Electronegativity, fractional ionic character and refractive index of binary compounds

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Received 20 January 2009; accepted 2 July 2009

An analysis is presented for the electronegativity, fractional ionic character and refractive index of binary compounds with monovalent, divalent and trivalent atoms. The values of electronegativity difference by investigating a relationship between fractional ionic character and electronegativities have been determined. More accurate values of ionicity based on the revised energy gap model have been used in the present study to obtain the new results. The values of electronegativity difference are found to be correlated well with the values of refractive index and energy gap in case of I-VII, II-VI and III-V binary compounds.

Keywords: Electronegativity difference, Binary compounds, Ionic character, Electronic polarizability, Magnetic susceptibility

1 Introduction

Electronegativity is defined as the power of an atom to attract an electron to itself. Pauling determined the electronegativity of different elements using thermochemical method based on the dissociation energies of molecules and compounds. The electronegativities were then refined by comparing the energies of real bonds in binary compounds with fractional covalent bonding for the same interatomic distances using the heat of formation and heat of sublimation of binary compounds. The stable arrangement for a binary compound or diatomic molecule corresponds to the largest values of the electronegativity difference, i.e. one atom with the highest value of electronegativity and the other atom with the lowest value of electronegativity.

Many attempts have been made to find several relationships between physical and chemical parameters both from the point of view of fundamental interest and technological applications. Batsanov proposed a method for calculating the electronegativity of metal atoms in crystalline solids from the thermochemical and structural parameters of inorganic materials. However, the values of electronegativity difference reported by earlier researchers are approximately similar even for such compounds for which the nature of chemical bond is much different. In fact, the electronegativity difference is a sensitive parameter depending on the fractional ionic character, ratio of ionic radii and other solid state properties of materials. Singh et al. have used a modified energy gap expression as derived by Grimes and Cowley in order to revise the estimates of ionicity parameters due to Phillips and Van Vechten. Their revised values of ionicity parameters obtained for type diatomic compounds are shown to exhibit systematic relationships with interatomic separations. The ionicity parameters are also found to correlate well with the photoelastic strain polarizability parameters.

Grimes and Cowley removed the shortcomings of the models due to Penn and Srinivasan. Penn derived a set of formulae based on an isotropic, nearly free electron model for the energy bands. The work of Penn was extended by Srinivasan. However, the model adopted by Penn as well as Srinivasan was so complicated that the dielectric function could not be evaluated analytically. They obtained approximate analytic expressions for the dielectric function after introducing several simplifications. Specifically, 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 the exact expressions. These drawbacks have been rectified by evaluating the sums 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 due to Grimes and Cowley\textsuperscript{17} is physically more plausible and consistent with the experimental data\textsuperscript{22}.

In the present study, we use the more accurate values of fractional ionic character reported by Singh et al.\textsuperscript{16} and determine values of electronegativity difference for I-VII, II-VI and III-V diatomic compounds. The values of electronegativity difference, thus, determined are found to correlate well with the physical quantities such as refractive index and energy gap parameters.

2 Theory

Grimes and Cowley\textsuperscript{17} modified the expression for energy gap ($E_g$) between bonding and antibonding states as follows:

\[
\varepsilon_n - 1 = \left(\frac{\hbar \omega_p}{E_g}\right)^2 S_0
\]

where $\omega_p$ is the plasma frequency, $\varepsilon_n$ the electronic dielectric constant and $S_0 = 0.62$ is the correction factor. Eq. (1) reduces to the original Penn model when $S_0$ is equal to one.

According to Phillips and Van-Vechten\textsuperscript{18,19}, in tetrahedrally coordinated crystals, energy gap $E_g$ between bonding and antibonding ($sp^3$) hybridized orbital, may be decomposed into contributions due to symmetric and antisymmetric parts by the potential within unit cell. These contributions are (i) heteropolar or ionic contribution represented by $C$ and (ii) homopolar or covalent contribution represented by $E_h$, in the following form:

\[
E_g^2 = E_h^2 + C^2
\]

The ionicity of chemical bond is expressed in terms of fractional ionic character $f_i$ as follows:

\[
f_i = \frac{C^2}{E_g^2}
\]

and fractional covalent character as:

\[
f_c = 1 - f_i = \frac{E_h^2}{E_g^2}
\]

Pauling\textsuperscript{1} developed a thermochemical method to formulate a reliable relationship between fractional ionic character or ionicity of a bond and the difference in electronegativities of two atoms forming the chemical bond. The description of a bond as a hybrid between a normal covalent bond and an extreme ionic bond is only an approximation. Following the theory due to Pauling, a relationship between fractional ionic character $f_i$ and electronegativity difference $\Delta X$ for diatomic compounds is considered as given below:

\[
f_i = \sin^2 \varphi = \frac{C^2}{E_g^2}
\]

and covalent fraction is:

\[
f_c = \cos^2 \varphi = \frac{E_h^2}{E_g^2}
\]

The values of $\Delta X$ from Eq. (9) have been calculated using the values of $f_i$ given in Tables 1-3 for I-VII, II-VI and III-V diatomic compounds. These values of $\Delta X$ are expected to be more precise and systematic as they are determined from the reliable values of fractional ionic character\textsuperscript{16,23} $f_i$. Now, we present a test of the results for $\Delta X$ by studying the correlations between $\Delta X$ and other properties of the materials.

3 Results and Discussion

The refractive index ($n$) is the most important optical property of materials. Its square ($n^2$) is equal to the electronic dielectric constant ($\varepsilon_n$), which is related to electronic polarizability ($\alpha$). We plot $n^2$ versus $\Delta X$ for I-VII, II-VI and III-V diatomic compounds. The results are shown in Fig. 1. These graphs are straight lines with different characteristics. For I-VII compounds, we get separate straight lines one for each group of compounds with common cations. The slopes of these straight lines are nearly similar except for silver
halides. The behaviour of silver halides is found to be different from that of other I-VII compounds. In case of II-VI compounds, we get the separate straight line plots for each group of compounds with common cations, but the slopes are significantly different from each other. On the other hand, for the III-V compounds, we get a single straight line for all the compounds, and no distinct behaviour is found depending on the cations or anions. This appears to be related to the fact that the III-V compounds are substantially covalent as far as the nature of chemical bond is concerned and the model based on individual ions does not remain valid. The linear relationship between \( n^2 \) and \( \Delta X \) can be represented as:

\[
n^2 = A_1 \Delta X + B_1 \quad \ldots (10)
\]

where \( A_1 \) and \( B_1 \) are constants determined by finding a regression line based on the data for a group of compounds.

Another property of central importance is the energy gap between bonding and antibonding states. We have studied and found that the dependence of \( E_g \) on \( \Delta X \) can be represented by a power law as well as by an exponential law. We have plotted (i) \( \ln E_g \) versus \( \ln \Delta X \) and (ii) \( \ln E_g \) versus \( \Delta X \) for different types of compounds. These are shown in Figs 2 and 3. Again, we find the cation dependent linear behaviour for I-VII and II-VI compounds, whereas a distinct behaviour is observed for the III-V compounds. The relationships between \( E_g \) and \( \Delta X \) can be written as follows:

\[
\ln E_g = A_2 \ln \Delta X + B_2 \quad \ldots (11)
\]

and

\[
\ln E_g = A_3 \Delta X + B_3 \quad \ldots (12)
\]

where \( A_2, B_2, A_3 \) and \( B_3 \) are constants for a group of materials. The values of these constants are extracted.

Table 1 — Values of fractional ionic character (\( f_i \)), electronegativity difference (\( \Delta X \)), energy gap (\( E_g \) in eV), refractive index (\( n^2 \)), electronic polarizability (\( \alpha \) in Å\(^3\)) and magnetic susceptibility (\( \chi_d \) in \( 10^{-6} \) cm mol\(^-1\)) for I-VII binary compounds

<table>
<thead>
<tr>
<th>Crystal</th>
<th>( f_i )</th>
<th>( \Delta X )</th>
<th>( E_g ) (eV)</th>
<th>( n^2 )</th>
<th>( \alpha ) (Å(^3))</th>
<th>( \chi_d ) ( (10^{-6} ) cm mol(^-1))</th>
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<td>8.730</td>
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<td>7.742</td>
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<td>5.976</td>
<td>3.02</td>
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<tr>
<td>CuF</td>
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<td>4.546</td>
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</table>
from the plots in Figs 2 and 3. Eq. (11) gives the power law as:

$$E_g = b_2 (\Delta X)^{b_2}$$

... (13)

whereas Eq. (12) gives the exponential law

$$E_g = b_3 e^{\Delta X}$$

... (14)

where $b_2$ and $b_3$ are related to $B_2$ and $B_3$ by $B_2 = \ln b_2$ and $B_3 = \ln b_3$. The values of the constants $B_2$ and $B_3$ are also presented in Table 4.

The electronic polarizability ($\alpha$) of a material is also related to the refractive index as follows:

$$\alpha = \left( \frac{n^2 - 1}{n^2 + 2} \right) \frac{3M}{4\pi Nd}$$

... (15)
Fig. 1 — $n^2$ versus $\Delta X$ for I-VII, II-VI and III-V binary compounds
Fig. 2 — $\ln (E_g)$ versus $\ln (\Delta X)$ for I-VII, II-VI and III-V binary compounds
Fig. 3 — $\ln (E_g)$ versus $\Delta X$ for I-VII, II-VI and III-V binary compounds
Fig. 4 — Polarizability (α) versus ΔX for I-VII, II-VI and III-V binary Compounds
Fig. 5 — Magnetic susceptibility ($\chi_d$) versus $\Delta X$ for I-VII, II-VI and III-V binary compounds
where $n$ is the refractive index of the substance, $d$ is its density at temperature $T$, $M$ is its molecular weight and $N$ is the Avogadro number. Eq. (15) for refractive index is based on the classical theory of the dielectric constant due to Clausius and Mosaussi, and the role of electronic polarizability is similar to that of the energy gap in quantum theory of solids. The plots of electronic polarizability ($\alpha$) versus electronegativity difference ($\Delta X$) for I-VII, II-VI and III-V diatomic compounds are shown in Fig. 4. The values of electronic polarizability ($\alpha$) determined from Eq. (15) are taken from the literature. The plots are linear and reveal that the electronic polarizability is related to the electronegativity difference as follows:

$$\alpha = A_1 (\Delta X) + B_4$$

(16)

The constants $A_1$ and $B_4$ are cation dependent in case of I-VII and II-VI compounds, and independent of cations or anions in III-V compounds.

Finally, the dependence of magnetic susceptibility on electronegativity difference has been studied. These plots are shown in Fig. 5 which indicate linear relationships with the electronegativity difference, similar to those for the energy gap. The diamagnetic susceptibility and electronic polarizability both depend essentially on the radial distribution of electrons around the nuclei, which would be different in covalent and ionic structures. The diamagnetic susceptibility and electronic polarizability are given below:

$$\chi_d = -2.01 \times 10^{-6} \sum_{0}^{\infty} \frac{n^2}{(Z-s)^2} \left[1 - \frac{3l(l+1)-1}{5n^2} \right]$$

(17)

and

$$\alpha = 0.281 \sum_{0}^{\infty} \frac{(5n^6 + 7n^4)(2l + 1)}{(Z-s)^4}$$

(18)

where $n$ and $l$ are the principal and orbital quantum numbers, $Z$ the number of electrons per atom and $s$ is an appropriate screening parameter which modifies the nuclear charge. The summation is being carried over all electrons in the atom. The values of the diamagnetic susceptibility have been taken from the literature.

Table 4 — Values of parameters extracted from the plots 1-4 for binary compounds

<table>
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<tr>
<th>Cations</th>
<th>$A_1$ (eV)</th>
<th>$B_1$</th>
<th>$A_2$ (eV)</th>
<th>$B_2$ (eV)</th>
<th>$A_3$ (eV)</th>
<th>$B_3$ (eV)</th>
<th>$A_4$ (Å$^3$)</th>
<th>$B_4$ (Å$^3$)</th>
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<td>19.7</td>
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4 Conclusions

In the present study, a relationship for the electronegativity difference in terms of fractional ionic character has been formulated. The values of electronegativity differences determined in the present study are systematic and precise since they are based on the values of fractional ionic character of the chemical bond obtained by Singh et al. using the revised model for the energy gap due to Grimes and Cowley. Various optoelectronic properties such as the refractive index ($n$), energy gap ($E_g$), electronic polarizability ($\alpha$) and diamagnetic susceptibility ($\chi_d$) have been shown to be related with the values of electronegativity difference in case of diatomic I-VII, II-VI and III-V compounds.

Acknowledgement

Authors are thankful to Prof Jai Shanker for valuable discussion. They are also thankful to Mrs Sudha Singh for her help in the computational work.
References