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Hjalmarson-Frenkel core excitonic resonances at III-V semiconductor surfaces

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Surface Hjalmarson-Frenkel core excitonic resonances are predicted to exist well above the conduction-band edges of the III-V semiconductors InSb, InAs, InP, AlSb, AlAs, and AlP.

Transitions to unoccupied surface states in III-V semiconductors have been observed with several techniques.[1–16] When the initial electronic state is a core state (e.g., a Ga 3*d* state in GaAs), the final state is often a Hjalmarson-Frenkel exciton,[17] as was first recognized by Lapeyre and Anderson.[4] (The Hjalmarson exciton of covalent semiconductors differs from the ordinary central-cell Frenkel exci-

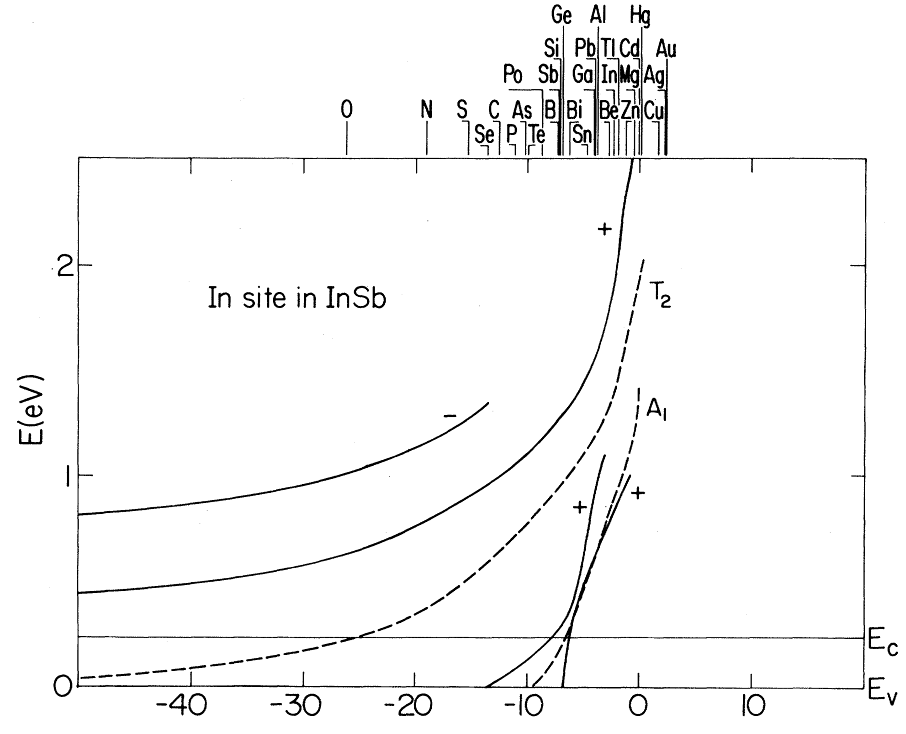

FIG. 1. Predicted energies of intrinsic (In) and extrinsic Hjalmarson-Frenkel core excitons (below E_c) and excitonic resonances (above E_c) at the In site in InSb. The branches are labeled according to the symmetry of the electron's wave function: The dashed curves represent bulk excitons with the electronic state having A_1 (*s*-like) or T_2 (*p*-like) symmetry. The solid lines represent excitons at the relaxed (110) surface with the electronic state having positive or negative parity with respect to the reflection plane perpendicular to the surface. E_v and E_c are the valence- and conduction-band edges. V_s is the *s* impurity potential (Ref. 28). To find the predicted energies for intrinsic Hjalmarson-Frenkel excitons (within the approximation of Ref. 29), drop a vertical line from the potential labeled In. Energies of extrinsic excitons are similarly given by the potentials corresponding to the various impurity atoms.

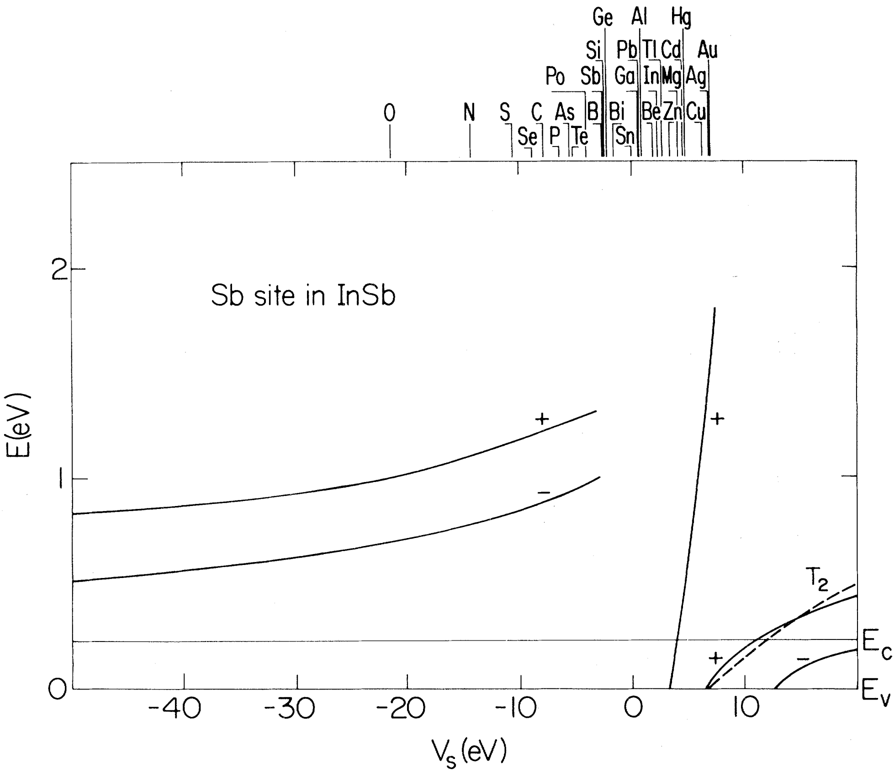

FIG. 2. Predicted energies of Hjalmarson-Frenkel core excitons at the Sb site in InSb.

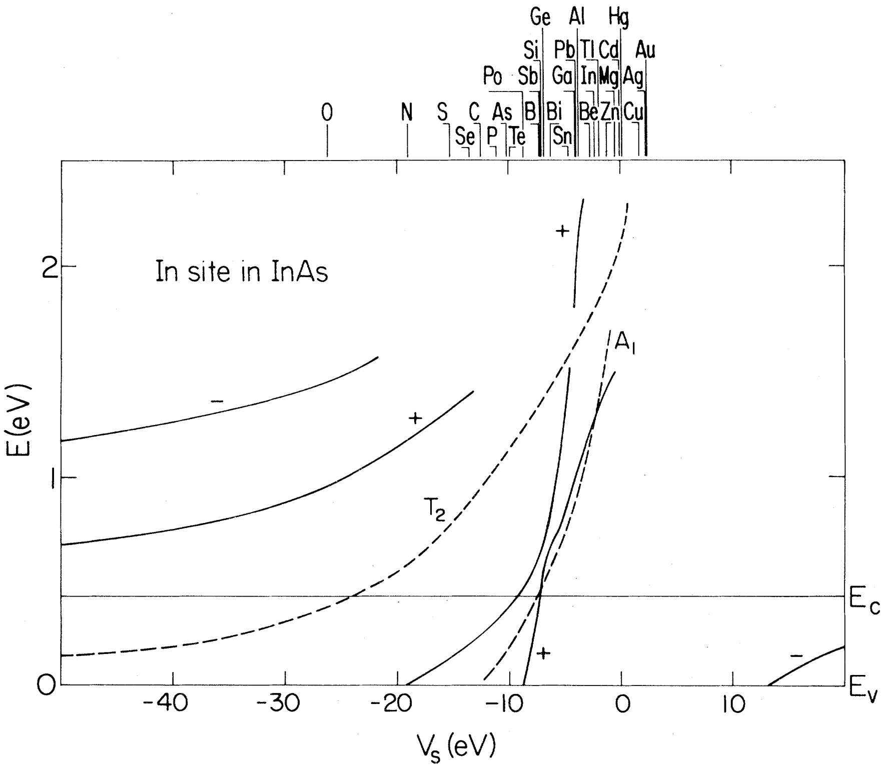

FIG. 3. Predicted energies of Hjalmarson-Frenkel core excitons at the In site in InAs.

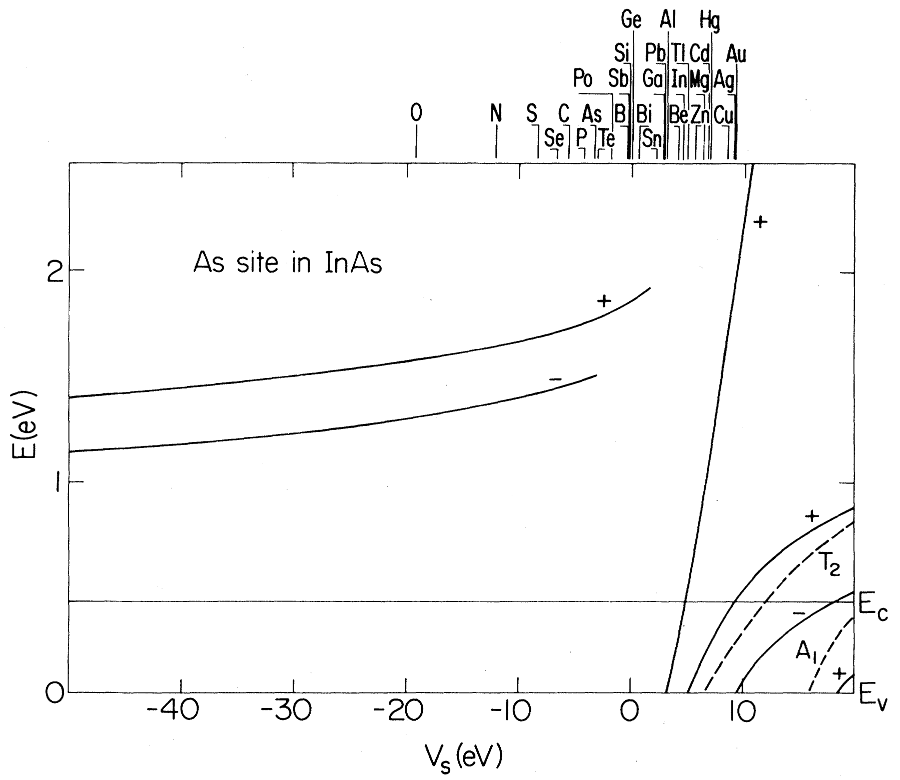

FIG. 4. Predicted energies of Hjalmarson-Frenkel core excitons at the As site in InAs.

ton found in molecular and ionic crystals because its electronic wave function has antibonding rather than molecular or ionic character.) In addition to bound excitons, lying within the band gap of the semiconductor, there can be excitonic resonances having energies above the conduction-band edge.[17] Such resonances are observed in the excitation of In $4d$ core electrons at the (110) surface of InSb and InAs (Refs. 1 and 2); i.e., in these materials surface Hjalmarson-Frenkel core excitons on the cation site are observed to lie above the conduction-band edge, whereas they lie within the band gap in the GaX

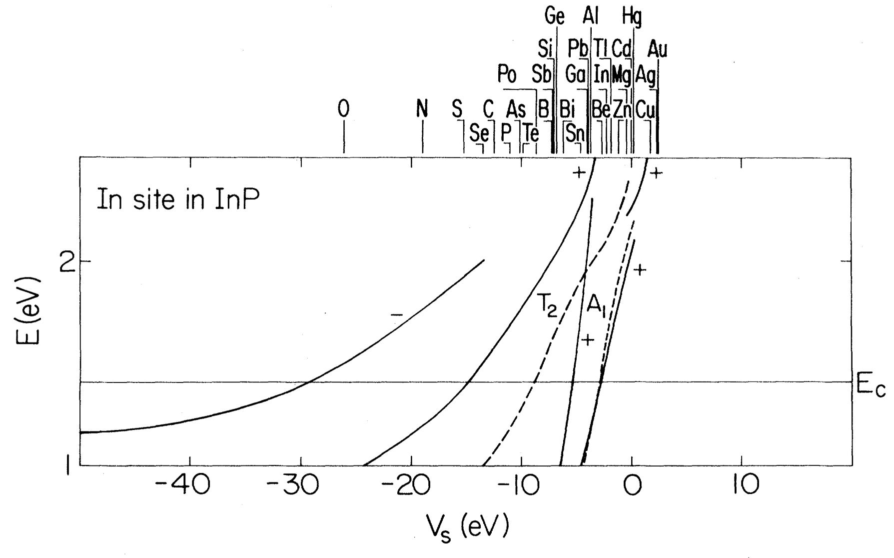

FIG. 5. Predicted energies of Hjalmarson-Frenkel core excitons at the In site in InP.

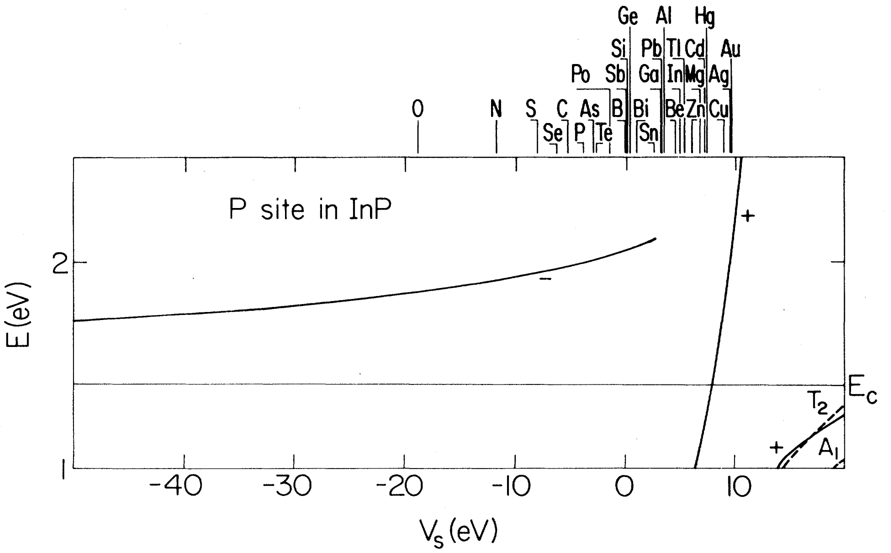

FIG. 6. Predicted energies of Hjalmarson-Frenkel core excitons at the P site in InP.

semiconductors, with X a group-V element. This experimental finding is in agreement with the theoretical study that we reported earlier.[18,19] Here we extend our theory of bound and resonant surface Hjalmarson-Frenkel core excitons to treat resonances above the conduction-band edge at higher energies than those previously considered.

The present theory, like that of core excitons in the bulk,[17] employs the "optical alchemy" or "$Z+1$" approximation, in which an excited atom of the perfect semiconductor is regarded as being equivalent to an impurity atom. For example, if an electron is excited from a $4d$ core state of an In atom in InAs, the small radius core hole is taken to be equivalent to a proton, and the excited atom—In*—is consequently approximated by a Sn impurity atom. The theory of core excitons then becomes isomorphic to the theory of impurity states in the

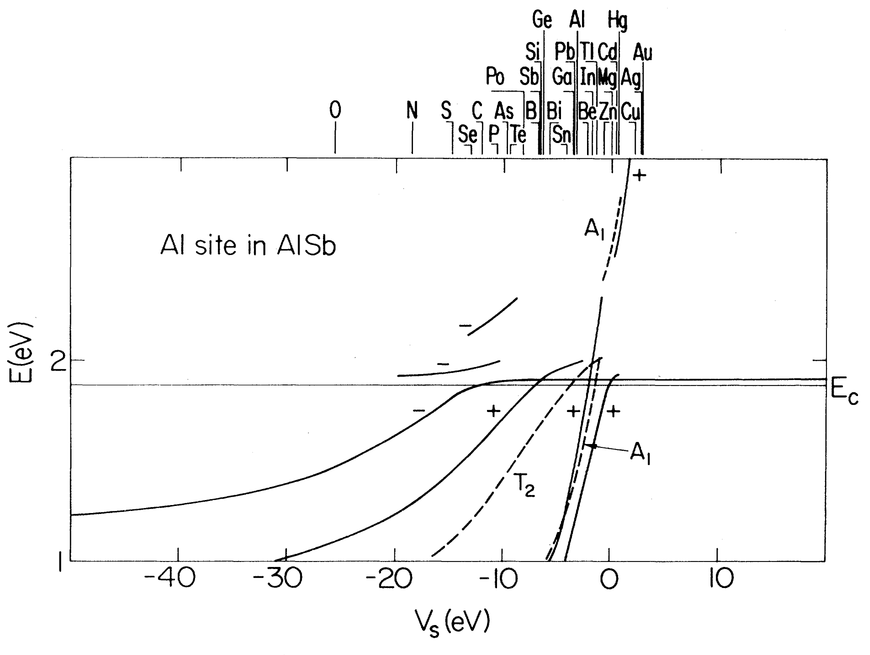

FIG. 7. Predicted energies of Hjalmarson-Frenkel core excitons at the Al site in AlSb.

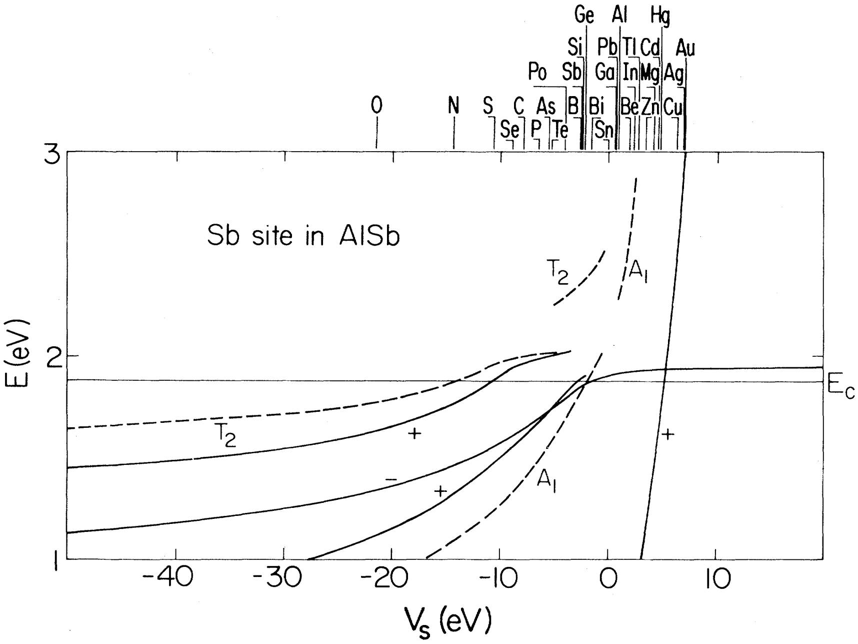

FIG. 8. Predicted energies of Hjalmarson-Frenkel core excitons at the Sb site in AlSb.

bulk[20] or at the surface.[21] As discussed previously,[18,19] there are three inputs to our calculations[22]: (i) the geometrical relaxation at the surface, which has been measured for several III-V's[23–26] and which is inferred for the others[27]; (ii) the bulk electronic structure of the semiconductor, which is represented by the sp^3s^* model of Vogl *et al.*,[28] and (iii) a table of atomic energies, which is used to model the "impurity" potential associated with the exciton, as in the bulk impurity theory of Hjalmar-

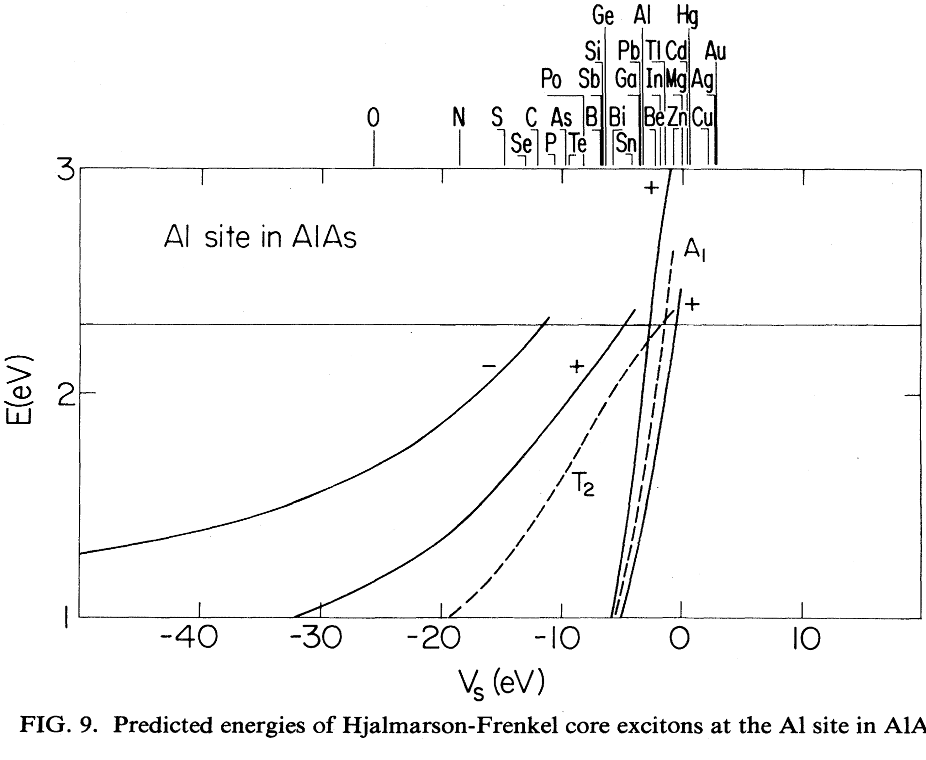

FIG. 9. Predicted energies of Hjalmarson-Frenkel core excitons at the Al site in AlAs.

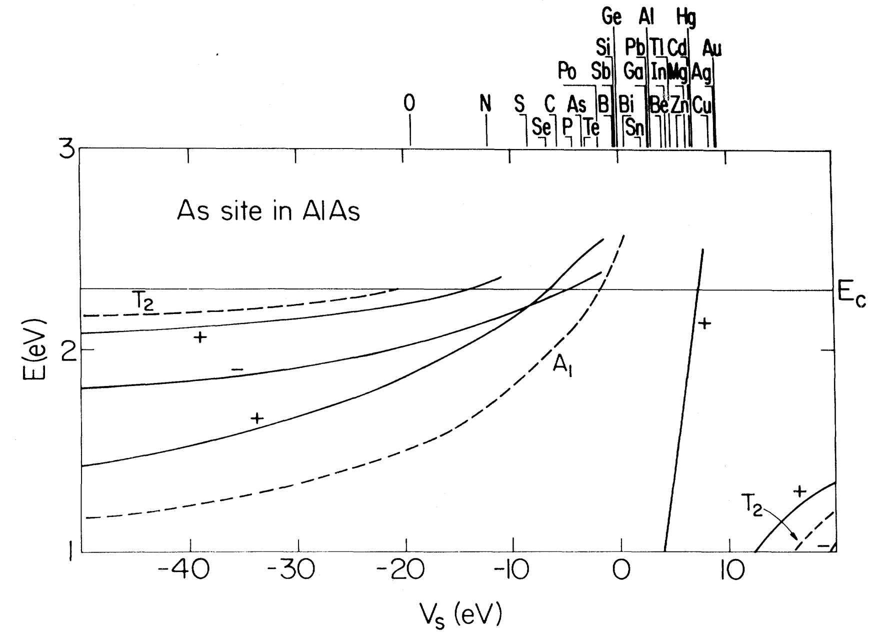

FIG. 10. Predicted energies of Hjalmarson-Frenkel core excitons at the As site in AlAs.

son *et al.*[20]

No current theory provides a quantitative description of excitations in a solid at energies far above the Fermi energy, and the present tight-binding model provides only a crude description of these states. For this reason, our results 1—5 eV above the conduction-band edge E_c should be regarded as only qualitative; at higher energies the predictions are unreliable. Near and below E_c, there are uncertainties in the theory of several tenths of an eV.

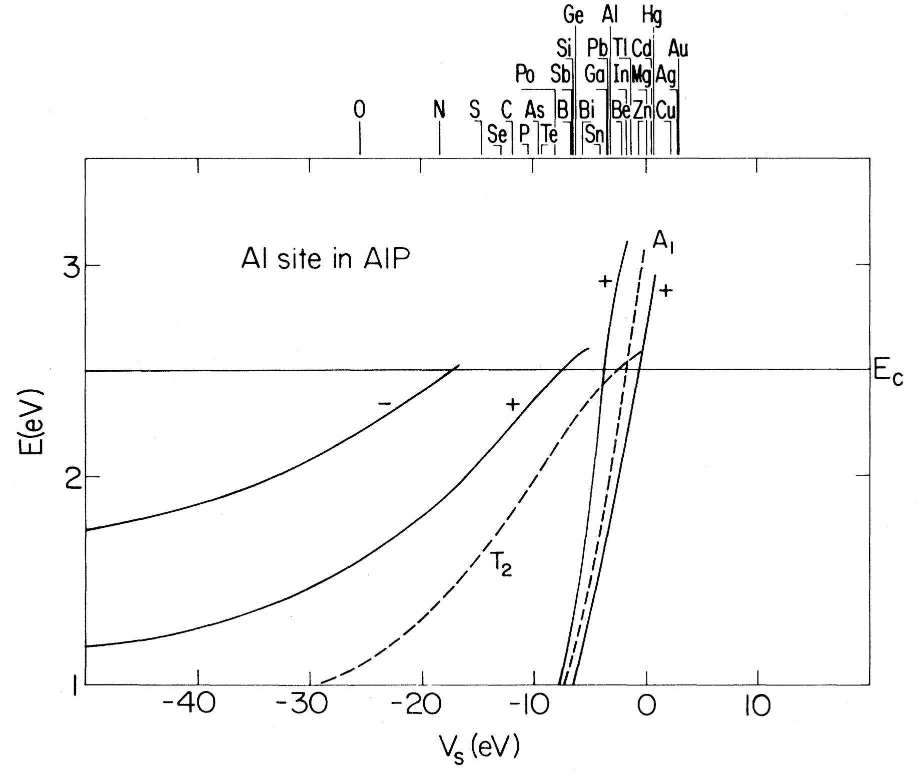

FIG. 11. Predicted energies of Hjalmarson-Frenkel core excitons at the Al site in AlP.

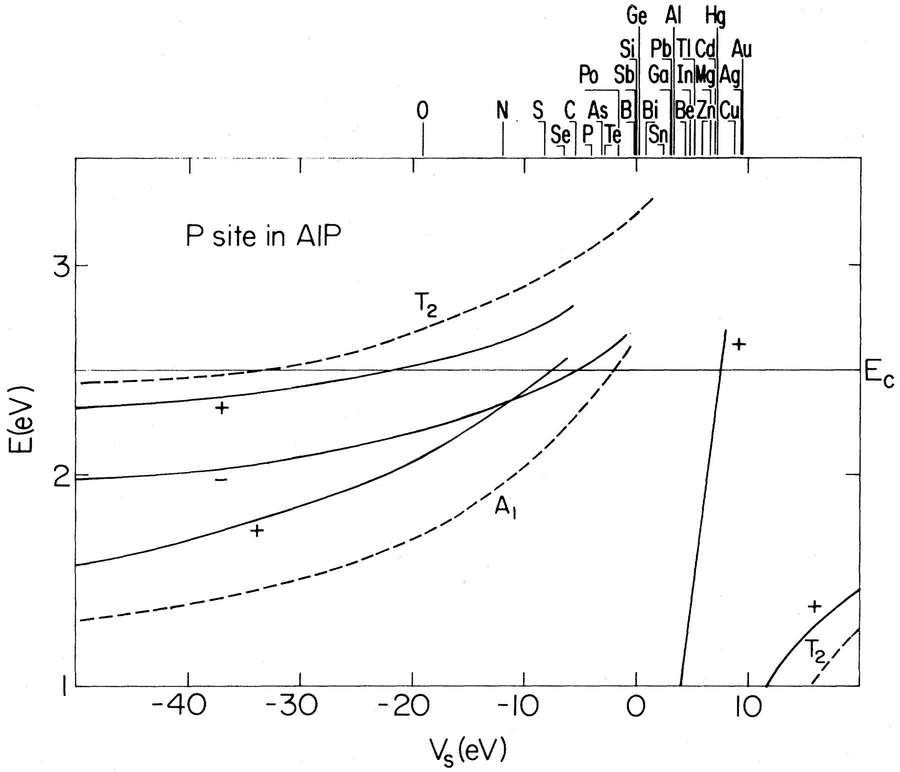

FIG. 12. Predicted energies of Hjalmarson-Frenkel core excitons at the P site in AlP.

Our results for the cation and anion sites in the In*X* and Al*X* semiconductors (with *X* a group-V element), shown in Figs. 1—12, exhibit many interesting features. The energy E of the Frenkel core exciton is plotted as a function of the *s*-electron "impurity" potential V_s, so that the results apply to extrinsic excitons, associated with impurity atoms, as well as the intrinsic excitons associated with the host atom on a given site. As described earlier,[18,19] the energy levels are obtained from the secular equation

$$\det\{[G(E)]^{-1}-V_d\}=0\ , \qquad (1)$$

where $G(E)$ is the surface Green's function and V_d is the change in the Hamiltonian associated with the "impurity" representing the exciton.[29]

In considering the results of Figs. 1—12, it is convenient to divide the materials into three groups: the narrow-gap semiconductors InSb and InAs, the larger-gap semiconductor InP, and the Al*X* semiconductors (with *X* a group-V element), of which two (AlAs and AlP) have indirect gaps and the third (AlSb) has a gap that is direct in our model,[28] but is very near to being indirect. One can see that the various branches of excitonic resonances persist well above the conduction-band edge E_c in InSb and InAs, somewhat above E_c in InP, and only slightly above E_c (for a number of the branches) in AlSb, AlAs, and AlP. The reason for this is that a resonance tends to be broadened and eventually lost as it enters an energy region where the density of states is high (for continuum states having the same symmetry as the exciton). There is only a rather gradual increase in the density of states associated with the direct minimum (occurring at the origin Γ of the bulk Brillouin zone), in contrast to the relatively sudden and large increase associated with the indirect minimum (occurring near the point *X* on the Brillouin-zone boundary). For reference, the direct and indirect minima, respectively, have the following values[28,30]: 0.23 and 1.71 eV (InSb), 0.43 and 2.28 eV (InAs), 1.41 and 2.44 eV (InP), 1.88 and 1.98 eV (AlSb), 3.04 and 2.30 eV (AlAs), and 3.60 and 2.50 eV (AlP).

On the cation site in InP, InAs, and InSb, the bulk T_2 (*p*-like) branch of excitonic resonances is predicted to persist to higher energies than the bulk A_1 (*s*-like) branch. The reverse is true in the other materials. This is due to the fact that the direct conduction-band minimum (at point Γ) is *s*-like, and the indirect conduction-band minimum (at point *X*) is *p*-like.

In some cases a branch of resonances vanishes as the energy is increased (or becomes so broad that the resonances are no longer well defined) and then reappears at still higher energies. This occurs for the "dangling-bond" branch associated with the In site in InAs and for several branches on the two sites in AlSb. Perhaps the most interesting conclusion illustrated by Figs. 1—12 is that, in many III-V semiconductors, it should be possible to observe excitonic resonances having energies well above the conduction-band edge.

ACKNOWLEDGMENT

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[27] Measured relaxations are available only for GaAs (Refs. 23—25), InSb (Ref. 25), InP (Ref. 25), and GaP (Ref. 26). However, all the III-V's appear to have similar relaxations, and we have consequently assumed a rigid rotational relaxation of 27.3° (see Refs. 23—26) for those materials whose relaxations have not been measured.

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[29] As discussed in Ref. 18, we use the approximation [H. P. Hjalmarson, R. E. Allen, H. Büttner, and J. D. Dow, J. Vac. Sci. Technol. 17, 993 (1980] $V_p = \frac{1}{2} V_s$ to generate the curves of Figs. 1—12, where V_s and V_p are, respectively, the s and p impurity potentials (Ref. 28). In Eq. (1), $G(E)$ is determined from the one-particle Dyson's equation, as described in Ref. 19, with the bulk Green's function obtained from the spectral representation for a model slab with periodic boundary conditions in the [110] direction (i.e., a discrete set, rather than a continuum, of energies is used, and no $+i\delta$ is required in the denominator of the spectral representation). A well-defined curve representing solutions to Eq. (1) is interpreted as a branch of excitonic resonances.

[30] These energies represent the band gaps at low temperature.