



Analysis of fractional ionic character and Ionic radii for polyatomic binary compounds

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Abstract

For investigating the nature of chemical bond, ionicity parameters and fractional ionic character parameters for polyatomic binary compounds, we have extended our knowledge from diatomic to polyatomic compounds. For calculating the values of fractional ionic character and other related parameters for polyatomic compounds the energy gap parameters E_g has been calculated. The values ionicity parameters have been obtained using the revised energy gap model due to Grimes and Cowley. Values of fractional ionic character parameters of the chemical bond are calculated for the A_2B , A_3B , AB_2 , A_3B_2 , AB_3 and A_2B_3 type polyatomic solids. In case of diatomic compounds these parameters are calculated from dielectric data. But for polyatomic compounds such data are not available. In present study we have calculated such parameters by using their universal relationship between interionic separations for the diatomic solids. The relation between fractional ionic parameters and ionic radii has also been investigated. In most cases the linear relationship between f_i and radius ratio r_c/r_a for diatomic as well as for polyatomic solids have played very useful role in understanding the relative stability for crystal structure.

Key Words :- Ionicity parameters, fractional ionic character, Energy gap parameters, polyatomic compounds

1. Introduction:-

The microscopic dielectric function of a solid plays the central role in the calculation of any property of the solid influenced by the screening effects of the valence and conduction electrons. Only for a small number of semiconductors, the detailed calculations have been made [1] by incorporating explicit knowledge of band structures of the particular material. In the absence of such knowledge of band structure Penn [2] derived a set of formulae based on an isotropic nearly free electron model for the energy bands. The work Penn was extended by Srinivasan [3]. However the model adopted by Penn as well as by Srinivasan was so complicated that the dielectric function could not be evaluated analytically. They obtained approximate expressions for the dielectric function after introducing several simplification specially the square matrix elements were replaced by interpolation formula chosen to reproduce the zero and long wave vector values and energies near the zone boundary were replaced by constant values rather than approximate expression. Grimes and Cowley [4] have rectified these shortcomings by evaluating the sum directly as integrals over the spherical Brillouin zone. Results thus obtained are sufficiently accurate at small, intermediate and large wave vectors. The modified expression for the energy gap between bonding and antibonding states obtained by Grimes and Cowley is physically more plausible and consistent with experimental data and pseudo potential calculations. Phillips and Van –

Vechten [6-7] have developed a compressive theory of ionicity of chemical bonding in binary solids using the revised energy gap expression originally due to Penn . In view of the modifications discussed above it become desirable to revise the calculations of Phillips and Van –Vechten for ionicity parameters. The studies of energy gap model and ionicity parameters have been the subject of current interest [8-10].In the present study we use the modified energy gap expression as obtained by Grimes and Cowley in order to revise the estimate of ionicity parameters due to Phillips . The revised values of ionicity parameters thus obtained for $A^N B^{8-N}$ type polyatomic solids depends on radius ratio in the same manner as they found in case of diatomic solids.

2. Method of Analysis

The energy gap E_g can be split in to an ionic (heteropolar) part ‘C’ and Covalent (homopolar) E_h such that [6]

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

The homopolar part E_h has been taken to depend universally on interionic separation R as

$$E_h = A R^{-k} \quad (2)$$

Here we have revised values of $A = 54.0$ J and $k = 2.52$ given by Grimes and Cowley [4] .The constant A and k were considered by Phillips and Van-Vechten to be universally constants for different crystals which were $A = 63.58$ and $k=2.48$. Values of E_h for polyatomic compounds can therefore be calculated with the help of equation (1) by taking appropriate values of R . The lattice parameters or interionic separation can be divided in to two parts by introducing the concepts of ionic radii such that

$$R = r_+ + r_- \quad (3)$$

Where R is the nearest neighbor interionic separation and r_+ (r_-) the radii of cation (anion) . In writing equation (3) it has been assumed that the ions are spherical and touching each other and this equation has been used by traditional workers [11-15] in addition to one more criteria relation to the radius ratio (r_+/r_-) with the ratio of polarizabilities of effective nuclear charge of ions . The electron density measurements [12] also reveal that ions are nearly spherical and one can make use of equation 930 to obtain additive radii characteristics of ions. It is evident that ionic radii estimated by traditional workers deviate significantly from corresponding values based on electron density measurements. These deviations have been explained by Tosi [3] in terms of Fagan’s rule for losing effect of cations and the tightening effect of anions in the crystalline state relative to the Free state. The ionic radii can also be related to the effective nuclear charge as

$$r_{+-} = [C_n / (Z-S)_{+-}] \quad (4)$$

Where C_n is a constant depending on the number of electrons in the ion. C_n is same for a sequence of isoelectronic ions. S is the size screening parameter. Z is the nuclear charge (Z-S) is then known as effective nuclear charge and + and – subscripts for cation and anion respectively.

Using Pauli’s relation values of C_n , the values of S can be calculated .When equation (4) is applied to a pair of isoelectronic ions yields

$$(r_+/r_-) = [(Z-S)_- / (Z-S)_+] \quad (5)$$

Equation (3) and (5) can be used to calculate radii taking experimental values of interionic separation in crystals composed of isoelectronic ions. Values of size screening parameters S have been taken to be the same as those for the corresponding isoelectronic alkali or halogen ions. Values of radii thus calculated for divalent and trivalent ions are given in table -1. The

radii for several other divalent and trivalent ions have also been deduced using the additivity rule (3) and experimental values of the lattice parameters for II-VI and III-V crystals, these values also included in Table -1.

For calculating the ionic (heteropolar) part C of the energy gap E_g we have to investigate the nature of dependence of C on R in diatomic compounds for which values of C have already been determined. For doing this we first plot 'ln C' versus 'ln R' for I-VII,II-VI and III-V diatomic crystals. These plots (Figures 1-3) are linear and systematic. They are cation dependent i.e. compounds with the same cations lie on the same line. In fact we can write the following relationship

$$C = BR^{-t}$$

(6)

Where 'B' and 't' are constant for given cation. Values of B and t for various cation are given in table -2. The values of B and t thus derived have been used to predict the values of heteropolar energy 'C' for polyatomic compounds with corresponding cations. Values of heteropolar energy 'C' derived from (6) and values of homopolar energy from equation (2) are used to obtain the values of energy gap E_g using equation (1). Calculated values of 'C', E_g and E_h are reported in Table -3

The ionicity of chemical bonds is defined in terms of fractional ionic character as given below

$$f_i = [C^2 / E_g^2] \quad (7)$$

The values obtained from equations (1) and (6) can be used to calculate the values of fractional ionic character which are reported in Table -3.

3. Result and Discussion

One of the most fundamental questions in the field of solid state physics is why a given solid crystallizes in a particular structure. In fact many important phenomena such as magnetism, superconductivity, ferroelectricity tend to occur in a definite structure and to be absent in other structures. The splitting of energy gap (E_g) into ionic (heteropolar) C and covalent (homopolar) E_h parts is made in a symmetrical manner (Equation -1) and it has been found that the values of fractional ionic character parameter can provide a criteria for distinguishing between the crystal structures with different coordination numbers. Thus the fractional character parameter f_i is an important parameter related to various crystalline state properties discussed by Phillips[6]. Here we have investigated a particular useful relation between fractional ionic character f_i and radius ratio of cation and anion r_+/r_- in table -4 in case of diatomic (I-VII),(II-VI) and (III-V) as well as for polyatomic binary compounds. In most of the cases the linear relationships are found [18-21]. We have plotted some figures for polyatomic compounds. It is interesting to mention here that the parameters f_i and r_c/r_a have played a very useful role in understanding the relative stability of the crystal structure. The values of f_i in polyatomic solids depend on the radius ratio in the same manner as they depend in case of diatomic solids [19-20]. This provides a support for the values of f_i calculated in the present study. It is the question to be investigated whether for the present study a distinction could be made between the four fold and six fold coordinated structures by using the concept for fractional ionic character as it has been made for the diatomic solids [14-16].

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Table-1Values of additive radii (in 10^{-1} nm) for ions

Cations	r_+	anions	r.	Cations	r_+	anions	r.	Cations	r_+	anions	r.
Li ⁺	0.93	F ⁻	1.13	Be ²⁺	0.43	O ²⁻	1.22	Ba ³⁺	1.54	P ³⁺	1.75
Na ⁺	1.18	Cl ⁻	1.63	Mg ²⁺	0.88	S ²⁻	1.67	B ³⁺	0.25	As ³⁺	1.83
K ⁺	1.51	Br ⁻	1.80	Ca ²⁺	1.16	Se ²⁻	1.80	Al ³⁺	0.60	Sb ³⁺	2.06
Rb ⁺	1.61	I ⁻	2.85	Zn ²⁺	0.69	Te ²⁻	1.96	Ga ³⁺	0.62		
Cs ⁺	1.90	---	----	Cd ²⁺	1.31	N ³⁻	1.26	In ³⁺	0.80		

Table -2

Values of constant 'B' and 't' for various cations calculated from the figures [1-3]

Cations	B (In Joules)	t
Li	270.5	3.00
Na	407.5	3.10
K	365.4	2.80
Rd	380.4	2.80
Cs	148.5	2.00
Be	607.9	3.36
Mg	230.5	3.31
Ca	252.2	3.14
Sr	275.9	2.67
Ba	176.0	5.09
Cd	934.5	2.62
Zn	781.3	4.73
Al	219.3	4.73
Ga	219.3	4.73
In	219.3	4.73

Table -3Calculated Values of ionicity parameters C, E_h and Energy gap E_g , f_i and radii ratio r_c/r_a

Crystal	C (10^{-19} J)	E_g (10^{-19} J)	E_h (10^{-19} J)	f_i	r_c/r_a
Li ₂ O	33.81	9.41	35.10	0.928	0.762
Li ₂ S	17.73	5.47	14.55	0.914	0.557
Li ₂ Se	15.39	4.86	16.14	0.909	0.517
Li ₂ Te	12.06	3.96	12.69	0.903	0.474
Na ₂ O	26.66	5.88	27.30	0.954	0.967
Na ₂ S	16.38	3.96	16.85	0.945	0.707
Na ₂ Se	14.25	3.54	14.68	0.942	0.656
Na ₂ Te	11.40	2.95	11.78	0.937	0.602
K ₂ O	20.66	4.07	21.06	0.962	1.238
K ₂ S	14.07	2.88	14.36	0.960	0.904
K ₂ Se	12.59	2.61	12.86	0.958	0.839
K ₂ Te	10.61	2.23	10.84	0.954	0.770
Rb ₂ O	18.91	3.63	19.36	0.964	1.344
Rb ₂ S	13.20	2.62	13.46	0.962	0.982
Rb ₂ Se	11.95	2.40	12.19	0.961	0.911
Rb ₂ Te	10.52	2.14	10.74	0.959	0.837

Cs ₂ O	15.26	3.07	15.57	0.961	1.557
Cs ₂ S	11.65	2.19	11.85	0.967	1.138
Cs ₂ Se	10.85	2.00	11.03	0.968	1.056
Cs ₂ Te	9.97	1.80	10.13	0.969	0.9693
Li ₃ N	25.75	7.49	26.82	0.922	0.768
Li ₃ P	17.31	5.37	18.12	0.913	0.531
Li ₃ AS	15.57	4.91	16.13	0.909	0.538
Li ₃ Sb	12.59	4.11	13.24	0.904	0.451
Na ₃ N	25.66	5.70	26.29	0.953	0.937
Na ₃ P	15.51	3.79	15.97	0.943	0.674
Na ₃ As	14.40	2.57	14.48	0.942	0.645
Na ₂ Sb	12.22	3.12	12.61	0.939	0.573
K ₃ N	21.08	4.14	21.18	0.963	1.198
K ₃ P	13.36	2.75	13.48	0.959	0.863
K ₃ AS	12.49	2.59	12.76	0.958	0.825
K ₃ Sb	11.13	2.33	11.37	0.957	0.733
Rb ₃ N	47.60	8.33	48.32	0.970	1.302
Rb ₃ P	12.45	2.49	12.70	0.961	0.937
Rb ₃ As	11.66	2.35	11.89	0.962	0.896
Rb ₃ Sb	9.75	2.00	9.95	0.960	0.796
BeF ₂	35.94	17.60	10.02	0.806	0.381
BeCl ₂	6.13	8.74	10.68	0.329	0.264
BeBr ₂	3.71	7.16	8.06	0.212	0.239
BeI ₂	1.88	5.47	5.78	0.106	0.210
MgF ₂	21.11	8.96	23.54	0.855	0.779
MgCl ₂	10.54	5.15	11.73	0.807	0.540
MgBr ₂	8.61	4.42	9.68	0.791	0.489
MgI ₂	6.49	3.57	7.41	0.767	0.429
Be ₃ N ₂	20.04	13.97	24.43	0.676	0.341
Be ₃ P ₂	4.54	7.75	8.98	0.256	0.246
Be ₂ AS ₂	3.40	6.92	7.71	0.194	0.235
Be ₃ Sb ₂	1.84	5.42	5.72	0.103	0.209
Mg ₃ N ₂	19.16	8.13	50.81	0.848	0.698
Mg ₃ P ₂	10.40	5.10	11.58	0.807	0.503
Mg ₂ AS ₂	9.51	4.77	10.64	0.799	0.181
Mg ₃ Sb ₂	7.45	3.96	8.44	0.799	0.427
AlF ₃	10.80	10.86	15.32	0.497	0.531
AlCl ₃	4.01	6.40	7.55	0.282	0.368
AlBr ₃	3.49	5.95	6.90	0.256	0.333
AlI ₃	2.18	4.63	5.12	0.181	0.293
GaF ₃	15.54	13.18	20.18	0.581	0.549
GaCl ₃	4.73	7.00	8.45	0.313	0.380
GaBr ₃	3.35	5.82	6.72	0.249	0.344
GaI ₃	2.11	4.55	5.02	0.177	0.302
InF ₃	1.36	3.60	3.85	0.125	0.708
InCl ₃	3.29	5.76	6.63	0.156	0.491
InBr ₃	2.29	4.86	5.42	0.194	0.444
InI ₃	1.55	3.86	4.16	0.139	0.390
Al ₂ O ₃	9.54	10.17	13.94	0.468	0.492

Al ₂ S ₃	4.54	6.84	8.23	0.306	0.359
Al ₂ Se ₃	3.49	5.95	6.90	0.256	0.333
Al ₂ Te ₃	2.57	5.05	8.67	0.205	0.306
Ga ₂ O ₃	9.09	9.91	16.45	0.457	0.508
Ga ₂ S ₃	4.36	6.69	7.99	0.298	0.371
Ga ₂ Se ₃	3.35	5.82	6.72	0.249	0.344
Ga ₂ Te ₃	2.48	4.96	5.55	0.200	0.316
In ₂ O ₃	5.87	7.85	9.80	0.359	0.656
In ₂ S ₃	3.04	5.53	6.31	0.232	0.479
In ₂ Se ₃	2.39	7.86	5.42	0.194	0.444
In ₂ Te ₃	1.80	4.18	4.55	0.152	0.388

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