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Analysis of Photoelastic behavior of $A^N B^{8-N}$ Type Binary Solids Using Ionicity Parameters

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Abstract

The strain derivatives of electronic dielectric constant are related to the Photoelastic behavior of Solids, have been studied with the help of iconicity parameters for binary Solids .Values of iconicity parameters have been obtained using revised energy gap model due to Grimes and Cowley. We have used a power law as well as exponential law for representing the dependence of homopolar energies on interionic distances. Values of fractional ionic character of the chemical bond have also been calculated for $A^N B^{8-N}$ type Binary Solids and the same has related to the Photoelastic behavior for the $A^N B^{8-N}$ type Binary Crystals.

Key Words:-Binary Crystals, Electronic dielectric constant, Photoelastic behavior .Ionicity parameter, Energy gap model.

.Introduction:-

The Photoelastic effect is related to the variation of refractive index or electronic dielectric constant of Solids under hydrostatic pressure. A theoretical analysis of this effect requires the strain derivatives pf electronic polarizabilities which are not easily deductible from the sophisticated polarization models [1-3].Even the theoretical approaches suggested in the past have been studied indirectly and can not be extended in a straight forward manner to include other families of crystals. 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 valance and conduction electrons. Only for small semiconductors, detailed calculation haven made by incorporating explicit knowledge of band structure of the particular material. In the absence of such knowledge Penn [2] derived a set of formulas based on an isotropic nearly free electron model for the energy bands The work Penn was extended by Sriniwasan [3]. However the model adopted by Penn as well as by Sriniwasan 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 Brillonin 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 iconicity 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 iconicity parameters. The studies of energy gap model and iconicity parameters have been the subject of current interest [8-10].In the present study we use modified energy gap expression as derived by Grimes and Cowley in order to revise the estimates of ionicity parameters due to Phillips .The revised values of ionicity parameters thus obtained for $A^N B^{8-N}$ type diatomic Solids are shown exhibit systematic relationships with interionic separations. The strain derivatives of electronic dielectric constant related to the Photoelastic behavior of Solids [13] are also studied with the help of ionicity parameters. The ionicity parameters are found to correlate well with the Photoelastic strain polarizabilty parameters.

Method of Analysis:-

The modified expression for energy gap between bonding and anti bonding states evaluated numerically has been found

$$\epsilon_\infty - 1 = \left(\frac{\hbar\, \omega_p}{E_g} \right) S_0 \qquad (1)$$

Where ϵ_∞ is the electronic constant, E_g is the average energy gap between bonding and antibonding states and ω_p is the plasma frequency which is given by

$$\omega_p^2 = \left(\frac{4\pi N e^2}{m} \right) \qquad (2)$$

Here ‘e’ and ‘m; are the electronic charge and mass respectively .N is the number of valance electrons per unit volume. In the original Penn model , the factor S_0 is taken nearly equal to unity. However, more accurate calculations performed Grimes and Cowley by taking $S_0 = 0.62$.This value of S_0 modifies the earlier estimates of ionicity parameters. The Energy gap E_g can be split in to an ionic (Heteropolar) part C and Covalent (Homopolar) part E_h such that

$$E^2_g = E^2_h + C^2 \qquad (3)$$

The Photoelastic behavior i.e. Volume derivatives of electronic dielectric constant can be studied using the Phillips –Van Vechten theory. Here we used the revised Penn Gap model due to Grimes and Cowley i.e. equation (1) to find the volume derivatives or interionic separation R of electronic dielectric constant. Differentiating equation (1) with respect to volume or interionic separation R, assuming S_0 remains constant.

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$$\frac{V}{\epsilon_\infty}\left(\frac{d\,\epsilon_\infty}{dV}\right)_{S_0} = \frac{R}{3\epsilon_\infty}\left(\frac{d\,\epsilon_\infty}{dR}\right)_{S_0} = \frac{2\,(\epsilon_\infty - 1)}{\epsilon_\infty}\left[\frac{R}{\omega_p}\left(\frac{d\,\omega_p}{dR}\right) - \frac{E_h^2}{E_g^2}\,\frac{R}{E_h}\left(\frac{d\,E_h}{dR}\right) - \frac{C^2}{E_g^2}\,\frac{R}{C}\left(\frac{d\,C}{dR}\right)\right] \quad (4)$$

In deriving equation (4) ,equation (3) has been used for energy gap. Thus equation (4) is based on the Phillips-Van Vechten dielectric theory and the modified Penn energy gap model. Equation (4) provides a method for studying the Photoelastic behavior since the volume derivative of electronic dielectric constant ϵ_∞ is related to the Photoelastic constant p_{11} and p_{12} of the material as follows

$$\frac{V}{\epsilon_\infty}\left(\frac{d\,\epsilon_\infty}{dV}\right) = \frac{\epsilon_\infty\,(p_{11} + 2p_{12})}{3} \quad (5)$$

The constant p_{11} and p_{12} are also known as piezo –optic or elasto –optic coefficients.

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

$$E_h = A\,R^{-k} \quad (6)$$

Where A and k are the constants i.e. remain unchanged in different Solids 'R' is the interatomic separation. The parameters A and k are then evaluated by applying equation (3) and (6) to purely covalent Solids viz. diamond and silicon which have heteropolar energy C = 0 and therefore $E_g = E_h$ .For diamond $\epsilon_\infty = 5.7$ and $R=1.54\ A^0$ whereas for silicon $\epsilon_\infty = 12.0$ and $R= 2.34\ A^0$ Here we have revised values of $A = 54.0 \times 10^{-19} J(A^0)$ 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 Solids which were $A = 63.58 \times 10^{-19} J\ (A^0)$ and k=2.48 .The parameter A and k are the evaluated by applying equation Values of E_h for binary Solids can therefore be calculated with the help of equation (6) 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

$$R = r_+ + r_- \quad (7)$$

Where R is the nearest neighbor interionic separation and r_+ (r_-) the radii of cation (anion). The terms appearing on right hand side of equation (4) can be evaluated as follows

$$\frac{R}{\omega_p}\left(\frac{d\,\omega_p}{dR}\right) = -1.5 \quad (8)$$

$$E_h^2 / E^2_g = 1 - f_i \ , \quad ; \quad C^2 / E^2_g = f_i \qquad (9)$$

From equation (4)

$$\frac{R}{E_h}\left(\frac{d E_h}{dR}\right) = -2.52 \qquad (10)$$

Equation n(8) follows grom the fact ω^2_p is proportional to V^{-1} or R^{-3} , so that ω_p is proportional to $R^{-1.5}$. equation (3) and (6) are written in the form of (9) and (10) . equation (10) follows from equation (4) . Equation (8), (9) and 910) when substituted in equation (4) yields

$$\frac{V}{\epsilon_\infty}\left(\frac{d\epsilon_\infty}{dV}\right) = \frac{R}{3\epsilon_\infty}\left(\frac{d\epsilon_\infty}{dR}\right) = \frac{2(\epsilon_\infty - 1)}{\epsilon_\infty}\left[2.52(1-f_i) - 1.5 - f_i\frac{R}{C}\left(\frac{dC}{dR}\right)\right] \qquad (11)$$

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 phenomenon such as magnetism, superconductivity, ferroelectricity tends to occur in a definite structure and to be absent in other structure .The splitting of energy gap (E_g) in to ionic (heteropolar) C and covalent (homopolar) E_h parts is made in a symmetrical manner (Equation -4) and it has 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].The critical values of ionicity parameter f_i is found to be equal to 0.787.The Solids with f_i smaller than 0.787 have the coordination number equal to four. This result has been verified by the power laws as well as exponential law .

The Photoelastic behavior of Solids can be studied with the help of equation (8 to 11) .Photoelastic effect in crystals have been the subject of much experimental and theoretical investigation [13,20-21]. Virtually all theoretical approaches have begun by considering alkali halides solids which were to be totally ionic. Hence the model for independently polarizable ions based on the Claussius –Mossotti relation and Lorentz and Lorentz relation has been used to study the Photoelastic behavior. This model becomes comparable with the experimental phtoelastic data on ionic solids such as alkali halides when the strain polarizabilities effects are taken in to consideration [22,23]. The Classius –Mossotti model yields the following relationship

$$\frac{V}{\epsilon_\infty}\left(\frac{d\epsilon_\infty}{dV}\right) = \frac{(\epsilon_\infty - 1)(\epsilon_\infty - 2)}{3\epsilon_\infty}(1-\lambda) \qquad (12)$$

Where λ is the strain polarizability parameter related to the volume derivative of the electronic polarizabilty (α) per ion pair

$$\lambda = (V/\alpha)(d\alpha/dV) \qquad (13)$$

We have considered some diatomic compounds of I-VII,II-VI and III-V types for which the experimental data of photoelastic constants p_{11} and p_{12} are available [24-26]. The values of (V/ ϵ_∞) (d ϵ_∞/dV) calculated from equation (5) are given in Table -2 along with the values of λ derived from equation (12). For II-VI and III-V compounds the strain polarizabilty parameter λ is grater than 1 and for I-VII compound λ is smaller than 1 . The electronic dielectric const ant (ϵ_∞) decreases with the decrease in volume or with increase in pressure for II-VI and III-V compounds where α increasers with the increase in pressure for I-VII compounds. On the basis of polarizabilty model, one can explain this distinct behavior of solids in terms of electronic polarizabilities of monovalent and multivalent ions . The strain effect of polarizabilities for divalent and trivalent ions contributing towards Photoelastic effects are substantially larger than those for monovalent ions . in Phillips van-Vechten dielectric theory of chemical bonding the concept of strain polarizabilty parameter is replaced by that of the strain derivatives hetropolar ionic nergy C ,i.e. (R/C)(dC/dR) appearing in equation (11) . The values of Photoelastic parameter (V/ ϵ_∞) (d ϵ_∞/dV) are calculated by equation (11) using the values of (R/C)(dC/dR) and reported in table -2. The values of Photoelastic coefficients are also calculated by using equation (5) and equation (12) and also reported in Table -2. From the comparative study of Photoelastic coefficients reported in table -2 ,it is found that the values of the parameter (V/ ϵ_∞) (d ϵ_∞/dV) are nearly same. From present study it is concluded that the Photoelastic parameters can easily be calculated by ionicity parameters as the values of polarizabilty λ and the values of elastic coefficients $p_{11}+ 2p_{12}$ are available easily in the literature.

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TABLE-1

Input data for the calculation of volume derivatives of electronic dielectric consent i.e. Photoelastic behavior for the $A^N B^{8-N}$ type Binary Cristals.

Crystals	Structure (CN)	R (A^0)	ε_∞	E_g (10^{-19}J)	E_h (10^{-19}J)		C (10^{-19}J)		f_i	
					(a)	(b)	(a)	(b)	(a)	(b)
LiF	NaCl (6)	2.01	1.93	34.1	9.30	9.79	32.8	12.6	0.926	0.917
LiCl	NaCl (6)	2.57	2.75	17.2	5.00	4.67	16.4	16.3	0.915	0.926
LiBr	NaCl (6)	2.75	3.16	14.0	4.22	3.69	13.3	13.5	0.909	0.930
LiI	NaCl (6)	3.09	3.80	10.8	3.39	2.65	10.2	10.4	0.991	0.939
NaF	NaCl (6)	2.31	1.74	31.0	6.55	6.59	30.3	30.3	0.955	0.955
NaC1	NaCl (6)	2.81	2.33	17.2	4.00	3.41	16.8	16.5	0.946	0.961
NaBr	NaCl (6)	2.98	3.60	14.4	3.45	2.72	14.0	14.1	0.943	0.961
NaI	NaCl (6)	3.23	3.01	11.4	2.81	1.96	11.0	11.2	0.939	0.970
KF	NaCl (6)	2.64	1.85	23.7	4.68	4.26	23.2	23.3	0.961	0.968
KCl	NaCl (6)	3.14	2.17	15.6	3.02	2.20	13.3	15.4	0.962	0.980

KBr	NaCl (6)	3.31	2.36	13.3	2.65	1.76	13.1	13.2	0.961	0.983
KI	NaCl (6)	3.56	2.65	10.9	2.20	1.27	10.6	10.8	0.959	0.986
RbF	NaCl (6)	2.77	1.93	21.1	4.14	3.59	20.6	20.7	0.961	0.971
RbC1	NaCl (6)	3.27	2.18	14.6	2.73	1.86	14.3	14.5	0.965	0.984
RbBr	NaCl (6)	3.44	2.34	12.2	2.40	1.48	12.4	12.6	0.964	0.986
RbI	NaCl (6)	2.69	2.58	10.5	2.01	1.07	10.3	10.5	0.963	0.990
CsF	NaCl (6)	3.03	2.16	18.8	3.30	2.35	18.5	18.6	0.969	0.982
CsC1	CsCl(8)	3.57	2.63	12.4	2.19	1.25	12.2	12.3	0.968	0.990
CsBr	CsCl(8)	3.70	2.78	11.2	2.00	1.05	11.4	11.2	0.969	0.991
CSI	CsCl(8)	3.95	3.05	9.56	1.69	0.76	9.41	9.52	0.781	0.738
CuF	Zb(4)	1.85	2.50	24.5	11.5	12.4	21.6	21.3	0.762	0.764
Cuci	Zb(4)	2.35	3.65	12.10	6.27	6.25	11.2	11.2	0.762	0.754
CuBr	Zb(4)	2.46	4.40	10.9	5.59	5.40	9.36	9.47	0.737	0.728
CUI	Zb(4)	2.62	5.50	8.38	4.77	4.38	6.9	2.15	0.677	0.968
AgF	NaCl (6)	2.46	2.90	17.6	5.59	5.40	16.7	16.8	0.899	0.902
AgCl	NaCl (6)	2.77	4.15	11.4	4.14	3.59	10.7	10.0	0.869	0.902
AgBr	NaCl (6)	2.89	5.00	9.53	2.72	3.06	8.77	9.02	0.847	0.897
AgI	Zb (4)	2.80	5.90	7.27	4.03	3.45	6.05	6.4	0.693	0.775
Beo	Wu (4)	1.64	3.00	31.5	15.5	16.0	27.4	27.2	0.757	0.744
Bes	Zb (4)	2.10	7.10	10.0	8.33	8.69	5.68	5.02	0.312	0.250
Bese	Zb (4)	2.20	8.50	8.44	7.40	7.62	4.05	3.64	0.231	0.186
BeTe	Zb(4)	2.41	11.6	6.19	5.88	5.77	1.93	2.24	0.097	0.830
MgO	NaCl (6)	2.10	2.95	22.0	8.33	8.69	20.4	20.2	0.857	0.844
MgS	NaCl (6)	2.60	5.10	11.0	4.86	4.49	9.90	10.1	0.806	0.834
MgSe	NaCl (6)	2.73	5.90	9.38	4.30	3.78	8.33	8.58	0.790	0.837
MgTe	WU (4)	2.75	7.00	6.09	4.22	3.69	5.70	6.06	0.646	0.730
CaO	NaCl (6)	2.40	3.33	16.5	5.95	5.85	15.4	15.4	0.870	0.874
CaS	NaCl (6)	2.84	4.50	10.5	3.89	3.27	9.70	9.93	0.862	0.902
CaSe	NaCl (6)	2.96	5.10	9.08	3.54	2.29	8.37	8.64	0.851	0.905
CaTe	NaCl (6)	3.17	6.30	7.20	2.95	2.12	6.57	6.89	0.832	0.914
SrO	NaCl (6)	2.57	3.30	15.0	5.00	4.67	14.1	14.2	0.888	0.903
SrS	NaCl (6)	2.94	4.40	10.1	3.57	2.87	9.42	9.65	0.875	0.919
SrSe	NaCl (6)	3.12	4.90	8.60	3.07	2.26	8.04	8.30	0.873	0.931
SrTe	NaCl (6)	3.24	5.80	7.33	2.79	1.93	6.77	7.07	0.855	0.907
BaO	NaCl (6)	2.75	3.00	12.0	4.18	3.64	11.2	11.4	0.878	0.942
BaS	NaCl (6)	3.18	7.10	8.65	2.93	2.09	8.14	8.39	0.886	0.947
BaSe	NaCl (6)	3.31	7.30	7.63	2.65	1.76	7.16	7.43	0.880	0.956
BaTe	NaCl (6)	3.56	11.6	6.52	2.30	1.37	6.10	6.37	0.876	0.874
ZnO	Wu(4)	1.95	3.75	16.2	10.0	10.6	12.8	12.3	0.618	0.574

ZnS	Zb(4)	2.36	5.20	10.2	6.20	6.17	8.04	8.06	0.627	0.631
ZnSe	Zb(4)	2.45	5.90	8.89	5.65	5.48	6.86	7.00	0.596	0.620
ZnTe	Zb(4)	2.63	7.30	7.05	4.72	4.32	5.23	5.57	0.551	0.624
CdO	NaCl (6)	2.35	4.63	13.6	13.6	6.25	12.1	12.1	0.789	0.79
CdS	Wu(4)	2.52	5.20	9.69	9.69	4.99	8.14	8.30	0.706	0.734
CdSe	Wu(4)	2.62	6.10	7.82	7.82	4.38	6.20	6.48	0.628	0.687
CdTe	Zb(4)	2.78	7.30	6.48	6.48	3.54	5.02	5.43	0.599	0.701
AlN	Wu(4)	1.86	4.80	15.3	15.3	11.9	10.2	9.50	0.451	0.388
AlP	Zb(4)	2.35	8.50	7.65	7.65	6.25	4.37	4.41	0.327	0.332
AlAs	Zb(4)	2.43	10.3	6.53	6.53	5.62	3.07	3.32	0.221	0.258
AlSb	Zb(4)	2.66	10.2	5.73	5.73	4.15	3.44	3.95	0.359	0.476
GaN	Wu(4)	1.94	5.00	14.0	14.0	10.7	9.55	8.91	0.469	0.408
GaP	Zb(4)	2.36	8.50	7.60	7.60	6.17	4.39	4.44	0.333	0.341
GaAs	Zb(4)	2.43	11.3	6.20	6.20	5.62	2.30	2.62	0.137	0.179
GasB	Zb(4)	2.65	14.4	4.78	4.78	4.21	1.17	2.26	0.060	0.225
InIN	Wu(4)	2.13	5.50	11.4	11.4	8.36	8.14	7.81	0.507	0.466
InP	Zb(4)	2.54	9.60	6.35	6.35	4.86	3.72	4.09	0.342	0.414
InAs	Zb(4)	2.62	12.3	5.29	5.29	4.38	2.30	2.98	0.188	0.316
InSb	Zb(4)	2.80	15.7	4.20	4.20	3.45	1.17	2.39	0.078	0.325

Table -2

Values of Strain derivatives of electronic constants based on Photoelastic data [24-26] and calculated values of Photoelastic parameters defined in the text. Values of Photoelastic coefficients are calculated (a) equation (10) (b) Equation (5) (c) Equation (11).

Cristal	(R/C)(dC/dR) Ref.14	$P_{11}+2p_{12}$ Ref. [21]	λ Ref. [19]	$(V/\ \epsilon_\infty)(d\ \epsilon_\infty/dV)$		
				(a)	(b)	(c)
LiF	-1.209	0.289	0.705	-0.186	-0.183	-0.184
NaF	-1·247	0.288	0.685	-0.167	-0.165	-0.166
NaCl	- 1.102	0.472	0.555	-0.367	-0.364	-0.365
NaBr	- 1.032	0.392	0.501	-0·471	-0.470	-0.469
KCl	-1.054	0.582	0·438	-0.421	-0.420	-0 423
KBr	- 1.046	0.579	0.456	-0.456	-0.453	-0.454
Kl	- 1.001	0.616	0.436	-0.544	-0.542	-0.543
RbCl	- 1.000	0.666	0.358	-0.484	-0.483	-0.482
RbBr	-0.984	0.676	0·363	-0 528	-0.527	-0.526
RbI	-0.996	0·638	0.413	-0.549	-0 550	-0.552
CsBr	-0.914	0.740	0.328	-0.686	·-0 687	-0 686
ZnO	-1.399	0.384	0.342	0.480	-0.480	-0 481
ZnS	-1.100	0.121	1.108	0.210	0.212	0.211
MgO	- 1.645	0.363	1.327	0·357	0.360	0.360
CdS	-1.662	0.386	1.346	0.670	0.667	0.665
CuCl	-0.486	0.632	0.437	-0.770	-0.771	-0.772
CuBr	-0.531	0·470	0.581	-0.690	-0.690	-0.689
CuI	-0.462	0.332	0.702	-0.610	-0.612	-0.611
GaP	-0.977	0·315	1.289	0.893	0.894	0.894
GaAs	-1.591	0.432	1.403	1.627	1.625	1.626

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