PHYSICAL REVIEW B VOLUME 36, NUMBER 9 15 SEPTEMBER 1987-II

# Ionicity in $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ semiconductors

V. Kumar Srivastava
*Department of Instrumentation, Central Mining Research Station, Barwa Road, Dhanbad 826 001, India*

(Received 31 October 1986; revised manuscript received 24 February 1987)

The dielectric theory of ionicity has been used to calculate the bond ionicity in the $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ semiconductors. Our calculated values of bond ionicities, dielectric constants, and homopolar and heteropolar energy gaps are in excellent agreement with the values reported by several workers.

In the last decade a considerable amount of experimental[1–3] and theoretical[4–21] work has been done to further the understanding of ionicity in solids. The dielectric description of ionicity developed by Phillips[5] and Van Vechten[6,7] has been successfully used in a wide variety of areas related to the crystal structures. Chemla[8] and several workers[9–11] have extended this theory to some complex crystals, neglecting the effect of noble-metal *d* electrons. Levine[12] has generalized the theory of bond ionicity in the case of various types of complexes, also considering the effect of *d* electrons, but it is difficult to generalize this theory for those compounds for which the experimental values of dielectric constants are unknown. Neumann[11] has derived these parameters, interpolating the curves between susceptibility and the square of the effective number of valence electrons ($\Delta Z^2$) for some of the $A^{\mathrm{I}}B^{\mathrm{III}}C_2^{\mathrm{VI}}$ compounds for which dielectric constants are unknown.

A simple model has recently been developed[22] based on plasma frequency formalism for the calculation of bond ionicity and other associated parameters for various rocksalt, zinc-blende and CsCl crystal structures. The results obtained have been compared with previous estimations. In this paper we extend the calculation of bond ionicities reported earlier in the case of $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{V}$ compounds. An excellent agreement has been obtained between the calculated values and the values reported by Levine.[12]

Several workers present clear pictures on ionicity and covalency. The ionic picture involves electron transfer from one atom to another giving rise to two closed-shell ions which interact mainly by Coulomb force and short-range repulsion, while the covalent picture involves sharing of electrons (bond change) between the atoms instead of charge transfer; directed hybrids and their chemical interaction describe the interactions. In order to determine the bond ionicity of $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ chalcopyrite crystals which are tetrahedrally coordinated, the average energy gap $E_{g,XY}$ of the $X$—$Y$ bond can be separated into the ionic $C_{XY}$ and covalent $E_{h,XY}$ parts as

$$E_{g,XY}^2 = C_{XY}^2 + E_{h,XY}^2 \,, \tag{1}$$

which yields the following relation for the bond ionicity:

$$f_{i,XY} = C_{XY}^2 / E_{g,XY}^2 \,. \tag{2}$$

Phillips,[5] Van Vechten,[7] and Levine[12] have given the relation for $E_{h,XY}$ and $C_{XY}$ according to which $E_{h,XY}$ depends on the bond length, and $C_{XY}$ on the difference between the screened Coulomb potentials of the atoms $X$ and $Y$ in the compound $XY$ and the Thomas-Fermi screening factor. Both the screening factor, which affects the chemical trend in a compound, and the bond length are related to the effective number of free electrons in a compound. The plasmon energy also depends directly on the effective number of free electrons in the valence band. Thus there must be some correlation between the physical process which involves the ionic and covalent contribution to the average energy gap and the plasmon energy of the compound. Therefore, the present author thought it would be of interest to correlate these parameters with the plasmon energy.

The Thomas-Fermi screening factor has been correlated with the plasmon energy, and the expression for the Thomas-Fermi momentum $K_s$ can be written as

$$K_{s,XY} = \left[ \frac{4}{a_B} \left[ \frac{3m}{(2\pi e)^2} \right]^{1/3} \right]^{1/2} (\hbar\omega_{p,XY})^{1/3} \,, \tag{3}$$

where $a_B$ is the Bohr radius.

The expressions for the ionic and covalent energy gaps, and the bond length for the $A$—$C$ bond in $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ semiconductors can be written in terms of plasmon energy as

$$E_{h,AC} = 0.051\,18(\hbar\omega_{p,AC})^{\nu}\ \mathrm{eV} \,, \tag{4}$$

$$C_{AC} = 5.904 b_{AC} (\hbar\omega_{p,AC})^{\mu} \times \exp[-5.971(\hbar\omega_{p,AC})^{-\mu/2}]\ \mathrm{eV} \,, \tag{5}$$

$$d_{AC} = 14.6337(\hbar\omega_{p,AC})^{-\mu} \quad (\hbar\omega_{p,AC}\ \text{in eV},\ d_{AC}\ \text{in Å}) \tag{6}$$

where $\nu = 1.6533$ and $\mu = \frac{2}{3}$ are the constants.

Similarly the expressions for the $B$—$C$ bond can be written as

$$E_{h,BC} = 0.041\,58(\hbar\omega_{p,BC})^{\nu}\ \mathrm{eV} \,, \tag{7}$$

$$C_{BC} = 1.81 b_{BC} (\hbar\omega_{p,BC})^{\mu} \times \exp[-6.4930(\hbar\omega_{p,BC})^{-\mu/2}]\ \mathrm{eV} \,, \tag{8}$$

$$d_{BC} = 15.9124(\hbar\omega_{p,BC})^{-\mu} \quad (\hbar\omega_{p,BC}\ \text{in eV},\ d_{BC}\ \text{in Å}) \tag{9}$$

TABLE I. Properties of the $A^{\mathrm{II}}C^{\mathrm{V}}$ bond in $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ compounds.

| | | $E_{h,AC}$ (eV) | | $C_{AC}$ (eV) | | $f_{i,AC}$ | | $\epsilon_{AC}$ | |
|---|---|---|---|---|---|---|---|---|---|
| Compounds | $\hbar\omega_{p,AC}$ (eV) | This work | Levine (Ref. 12) | This work | Levine (Ref. 12) | This work | Levine (Ref. 12) | This work | Levine (Ref. 12) |
| $ZnSiP_2$ | 15.294 | 4.650 | 4.65 | 4.584 | 4.10 | 0.4927 | 0.438 | 6.486 | 6.84 |
| $CdSiP_2$ | 13.659 | 3.857 | 3.86 | 3.875 | 4.17 | 0.5023 | 0.539 | 7.239 | 6.99 |
| $ZnGeP_2$ | 15.198 | 4.602 | 4.58 | 4.541 | 4.08 | 0.4932 | 0.442 | 6.526 | 6.84 |
| $CdGeP_2$ | 13.675 | 3.865 | 3.87 | 3.882 | 4.12 | 0.5023 | 0.532 | 7.232 | 6.99 |
| $ZnSnP_2$ | 14.907 | 4.457 | 4.46 | 4.414 | 4.07 | 0.4951 | 0.455 | 6.648 | 6.84 |
| $CdSnP_2$ | 13.446 | 3.758 | 3.76 | 3.785 | 4.04 | 0.5035 | 0.536 | 7.355 | 6.99 |
| $ZnSiAs_2$ | 14.473 | 4.245 | 4.25 | 4.225 | 3.73 | 0.4976 | 0.436 | 6.839 | 7.95 |
| $CdSiAs_2$ | 13.050 | 3.577 | 3.58 | 3.618 | 3.98 | 0.5057 | 0.553 | 7.579 | 8.22 |
| $ZnGeAs_2$ | 14.316 | 4.169 | 4.17 | 4.157 | 3.71 | 0.4986 | 0.442 | 6.913 | 7.95 |
| $CdGeAs_2$ | 13.035 | 3.570 | 3.57 | 3.612 | 3.94 | 0.5058 | 0.549 | 7.588 | 8.22 |
| $ZnSnAs_2$ | 14.094 | 4.062 | 4.06 | 4.061 | 3.68 | 0.4999 | 0.450 | 7.021 | 7.95 |
| $CdSnAs_2$ | 12.831 | 3.520 | 3.48 | 3.527 | 3.87 | 0.5008 | 0.553 | 7.730 | 8.22 |

where $\hbar\omega_{p,BC}$ is the plasmon energy for the $B$—$C$ compound and $b_{BC}$ is the prescreening factor. The plasma frequency is obtained from the number of valence electrons $N_e$ per unit volume, using the relation

$$\omega_{p,XY}^2=4\pi N_{e,XY}e^2/m\;. \tag{10}$$

The $N_{e,XY}$ can be expressed in terms of individual bond properties, as

$$N_{e,XY}=(Z_X/N_{cX}+Z_Y/N_{cY})/v_{b,XY}\;, \tag{11}$$

where $Z_X$ and $Z_Y$ are the numbers of valence electrons of the atoms $X$ and $Y$, $N_{cX}$ and $N_{cY}$ are the coordination numbers of the atoms, and $v_{b,XY}$ is the bond volume. In the case of $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ crystals, $N_{cA}=N_{cB}=N_{cC}=4$, $v_{b,XY}=4d_{XY}^3/3\sqrt{3}$, and the average value of prescreening constant $b$ has been taken as 1.3966 (Ref. 12) and 2.4516 (Ref. 12) for the $A$—$C$ and $B$—$C$ bond, respectively. The details of Eqs. (4)–(11) have been given by the author in his previous publications[22,23] and by several other workers.[5–13]

The dielectric constant $\epsilon_{XY}$ of the $X$—$Y$ bond is given by the well-known relation[5,12,17]

$$\epsilon_{XY}=1+(\hbar\omega_{p,XY})^2/E_{g,XY}^2\;. \tag{12}$$

Using Eqs. (1)–(12), the bond ionicity, homopolar (covalent) and heteropolar (ionic) energy gaps, and dielectric constants of the $A$—$C$ and $B$—$C$ bonds in $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ chalcopyrite compounds have been calculated. The results are presented in Tables I and II, together with the values obtained by Levine[12] from interpolating the curve between known compounds. The calculated values are in fair agreement with the values reported by Levine.[12] In the present model, $E_{h,XY}$, $C_{XY}$, $f_{i,XY}$, and $\epsilon_{XY}$ can be calculated without having any knowledge of the experimental value of the dielectric constant while the earlier models require this value in

TABLE II. Properties of $B^{\mathrm{IV}}C^{\mathrm{V}}$ bond in $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ compounds.

| | | $E_{h,BC}$ (eV) | | $C_{BC}$ (eV) | | $f_{i,BC}$ | | $\epsilon_{BC}$ | |
|---|---|---|---|---|---|---|---|---|---|
| Compounds | $\hbar\omega_{p,BC}$ (eV) | This work | Levine (Ref. 12) | This work | Levine (Ref. 12) | This work | Levine (Ref. 12) | This work | Levine (Ref. 12) |
| $ZnSiP_2$ | 18.757 | 5.294 | 5.3 | 2.720 | 2.45 | 0.2088 | 0.177 | 10.931 | 10.41 |
| $CdSiP_2$ | 18.845 | 5.335 | 5.34 | 2.739 | 2.59 | 0.2085 | 0.191 | 10.874 | 10.41 |
| $ZnGeP_2$ | 17.944 | 4.920 | 4.91 | 2.546 | 2.60 | 0.2112 | 0.219 | 11.494 | 11.55 |
| $CdGeP_2$ | 17.905 | 4.902 | 4.90 | 2.538 | 2.68 | 0.2113 | 0.231 | 11.521 | 11.55 |
| $ZnSnP_2$ | 16.203 | 4.156 | 4.16 | 2.183 | 2.71 | 0.2162 | 0.298 | 12.93 | 12.65 |
| $CdSnP_2$ | 16.194 | 4.152 | 4.15 | 2.181 | 2.71 | 0.2163 | 0.298 | 12.922 | 12.65 |
| $ZnSiAs_2$ | 17.620 | 4.774 | 4.77 | 2.478 | 2.54 | 0.2122 | 0.220 | 11.731 | 11.80 |
| $CdSiAs_2$ | 17.642 | 4.784 | 4.78 | 2.543 | 2.64 | 0.2202 | 0.234 | 11.603 | 11.80 |
| $ZnGeAs_2$ | 16.997 | 4.498 | 4.50 | 2.347 | 2.12 | 0.2140 | 0.182 | 12.223 | 14.29 |
| $CdGeAs_2$ | 16.850 | 4.434 | 4.43 | 2.317 | 2.21 | 0.2144 | 0.199 | 12.343 | 14.29 |
| $ZnSnAs_2$ | 15.524 | 3.872 | 3.87 | 2.045 | 1.53 | 0.2180 | 0.135 | 13.568 | 18.08 |
| $CdSnAs_2$ | 15.388 | 3.816 | 3.82 | 2.017 | 1.59 | 0.2184 | 0.148 | 13.710 | 18.08 |

their calculations.

Hence it is possible to calculate the bond ionicities and other associated parameters in $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ crystals from their plasmon energies even if the experimental values of dielectric constants are unknown.

The author wishes to express his sincere thanks to Dr. B. Singh, Director, Central Mining Research Station, Dhanbad for continuous inspiration and giving permission to publish this part of the work. The author is also grateful to Dr. S. C. Srivastava for his cooperation.

---

[1] J. J. Verbist, in *Solid State Chemistry, 1982,* Proceedings of the Second European Conference, Veldhoven, The Netherlands, 1982, edited by R. Metselaar, H. J. M. Heijligers, and J. Schoonman (Elsevier, Amsterdam, 1983).

[2] P. R. Sarode, Phys. Status Solidi B **88**, K35 (1978).

[3] S. V. Adhyapak, S. M. Karnetkar, and A. S. Nigavekar, Nuovo Cimento **35**, 179 (1976).

[4] L. Pauling, Phys. Rev. Lett. **23**, 480 (1969); Phys. Today **22**(2), 9 (1969); *The Nature of Chemical Bond* (Cornell, Ithaca University, 1960).

[5] J. C. Phillips, *Highlights of Condensed-Matter Theory LXXXIX Corso* (Soc. Italiana di Fisica, Bologna, Italy, 1985), p. 177; Phys. Rev. B **29**, 5683 (1984); Rev. Mod. Phys. **42**, 317 (1970).

[6] J. C. Phillips and J. A. Van Vechten, Phys. Rev. B **2**, 2147 (1970); Phys. Rev. **183**, 709 (1969).

[7] J. A. Van Vechten, Phys. Rev. **182**, 891 (1969); **187**, 1007 (1969); Phys. Rev. B **1**, 3351 (1970).

[8] D. S. Chemla, Phys. Rev. Lett. **26**, 1441 (1971).

[9] J. E. Fischer, M. Glickman, J. A. Van Vechten, *Physics of Semiconductors,* Proceedings of the International Conference on the Physics of Semiconductors, Roma, 1976, edited by F. G. Fumi (Tipographia Marves, Rome, 1976), p. 541.

[10] M. J. Bernard, Phys. Suppl. **36**, C3 (1975).

[11] H. Neumann, Cryst. Res. Tech. **18**, 1299 (1983); **18**, 1391 (1983); **18**, 665 (1983); **18**, 901 (1983).

[12] B. F. Levine, Phys. Rev. B **7**, 2591 (1973); J. Chem. Phys. **59**, 1463 (1973); Phys. Rev. B **7**, 2600 (1973); Phys. Rev. Lett. **25**, 44 (1970).

[13] S. H. Wemple and D. M. Domenica, Jr., Phys. Rev. B **3**, 1338 (1971).

[14] J. T. Devreese, P. E. Van Camp, and V. E. Van Doren, Solid State Commun. **35**, 857 (1980).

[15] D. A. Kleinman, Phys. Rev. B **2**, 3139 (1970).

[16] C. R. A. Catlow and A. M. Stoneham, J. Phys. C **16**, 4321 (1983).

[17] D. R. Penn, Phys. Rev. **128**, 2093 (1962).

[18] M. L. Cohen, Phys. Rep. **110**, 293 (1984).

[19] J. R. Chelikowsky and J. K. Burdett, Phys. Rev. Lett. **56**, 961 (1986); J. R. Chelikowsky and J. C. Phillips, Phys. Rev. B **17**, 2453 (1984).

[20] P. Enders, Phys. Status Solidi B **131**, 489 (1985).

[21] G. Srinivasan, Phys. Rev. **178**, 1244 (1969).

[22] V. Kumar Srivastava, Phys. Rev. B **29**, 6993 (1984); Phys. Lett. **102A**, 127 (1984); J. Phys. C **19**, 5689 (1986).

[23] K. S. Srivastava, R. L. Shrivastava, O. K. Harsh, and V. Kumar, Phys. Rev. B **19**, 4336 (1979); J. Phys. Chem. Solids **40**, 489 (1979).