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Plasmon energy, homopolar energy gap, heteropolar energy gap and ionicity of binary tetrahedral semiconductors and ionic compounds

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ABSTRACT The homopolar energy gap (E_h) and heteropolar energy gap (C) of binary tetrahedral semiconductors and ionic crystals having rock salt structure is calculated from plasmon energy of solids. Later on Phillips, Van Vechten and Levine (PVL) theory is used to estimate the ionicity of binary tetrahedral semiconductors and ionic compounds. The calculated values are in excellent agreement with the values reported by different researchers.

KEYWORDS Plasmon energy, ionicity, binary tetrahedral semiconductors, ionic compounds

1.Introduction

There have been several attempts made at understanding the homopolar (covalent) and heteropolar (ionic) energy gap in semiconductors. Phillips [1, 2] Van Vechten [2-3], Levine [4] and several researchers [5-9] have developed various theories and calculated these gaps for the case of simple compounds. From these gaps they have calculated ionicity of the compounds. Recently, several authors [10-13] have made at attempt to understand the electronic, mechanical, elastic and optical properties of zinc compounds. This is because of interesting semiconducting properties and various applications in the field of electronics, photovoltaic detectors, light emitting diode and solar cells. In this paper an attempt has been made for partially ionic and partially covalent compounds. The covalent and ionic contribution to energy gap has been calculated by Phillips and Van Vechten [1-3] originated by one dimensional pen gap model. In this model the average energy gap has been separated into homopolar energy gap (E_f ' _l b f crcpmnj_p cl cpew e_n &C). The homopolar energy energy gap is a function of nearest neighbor distance only [1] while heteropolar energy gap is estimated on electronegativity difference between elements of compounds.

2. Calculation of bond ionicity

According to the following relation [1-2] the average energy gap can be separated into the homopolar and heteropolar parts:

$$E_g^2 = E_h^2 + C^2 \qquad (1)$$

$$f_i = \frac{C^2}{E_g^2}, \quad f_c = \frac{E_h^2}{E_g^2} \qquad (2)$$

$$E_h = 39.74/d^{2.48} \qquad (3)$$

and

$$C = 14.4b\left[\frac{z_A}{r_A} - \frac{n}{m}\frac{z_B}{r_B}\right] e^{-k_s r_0} \qquad (4)$$

where E_g is the average energy gap of a crystal , f_i and f_c are the fractional ionicity and covalency of the bonds, d is the nearest neighbors distance (bond length) , C the heteropolar part of the average energy gap for binary compounds, b is the prescreening factor. $e^{-k_s r_0}$ the Thomas – Fermi screening factor and $r_0 = \frac{1}{2}d$. The numerical factor in equation (3) and equation (4) are given in which d is expressed in A^0 and the energy in eV. The most generalized form of the above equation has been discussed by Levine [4] in detail. The equations given by Levine reduce to those of PV when only one type of bond is present in the crystal. The physical meaning of equation (4) is that C is given by the difference between the screened coulomb potentials of atoms A and B having core charges Z_A and Z_B . These potentials are to be evaluated at the covalent radii r_0 . Only a small part of the electrons are in the bond, the rest screens the ionic cores, reducing their charge by Thomas – Fermi screening factor, $e^{-k_s r_0}$ which effects the chemical bond in a compound. This screening factor, as well as the bond length is related to the effective number of free electrons in the valence band. Thus, there must be some correlation between the physical process which involves the ionic contribution C to the average energy gap E_g and plasmon energy of a compound. Krishnan-Roy [14]. J.Jayaraman et al. [15] and Srideshmukh et al. [16] found that substationally reduced ionic charges must be used to get better agreement with experimental values. The crystal ionicity of binary tetrahedral compounds and ionic compounds exhibit a linear relationship when plotted against nearest neighbor distance but fall on three nearly straight lines which is presented in the figure 1. Using this idea for getting better agreement with the theoretical data for ionic gap (C) homopolar energy gap (E_h), total energy gap (E_g) and crystal ionicity.The homopolar energy gap (E_h) may be expressed as follows:

$$E_h = A(\omega_p)^B \qquad (5)$$

The values of A and B have been estimated considering the regressional analysis of plasmon energies of elemental semiconductors C,Si,Ge,Sn with homopolar energy estimated by Phillips[2].From which one gets A=0.448 and B=1.6609.The calculated values are given in table 17 for the comparison. This relation has been utilized in evaluating E_h in compound semiconductors (II-VI, III-V) and I-VII ionic compounds. The free electron plasmon energy (ω_p) of binary tetrahedral semiconductors and ionic compounds is given by

$$\omega_p = \frac{4\Pi N e^2}{m} \qquad (6)$$

where N is the effective number of free electrons taking part in plasma oscillation e is the charge and m is the mass of the electron. The plasmon energy can be written as

$$\omega_p = 28.8\sqrt{\frac{Z\sigma}{M}} \quad \text{(eV)} \qquad (7)$$

where Z is the effective number of valence electrons taking part in plasma oscillation, σ is the specific gravity and M is the molecular weight. ω_p is the plasmon energy of the compounds.

The ionic energy gap is estimated by the following proposed empirical relation:

$$C = Ae^{-B(\omega_P)^{-\frac{1}{3}}} \qquad (8)$$

where A and B are constants and their values are A =641.534, B =11.499 for II-VI compounds, A =313.535, B = 11.441 for III-V compounds, A =724.1767, B =10.1686 for I-VII compounds.

Using equation (1) and (2) one can calculate the total energy gap (E_g) and ionicity (f_i) of binary tetrahedral semiconductors and I-VII ionic compounds .The results are presented in table [11-13] and table [1-3]. Earlier models require the experimental values of the optical dielectric constants for the calculation of E_h, C, f_i but in current model one can predict the order of these parameters without having any knowledge of the experimental values of dielectric constants.

Conclusion

Using equation (5), (7), (8) and (2) the homopolar energy, heteropolar energy, plasmon energy and ionicity of binary tetrahedral semiconductors and ionic compounds have been estimated which is given in table 1 to table 16. Our calculated values of E_h and C for most materials agree with previous estimation. The ionicity of II-VI, III-V binary semiconductors and I-VII ionic solids has been estimated which is given in Table 1 to table 3 and corresponding graph in figure 2 and figure 3 using PVL theory.

For isoelectronic sequence the ionicities are like f_i (Ge) =0.0, f_i(GaAs) =0.347 and f_i(ZnSe) =0.673 we observe that in III-V semiconductors C is nearly less than E_h and the bond is predominantly covalent. For most II-VI and III-V crystals however, C is larger than E_h and the bonding is predominantly ionic. When the bond is sufficiently ionic i.e. f_i(AB)> F_i the crystal will have a structure in which each ion is more than four fold coordinated. Here f_i is critical or threshold ionicity for transition from a covalent Zinc blende or Wurtzite structure to ionic rock salt structure.

In this case critical ionicity is obtained as f_i=0.832. Besides this critical ionicity, it is observed the sub critical ionicity which divides II-VI semiconductor with f_i = 0.680 and III-V compounds with f_i =0.345 which is observed from the graph plotted in figure2 and figure 3.It is found that proposed relations are simpler widely applicable and values are better agreement with reported data as compared to empirical relation proposed by previous researchers. The method presented in this work will be helpful to the material scientist for finding new materials with desired ionic gap (C), average ionic gap (E_g), crystal ionicity (f_i) among the series of structurally similar materials.

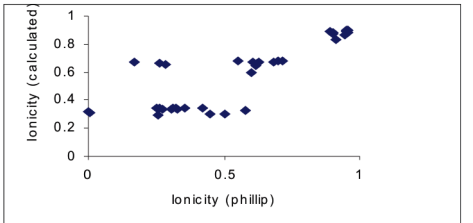

Figure 2. Plot of ionicity (calculated) versus ionicity (phillip)

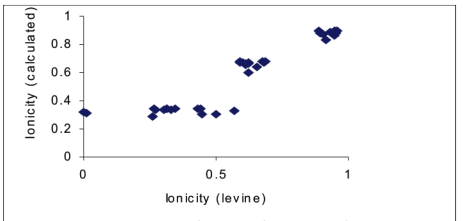

Figure 3. Plot of ionicity (calculated) versus ionicity (levine)

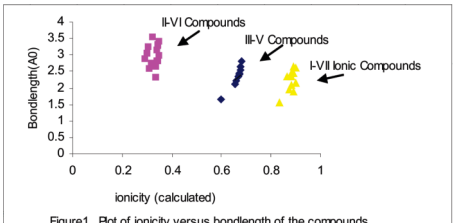

Figure1. Plot of ionicity versus bondlength of the compounds

Table 1. Ionicity of II-VI binary tetrahedral semiconductors.

Compounds	ω_p (eV)	fi Calculated	fi Phillip	fi Levine	fi Christensen
BeO	28.26	0.599	0.602	0.620	0.798
BeS	19.52	0.655	0.286	0.611	0.537
BeSe	18.39	0.661	0.261	0.610	0.420

BeTe	16.12	0.671	0.169	0.592	0.222
ZnO	21.48	0.643	0.616	0.653	
ZnS	16.71	0.668	0.623	0.621	0.764
ZnSe	15.78	0.673	0.630	0.623	0.740
ZnTe	14.76	0.676	0.609	0.599	0.560
CdS	14.88	0.675	0.685	0.649	0.794
CdSe	14.01	0.678	0.699	0.684	0.841
CdTe	13.09	0.680	0.717	0.675	0.739
MgTe	12.97	0.680	0.554	0.589	

Table2. Ionicity of III-V binary tetrahedral semiconductors

Compounds	ω_n (eV)	fi Calculated	fi Phillip	fi Levine	fi Christensen
LiF	25.96	0.382	0.915	0.914	0.9136
LiCl	17.99	0.875	0.903	0.903	0.9043
LiI	13.25	0.881	0.899	0.896	0.8944
NaCl	15.68	0.893	0.890	0.890	0.8889
NaBr	14.37	0.865	0.946	0.946	0.9462
NaI	12.79	0.884	0.935	0.936	0.9261
KF	16.83	0.889	0.934	0.933	0.9319
KCl	13.29	0.895	0.927	0.929	0.9292
KBr	12.38	0.880	0.955	0.954	0.9585
KI	11.17	0.893	0.953	0.951	0.9508
RbF	15.03	0.896	0.952	0.953	0.9522
RbCl	12.40	0.900	0.950	0.948	0.9479
RbBr	11.59	0.898	0.955	0.955	0.9583
RbI	10.53	0.901	0.957	0.954	0.9538

Table 3. Ionicity of I-VII Ionic compounds

Compounds	ω_n (eV)	fi Calculated	fi Phillip	fi Levine	fi Christensen
BN	24.75	0.291	0.256	0.261	0.383
BP	21.71	0.309	0.006	0.008	0.001
BAs	20.12	0.317	0.002	0.002	0.002
AlN	22.97	0.301	0.449	0.445	
AlP	16.65	0.337	0.307	0.303	0.421
AlAs	15.75	0.340	0.274	0.273	0.367
AlSb	13.72	0.348	0.250	0.440	0.163
GaN	21.98	0.306	0.500	0.500	
GaP	16.50	0.335	0.327	0.330	0.361
GaAs	15.35	0.341	0.310	0.313	0.310
GaSb	13.38	0.346	0.261	0.264	0.108
InN	18.82	0.325	0.578	0.569	
InP	14.76	0.343	0.421	0.432	0.534
InAs	14.07	0.345	0.357	0.347	0.553
InSb	12.73	0.348	0.321	0.315	0.303
RbBr	11.59	0.898	0.955	0.955	0.9583
RbI	10.53	0.901	0.957	0.954	0.9538

Table 4. Homopolar energy gap of II-VI binary tetrahedral semiconductors.

Compounds	ω_n (eV)	Eh Calculated	Eh Phillip	Eh Van Vechten	Eh Levine
BeO	28.26	11.5	11.5	11.5	11.5
BeS	19.52	6.23	6.31	6.3	6.31
BeSe	18.39	5.64	5.65	5.7	5.65
BeTe	16.12	4.54	4.54	4.5	4.54
ZnO	21.48	7.31	7.33	7.3	7.33
ZnS	16.71	4.82	4.8	4.81	4.82
ZnSe	15.78	4.37	4.29	4.3	4.29
ZnTe	14.76	3.41	3.59	3.6	3.59
CdS	14.88	3.47	3.97	4.0	3.47
CdSe	14.01	3.59	3.61	3.6	3.60
CdTe	13.09	3.20	3.08	3.1	3.08
MgTe	12.97	3.16	3.20	3.2	3.20

Table5. Homopolar energy gap of III-V binary tetrahedral semiconductors.

Compounds	ω_n (eV)	Eh Calculated	Eh Phillip	Eh Van Vechten	Eh Levine
BN	24.75	9.24	13.1	13.1	13.1
BP	21.71	7.43	7.44	7.4	7.44
BAs	20.12	6.55	6.55	6.6	6.55
AlN	22.97	8.17	8.17	8.2	8.17
AlP	16.65	4.78	4.72	4.7	4.72
AlAs	15.75	4.36	4.38	4.4	4.38
AlSb	13.72	3.46	3.53	3.5	3.52
GaN	21.98	7.59	7.64	7.6	7.65
GaP	16.50	4.71	4.73	4.7	4.72
GaAs	15.35	4.18	4.32	4.3	4.31
GaSb	13.38	3.32	3.55	3.5	3.55
InN	18.82	5.86	5.93	5.9	5.93
InP	14.76	3.91	3.93	3.9	3.93
InAs	14.07	3.61	3.67	3.7	3.67
InSb	12.73	3.06	3.08	3.1	3.08

Table6. Homopolar energy gap of I-VII ionic Compounds

Compounds	ω_n (eV)	Eh Calculated	Eh Van Vechten	Eh Levine
LiF	25.96	10.1	7.0	7.05
LiCl	17.99	5.44	3.8	3.84
LiBr	16.27	4.61	4.2	4.23
LiI	13.25	3.27	2.6	2.61
NaF	20.11	6.54	5.0	4.98
NaCl	15.68	4.33	3.1	3.04
NaBr	14.37	3.74	2.6	2.63
NaI	12.79	3.08	2.2	2.16
KF	16.83	4.87	3.5	3.47
KCl	13.29	3.29	2.3	2.32
KBr	12.38	2.92	2.1	2.06
KI	11.17	2.46	1.7	1.74
RbF	15.03	4.03	3.0	3.04
RbCl	12.40	2.93	2.13	2.07
RbBr	11.59	2.62	1.9	1.87
RbI	10.53	2.23	1.6	1.58

Table7. Heteropolar energy gap of II-VI binary tetrahedral semiconductors.

Compounds	ω_n (eV)	C Calculated	C Phillip	C Van Vechten	C Levine
BeO	28.26	14.10	13.9	14.1	18.28
BeS	19.52	8.59	3.99	4.0	7.13
BeSe	18.39	7.88	3.36	3.4	5.84
BeTe	16.12	6.48	2.05	2.1	3.26
ZnO	21.48	9.82	9.30	9.3	
ZnS	16.71	6.84	6.20	6.2	8.57
ZnSe	15.78	6.27	5.60	5.6	12.51
ZnTe	14.76	5.66	4.48	4.5	5.60
CdS	14.88	5.73	5.90	5.9	9.19
CdSe	14.01	5.73	5.50	5.5	8.35
CdTe	13.09	4.67	4.90	4.4	6.35
MgTe	12.97	4.61	3.58	3.6	

Table8. Heteropolar energy gap of III-V binary tetrahedral semiconductors

Compounds	ω_n (eV)	C Calculated	C Phillip	C Van Vechten	C Levine
BN	24.75	5.92	7.71	7.8	9.35
BP	21.71	4.97	0.68	0.7	0.254
BAs	20.12	4.47	0.38	0.3	0.35
AlN	22.97	5.37	7.30	7.3	
AlP	16.65	3.41	3.14	3.1	5.16
AlAs	15.75	3.13	2.67	2.7	4.50
AlSb	13.72	2.53	2.07	3.1	2.38
GaN	21.98	5.05	7.64	7.6	
GaP	16.50	3.35	3.50	3.3	5.00

GaAs	15.35	3.01	2.90	2.9	4.29
GaSb	13.38	2.42	2.10	2.1	2.08
InN	18.82	4.07	6.78	6.8	
InP	14.76	2.83	3.84	3.4	6.15
InAs	14.07	2.24	2.74	2.1	5.06
InSb	12.73	2.24	2.10	2.1	3.39

Table 9. Heteropolar energy gap of I-VII ionic Compounds

Compounds	$\hbar\omega_p$ (eV)	C Calculated	C Van Vechten	C Levine
LiF	25.96	22.5	23.0	22.9
LiCl	17.99	14.4	11.6	11.8
LiBr	16.27	12.6	9.3	9.48
LiI	13.25	9.49	7.4	7.41
NaF	20.11	16.57	20.9	20.9
NaCl	15.68	12.00	11.8	11.6
NaBr	14.37	10.63	9.8	9.81
NaI	12.79	9.02	7.8	7.83
KF	16.83	13.2	16.1	15.7
KCl	13.29	9.53	10.4	10.2
KBr	12.38	8.61	9.3	9.29
KI	11.17	7.38	7.4	7.41
RbF	15.03	11.32	13.9	13.9
RbCl	12.40	8.62	9.7	9.68
RbBr	11.59	7.81	8.9	8.65
RbI	10.53	6.74	7.1	7.16

Table10. Total energy gap of II-VI binary tetrahedral semiconductors.

Compounds	$\hbar\omega_p$ (eV)	Eg Calculated	Eg Van Vechten	Eg Levine
LiF	25.96	24.66	24.04	23.96
LiCl	17.99	15.39	12.20	12.40
LiBr	16.27	13.41	10.20	10.38
LiI	13.25	10.03	7.84	7.85
NaF	20.11	17.81	21.48	21.48
NaCl	15.68	12.75	12.21	11.99
NaBr	14.37	11.26	10.13	10.15
NaI	12.79	9.53	8.10	8.12
KF	16.83	14.06	16.47	16.07
KCl	13.29	10.08	10.65	10.46
KBr	12.38	9.09	9.53	9.51
KI	11.17	7.77	7.59	7.61
RbF	15.03	12.01	14.22	14.22
RbCl	12.40	9.10	9.93	9.89
RbBr	11.59	8.23	9.11	8.84
RbI	10.53	7.09	7.27	7.33

Table11. Total energy gap of III-V binary tetrahedral semiconductors.

Compounds	$\hbar\omega_p$ (eV)	Eg Calculated	Eg Phillip	Eg Van Vechten	Eg Levine	Eg Christensen
BeO	28.26	18.21	18.04	18.19	18.66	20.46
BeS	19.52	10.61	7.46	7.46	10.11	9.72
BeSe	18.39	9.69	6.57	6.63	9.05	9.00
BeTe	16.12	7.91	4.98	4.96	7.11	6.96
ZnO	21.48	12.24	11.84	11.82	12.47	
ZnS	16.71	8.36	7.85	7.84	7.82	9.81
ZnSe	15.78	7.64	7.05	7.06	6.98	14.53
ZnTe	14.76	6.87	5.74	5.76	5.66	7.48
CdS	14.88	6.97	7.11	7.12	7.01	10.30
CdSe	14.01	6.32	6.57	6.57	6.41	9.10
CdTe	13.09	5.66	5.78	5.38	5.39	7.38
MgTe	12.97	5.88	4.80	4.81	4.99	

Table12. Total energy gap of I-VII ionic Compounds

Compounds	$\hbar\omega_p$ (eV)	Eg Calculated	Eg Phillip	Eg Van Vechten	Eg Levine	Eg Christensen
BN	24.75	10.97	15.21	15.24	15.26	15.11
BP	21.71	8.93	7.47	7.43	7.62	8.71
BAs	20.12	7.92	6.56	6.60	6.84	8.33
AlN	22.97	9.77	10.95	10.97	10.96	
AlP	16.65	5.87	5.66	5.63	6.03	7.94
AlAs	15.75	5.36	5.12	5.16	5.81	7.41
AlSb	13.72	4.28	4.09	4.67	4.67	6.81
GaN	21.98	9.11	10.80	10.74	10.81	
GaP	16.50	5.77	5.76	5.74	6.38	8.32
GaAs	15.35	5.15	5.20	5.18	5.21	7.7
GaSb	13.38	4.10	4.12	4.08	4.13	6.31
InN	18.82	7.13	9.00	9.01	8.38	
InP	14.76	7.13	5.15	5.17	5.16	8.37
InAs	14.07	4.82	4.58	4.58	4.58	6.81
InSb	12.73	4.46	3.72	3.74	3.74	6.14

Table 13.Plasmon energy of III-V Compounds

Compounds	Mol.Wt Ref.[17,18]	Density Ref.[17,18]	Bond length Ref.[17,18]	$\hbar\omega_p$ (eV)
BN	24.82	3.49	1.565	24.75
BP	41.78	2.9	1.965	21.71
BAs	85.73	5.23	2.068	20.12
AlN	40.99	3.26	1.892	22.97
AlP	57.95	2.42	2.360	16.65
AlAs	101.90	3.81	2.433	15.75
AlSb	148.73	4.218	2.656	13.72
GaN	83.73	6.10	1.94	21.98
GaP	100.69	4.13	2.360	16.50
GaAs	144.64	5.316	2.450	15.35
GaSb	191.47	5.618	2.649	13.38
InN	128.83	6.88	2.154	18.82
InP	145.79	4.787	2.154	14.76
InAs	189.74	5.66	2.614	14.07
InSb	236.57	5.775	2.805	12.73

Table 14. Plasmon energy of II-VI Compounds

Compounds	Mol.Wt Ref.[17,18]	Density Ref.[17,18]	Bond length Ref.[17,18]	$\hbar\omega_p$ (eV)
BeO	25.01	3.01	1.65	28.26
BeS	41.08	2.36	2.10	19.52
BeSe	87.97	4.315	2.20	18.39
BeTe	136.61	5.09	2.40	16.12
ZnO	81.37	5.66		21.48
ZnS	97.43	4.1	2.34	16.71
ZnSe	144.34	5.42	2.45	15.78
ZnTe	192.99	6.34	2.64	14.76
CdS	144.46	4.82	2.53	14.88
CdSe	191.36	5.66	2.63	14.01
CdTe	240.00	5.86	2.81	13.09
MgTe	151.9	3.85		12.97

Table 15. Plasmon energy of I-VII Ionic compounds

Compounds	Mol.Wt Ref.[17,18]	Density Ref.[17,18]	Bond length Ref.[17,18]	$\hbar\omega_p$ (eV)
LiF	25.93	2.635	2.87	25.96
LiCl	42.39	2.068	2.57	17.99
LiI	133.84	3.494	3.032	13.25
NaCl	58.44	2.165	2.81	15.68
NaBr	102.89	3.203	2.97	14.37
NaI	149.89	3.667	3.23	12.79
KF	58.10	2.480	2.66	16.83
KCl	74.55	1.984	3.14	13.29
KBr	119.00	2.750	3.29	12.38

KI	166.00	3.130	3.53	11.17
RbF	104.46	3.557	2.82	15.03
RbCl	120.92	2.800	3.27	12.40
RbBr	165.37	3.350	3.42	11.59
RbI	212.34	3.550	3.66	10.53

Table 16. Plasmon energy of elemental semiconductors

Elements	At.Wt.	Density	Bond length(A^0)	Plasmon energy
C	12.01	3.52	1.54	31.2
Si	28.086	2.329	2.35	16.5
Ge	72.59	5.3234	2.45	15.6
Sn	118.69	7.030	2.84	12.7

Table 17. Homopolar energy of elemental semiconductors.

Elements	Plasmon energy	E_h (cal)	E_h (Philip)	E_h(Christensen)
C	31.2	13.5	13.5	13.31
Si	16.5	4.71	4.77	6.82
Ge	15.6	4.29	4.31	6.38
Sn	12.7	3.05	3.01	5.18

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