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Quantum-dielectric behavior of $A^N B^{8-N}$ binary solids

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The quantum-dielectric–ion-dependent model for $A^N B^{8-N}$ binary solids has been analyzed and used to predict the average energy gaps between the bonding and antibonding states. The results are in excellent agreement with the available experimental values.

In recent developments on the dielectric behavior of $A^N R^{8-N}$ binary solids, ion-dependent models have been produced through semiempirical formulations. Pantelides[1] has shown that the dielectric behavior of ionic compounds depends upon their cations. The theoretical predictions of the electronic dielectric constants for the solids with fluorite and antifluorite structures are in good agreement with the experimental data. On the other hand, Goyal and Sarkar[2] have extended an anion-dependent model for the covalent compounds which could subsequently predict accurate values for the pressure derivatives of electronic dielectric constants in the III-V family.[3] The anion dependence in tetrahedral covalent solids has been supported by the theoretical bond-orbital model of Pantelides and Harrison.[4,5] The present study is a supplement to the said models for the ionic and covalent cases, both of which accurately predict the values of the average energy gap between the bonding and antibonding states.

The average energy band gap E_g between the bonding and antibonding states has been shown to have two parts.[6,7] One is associated with the ionic bonds known as the heteropolar or electronegativity part C and the other is the homopolar part E_h associated with the covalent bonds. The split assumes a square law given by

$$E_g^2 = E_h^2 + C^2 . \tag{1}$$

Van Vechten[6] has empirically calculated and reported the values of E_h and C for all related binary solids. His table shows that all I-VII solids have much larger contributions from C than from E_h. All these compounds have rocksalt structure. II-VI solids have significant contributions from both E_h and C. Those with rocksalt structure have larger values of C than E_h, while the tetrahedral-structure solids (wurtzite and zinc blende) have comparable values, C being generally greater than E_h. In III-V solids the values of E_h are larger than C, and all these have tetrahedral structures. C has been reported to be zero in IV-IV solids, which have diamond structures. It may be inferred, therefore, that there is a gradual change from ionic to covalent nature as one moves from I-VII to IV-IV binary solids.

The Pantelides study[1] considers all the I-VII alkali halides and II-VI alkaline-earth chalcogenides together in one figure. All these are significantly ionic with rocksalt structure. In the present study I-VII, II-VI, and III-V solids have been separated in Figs. 1, 2, and 3, respectively. The experimental values of the electronic dielectric constant ϵ and the interionic separation R have been taken, respectively, from Van Vechten's[6] Table III and Slater's compilation.[8] With an analytical difference, Fig. 1 reiterates a part of the Pantelides figure.[1] Figure 3 is a complete replot for III-V solids, which appeared in an incomplete form in one of our previous papers.[2]

In Fig. 1 a $\log(\epsilon - 1)$-vs-$\log R$ plot for I-VII solids, we have four parallel straight lines, each having the same cation compounds. Obviously the slope is constant for all solids, while the intercepts on the $\log(\epsilon - 1)$ axis are characteristic constants for the same cation solids. The broken lines show that average straight lines may be drawn with the same anion solids around each of them, but they do not fall exactly on the lines as they did with respect to cations. Also, the lines do not have the same slope.

In Fig. 2 we find that, with the exception of few solids like CdO, MgTe, and all Be compounds, all II-VI solids readily fall on their respective cation lines with same slope. The dotted lines reveal that up to some point they show anion-dependent behavior also. Although all the six oxides disagree completely, we get average S, Se, and Te lines with little deviation. The beauty we find in this family is the parallelism in anion lines also not observed in I-VII solids. Thus the II-VI family has the tendency both toward cation and anion dependences.

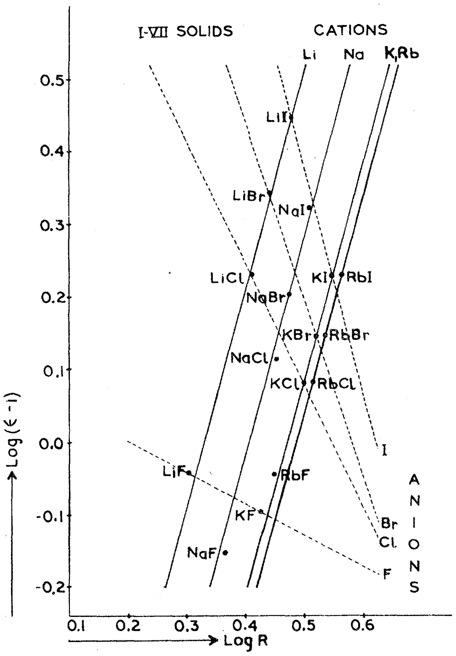

FIG. 1. Variation of $\log(\epsilon-1)$ with $\log R$ in the I-VII family.

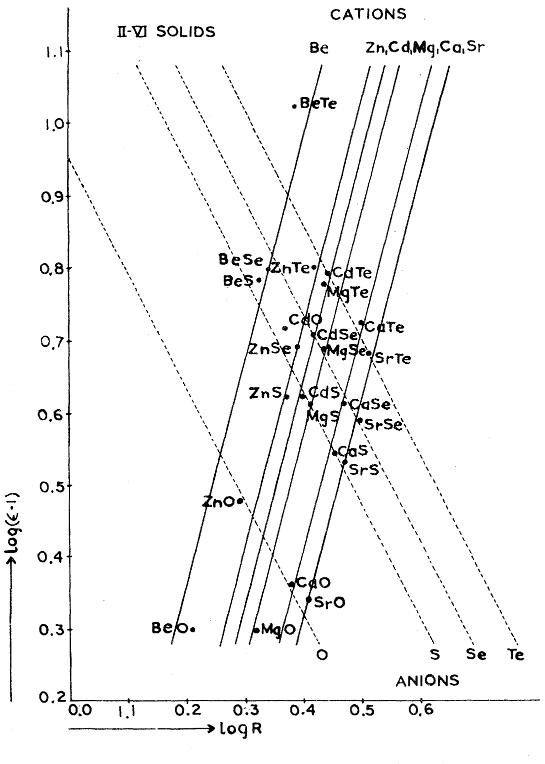

FIG. 2. Variation in the II-VI family.

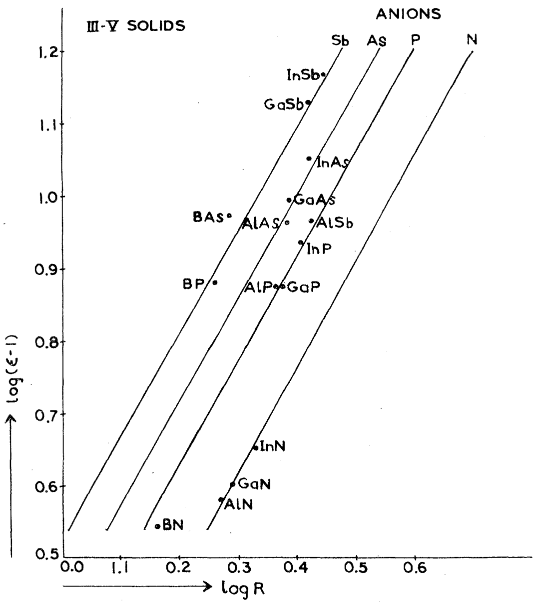

FIG. 3. Variation in the III-V family.

III-V solids in Fig. 3 show anion-dependent behavior with AlSb and boron compounds as exceptions. In this case the $\log(\epsilon-1)$-axis intercepts are the characteristic constants for the same anion solids.

It may be inferred, therefore, that the solids having large heteropolar contribution (I-VII) show pure cation-dependent dielectric behavior. As we move toward the II-VI family, in which the members have comparable amounts of E_h and C, tendencies toward both cation and anion dependences are observed, while in the III-V ones with large homopolar contribution we have anion dependence. Thus, with the transition from ionic to covalent nature, the dependence gradually changes from cation to anion.

It is interesting to analyze the exceptions in the II-VI and III-V families which actually support our inference. We refer to Van Vechten's[6] Table III for the discussion that follows. Among II-VI solids, all Cd salts have tetrahedral structure, except CdO which has rocksalt structure. CdO is much more ionic as compared to others which have a greater percentage of E_h. Thus CdO deviates from the Cd line. Similarly all Mg salts have large C except MgTe, which has comparable amounts of E_h and C. Obviously all Mg solids have rocksalt structure while MgTe is wurtzite. Thus, a much more covalent MgTe falls away from the Mg line. Among Be solids, BeO has larger C, BeS and BeSe have a larger E_h, while, in BeTe, E_h and C are equal. All four together are neither more ionic nor more covalent and, thus refuse to

TABLE I. Schematic information obtained from the three figures. Unit of B' is $(\text{Å})^{-s'}$, with corresponding value of s'.

Family and type of solids	Characteristic dependence	s'	Ion	B'
I-VII rocksalt	cation	3.00	Li	0.105
			Na	0.060
			K	0.038
			Rb	0.034
II-VI rocksalt	cation	3.00	Mg	0.233
			Ca	0.160
			Sr	0.133
	anion	−1.59	O	
			S	18.401
			Se	23.588
			Te	31.503
II-VI tetrahedral	cation	3.00	Be	0.592
			Zn	0.333
			Cd	0.283
	anion	−1.59	O	
			S	18.401
			Se	23.588
			Te	31.503
III-V tetrahedral	anion	1.45	N	1.514
			P	2.208
			As	2.588
			Sb	3.281

form a proper cation line. Among III-V solids, AlSb falls off the Sb line, as it has an almost equal contribution from E_h and C, unlike GaSb and InSb, which have a larger value of E_h than C. One may ask whether with only two points a straight line graph is justified. Our argument is that it is not only a question of two points, but that the major consideration is the parallelism of the four anion lines, which is readily shown by GaSb and InSb with respect to all other solids. As regards the boron solids, BN (zinc blende) has a very large contribution from E_h, while other nitrides (wrutzite) have comparable amounts of E_h and C. In BP and BAs the contribution of C is negligible, unlike other phosphides and arsenides. These two must have a behavior like IV-IV solids. Thus the boron solids deviate from their respective anion lines. In separate studies concerned with effective charge and ionicity Lawaetz[9] and Wemple[10] have also reported that SiC (IV-IV) and first row III-V compounds (boron solids) are somewhat exceptional. Recently, Sharma *et al.*[11] have produced a plot for III-V solids showing a single average straight line with all compounds around that. In fact, this has been enforced by compressing the log$R$ axis, which has reduced the accuracy, and the plot should obviously have a large value of root-mean-square deviation. A constant intercept on the log$(\epsilon - 1)$ axis for all III-V solids has not been physically attained.

Now we turn to the prediction of the average energy-gap values with the help of the ion-dependent models. All three figures obviously propose an easy relation between ϵ and R given by

$$\epsilon = 1 + B'R^{s'} . \tag{2}$$

In any of the three figures s', the slope, is constant for all the members in one family. It is the cation slope in I-VII and the anion slope in III-V solids. In II-VI we have different s' values for the cation and anion slopes. Similarly B' values, the intercepts on the log$(\epsilon - 1)$ axis, are the cation characteristics in I-VII, anion characteristics in III-V, and both types in II-VI. Now we recall the one-gap model for electronic band structure given by Van Vechten[6] which leads to the following formulation:

$$\epsilon = 1 + 4\pi e^2\hbar^2 N_{\text{eff}}/mE_g^2 . \tag{3}$$

Here N_{eff} is the effective density of valence electrons, which includes the overlapping effect of core d electrons. The unit volume is given by $\frac{1}{2}kR^3$ with k as a structural constant. A comparison of the experimental equation (2) with the theoretical equation (3) suggests a trivial equation for E_g,

$$E_g = BR^{-s} , \tag{4}$$

where B and s are constants. Similar dependence of E_g, E_h, and C on R has been supported by Van Vechten and others.[12-15] Thus, Eq. (3) takes its final shape in the form

$$\epsilon = 1 + 8\pi e^2\hbar^2 N_{\text{eff}} R^{(2s-3)}/mkB^2 . \tag{5}$$

A comparison with Eq. (2) leads to

$$s' = 2s - 3 \tag{6}$$

and

$$B' = 8\pi e^2\hbar^2 N_{\text{eff}}/mkB^2 . \tag{7}$$

Constants s' and B', reported in Table I, are obtained directly from the three figures, which use the experimental values of ϵ and R. From these, we evaluate the values of s and B using Eqs. (6) and (7), respectively. The values of N_{eff} are taken from Van Vechten's compilation.[6] The obtained values of s and B are then put into Eq. (4) to get E_g for different solids. Obviously we have single-set results in the cases of I-VII and III-V families which assume pure-cation and pure-anion dependence, respectively. II-VI solids have, however, double-set results due to their dependence on

TABLE II. Calculated and experimental values of E_g.

Family	Solids	E_g (eV) (cal) Through cation	E_g (eV) (cal) Through anion	E_g (eV) (expt)	Solids	E_g (eV) (cal) Through cation	E_g (eV) (cal) Through anion	E_g (eV) (expt)
I-VII	LiF	28.21			KF	20.00		
	LiCl	13.50			KCl	12.18		12.6[a]
	LiBr	11.02			KBr	10.60		11.5[a,b]
	LiI	8.49			KI	8.70		9.3[b]
	NaF	24.59			RbF	17.95		
	NaCl	13.51			RbCl	11.30		
	NaBr	11.45		11.0[b]	RbBr	10.46		10.9[b]
	NaI	8.91			RbI	8.61		
II-VI	MgO	16.60	•••		BeO	17.29	•••	
	MgS	8.75	8.78		BeS	8.24	8.08	
	MgSe	7.92	7.86		BeSe	7.51	7.24	
	MgTe	•••	•••		BeTe	5.71	5.87	
	CaO	13.42	•••		ZnO	14.39	•••	
	CaS	8.10	8.24		ZnS	8.12	7.80	7.6[c]
	CaSe	7.50	7.42		ZnSe	7.58	7.00	6.4[d,e]
	CaTe	6.11	6.11		ZnTe	6.12	5.76	5.3[e]
	SrO	11.99	•••		CdO	•••	•••	
	SrS	8.01	8.04		CdS	7.23	7.45	7.8[f]
	SrSe	7.03	7.15		CdSe	6.72	6.75	6.9[f]
	SrTe	6.27	6.02		CdTe	5.85	5.50	5.0[d]
III-V	BN		•••		BAs		•••	
	AlN		12.0		AlAs		5.3	
	GaN		11.5		GaAs		5.5	5.0[g]
	InN		9.7		InAs		4.9	4.7[e,g]
	BP		•••		BSb		•••	
	AlP		5.9	5.5[h]	AlSb		4.0	4.2[g]
	GaP		6.1	5.3[g]	GaSb		4.2	4.2[d,g]
	InP		5.4	5.1[e,g]	InSb		3.9	4.1[e,g]

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both. The calculated and available experimental values are reported in Table II.

The experimental data for ionic solids are unfortunately not as conclusive as one might hope. However, with those available for I-VII solids, we find good agreement. In III-V covalent solids we also get excellent agreement. In the II-VI tetrahedral family, which has comparatively more covalent members, we find the values calculated through anion dependence in closer agreement than those through cation dependence, as expected.

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