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Relation between Energy gap and refractive index for Alklai Halides and II-VI and III-V Group Compound Semiconductors

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Abstract

In the present study we have studied the variation between the energy gap and refractive index of the material using the relations given by Moss and ravindra et.al[9]. The two most interesting optical properties of semiconductors are the absorption edge, or optical energy gap, and the refractive index. It is therefore natural that attempts have been made to find a general relationship between these parameters, both from the point of view of fundamentals interest and also as a technological aid in estimating the refractive index if only the energy gap is known. The first proposal was made by Moss[10] on very general grounds that all energy level in a solid are scaled down by a factor($1/\varepsilon^2_\infty$),where $\varepsilon_\infty=n^2$ is the optical dielectric constant.

Key Words:- Energy gap. Refractive index, Moss relation. Absorption edge, Dielectric constant, Compound Semiconductors.

Method of Analysis

The data on the then known materials were correlated and as a result the so called Moss relation.

$$n^4/\lambda_g = 77\ \mu\ m^{-1} \qquad (1)$$

was proposed .In terms of energy gap E_g this is equivalent to

$$n^4 E_g = 95\ \text{eV} \qquad (2)$$

Subsequently there has been renewed interest in this topic, especially by various coworkers [1-6]. From an analysis of more data, Ravidera and Srivastava[9] proposed a revised value of the constant giving the modified relation

$$n^4 E_g = 108\ \text{eV} \qquad (3)$$

From a study of wide range of materials, Ravidera et.al.[9] have proposed an alternative empirical relationship of linear form ,namely

$$n = 4.084 - \varphi E_g \qquad (4)$$

Where φ is a constant equal 0.62 eV. The optical constants of a material are not independent but are related. The most useful interrelation, namely that between n and K was derived by Moss [10].

$$n_a - 1 = (1/2\square^2)\int_0^\infty k\, d\lambda/(1 - 2\lambda^2_a) \qquad (5)$$

Which for the long wavelength, zero frequency, index becomes

$$n - 1 = (1/2\square^2)\int_0^{\lambda} k\, d\lambda \qquad (6)$$

In the present context, a significant feature of this function is the fact that it is integrated over wavelength not with energy. Thus, if for example a given level of absorption persists over a given energy interval as occurs between two allowed energy bands then smaller the width of the forbidden zone the greater will be the spread of absorption in wavelength, resulting in a greater value of the integral and a larger n. Taking a simple, hypothetical absorption spectrum which has constant K at a level K_0 from essentially zero wavelength to the band edge at λ_g, we would have

$$2\square^2(n - 1) = \int_0^{\lambda g} K0\ d\,\lambda \ = k_0\,\lambda_g \qquad (7)$$

i.e. the refractive index would be proportional to the wavelength of the absorption edge. Thus this highly idealized example show how a strong dependence of the refractive index on the long wavelength edge could arise in the fact; this example shows a much stronger dependence than the Moss relation [10]. i.e. n is approximately equal to $\lambda_g^{1/4}$. Now consider the contribution of real absorption spectra to the refractive index for example the InSb where the absorption has been measured accurately over a wide wavelength range from 1.56 μm to beyond the edge at 7μm. The results are given together with results from InAs to the same scale .From the difference in area under consideration we can calculate the extra contribution to the refractive index arising from the absorption in the InSb tail band beyond 3.4 μm we find $\int_{InAs}^{InSb} K.d\lambda = 1.1$ So that the contribution to the refractive index is 0.055.Now the measured indices are:InSb 3.96;InAs=3.44 giving a measured value for Δn =0.52.Hence the contribution to the refractive index from the extra long wavelength absorption in InSb is barely 10% of the actual increase in refractive index. Noting that we are studying precise theoretical inter relations , the calculated Δ n can be considered quite accurate as are the measured indices .It is concluded that InSb tail band absorption i.e. that lying beyond the long wavelength edge of InAs. This analysis of the InSb absorption spectrum can be extended to shorter wavelength. It may be noted that this is approximately the excess absorption tail of InSb relative to GaAs,in contrast to the actual difference in indices of n=0.66.The clear implification of this analysis is that the majority of the refractive index arises from a relatively narrow band of intense absorption at wavelength well below 1 μm i.e. at very short wavelengths compared with the absorption edge [8-11].

As a model to provide such resonant absorption, we may consider the simple classical oscillator. For this, the optical constants are given by

$$n^2 - k^2 - 1 = [(\omega^2_0 - \omega^2)(Ne^2F/m)\varepsilon_\infty]/[(\omega^2_0 - \omega^2)^2 + \Upsilon^2\omega^2] \qquad (8)$$

Which for ω=0 gives

$$n^2 - 1 = (Ne^2F/m)\varepsilon_\infty\, \omega^2_0 \qquad (9)$$

Where N is the density of oscillations and F is the oscillator strength, i.e. essentially the number of valance electrons per atom, ω_0 is the angular frequency at resonance and ε_∞ is the dielectric constant of free space. Note that the index does not depend on the oscillator band width ϓ but only on the resonant frequency..The fact that this simple classical oscillator model could give a good quantitative explanation of the refractive index of Ge was pointed out by Moss[10].From the analysis of ultraviolet reflection spectra Phillips and Ehrenreich [6] showed that for Ge there is a strong peak in the absorption spectrum per atom, assuming any possible contribution from inner shell electrons is negligible, we calculate n^2-1=13.6 or n=3.84.Considering that the ultraviolet spectrum has considerable structure although the main peak is well pronounced this is very satisfactory agreement with the experimental value. Similarly, for very high index material PbTe, the measured peak of reflectivity is at 204 eV. The absorption peak will be at almost the same energy so,

$\omega_0 = 3.5\text{x}10^{15}$ and f= 2+6 electron/molecule

$n^2 - 1 = 30.6$ or n=5.62

Again very close to the known value

Equation (9) may also be written as

$$\varepsilon_\infty - 1 = n^2 - 1 = (\hbar\, \omega_p / E_g)^2 \qquad (10)$$

Where $\omega^2_p = [Nfe^2/m\, \varepsilon_\infty]$ is the valance electron plasma frequency and $E_g = \hbar\, \omega_p$ is the energy of the ultraviolet resonance. Penn gave a modified expression for the refractive index viz,

$$n^2 - 1 = (\hbar\, \omega_p / E_g)^2 S_0 \qquad (11)$$

Where the factor

$$s_0 = 1 - E_g/4Er + 1/3\ (E_g + 4\ E_f)^2 \qquad (12)$$

From the most materials there is little net contribution from the second and third term and Penn proposed that S_0 could be taken as unity. Also Heine and Jones [15] confirms that the energy E_g in the above expression should be identified with ultraviolet absorption peak. Ravindra et.al. gives a discussion of the influence of inner shell.The following relationships are found suitable for the estimation of valance electron plasma energy. Plasma energy $\hbar\, \omega_p$ can be related to the interionic distance by following equations,assuming that they are applicable to comound semiconductors and alkali halides [12]

$\hbar\, \omega_p = -8.08\ (r_0 + 39.10$ for alkali Halides I-VII group (13)

$\hbar\, \omega_p = -6.78\ (r_0) + 34.44$ group II-VI semiconductors (14)

$\hbar\, \omega_p = -8.99\ (r_0) + 37.80$ group III-V semiconductors (15)

Where $\hbar\,\omega_p$ and r_0 are the valance electron plasma energy in eV and interionic distance in A^0.

Results and conclusions

From above analysis it is concluded that the intense, relatively narrow absorption band which semiconductors have in ultraviolet region i.e. in far removed from the long wavelength absorption edge, is the absorption feature which essentially determines the refractive index. There are two important consequences of this finding (i) Any relationship between the refractive and the long wavelength absorption edge must arise from some relation between the ultraviolet oscillator frequency and the energy gap and (ii) Modification of the absorption edge which do not at the same time vary the resonance frequency cannot be expected to produce change in the refractive index.

The simplest assumption in mathematical terms, which can make to relate the resonant energy to the energy gap is to say that there is a constant difference the two i.e.

$$E_g = E_0 - B \tag{16}$$

This possibility was first postulated by Moss [10] and such an assumption has been made by Ravindera[9]. On the ground that the valance the valance and conduction bands are more or less parallel to each other. The consequences of this assumption will be considered, We have

$$E_0 = B\,(1 + E_g/B) \tag{17}$$

And writing (9)

$$n^2 - 1 = (\hbar\,\omega_p / E_g)^2$$

Then if we ignore unity compared with n^2 and also assume that $E_g \ll B$, both reasonable assumptions for many semiconductors, we obtain

$$n = (\hbar\,\omega_p / B) - (\hbar\,\omega_p / \omega)^2 E_g \tag{18}$$

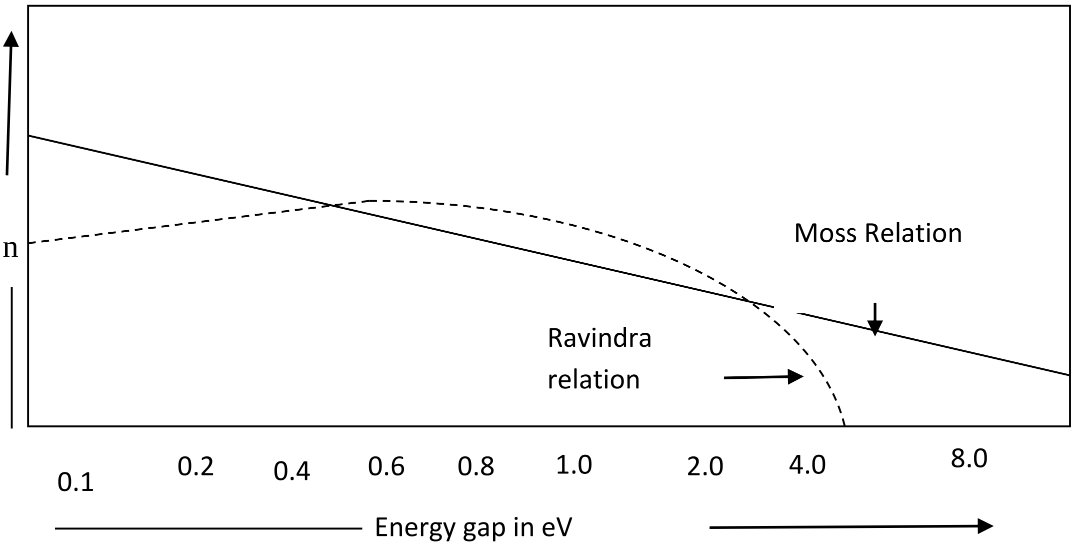
This form of relationship closely resembles the linear relation (5),put forward by Ravindra and Co-workers. However, it has significant disadvantage in comparison with the Moss relation.

As stated in the introduction, the two important attempts to relate the refractive index with the energy gap are the Moss relation given in equation (1) with the revised value of constant (equation 3) and Ravinder et.al. linear relation equation (4). The linear form of relationship has the slight disadvantage that it has two arbitrary constants compared with one in (equation 3),it has two more serious effects namely the behavior at high and low values of n respectively

For materials with high value of n the relation indicates that $n \geq 4$ cannot occur where as it is well known that the materials with much higher indices exist e.g. Pbse,n=4.7 and n=7.00 the latter being probable the highest reliably known index. In contrast, the Moss relation using the revised constant (equation -3) gives Pbse (E_g = 0.25 Ev),n=4.6;PbSnTe(Eg=0.032 eV)n=6.03 ,which are very reasonable predictions. The assumption of an approximately constant difference (B) between the resonance energy and the band energy on the grounds that the valance band and conduction bands are roughly context. It is necessary for any variation in B to be small compared with the change in E_g between two materials. In contrast for the ten materials listed by Gupta and Ravindra [11] the energy difference varies from 3.5 to 4.5 eV, while for PbTe it is only 2.1 eV. Hence the assumption of a constant energy difference is not justified for low gap (high index) materials.

For materials with low value of n here again the linear formula equation (4) gives unrealistic results, predicting that the index would become zero for E_g = 6.6 eV where as equation (1) would requires an infinite gap.For the conduction n=1 the linear relation requires E_g=5 eV only a values exceeded by many materials, although unity index is of course impossible in a material . By contrast equation (3) it would need Eg greater than 100 eV much larger than any real material more realistically, if we consider the highest energy gaps likely to exist (nearly 20 to25 eV) and the smallest indices found in solids (approximately 1.4).We find these two parameters quite compatible with the Moss relation.

These points are well illustrated by the fig(1) where a wide range of values of E_g and n is shown on a log –log plot. Most of the data is taken from Ravindra and his coworkers [], with Gopal's data for the Pb/Sn chalcogenides. On this plot the Moss relation is shown by full straight line and Ravindra relation is shown by dashed curve. It is clear from this fig. (1) That there is no sign of the sharp fall in n at high energy gaps If anything the indices rise sharply more rapidly than predicted by equation (1) and straight line corresponding to $(1/E_g) \alpha\, n^{3.4}$ might be an improvement . Plotting the data in this way thus shows very clearly that the Moss relation is superior and gives a good general representation of the data over the whole range of measured energy gaps. Clearly for the materials with low index and corresponding high energy gap the approximations $n^2 >> 1$ and $E_g << B$ are inadequate. Also identification of (4) with (15) implies that $(\hbar\, \omega_p /B)$ is a constant. Although for many materials the variation is plasma energy is small. It lies between 12.7 for InSb and 16.6 for Si for a wide range of semiconductors, It does depend directly on the lattice constant and has considerably larger values for low index solids e.g. AIN =23 ; diamond =31.Finally the two constants found empirically by Ravidra in relation equation (4), can be compared quantitatively with relation of equation (15). The mean value of $\hbar\, \omega_p$ for ten well known materials given by Gupta and Ravindra is 14.9 eV and the calculated values for the different binary crystals are given in Table (1-3) and also the mean energy difference is B=3.82 eV. Hence (a) First Ravindra term should be 14.9/3.82=3.9,which is not far from Ravindra value of 4.084 and (b) The second term should be $(\hbar\, \omega_p /B^2)$=1.023. This is much higher than Ravindra value $0.62E_g$. Alternatively this value implies that B should be 6.6eV.The main variables concerned are pressure, temperature and doping, of these doping and temperature effects arer the most marked and are of technological significance .Doping is most pronounced in very low energy gaps and low mass materials e.g. InSb, where filling the lower levels in the conduction band, thius effectively preventing optical transitions at energies below the Fermi level, produces a marked Burstein – Moss shift of the absorption edge.



[-Refractive index versus Energy gap relation Full line Moss relation and Dashed line Ravindra relation]

[Fig-1]

This effect of course always produces a positive dE/dN effect and there is corresponding negative dn/dN change. By contrast, the temperature change in E_g can be either negative or positive, the lead salts in particular showing a marked increase in the long wavelength absorption edge on cooling in contradiction to most other materials.In terms of predicting the variation in n for a known variation in E_g from equation(2)

$$(dn/dE_g)_{Moss} = (-n/4E_g) \tag{19}$$

And from equation (4)

$$(dn/dE_g)_{Moss} = 0.62 \tag{20}$$

These derivatives are thus equal when E_g = 1.23 eV and n=3.1 and the difference between the two predictions will be most marked for very small or very large values of E_g. In future work one can find the relationship between refractive index with density under the variation of pressure and temperature.

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Table -1

Calculated values of valance Plasma energies, energy gap and refractive index of Alkali Halides

Crystals	Structure (CN)	(Interatomic separation) R (A^0)	Plasma Energy $\hbar\omega_p$ (eV) (Equation (13)	Energy gap E_g (eV)	$\varepsilon_\infty = n^2$ Refractive index
LiF	NaCl (6)	2.01	22.84	9.49	1.93
LiCl	NaCl (6)	2.57	18.33	7.02	2.75
LiBr	NaCl (6)	2.75	16.87	5.91	3.16
Lil	NaCl (6)	3.09	14.62	4.38	3.80
NaF	NaCl (6)	2.31	20.43	9.99	1.74
NaC1	NaCl (6)	2.81	16.33	8.13	2.33
NaBr	NaCl (6)	2.98	14.98	7.21	3.60
Nal	NaCl (6)	3.23	13.96	6.00	3.01
KF	NaCl (6)	2.64	18.54	9.77	1.85
KCI	NaCl (6)	3.14	13.70	8.59	2.17
KBr	NaCl (6)	3.31	12.46	7.96	2.36
Kl	NaCl (6)	3.56	10.57	6.88	2.65
RbF	NaCl (6)	2.77	16.32	9.43	1.93
RbC1	NaCl (6)	3.27	12.52	8.56	2.18
RbBr	NaCl (6)	3.44	11.32	8.02	2.34
Rbl	NaCl (6)	2.69	17.55	7.15	2.58
CsF	NaCl (6)	3.03	14.78	8.65	2.16
CsC1	CsCl(8)	3.57	10.30	7.50	2.63
CsBr	CsCl(8)	3.70	9.06	6.95	2.78
CSI	CsCl(8)	3.95	7.13	5.88	3.05

Table -2

Calculated values of valance Plasma energies, energy gap and refractive index of II-VI group semiconducting compounds

Crystals	Structure (CN)	(Interatomic separation) R (A^0)	Plasma Energy $\hbar\omega_p$ (eV) (Equation (13))	Energy gap E_g (eV)	$\varepsilon_\infty = n^2$ Refractive index
CaO	NaCl (6)	2.40	18.13	6.15	3.33
CaS	NaCl (6)	2.84	15.14	5.40	4.50
CaSe	NaCl (6)	2.96	14.36	5.00	5.10
CaTe	NaCl (6)	3.17	12.89	4.20	6.30
SrO	NaCl (6)	2.57	16.95	5.80	3.30
SrS	NaCl (6)	2.94	14.03	4.80	4.40
SrSe	NaCl (6)	3.12	13.27	4.60	4.90
SrTe	NaCl (6)	3.24	11.81	4.00	5.80
BaO	NaCl (6)	2.75	15.66	4.20	3.00
BaS	NaCl (6)	3.18	13.78	4.00	7.10
ZnO	Wu(4)	1.95	21.22	3.20	3.75
ZnS	Zb(4)	2.36	18.11	3.70	5.20
ZnSe	Zb(4)	2.45	17.83	2.58	5.90
ZnTe	Zb(4)	2.63	16.61	2.10	7.30
CdO	NaCl (6)	2.35	18.51	2.60	4.63
CdS	Wu(4)	2.52	14.57	2.40	5.20
CdSe	Wu(4)	2.62	14.03	1.70	6.10

Table -3

Calculated values of valance Plasma energies, energy gap and refractive index of III-VI group semiconducting compounds

Crystals	Structure (CN)	(Interatomic separation) R (A^0)	Plasma Energy $\hbar\omega_p$ (eV) (Equation (13))	Energy gap E_g (eV)	$\varepsilon_\infty = n^2$ (Refractive index)^2
AlN	Wu(4)	1.86	21.08	3.80	4.80
AlP	Zb(4)	2.35	16.67	3.00	8.50
AlAs	Zb(4)	2.43	15.95	2.40	10.3
AlSb	Zb(4)	2.66	13.89	1.50	10.2
GaN	Wu(4)	1.94	20.36	3.40	5.00
GaP	Zb(4)	2.36	16.58	2.24	8.50
GaAs	Zb(4)	2.43	15.95	1.40	11.3
GasB	Zb(4)	2.65	13.95	0.07	14.4
InIN	Wu(4)	2.13	18.65	2.40	5.50
InP	Zb(4)	2.54	14.97	1.25	9.60
InAs	Zb(4)	2.62	14.25	0.33	12.3
InSb	Zb(4)	2.80	12.63	0.18	15.7

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