier transition should begin to occur. A com-

plete discussion of the model and its limitations may be found in the deep-trap literature.^{6,7}

V. APPLICATION

Numerous core-exciton spectra have been reported for semiconductors, primarily for intrinsic excitons (measurements of extrinsic spectra associated with isolated impurities are currently difficult). Here we consider the intrinsic core-exciton binding energies reported for the Ga $3d$ core excitons in GaP, GaAs, and GaSb,^{10,11} and for the $2p$ edge of Si which has been studied extensively.^{12–14}

The Ga $3d$ core-exciton binding-energy data of Aspnes, Olson, and Lynch^{10,11} exhibit trends as the host anion is altered from P to As to Sb; such trends are ideally suited for analysis by the present theory. Aspnes *et al.* obtained their binding energies by comparing Ga $3d$ electroabsorption-edge data¹⁵ with valence-band photoemission spectra. The photoemission transitions involved a delocalized valence hole, not a localized Ga $3d$ hole; hence, in their data analyses, they have assumed the same hole self-energy for the $3d$ and for the valence transitions—differences in level shifts associated with electron-electron interactions have been neglected. Likewise, the present theory assumes that hole self-energy shifts can be neglected. It is possible and perhaps likely that these assumptions of the theory and the data analyses are not justifiable. Uncertainties of tenths of electron volts in the core-exciton binding energies could result. However, if the self-energy shifts are approximately equal for GaP, GaAs, and GaSb, then these uncertainties will not alter the *trends* in the data.

The Ga $3d$ core-exciton energies *with respect to the primary band gap* are listed in Table I together with their large experimental uncertainties.¹⁶ (The energies of Ref. 10 are given with respect to the indirect X minimum in the conduction band; for direct-gap GaAs and GaSb the entries in Table I differ from those energies by the $\Gamma-X$ energy differences of 0.48 and 0.43 eV, respectively.)

The experiment shows a genuine bound state for the Ga-site core exciton in (indirect gap) GaP; this state has a moderately large binding energy, 0.17 ± 0.15 eV, relative to the primary band edge and thus lies within the primary band gap, i.e., below the X point. In contrast, the experiment does not resolve core-exciton state bound within the primary band gap (i.e., bound to the Γ point) in either of the direct-gap semiconductors GaAs or

TABLE I. Energies of intrinsic Ga $3d$ core excitons in Ga-V semiconductors (in eV), and reference energies E_{gap} , the primary band gap, and E_X , the X -point gap.

	GaP	GaAs	GaSb
$E - E_X$ (experiment ^a)	-0.17 ± 0.15	-0.09 ± 0.2	-0.09 ± 0.25
$E_{\text{gap}} - E_X$ ^b	0.0	-0.48	-0.43 ^c
$E - E_{\text{gap}}$ (experiment ^{a,b})	-0.17	+0.39	+0.34
$E - E_{\text{gap}}$ (theory)	-0.05	+0.35	+0.33

^aReference 10.

^bFor a discussion of the $\Gamma - X$ energy difference, together with citations of the relevant literature, see Ref. 7.

^cD. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B **14**, 4450 (1976). A slightly different value, -0.315 eV, has been reported by B. B. Kosicki, A. Jayaraman, and W. Paul, Phys. Rev. **172**, 764 (1968), but our results and the agreement with experiment are not significantly affected by such modest differences in band structure. We thank S. Kelso and D. Aspnes for calling our attention to these modern values of the band gap in GaSb, which differ significantly from the previously accepted values used in Ref. 7.

GaSb, but rather shows evidence for resonance states in the conduction band seemingly bound to the X point by energies of 0.09 ± 0.20 eV for GaAs and 0.09 ± 0.25 eV for GaSb. These energies lie above the direct gap by 0.39 and 0.34 eV, respectively.

Impurity data for Ge (=Ga*) replacing Ga in GaP, GaAs, and GaSb are of little assistance in interpreting these core-exciton spectra. Ge levels within the band gaps of GaAs and GaSb have not been identified (to our knowledge) and are not predicted to occur. Substitution of Ge on a Ga site in GaP is known to produce a level at -0.200 eV (Ref. 17) whose symmetry is A_1 (Ref. 18); this is in good agreement with the theory⁶ for an A_1 -symmetric (s -like) level. The present theory predicts a T_2 level for excited Ga (viz., Ge) at nearly the same energy as the A_1 level. It is this T_2 state that is involved in dipole transitions from the $3d$ core. (For the theoretical expectations see Figs. 2 and 4 for Ga in GaP, GaAs, and GaSb.) Thus the idea of optical alchemy by itself, without calculations such as those presented here, is insufficient to solve the problem of interpretation posed by these data.

The theory reproduces the chemical trends in the Ga $3d$ core-exciton data quite well. The major qualitative experimental fact is that the GaP Frenkel exciton lies bound within the primary band gap, whereas the corresponding GaAs and GaSb Frenkel levels are resonant with the conduction

band. Thus, the Ga $3d$ core exciton at the primary absorption edge of GaP is a Frenkel exciton but the primary-edge excitons in GaAs and GaSb are of the Wannier type. The theory predicts just that. To determine the predictions of the theory we examine Fig. 4 (excitons at the Ga site with p -like electrons) because the dipole selection rules require the optical electron from the $3d$ core to reside in a T_2 -symmetric final state. Excited Ga in GaP is predicted to have a binding energy of 0.05 eV (the intersection of the GaP curve and the transmutant's p -orbital energy, labeled Ga). According to Fig. 4 the Ga core excitons in GaAs and GaSb are Wannier type at the primary gap. These two materials, unlike GaP, are direct-gap semiconductors, and in each of them a remnant of the Frenkel exciton should appear as a resonance above the direct (Γ) minimum and below the indirect (X) minimum in the conduction band. The trends for bound-exciton energies can be extrapolated somewhat into the continuum for resonances,¹⁶ and the calculated energies of the main resonance peaks with respect to the primary band gap are given in Table I. Observe that the theory with resonance states included does reproduce the trends in these energies.

The predicted energies of the bound and resonant Frenkel excitons are in excellent agreement with the observations, as shown in Fig. 6 and Table I. In fact the agreement between theory and experiment is better than one should expect in view of the theoretical uncertainties. More importantly,

the theory reproduces the trends in the data. As observed experimentally¹⁰ [(see Table I), the bound and resonant core excitons follow the X conduction minimum to a good approximation because the bulk of the conduction-band density of states lies near X . This behavior, of following the density of states and not the lowest conduction-band edge, has been emphasized by Hsu *et al.*¹⁹ and by Hjalmarson *et al.*⁶ as a signature of a “deep” level.

The valence excitons at the primary edges in GaP, GaAs, and GaSb are all Wannier excitons, yet the primary-edge core exciton in GaP is a Frenkel state and Frenkel resonances occur between the Γ and X conduction-band edges in GaAs and GaSb. Moreover, the theory predicts that the primary-edge core excitons with A_1 electrons and with holes attached to anions in GaAs and GaSb (Ref. 20) will all be Wannier type; the exciton binding energies will be small effective-mass values. Thus in the present theory we have a simple and natural means for obtaining coexisting Frenkel and Wannier states, and for producing quite different primary-edge exciton binding energies for different ion sites in the same host and for different but similar hosts.

The core Frenkel exciton states predicted in the present work are different from the ordinary Frenkel excitons discussed most widely² in that they have hybrid, antibonding character rather than being atomic or ionic in nature. Moreover, the Frenkel excitonic resonances in GaAs and

GaSb offer an explanation of one of the paradoxes of contemporary synchrotron-radiation physics: A primary-gap Wannier valence exciton may coexist with a Frenkel excitonic resonance at higher energy, the Wannier exciton may be unresolved experimentally, and the Frenkel resonance may produce a line shape drastically different from that predicted for Wannier state using effective-mass theory. The Frenkel excitons are the ones most often identified as the “core excitons.” Hence, if the Frenkel resonance lies at an energy immediately above the Wannier exciton and the band edge, then the Frenkel state may be the only exciton state resolved in experiments.

The success of the theory in describing the binding-energy trends for GaP, GaAs, and GaSb suggests that these ideas can be fruitfully applied to the somewhat controversial problem of the $2p$ core exciton in Si. If one is guided exclusively by the optical alchemy approximation, then one expects this exciton to be of the Wannier type because Si's transmutant, P, is a shallow donor in Si with a 45-meV binding energy.²¹ The calculations presented in Fig. 1 indicate that the Si $2p$ exciton at the primary core edge should be of the Wannier type, in agreement with the P-donor data. The predicted Frenkel core-exciton level does not lie in the band gap, but yields a conduction-band resonance only 0.02 eV above the primary gap, as can be seen by extrapolating the theory of Fig. 1. Clearly, the intrinsic Si primary-edge core exciton is predicted to be on the verge of the transition from Wannier to Frenkel-type. If the central-cell potential were slightly more attractive, then the predicted Si primary-gap core exciton would be of the Frenkel type. The borderline nature of the Si $2p$ core exciton in our theory actually means that the theory, with its significant uncertainties, is incapable of predicting unambiguously whether the primary-edge core exciton is of the Wannier or Frenkel type. The present theory omits the effects of the surface, and the optical alchemy approximation neglects the long-ranged Coulomb electron-hole interaction and the effects of other static and dynamical electron-electron interactions. These effects could all be important in such a borderline case.

The experimental values of the Si $2p$ exciton binding energies range from 0.15 eV by Brown *et al.*¹² to 0.8 eV by Margaritondo *et al.*,¹³ with an intermediate value of 0.3 eV reported by Bauer *et al.*¹⁴. These energies are typically obtained by taking the difference between large transition ener-

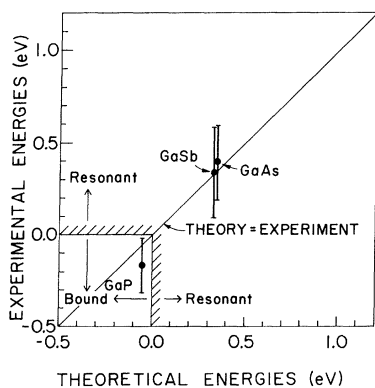


FIG. 6. Comparison of theoretical and experimental energies for Ga $3d$ Frenkel excitons, namely the bound Frenkel primary-edge exciton in GaP and the Frenkel resonances in GaAs and GaSb. The zero of energy for each material is the primary band gap, i.e., corresponds to the X point in GaP and the Γ point in GaAs and GaSb.

gies, and may differ from the predicted energy due to the size of the hole self-energy (electron-electron correlations) or to surface effects as proposed by Margaritondo *et al.*¹³. A more direct determination of the exciton binding energy involves fixing the energy of the exciton relative to the band edge and requires quantitative line-shape analysis. Perhaps the best way to resolve the Si 2*p* dilemma is to systematically determine the trends in the Si 2*p* excitation energies for a variety of Si environments and to extrapolate these trends to crystalline Si using a theory such as the present one.

Comparison of core-exciton energies for excitation of a common atom in a sequence of host semiconductors has provided a valuable test of the theory of trends presented here. Ideally an even better way to test the theory would be to study a sequence of impurity core excitons at a common site in a single host. Such experiments are currently difficult.

The data of Aspnes *et al.* and the present theory suggest that experimenters should search for the Ga 3*d*-to-*A*₁ core exciton in GaP, which is dipole forbidden and absent from synchrotron-radiation spectra. However, in electron energy-loss spectra the dipole selection rule is broken for large-angle, large-momentum-transfer scattering (see Appendix B). At large-angle electron scattering, one expects to observe an energy loss associated with both the dipole-forbidden 3*d*-to-*A*₁ exciton and the 3*d*-to-*T*₂ core exciton whose energies are predicted to be close to one another. Simultaneous observation of the Ga 3*d*-to-*A*₁ and 3*d*-to-*T*₂ core excitons would provide striking confirmation of the present theory.

VI. SUMMARY

In summary, we have proposed the existence of new antibonding Frenkel core excitons, predicted their energies in zinc-blende- and diamond-structure semiconductors, and obtained a criterion for the transition from Wannier to Frenkel exciton behavior at the primary core absorption edge. Future work should test the theory experimentally, re-

fine the theoretical calculations, and extend the predictions of the model to other crystal structures.

Note added in proof. There have been two recent developments. (1) M. Piacentini has called our attention to data which have been interpreted as showing a negative "binding energy" for the In 4*d* core exciton in InSe.²² The present theory has not yet been extended to such layered compounds. We note, however, that the Frenkel resonances of the present theory, since they lie above the conduction-band edge, do have what appear to be negative binding energies. Ordinary one-band effective-mass theory always produces positive binding energies. (2) R. E. Allen and one of us²³ have successfully applied this theory to core excitons at the (110) surfaces of Ga-V and In-V compound semiconductors, thereby providing the first natural interpretation of both bulk and surface core-exciton data.

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APPENDIX A: METHOD OF CALCULATION

The calculation of core-exciton energies proceeds along established lines⁶ as follows: We first parametrize the host energy band using the sp^3s^* , ten-band, empirical, tight-binding sp^3s^* model.⁸ The Bloch-type states

$$|ib\vec{k}\rangle = N^{-1/2} \sum_j \exp(i\vec{k} \cdot \vec{R}_j) |ib\vec{R}_j\rangle$$

are formed from the localized basis set $|ib\vec{R}\rangle$. Here \vec{R} specifies the unit cell, b is anion or cation, and $i = s, p_x, p_y, p_z$, or s^* . In the Bloch-type basis the host Hamiltonian matrix is

	$ sa\rangle$	$ sc\rangle$	$ p_xa\rangle$	$ p_ya\rangle$	$ p_za\rangle$	$ p_xc\rangle$	$ p_yc\rangle$	$ p_zc\rangle$	$ s^*a\rangle$	$ s^*c\rangle$
$ sa\rangle$	$E(s,a)$	$V(s,s)g_0$	0	0	0	$V(sa,pc)g_1$	$V(sa,pc)g_2$	$V(sa,pc)g_3$	0	0
$ sc\rangle$	$V(s,s)g_0^*$	$E(s,c)$	$-V(pa,sc)g_1^*$	$-V(pa,sc)g_2^*$	$-V(pa,sc)g_3^*$	0	0	0	0	0
$ p_xa\rangle$	0	$-V(pa,sc)g_1$	$E(p,a)$	0	0	$V(x,x)g_0$	$V(x,y)g_3$	$V(x,y)g_2$	0	$-V(pa,s^*c)g_1$
$ p_ya\rangle$	0	$-V(pa,sc)g_2$	0	$E(p,a)$	0	$V(x,y)g_3$	$V(x,x)g_0$	$V(x,y)g_1$	0	$-V(pa,s^*c)g_2$
$ p_za\rangle$	0	$-V(pa,sc)g_3$	0	0	$E(p,a)$	$V(x,y)g_2$	$V(x,y)g_1$	$V(x,x)g_0$	0	$-V(pa,s^*c)g_3$
$ p_xc\rangle$	$V(sa,pc)g_1^*$	0	$V(x,x)g_0^*$	$V(x,y)g_3^*$	$V(x,y)g_2^*$	$E(p,c)$	0	0	$V(s^*a,pc)g_1$	0
$ p_yc\rangle$	$V(sa,pc)g_2^*$	0	$V(x,y)g_3^*$	$V(x,x)g_0^*$	$V(x,y)g_1^*$	0	$E(p,c)$	0	$V(s^*a,pc)g_2$	0
$ p_zc\rangle$	$V(sa,pc)g_3^*$	0	$V(x,y)g_2^*$	$V(x,y)g_1^*$	$V(x,x)g_0^*$	0	0	$E(p,c)$	$V(s^*a,pc)g_3$	0
$ s^*a\rangle$	0	0	0	0	0	$V(s^*a,pc)g_1$	$V(s^*a,pc)g_2$	$V(s^*a,pc)g_3$	$E(s^*a)$	$V(s^*,s^*)g_0$
$ s^*c\rangle$	0	0	$-V(pa,s^*c)g_1^*$	$-V(pa,s^*c)g_2^*$	$-V(pa,s^*c)g_3^*$	0	0	0	$V(s^*,s^*)g_0^*$	$E(s^*,c)$

where we have

$$\begin{aligned}
 g_0(\vec{k}) &= \cos(q_1)\cos(q_2)\cos(q_3) \\
 &\quad - i \sin(q_1)\sin(q_2)\sin(q_3), \\
 g_1(\vec{k}) &= -\cos(q_1)\sin(q_2)\sin(q_3) \\
 &\quad + i \sin(q_1)\cos(q_2)\cos(q_3), \\
 g_2(\vec{k}) &= -\sin(q_1)\cos(q_2)\sin(q_3) \\
 &\quad + i \cos(q_1)\sin(q_2)\cos(q_3), \\
 g_3(\vec{k}) &= -\sin(q_1)\sin(q_2)\cos(q_3) \\
 &\quad + i \cos(q_1)\cos(q_2)\sin(q_3),
 \end{aligned}$$

and $q_j = k_j a_L \pi / 2$.

The matrix elements of the empirical Hamiltonian have been tabulated.^{7,8} The off-diagonal matrix elements depend only on the bond length and not on the constituents of the host, as proposed by Harrison.⁵ The diagonal matrix elements are functions of atomic-orbital energies and hence exhibit manifest chemical trends.

The defect potential associated with the core hole is diagonal in the $|ib\bar{R}\rangle$ basis because the bond length is unaltered during the optical transition, according to the Franck-Condon principle. For a cation site defect or core hole it has the form $V = (0, V_s, 0, 0, 0, V_p, V_p, V_p, 0, 0)$, where V_s (V_p) is 0.8 (0.6) times the atomic s (p)-orbital energy difference between the "transmutant" atom with charge $Z + 1$ and the host atom with Z . The proportionality constants have been deduced from empirical fits to a variety of semiconductor bands.^{4,7,8} The contribution of the Coulombic electron-hole interaction from outside the central cell has been neglected, as it should be in a theory that seeks to explain trends with an accuracy of ~ 200 meV.

The secular equation for the exciton energy E is

$$\det[1 - (E - H_0)^{-1}V] = 0$$

or

$$\det \left[1 - \int_{-\infty}^{\infty} (E - E')^{-1} \delta(E' - H_0) dE' V \right] = 0,$$

where E is to be interpreted as having a positive imaginary infinitesimal added to it. The secular determinant factors into subdeterminants associated with each irreducible representation whenever there is symmetry. For tetrahedral symmetry we find A_1 (s -like) and T_2 (p -like) irreducible representations,

and we project the spectral density operator $\delta(E' - H_0)$ onto the manifold of such states using standard numerical techniques⁷ to evaluate the projected spectral densities of states $D_f(E')$ and equations of the form Eq. (1). Details of the numerical methods, including all relevant FORTRAN programs, are given in Ref. 7.

APPENDIX B: SELECTION RULES AND FERMI STATISTICS

In applying the theory, especially to impurity excitons, one must be certain that the Frenkel exciton final states are not forbidden by the Pauli principle. This is most easily done experimentally by using p -doped samples which "drain" electrons from the impurity levels, making the levels accessible to the optical electron. Theoretically, for nearly intrinsic semiconductors one needs to count electrons. For example, consider a core excitation of Se impurity in Si. The optical transmutant of Se is $\text{Se}^* = \text{Br}$ and the defect molecule consisting of Se^* and one-quarter of each of its four neighboring Si atoms has eleven s and p electrons. At low temperatures two of these will occupy the A_1 -symmetric bonding level and six will fill the T_2 bonding spin orbitals of the defect molecule. In the lowest exciton state the remaining three electrons, one of which is the optical electron, must occupy some combination of the two A_1 and six T_2 antibonding spin orbitals. If, as is almost certainly the case, the two A_1 antibonding spin orbitals are already full when Se is unexcited then, regardless of the dipole selection rules, the lowest energy orbital accessible to the optical electron in a normal transition is a T_2 antibonding orbital and the transition to the A_1 Frenkel core exciton is Pauli forbidden. Of course if the core hole is p -like, optical transitions to the T_2 orbital are dipole forbidden. The Pauli-forbidden transition can be restored by doping the sample sufficiently p -type that the electrons are drained out of the Se antibonding A_1 states. In this case transitions from p cores to the A_1 state are dipole allowed. The dipole selection rule can also be avoided in cases such as transitions from an s core of Se embedded in Si. This is most easily done by performing large-angle inelastic-electron scattering measurements in which case the transition operator is the Fourier transform of the charge density, $\exp(i\vec{q} \cdot \vec{r})$, rather than the dipole operator \vec{r} .

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