Correlation Between the Ionicity and the Polarity in Semiconductors

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ABSTRACT

Using the polarity with respect to energy gap Egrx, an empirical formula of ionicity factor is obtained for a specific class of semiconductors. The computation of ionicity character is distinguished with high degree of accuracy reaches that of other calculations like ab initio methods. Systematic behaviours are noticed in the calculated values of ionicities. It is seen that the experimental and calculated discrepancies for III-V compounds are three times as for II-VI ones. The results are in good agreement with that of Phillips and other authors.

INTRODUCTION

The systematic theoretical studies of the electronic structures, optical properties, and charge distributions have been already reported in the literature [1,2]. However, detailed calculations on covalent and ionic bonds have not reached the same degree of a prior completeness as can be attained in the case of metallic properties. The difficulty in defining the ionicity of a bond is transforming a qualitative or verbal concept into a quantitative, mathematical formula. Several empirical approaches have been developed [3] where yield analytic results which can be used for exploring trends in materials properties. In many applications, these empirical approaches do not give highly accurate results for each specific material, but they still can be very useful. Phillips'[3] stimulating assumption concerning the relationship of the macroscopic characteristics of a covalent crystal (dielectric constant, structure) and the microscopic ones (band gap, covalent and atomic charge densities) is based essentially on the isotropic model of a covalent semiconductors, whereas Christensen et al. [4] performed self-consistent calculations but used model potentials which were derived from a realistic GaAs potential where additional external potentials were added to the anion and cation sites. However, in general the ionicities found by Christensen tend to be somewhat larger than those of Phillips. Also Garcia and Cohen [5] achieved the mapping of the ionicity scale by an unambiguous procedure based on the measure of the asymmetry of the first principle valence charge distribution [6]. As for Christensen scale, their results were somewhat larger than those of the Phillips scale. Zaoui et al. [7] established an empirical formula for the calculation of the ionicity, based on the measure of the asymmetry of the total valence charge density. Their results are in agreement with those of the Phillips scale.

In this paper, we have established an empirical formula for the calculation of the ionicity f_i of a specific class of materials. The theory yields formulae with three attractive features. Only the polarity α_p and energy gap Eg_{rx} are required as input, the computation of f_i itself is trivial and the accuracy of the results reaches that of ab initio calculations. It considers

hypothetical structure and simulation of experimental condition that are difficult to achieve in the laboratory, e.g. very high pressure where make it an attractive option.

RESULTS AND DISCUSSION

The goal of our study is to understand how qualitative concepts, such as ionicity, can be related to polarity α_p with respect to energy gap $Eg_{\Gamma X}$. Our calculation is based upon polarity which have been reported previously [8]. An important observation for studying f_i is the distinguished difference between the values of polarity and energy gaps $Eg_{\Gamma X}$ in going from the group-IV to III-V and II-VI semiconductors as seen in table 1.

Table 1. The values of polarity and energy gaps along $\Gamma \rightarrow X$ for group-IV, III-V and II-VI semiconductors.

Compound	α_p [8]	$Eg_{\Gamma X}$ (eV) [9]
Si	0.00	1.11
GaSb	0.44	2.1
GaAs	0.50	2.6
InSb	0.51	2.5
GaP	0.52	2.4
InAs	0.53	2.8
AlSb	0.54	1.9
InP	0.58	2.82
ZnTe	0.72	4.8
ZnSe	0.72	4.9
ZnS	0.73	5.0
CdTe	0.76	5.5
CdS	0.77	5.1

Hence, the polarity is predominantly dependent on f_i. The differences between the polarity and energy gaps $Eg_{\Gamma X}$ have led to consider this model.

The basis of our model is the polarity as seen in upon table. The fitting of these data give the following empirical formulas:

$$f_i = \lambda \left[\frac{\alpha_P \cdot E_{g\Gamma X}}{4} \right] \qquad \text{(a)}$$

where α_p is the polarity, the energy gap $Eg_{\Gamma X}$ is in (eV), 4 is in (eV), and λ is a parameter separating the strongly ionic materials from the weakly ionic ones. Thus, an appropriate for the group-IV ($\lambda = 0$), III-V ($\lambda = 1$), and II-VI ($\lambda = 0.7$) semiconductors. The calculated ionicity values compared with those of Phillips [3], Christensen et al. [4], Garcia and Cohen [5], and Zaoui et al. [7] are given in table 2.

Table 2. The calculated ionicity factors along with those of other authors; Phillips [3], Christensen et al. [4], Garcia and Cohen [5] and Zaoui et al. [7].

Compound	f_i cal.	f_i [3]	f_i [4]	f_i [5]	f_i [7]
Si	0	0	0	0	0
GaSb	0.231	0.261	0.108	0.169	0.264
GaAs	0.325	0.310	0.310	0.316	0.312
InSb	0.318	0.321	0.303	0.294	0.301
GaP	0.312	0.327	0.361	0.371	0.377
InAs	0.371	0.357	0.553	0.450	0.357
AlSb	0.256	0.250	0.163	0.230	0.245
InP	0.409	0.421	0.534	0.506	0.405
ZnTe	0.604	0.600	0.560		0.684
ZnSe	0.617	0.630	0.740	0.597	0.639
ZnS	0.638	0.623	0.764	0.673	0.677
CdTe	0.731	0.717	0.739		0.713
CdS	0.687	0.685	0.794		0.729
CdSe	0.727	0.699	0.841		0.737

We may conclude that, the present ionicities are in good agreement with the empirical ionicity values as seen in figure 1, calculated in a different way than the definition of Phillips and exhibit the same chemical trends as those found in the values derived from the Phillips theory or those of Christensen et al. [4], Garcia and Cohen [5], and Zaoui et al. [7] as seen in table 2.

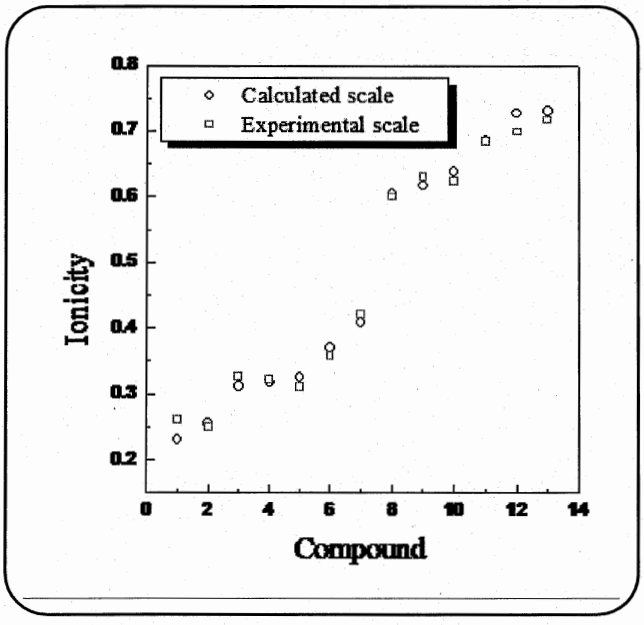

Figure 1. The experimental and our calculated ionicity factor scales by using formula (1) for different semiconductors.

Some systematic behavior is observed in the results of the calculated values. For the II-VI compounds, the differences between the experiment and theory are less than 4% and the discrepancies are three times approximately as larger for III-V compounds semiconductors, as shown in tables 3 and 4 , respectively.

Table 3. Comparison of calculated [using Eq. (1)] and empirical values of the ionicities of III-V compounds.

Compound	f_i cal.	f_i [3]	(%)
GaSb	0.231	0.261	11.4
GaAs	0.325	0.310	4.6
InSb	0.318	0.321	0.9
GaP	0.312	0.327	4.5
InAs	0.371	0.357	3.7
AlSb	0.256	0.250	2.3
InP	0.409	0.421	2.8

Table 4. Comparison of calculated [using Eq. (1)] and empirical values of the ionicities of II-VI compounds.

Compound	f_i cal.	f_i [3]	(%)
ZnTe	0.604	0.600	0.6
ZnSe	0.617	0.630	2.0
ZnS	0.638	0.623	2.3
CdTe	0.731	0.717	1.4
CdS	0.687	0.685	0.2
CdSe	0.727	0.699	3.8

The calculation estimates are larger than the measured values for the III-V compounds, and the tendency is similar for the II-VI compounds. Although it can be argued that for many of these compounds the calculation-empirical differences are the same order as differences between reported measured values, it is expected that these trends are real [10]. In conclusion, the empirical models obtained for the ionicity give results in good agreement with the results of other scales, which in turn demonstrate the validity of our model to predict some other physical properties of such compounds.

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