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Electronic Charge Densities in Semiconductors*

by

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Abstract

Electronic charge densities are calculated as a function of position in the unit cell for several diamond and zincblende semiconductors using wavefunctions derived from pseudopotential band structure calculations. The covalent bonding charge is also calculated for these crystals and is plotted against the ionicity scales of Phillips and VanVechten and of Pauling. It is shown that an extrapolation to zero covalent bonding charge yields a critical value of the ionicity which separates 4-fold coordinated and 6-fold coordinated diatomic crystals. This value is in agreement with the empirical value obtained by Phillips and Van Vechten.

The bonding and chemical nature of semiconductors and insulators[1-5] has recently been a focal point of interest for solid state physicists. The emphasis[6,7] on bonding is motivated by the belief that a detailed knowledge of the distribution of electronic charge in solids will lead to a better understanding of the physical and chemical properties of these solids. Despite the existence of accurate band structure calculations, accurate charge

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density calculations have not been previously available. We present here the results of such calculations for Ge, GaAs, ZnSe, α-Sn, InSb and CdTe (although space allows only detailed plots for Ge and GaAs). The calculated charge density distributions are used to compute covalent bonding charges, which in turn are used to compute the critical ionicity, f_c, which separates 4-fold coordinated and 6-fold coordinated diatomic crystals.

The spatial charge density distribution for valence band n may be written

$$\rho_n(\vec{r}) = e \sum_{\vec{k}} |\psi_{n,\vec{k}}(\vec{r})|^2 , \qquad (1)$$

where the summation is over all available states $\vec{k}$ in band n. $\psi_{n,k}$ is obtained from empirical pseudopotential band structure calculations[8] for Ge, GaAs, ZnSe, α-Sn, InSb, and CdTe.[9] To obtain proper convergence for the accurate calculation of charge density distributions, it is necessary to expand $\psi_{n,k}$ in a basis of approximately 90 plane waves.[10] The wavefunctions are evaluated on a grid of 3360 points in the Brillouin zone.

By using Eq. (1), the charge density $\rho_n(\vec{r})$ is evaluated at over 1600 points in a plane which intersects both atoms in the primitive cell (a (1,-1,0) plane). A diagram of the primitive cell and the orientation of this plane is shown in the insert in Fig. 1. The charge density is plotted on contour maps in units of (e/Ω), where $\Omega = \frac{1}{4}a^3$ is the volume of the primitive cell.

The results of the calculations are shown in detailed contour maps of the total valence charge density (Figs. 1 and 2). The contours are

striking and can be used to describe selected physical properties of crystals to a more general audience. One can definitely see tetrahedral covalent bonding in germanium, where the charge density is concentrated halfway between the two atoms. Ionic trends in the bonding may be seen by comparing the total valence charge density for Ge and GaAs. For GaAs, the center of the bonding charge has moved toward the As ion. Another trend that is noticeable is that the amount of bonding charge decreases in going from Ge to GaAs. Thus the covalent bonding becomes weaker as the crystals become more ionic.

The covalent bonding charge Z_b may be calculated as follows:

$$Z_b = \int (\rho(\vec{r}) - \rho_0)\, d^3r \quad , \tag{2}$$

where ρ_0 is the charge density at the outermost close contour of the bonding charge density. The integration extends over the volume defined by this outermost contour.

For the purposes of our calculations we choose two series of crystals. The first series, composed of Ge, GaAs, and ZnSe, lies in the fourth row of the Periodic Table. The second series, composed of α-Sn, InSb, and CdTe, lies in the fifth row of the Periodic Table. Since spin-orbit effects have been neglected in our calculations and since spin-orbit effects are relatively large in the second series of crystals, the results for the second series are not expected to be as good as for the first series. For the crystals of each series the lattice constant is practically the same and the ion-cores are identical. The values we calculate for Z_b (in units of e)

are 0.146 for Ge, 0.080 for GaAs, 0.026 for ZnSe, 0.123 for Sn, 0.091 for InSb, and 0.027 for CdTe.

Phillips and Van Vechten[1, 2] define ionicity f_i using homopolar, heteropolar and average energy gaps, E_h, C, and E_g, respectively, where $E_g^2 = E_h^2 + C^2$. Their ionicity factor $f_i = C^2/E_g^2$ varies between zero and one: $f_i = 0$ designates a completely covalent-bonded crystal and $f_i = 1$ designates a completely ionic crystal. The important result is that for Phillips' sample[2] of 68 binary crystals, the ionicity value $f_c = 0.785 \pm 0.01$ neatly separates the more covalent crystals of 4-fold coordination (zinc-blende and wurtzite structures) from the more ionic crystals of 6-fold coordination (rocksalt structure). As Phillips notes in his review article,[2] this critical value of the ionicity f_c is determined completely empirically.

We have attempted to obtain f_c from our calculation of bonding charge. The idea is that the atoms in crystals of 4-fold coordination form tetrahedrally-directed covalent bonds through hybridization of (e.g. (sp^3) in Ge) orbitals, and that crystals of 6-fold coordination no longer form directed bonds but are held together by electrostatic forces. For an homologous series of crystals of increasing ionicity, the covalent bonding weakens as the ionic bonding becomes stronger. When the amount of charge in the covalent bond approaches zero, the configuration of tetrahedrally-directed bonds is no longer stable. Consequently, it is reasonable to speculate that a phase transition to a different crystalline structure occurs as the covalent bonding charge goes to zero.

To test this hypothesis we have plotted our calculated values of Z_b versus the ionicity of Phillips and Van Vechten. The points of the series Ge,

The points of the series Sn, InSb, and CdTe are also connected using a smooth curve, which when extrapolated gives zero bonding at an ionicity of $f_c = 0.79$.

GaAs, and ZnSe[11] are connected with a smooth curve, which when extrapolated gives zero bonding at an ionicity of $f_c = 0.78$. These two values of critical ionicity ($f_c = 0.79$ and $f_c = 0.78$) should be compared with Phillips' empirical value of the critical ionicity, namely, $f_c = 0.785 \pm 0.01$.

When the bonding charge Z_b is plotted against Pauling's ionicity scale,[12] the curve passing through the series Ge, GaAs, and ZnSe gives a zero-covalent-bonding ionicity of 0.80, which is the empirically determined critical ionicity on Pauling's scale. The curve passing through the series Sn, InSb, and CdTe gives a critical ionicity of 0.61, which does not agree with Pauling's empirical value. For the crystals we have studied it appears that the ionicity scale of Phillips and Van Vechten is in better agreement with our results than the ionicity scale of Pauling.

We wish to thank Dr. J. C. Phillips, Professor L. M. Falicov and Professor C. Kittel for stimulating discussions and helpful comments.

References

1. J. C. Phillips, Phys. Rev. Letters 20, 550 (1968); J. C. Phillips and J. A. Van Vechten, Phys. Rev. Letters 22, 705 (1969); J. A. Van Vechten, Phys. Rev. 182, 891 (1969).
2. An excellent review article is J. C. Phillips, Rev. Modern Phys. 42, 317 (1970).
3. S. H. Wemple and M. DiDomenico, Phys. Rev. Letters 23, 1156 (1969).
4. J. J. Hopfield, Phys. Rev. B2, 973 (1970).
5. R. W. Shaw, Jr., Phys. Rev. Letters 25, 818 (1970).
6. J. C. Phillips, Covalent bonding in crystals, molecules and polymers

(University of Chicago Press, Chicago) 1970.

7. J. Platt, "The chemical bond", Handbuch der Physik 37 (Springer-Verlag, 1960), esp. pp. 173-181.

8. See M. L. Cohen and V. Heine in Solid State Physics 24, H. Ehrenreich, F. Seitz, and D. Turnbull (eds.), (Academic Press, New York), 1970, and references therein.

9. The pseudopotential form factors are taken from the following papers: Ge and Sn: M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966); GaAs: R. R. L. Zucca, J. P. Walter, Y. R. Shen, and M. L. Cohen, Solid State Communications 8, 627 (1970); ZnSe: J. P. Walter, M. L. Cohen, Y. Petroff, and M. Balkanski, Phys. Rev. B 1, 2661 (1970); InSb: R. Boyd, J. P. Walter and M. L. Cohen, (to be published); CdTe: D. Chadi, J. P. Walter, and M. L. Cohen (to be published).

10. Since the wavefunctions are obtained using a pseudopotential (core states are not included), $\rho_n(r)$ is not expected to be accurate in the neighborhood of the ion-core.

11. The ionicity of ZnSe on Phillips' scale is 0.63. J. C. Phillips, (private communication).

12. L. Pauling, The nature of the chemical bond, (Cornell University Press, Ithaca, New York), 1939. Discussion of Pauling's ionicity scale is also included in Ref. 2.

Figure Captions

Fig. 1. Valence electron density contour map (in units of e per primitive cell) for Ge in the (1, -1,0) plane. The orientation of the plane (dashed lines) with respect to the primitive cell is shown in the inset. The radii of the cores for Ge is 0.20 of the Ge-Ge distance. This radius is that of a sphere containing 80% of the outermost shell of core electrons.

Fig. 2. Valence electron density contour map (in units of e per primitive cell) for GaAs in the (1, -1, 0) plane. See inset of Fig. 1. The core radii for Ga and As are 0.23 and 0.18 of the Ga-As distance. The radii are those of spheres containing 80% of the outermost shell of core electrons.

Fig. 3. Bonding charge versus ionicity (Phillips-Van Vechten scale). The bonding charge is in units of e per bond. The calculations do not include spin-orbit effects.

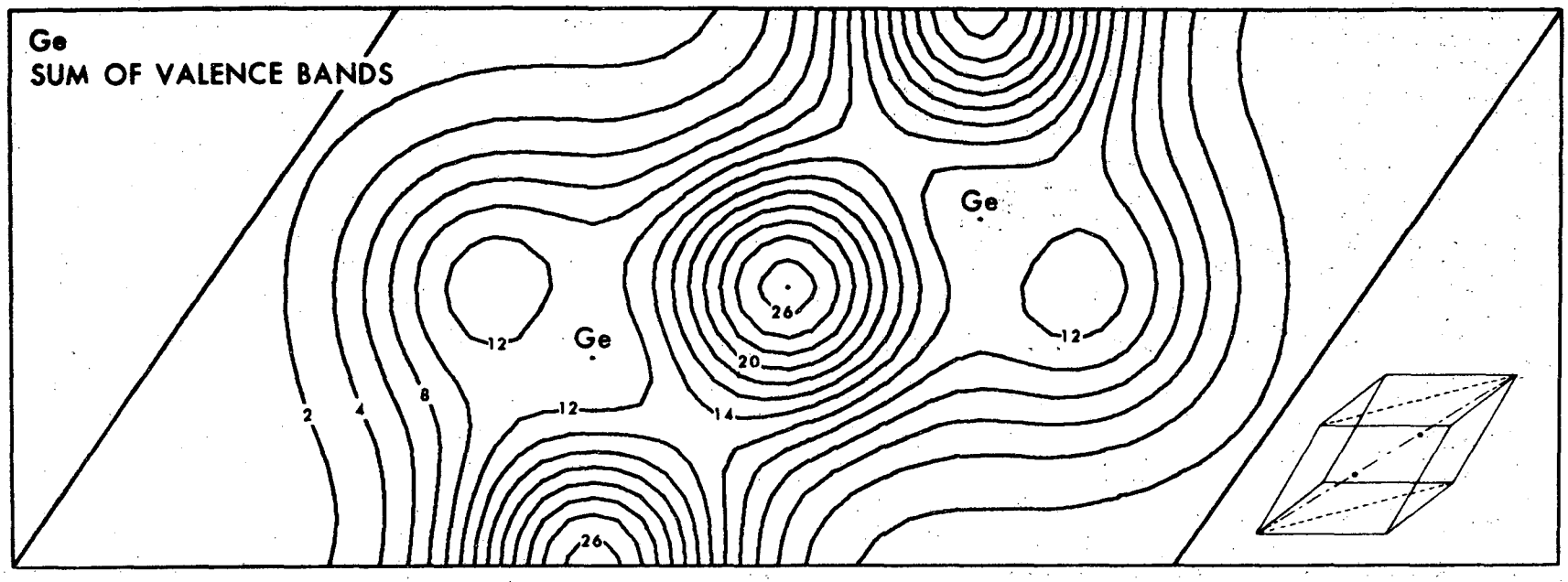

Fig. 1

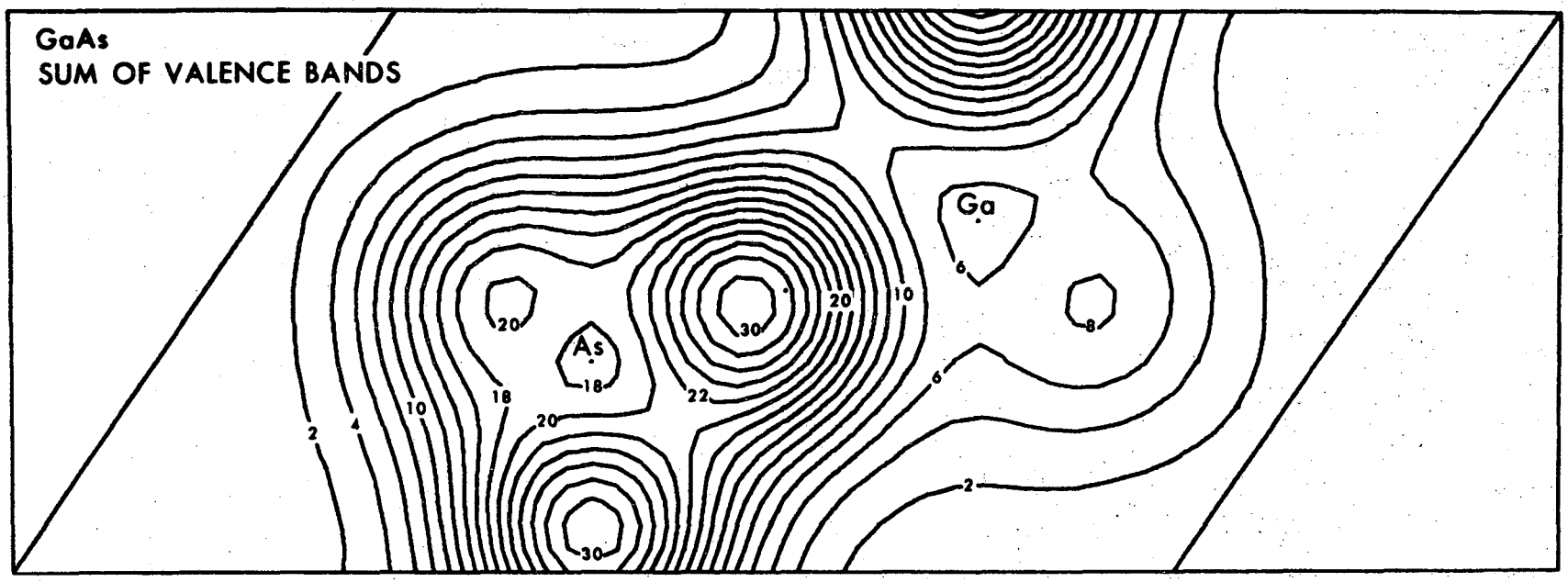

Fig. 2

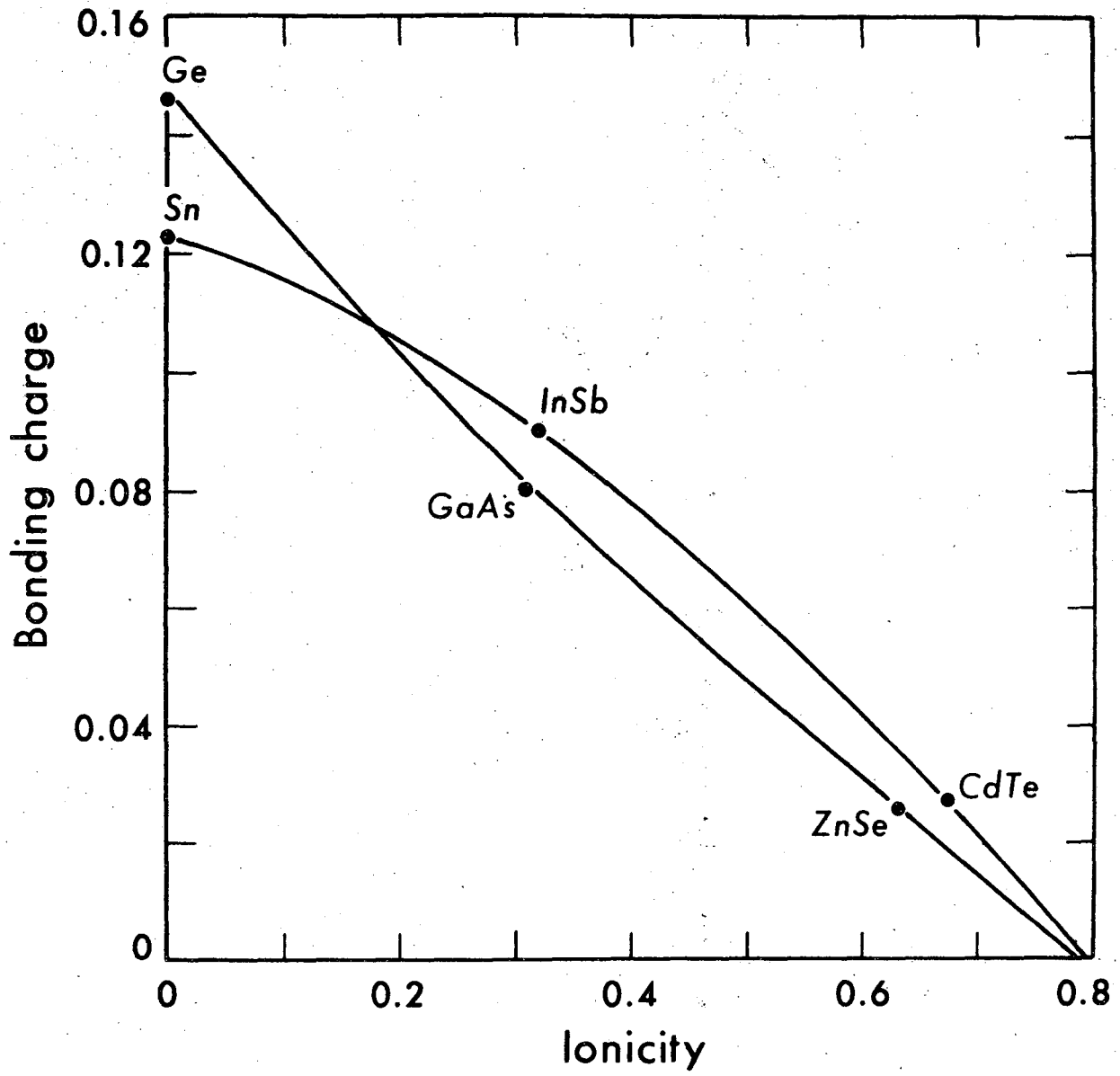
0.16
0.12
0.08
0.04
0
Bonding charge
Ge
Sn
InSb
GaAs
CdTe
ZnSe
0
0.2
0.4
0.6
0.8
Ionicity

Fig. 3

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