

Conduction-band-edge charge densities in elemental and compound semiconductors

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The empirical pseudopotential method is used to compute electronic charge densities at the Γ , L , and X \mathbf{k} points of the conduction-band edge in selected group-IV elemental (Si, Ge, α -Sn) and III-V compound (GaP, GaAs, GaSb, InP, InAs, InSb) semiconductors. We find that these charge distributions are essentially independent of the system under study and are strongly dependent upon the symmetry of the wave function of a particular state. As a direct consequence of this analysis, we find that the Γ_1^c conduction-band state for the heteropolar semiconductors contains an abundance of charge density associated with the anion as opposed to the cation in support of a previous observation by Baldereschi and Maschke, and that the symmetry of the wave function of the conduction-band edge at X^c for GaSb is actually X_5^c , and not X_1^c as has been previously assigned in the literature. We therefore predict an increase in both the direct and indirect band gaps of the Nowotny-Juza alloy α -LiZnSb upon applying the interstitial insertion rule of Wood, Zunger, and de Groot to GaSb.

Recent interest in the modification of the electronic band structures of tetrahedral semiconductors by interstitial impurities has renewed efforts to obtain detailed analyses of the topologies of electron charge densities at selected high-symmetry \mathbf{k} points along the conduction-band edge of these materials.¹⁻¹⁰ Such charge distributions have been shown to depend strongly on the particular \mathbf{k} point under consideration. For example, the charge densities at the X point of the conduction-band edges (X^c) of Si,⁶ Ge,¹⁰ GaP,⁶ GaAs,¹⁻⁵ ZnSe,⁹ and CdTe (Ref. 9) differ considerably from those at L^c or Γ^c .

In an attempt to provide a more systematic understanding of this behavior in elemental and compound semiconductors, this paper studies the charge densities of the conduction-band edge at Γ^c , L^c , and X^c for the representative group-IV elemental semiconductors Si, Ge, and α -Sn and for the representative III-V compound semiconductors GaP, GaAs, GaSb, InP, InAs, and InSb. Both the qualitative and quantitative differences in these antibonding charge-density topologies are discussed with the intent of stimulating further research as to how impurities can selectively modify the electronic band structure of semiconductors, and how specific bands respond to external perturbations.

The method of calculation used to compute the charge densities at selected \mathbf{k} points has been reviewed elsewhere, hence we shall only outline it briefly here.^{2,3,11} The non-local empirical pseudopotential method (EPM) is employed to solve the one-electron Hamiltonian for the eigenvalues and wave functions of the selected nine semiconductors. The charge density is then computed at a selected \mathbf{k} point in the Brillouin zone by using the appropriate wave function $\psi_{n,\mathbf{k}}$ for the band n at the point \mathbf{k} in the Brillouin zone:

$$\rho_{n,\mathbf{k}}(\mathbf{r}) = 2e |\psi_{n,\mathbf{k}}(\mathbf{r})|^2. \quad (1)$$

The results for the Γ^c , L^c , and X^c \mathbf{k} points of Si, Ge, α -Sn, GaP, GaAs, GaSb, InP, InAs, and InSb are illustrated in the charge-density contour plots of Figs. 1-10.

In studying the conduction-band-edge charge densities for Si, Ge, and α -Sn as shown in Figs. 1, 2, and 3, we see that at the conduction-band state Γ^c the electron charge density is similar for Ge and α -Sn, but different for Si. This is easily understood because although the symmetry of the wave function is the same for Ge and α -Sn, (viz. Γ_2^c)¹², it is Γ_{15} for Si. The Γ_2^c antibonding states for Ge and α -Sn are s -like and localized about the ions with a minimum of charge density halfway along the internuclear separation between the ions, suggesting the appearance of a nodal plane which is often observed in antibonding electronic charge distributions. Because the Γ_{15}^c state of Si contains more p and d character than the Γ_2^c states

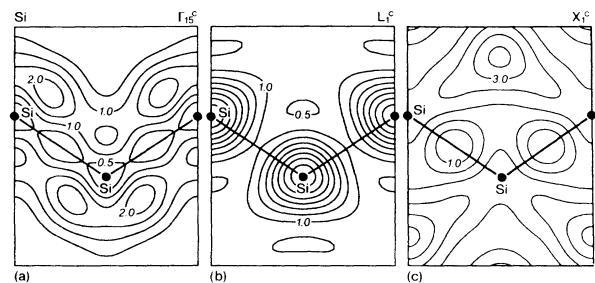


FIG. 1. Electronic charge-density contours for Si in the $(1\bar{1}0)$ plane at the Γ , L , and X \mathbf{k} points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for all three plots is in units of 0.5 electron per primitive cell.

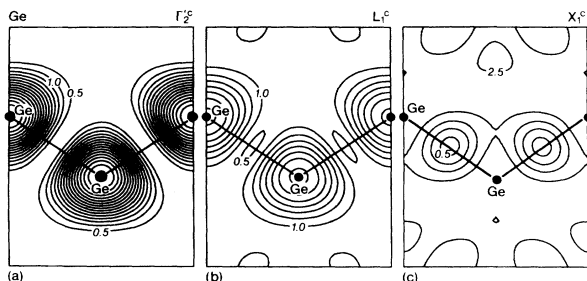


FIG. 2. Electronic charge-density contours for Ge in the $(1\bar{1}0)$ plane at the Γ , L , and X k points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for all three plots is in units of 0.5 electron per primitive cell.

of Ge and α -Sn, the charge density at the Γ_{15}^c state for Si is slightly more delocalized following the zigzag pattern of the bonding chain. However, all three elements show a dramatic change in going from L^c , which contains slightly more d character than the Γ_2^c states of Ge and α -Sn, to X^c where the abundance of d character is highest and thus the electronic charge density is more delocalized or free-electron-like throughout the unit cell. Furthermore, we observe through an angular momentum decomposition of these states^{2,3} that the amount of p and d character significantly increases in going from the conduction-band states at L^c to those at X^c . Finally, there is a buildup of charge density in the interstitial region which becomes more significant in going from the X^c state of Si to the X^c state of α -Sn. The appearance of this increased electronic charge density in the interstitial region at X^c has been observed previously in Si (Ref. 6) and Ge (Ref. 10), and its interesting implications for modifying the electronic band structure of semiconductors when closed-shell atoms are substituted at interstitial sites have been recently discussed.^{1,2,3,6-8}

When making the transition from the group-IV elemental semiconductors with diamond symmetry to the zinc-

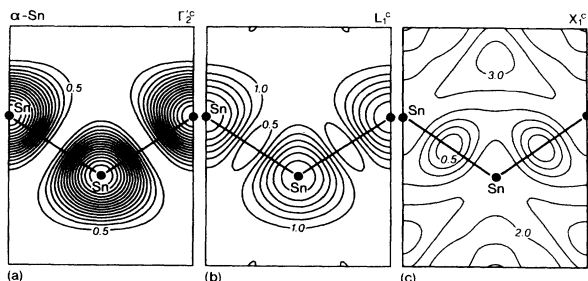


FIG. 3. Electronic charge-density contours for α -Sn in the $(1\bar{1}0)$ plane at the Γ , L , and X k points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for all three plots is in units of 0.5 electron per primitive cell.

blende III-V compound semiconductors, we can directly observe the consequences of the lack of inversion symmetry upon the charge densities at Γ^c , L^c , and X^c . For GaP, GaAs, and GaSb (cf. Figs. 4, 5, and 6), the computed charge distributions are still antibonding and s like at Γ^c , but there is more electronic charge density surrounding the anion than the cation. This is consistent with previous studies of charge distributions in II-VI⁹ and III-V compound semiconductors¹⁻³ and ionic crystals,¹³ and tends to support the observation of Baldereschi and Maschke that restricted tight-binding calculations did not produce accurate charge densities for conduction-band states.¹⁴ The charge densities at L_1^c are similar to those at Γ_1^c , although they do contain some p and d character which reflects some minor differences, particularly in the interstitial region.

The situation at X^c is quite interesting in that not only do we find the charge distributions to be more delocalized throughout the unit cell as with the group-IV semiconductors, but we also find that the actual charge-density topologies are different with the symmetry being X_1^c for GaP and GaAs, but X_3^c for GaSb. This difference has important physical consequences for the electron charge-density topology because at the X^c point in GaP and GaAs, the s and d_{z^2} orbitals of the anion and p_z and d_{xy} orbitals of the cation combine to form an antibonding state,^{15,16} where the s -like distribution about the anion is evident in Figs. 4(c) and 5(c). For GaSb, however, the charge distribution involves s and d_{z^2} orbitals from Ga and p_z and d_{xy} orbitals from Sb with a s -like charge distribution surrounding the cation as shown in Fig. 6(c).

This difference has immediate consequences for the effect of interstitial impurities on the electronic structure of GaSb. As first studied by Rompa, Schuurmans, and Williams for GaAs,¹ and later investigated by Wood, Zunger, and de Groot (WZG) for GaP (Ref. 6) and other so-called "filled tetrahedral semiconductors" (FTS),^{7,8} the substitution of the interstitial sites of tetrahedral compounds with atoms possessing repulsive s and attractive non- s effective potentials (e.g., H, He, Li^+) can raise (lower) the energy of the lowest conduction-band state at X^c if that state has s (non- s) charge-density character at the interstitial site.

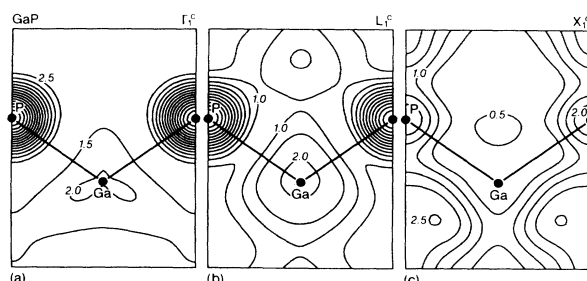


FIG. 4. Electronic charge-density contours for GaP in the $(1\bar{1}0)$ plane at the Γ , L , and X k points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for all three plots is in units of 0.5 electron per primitive cell.

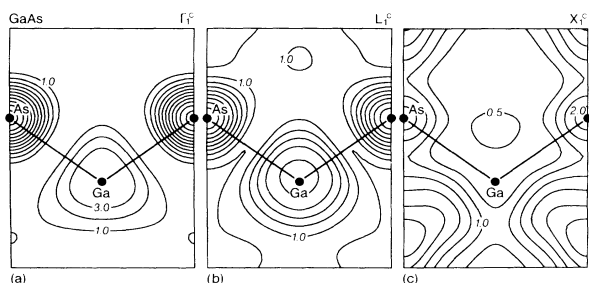


FIG. 5. Electronic charge-density contours for GaAs in the $(1\bar{1}0)$ plane at the Γ , L , and X k points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for 5(a) is in units of 1.0 electron per primitive cell while the intervals for (b), (c) are in units of 0.5 electron per primitive cell.

WZG showed that GaP could be turned into the FTS, $V_c\text{GaPV}_a$, where V_c is the interstitial site nearest the cation (Ga), and V_a is the interstitial site nearest the anion (P). By inserting He atoms at each of the V_c and V_a sites of the crystal, they predicted that GaP could be transformed from an indirect-gap semiconductor to the direct-gap semiconductor HeGaPHe. As we observe from the charge-density plot for GaP at X_1^c in Fig. 7, there is an abundance of s -like charge density at V_c while there is a local minimum of charge density at V_a . Because these interstitial sites contain more s -character charge density than those at Γ_1^c [cf. Fig. 4(a)], the insertion of He atoms at V_c raises the X_1^c conduction-band state more than that at Γ^c , thus forcing the semiconductor to become direct at Γ . This argument was subsequently applied to LiZnP (Ref. 7) and α -LiZnAs (Ref. 8) where it was suggested that these so-called Nowotny-Juza alloys should have larger direct band gaps than GaP and GaAs, respectively, but smaller indirect band gaps because the symmetry of the states at X^c was still X_1^c . We predict that because the symmetry of the conduction-band-edge state at X for GaSb is X_3^c and not X_1^c , as in GaP and GaAs, the analogous Nowotny-Juza compound for GaSb, α -LiZnSb, should also have a larger direct gap at Γ than GaSb, fol-

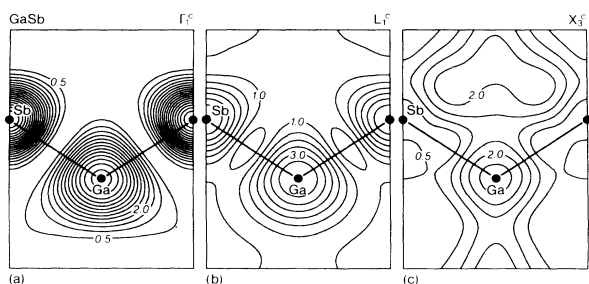


FIG. 6. Electronic charge-density contours for GaSb in the $(1\bar{1}0)$ plane at the Γ , L , and X k points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for all three plots is in units of 0.5 electron per primitive cell.

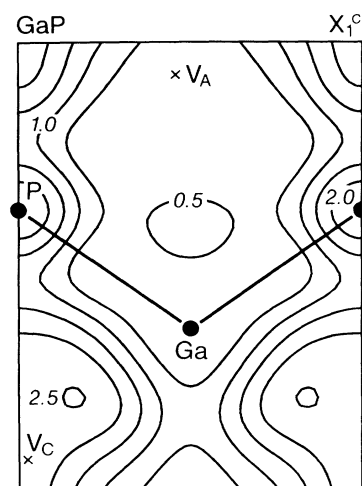


FIG. 7. Electronic charge-density contours for GaP in the $(1\bar{1}0)$ plane at the X k point of the first conduction band. The interstitial impurity sites are labeled V_c and V_a , respectively. The symmetry of this state is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for this plot is in units of 0.5 electron per primitive cell.

lowing the interstitial insertion rule of WZG, but that the indirect band gap between Γ and X should be larger because the X_3^c state is pushed upward when the Li^+ "impurity" is added. Since little is known about the electronic and optical properties of α -LiZnSb, we hope that these results would prompt further experimental interest. Perhaps a less exotic confirmation of the symmetry assignment of X_3^c in GaSb would be experimental information obtained from photoemission spectroscopy and measured band-gap pressure coefficients.

Finally, the charge distributions for InP, InAs, and InSb are quite similar to those of their gallium analogues, as shown in Figs. 8, 9, and 10 with the sole difference being that the symmetries of all the conduction states at X^c

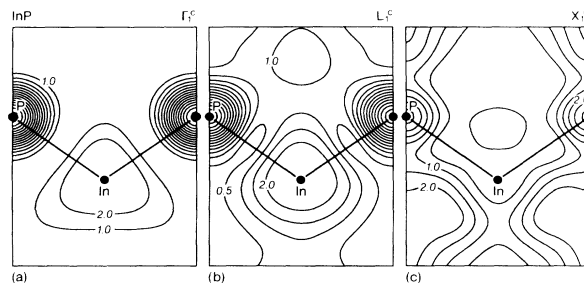


FIG. 8. Electronic charge-density contours for InP in the $(1\bar{1}0)$ plane at the Γ , L , and X k points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for (a) is in units of 1.0 electron per primitive cell while the interval for (b) and (c) is in units of 0.5 electron per primitive cell.

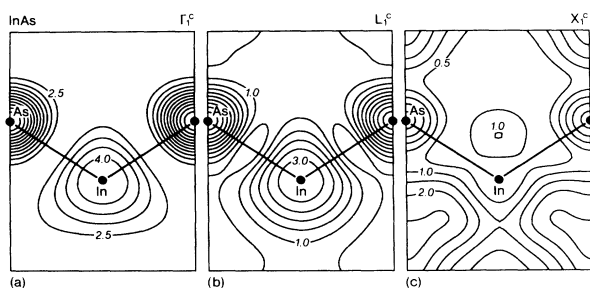


FIG. 9. Electronic charge-density contours for InAs in the $(1\bar{1}0)$ plane at the Γ , L , and X k points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for all three plots is in units of 0.5 electron per primitive cell.

were found to be X_1^c . Thus upon applying the analysis of WZG to these compounds, we predict that, for example, the alloys HeInPHe, HeInAsHe, and HeInSbHe would also have larger direct band gaps than their parent compounds InP, InAs, and InSb, respectively, but smaller $\Gamma^v \rightarrow X^c$ indirect band gaps because of the X_1^c symmetry of the conduction-band edge at X . In addition to α -LiZnAs, HeGaAsHe, and HeSiHe, these indium alloys, along with α -LiZnSb, would represent a new class of electronic materials whose properties were determined by the nature of the charge density along the conduction-band edge of III-V and group-IV semiconductors.

In conclusion, we have studied the electronic charge distributions for a number of representative elemental and compound semiconductors, and have discovered that it is the symmetry of the wave function at a particular k point which is primarily responsible for the general topology of the charge distribution. This fact has important consequences for optical processes which depend on the symmetry of the initial and final wave functions of a particular transition as well as band-structure modifications by interstitial impurities. Furthermore, our calculations sup-

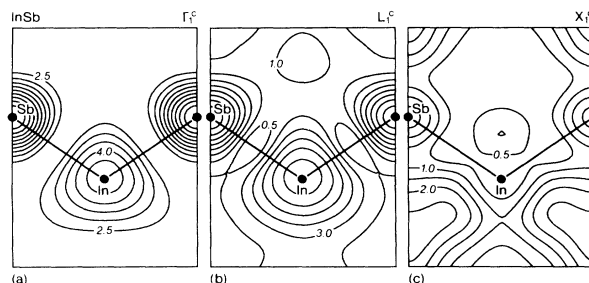


FIG. 10. Electronic charge-density contours for InSb in the $(1\bar{1}0)$ plane at the Γ , L , and X k points of the first conduction band. The symmetry of each of these states is also indicated as confirmed by an angular momentum decomposition analysis. The contour interval for all three plots is in units of 0.5 electron per primitive cell.

port previous ideas in the literature about the antibonding nature of conduction-band states in heteropolar semiconductors, and predict interesting consequences for filled tetrahedral semiconductors such as α -LiZnSb due to the identification of X_3^c as the correct symmetry for the conduction-band edge in GaSb.

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¹²In our study of α -Sn, we ignored relativistic effects so that the Γ_2^c state in α -Sn actually lies roughly 0.1 eV below the valence-band edge. However, in a relativistic calculation, the lowest conduction and highest valence bands actually coincide, giving a zero band gap with the symmetry of the upper band being Γ -like.
¹³M. S. Hybertsen and S. G. Louie (unpublished).
¹⁴A. Baldereschi and K. Maschke, in *Proceedings of the 14th International Conference on the Physics of Semiconductors, Edinburgh, 1978*, edited by B. L. H. Wilson (IOP, Bristol, 1978), p. 1167.
¹⁵The group-theoretical labels for the symmetry of a particular

state (viz., X_1 and X_3) are arbitrary and depend upon a convention, namely the choice of origin for the group-theoretical analysis. (In particular, Refs. 6 and 7 both use a convention different from that of Ref. 8.) We follow the single-group convention of, for example, F. Bassani in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), where the origin is chosen to be at the anion. One should also realize that although the choice of coordinates for the X point, $(2\pi/a)(1,0,0)$ and $(2\pi/a)(0,0,1)$, are equivalent by symmetry, Bassani has used

the former in his discussion while we have chosen the latter.

¹⁶It should be noted that although the symmetry of the conduction band state at X^c is X_1^c for GaAs as shown in Fig. 5(c), a similar charge density plot for GaAs in Fig. 4 of Ref. 3 suggests that the symmetry of the charge distribution is X_3^c . This is simply a reflection of the choice of the model potential in this paper which reverses the symmetry of the first and second conduction band states at X^c . We are grateful to Dr. Gerald Martinez for reminding us of this interesting point in a recent discussion.