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Applications of the ion-dependent quantum dielectric model for binary solids

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Two important applications of the previously established ion-dependent dielectric model have been incorporated. One is the accurate prediction of the electronic dielectric constant of normal-valence compounds with complicated structures. The other one provides a modification to the Phillips–Van Vechten theory for the heats of formation of binary compounds which facilitates a better agreement between the calculated and the experimental data.

I. INTRODUCTION

The ion-dependent quantum dielectric model for normal-valence compounds, which has recently been established by Sarkar and Goyal,[1] has produced manyfold applications, such as the prediction for the strain derivatives of these compounds,[2,3] the calculation of the energy gap between bonding and antibonding states,[1] etc. Only the cation dependence in ionic solids had been used by Pantelides[4] to predict the values of electronic dielectric constant ϵ_∞ of fluorite- and antifluorite-structured solids. All these predictions agree appreciably with the experimental data. In the first part of this paper we further apply this model to predict ϵ_∞ for a large number of cross compounds with comparatively complicated structures, using both anion and cation dependence in covalent and ionic solids, respectively. We will include structures like fluorite, antifluorite, and rutile (A_2B and AB_2 crystals), Na_3As, and Tl_2O_3 (A_3B and A_3B_2 solids). The dielectric study of such complicated structures has been quite inconclusive until now. In the second part we use the same model to predict the heats of formation of A^NB^{8-N} tetrahedral semiconductors which is a very useful structural property of solids.

II. ϵ_∞ OF CROSS COMPOUNDS

The semiempirical formulation for the ion dependence of ϵ_∞ of A^NB^{8-N} binary solids is given by[1]

$$\epsilon_\infty = 1 + BR^s , \qquad (1)$$

where R is the interatomic separation. Among the three families (I-VII, II-VI, and III-V), s is shown to be a characteristic constant in each separately, while the constant B is a cation characteristic in ionic solids and an anion property in covalent ones. Parameters B and s are not adjustable but their values are readily obtained from the experimental values of ϵ_∞ and R.[1] From these known values of B and s for binary solids, we may predict the same for complicated cross compounds such as A_2B, AB_2, A_3B, and A_3B_2 structures, and subsequently they may be put in Eq. (1) to obtain their ϵ_∞ values.

The procedure is as follows. Let us consider A_3B compounds which consist of four interpenetrating lattices, one for each element in the chemical formula. Now proceeding through anion dependence, we may compare them with the same anion III-V solids which are covalent in nature. For example, Li_3Sb may be compared with InSb. Li_3Sb, having a group V anion, should have its s value the same as that given for the III-V family. All antimonides have the same value of B. Both Li_3Sb and InSb have excited states of Sb, but for each p electron InSb has three times the number of Sb excited states as in Li_3Sb. Thus, the value of B for Li_3Sb should be one-third of the anion characteristic B obtained for binary antimonides. All A_3B solids will, therefore, have the same value of s and one-third the value of B, for the same anion AB crystal.

An approach through cation dependence may also be applied by comparison with the same cation ionic I-VII solids. With the same reasoning, B for Li_3Sb should be thrice that for LiCl or other lithium halides. However, the value of s to be used in this calculation should be that of I-VII compounds. This prescription may be used to get the values of B and s for all A_2B, AB_2, and A_3B_2 solids which may then be put into Eq. (1) to predict their ϵ_∞. The values calculated by this procedure agree with available experimental data in an impressive manner. The calculated values are reported in Table I.

A brief discussion of the results is necessary here. We have already seen that the solids with larger percentage of heteropolar energy C (ionic ones) incline toward cation dependence, while compounds with larger homopolar energy E_h (covalent ones) show anion dependence.[1-3] In the case of $ZnCl_2$, ϵ_∞ has been calculated through the cation dependence of II-VI solids and a deviation of about 30% from the experimental value is observed. This may suggest that the percentage of homopolar energy in this solid is definitely larger than that of the heteropolar contribution. We further note that for A_2B, A_3B, and A_3B_2 compounds, there are differences between the two sets of values calculated through anion and cation dependences. It is a matter of further study to calculate the value of E_h and C of these solids which will enable us to predict the correct value out of the two. A solid with E_h greater than C will have its correct value determined through an anion-dependent calculation, and for C greater than E_h, cation dependence will give a correct result. If the experimental data is made available, a comparison will predict whether a particular solid is more ionic or more covalent. For example, in Li_2O (the only solid for which the experimental value is available), the result calculated using cation-dependent I-VII solids is much more convincing than that calculated using anion-dependent II-VI ones, suggesting that Li_2O is more ionic in nature with a less covalent contribution.

It may be noted here that the I-VII family is exclusively cation dependent, hence we get parallel lines for cation sets only.[1] The negligible amounts of homopolar energy in these solids suggest the nonparallelism of anion lines (see Fig. 1 of Ref. 1). In order to calculate ϵ_∞ for AB_2 (II-VII$_2$) solids through I-VII compounds, our procedure will require comparison of anions which can not be done simply, because for the same anions, the exponent s for I-VII and II-VII$_2$ solids will have no fixed value.

Since the experimental data for all of these solids are not available, we will prove the validity

TABLE I. Calculated and available experimental values of some A_2B, A_3B, A_3B_2, and AB_2 solids.

A_2B solids	Value of ϵ_∞ through I-VII	through II-VI	Expt.	A_3B solids	Value of ϵ_∞ through I-VII	through III-V	Expt.
Li_2O	2.73	2.50	2.70	Li_3P	5.8	3.7	
Li_2Se	4.80	3.58		Na_3P	5.3	4.5	
Li_2Te	5.84	4.03		Li_3As	6.3	4.4	
Na_2S	3.65	2.77		Na_3As	5.7	5.2	
K_2S	3.49	2.48		K_3As	5.4	5.9	
K_2Se	3.81	2.74		Li_3Sb	7.5	5.7	
Rb_2O	2.69	1.81		Na_3Sb	5.8	6.7	
Rb_2S	3.49	2.36		K_3Sb	6.0	7.7	

A_3B_2 solids	Value of ϵ_∞ through II-VI	through III-V	Expt.	AB_2 solids	Value of ϵ_∞ through II-VI	Expt.
Be_3N_2	5.4	3.2		MgF_2	1.92	1.90
Mg_3N_2	4.3	4.0		$MgCl_2$	2.88	2.81
Mg_3P_2	6.8	6.7		$MgBr_2$	3.26	
Mg_3As_2	7.3	8.0		CaF_2	2.06	2.06
Mg_3Sb_2	10.1	11.6		$CaCl_2$	2.65	2.56
Ca_3N_2	3.6	4.2		$ZnCl_2$	4.00	3.00
Zn_3P_2	7.5	6.1		SrF_2	2.04	2.07
Cd_3As_2	8.4	7.9		$SrCl_2$	2.82	2.72
				CdF_2	2.76	2.43

of these results by classifying them according to the predicted values of ϵ_∞ and their directional bond properties. Since the directional properties of these solids depend on two factors; namely the average quantum number of the valence electrons and the electronegativity difference of the component atoms, Mooser and Pearson[5] plotted the average quantum number against the electronegativity difference in order to classify the more and less directionally bonded crystals. They found a sharp line of separation between more ionic and more covalent solids. ϵ_∞ may be taken to be directly concerned with the electronegativity difference, as the electronegativity difference of component atoms is roughly proportional to the dipole moment of molecules. Thus, if one plots our calculated values of ϵ_∞ against the average quantum number, it will be readily seen that the more and less directionally bonded solids are separated by a sharp line. This approximately confirms the validity of the calculated values of ϵ_∞. Since the structures of valence compounds depend upon the directional characteristics of bonds, the structure of any such solid may be predicted with help of this classification.

III. HEATS OF FORMATION OF BINARY TETRAHEDRAL SOLIDS

We start with a critical analysis of the theory formulated by Phillips and Van Vechten (PVV) for the heats of formation,[6] $H(AB)$, of binary tetrahedral A^NB^{8-N} solids. The formulation given by PVV is

$$H(AB) = -68.6 f_i \left[\frac{R_{\mathrm{Ge}}}{R_{AB}}\right]^3 \left[1 - b\left[\frac{2E_g}{E_0+E_1}\right]^2\right] \tag{2}$$

where f_i is the Phillips ionicity,[7] and R_{Ge} and R_{AB} is the interatomic separation in the Ge and A^NB^{8-N} molecules, respectively. E_g, E_0, and E_1 are specific optical energies, and b is a constant related to the optical energy of gray tin.

The factor R_{AB}^{-3} in Eq. (2) is questionable. While prescribing this factor, PVV assume that (i) the ionic energy C in all tetrahedral binary solids is negligible as compared to its covalent part E_h, and (ii) E_h scales as $R^{-2.5}$ for all AB solids. These two assumptions give $R^{-2.5}$ dependence for E_g, the average gap between bonding and antibonding states. PVV show $H(AB)$ to be proportional to E_g^2/E_f, E_f being Fermi energy with R^{-2} dependence. This finally leads to R^{-3} dependence of $H(AB)$.

TABLE II. Values of $H(AB)$ given by PVV and calculated through present modification compared with the experimental data.

Solids	Values of $H(AB)$ in kcal/mole Expt.	Present	PVV
ZnO	83.2	91.0	72.5
ZnS	49.2	43.7	42.1
ZnSe	39.0	39.8	39.8
CdTe	22.1	22.1	25.1
GaP	24.4	24.3	24.8
InP	21.2	20.7	20.3
InAs	14.0	12.0	11.5
GaAs	10.0	9.9	9.5

However, PVV themselves have reported their calculated values of E_h and C for all binary tetrahedral solids,[8] which shows that C cannot be neglected in most of the tetrahedral semiconductors, as their E_h and C are comparable. Also it has been shown earlier that the $R^{-2.5}$ dependence of E_h is quite inappropriate.[2] The ion-dependent model, on the other hand, gives the dependence of E_g on R directly without any references to E_h.[1] Thus, if the factor $(R_{\mathrm{Ge}}/R_{AB})^3$ in Eq. (2) is replaced by $(R_{\mathrm{Ge}}/R_{AB})^r$, the value of r can be readily obtained from E_g^2/E_f dependence. We find r to be equal to 2.44 for the covalent III-V family through anion dependence, and 4.0 for II-VI family members through cation dependence since this family shows more inclination towards ionic nature. In Table II the values calculated through this prescription are compared with those given by PVV with respect to the experimental ones. It can be seen that the present model provides a better agreement which proves a difinite improvement in the formulation for $H(AB)$.

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