

Energy gap–refractive index relations in semiconductors – An overview

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Abstract

An overview of the understanding of correlations between energy gap and refractive index of semiconductors is presented here. The atomic approach of Moss, the nearly free electron model of Penn, the oscillator concept of Wemple and the optical polarizability approach of Finkenrath are considered in this study. The Ravindra relation is discussed in the context of alternate approaches that have been presented in the literature. Case studies of applications of these relations to infrared materials and wide band gap semiconductors are presented.

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1. Introduction

The refractive index and energy gap of semiconductors represent two fundamental physical aspects that characterize their optical and electronic properties. The applications of semiconductors as electronic, optical and optoelectronic devices are very much determined by the nature and magnitude of these two elementary material properties. These properties also aid in the performance assessment of band gap engineered structures for continuous and optimal absorption of broad band spectral sources. In addition, devices such as photonic crystals, wave guides, solar cells and detectors require a pre-knowledge of the refractive index and energy gap. Application specific coating technologies (ASPECT™) [1] including antireflection coatings and optical filters [2] rely on the spectral properties of materials.

The energy gap determines the threshold for absorption of photons in semiconductors. The refractive index in the semiconductor is a measure of its transparency to incident spectral radiation. A correlation between these two fundamental properties has significant bearing on the band structure of semiconductors. In 1950, Moss [3] proposed a basic

relationship between these two properties using the general theory of photoconductivity which was based on the photo effect studies of Mott and Gurney [4], Smekal [5], Zwicky [6], Gudden and Pohl [7] and Pearson and Bardeen [8]. According to this theory, the absorption of an optical quantum will raise an electron in alkali halides to an excited state rather than freeing it from the center. Thermal energy then moves this electron to the conduction band from the lattice. Such a photo effect takes place in imperfections at certain lattice points, and thus, the electron behaves similar to an electron in an isolated atom with a dielectric constant of the bulk material. As a result of this effective dielectric constant, ϵ_{eff} , the energy levels of the electron are scaled down by a factor of $1/\epsilon_{\text{eff}}^2$ which approximately corresponds to the square of the refractive index, n . This factor, thus, should be proportional to the energy required to raise an electron in the lattice to an excited state as given by the Bohr formula for the ionization energy, E , of the hydrogen atom, $E = 2\pi^2 m^* e^4 / \epsilon^2 h^2$, where, m^* is the electron effective mass, e is the electronic charge, ϵ is the relative permittivity and h is the Plank constant. This minimum energy determines the threshold wavelength, λ_e , which then varies as the fourth power of the refractive index. Experimental data on different photoconductive compounds show that the values of n^4/λ_e were close to 77 throughout a range of refractive indices. The

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similarities in the quotient show that the photoelectrons stem from the same type of lattice imperfections, or alternatively, the binding energies to the different types of hydrogen-like centers are similar. Thus the Moss relation was formulated as [3]:

$$\frac{n^4}{\lambda_e} = 77/\mu\text{m} \quad (1)$$

where n is the refractive index and λ_e is the wavelength corresponding to the absorption edge. In terms of energy gap, this is [9]:

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

According to this relation, the refractive index of a semiconductor can be determined with a known energy gap, E_g . This relation, again, was based on the general assumption that all energy levels in a solid are scaled down by a factor of $1/\epsilon_{\text{eff}}^2$.

2. Penn model

In 1962, Penn [10] proposed a simple model for an isotropic semiconductor with electrons in a sphere of momentum space and are characterized by an isotropic energy gap. In his investigation of a nearly free electron model for a semiconductor, Penn showed that two common assumptions were flawed in Callaway's approximation of the static dielectric constant [11]. Previous semiconductor models did not allow for the formation of standing waves in the Brillouin zone. The Umklapp process was neglected. The energy, E , and wave function, ψ , with respect to the state k for this model are given by,

$$E_{\mathbf{k}}^{\pm} = \frac{1}{2} \{ E_{\mathbf{k}}^0 + E_{\mathbf{k}'}^0 \pm [(E_{\mathbf{k}}^0 - E_{\mathbf{k}'}^0)^2 + E_g^2]^{1/2} \}$$

$$\psi_{\mathbf{k}} = (e^{i\mathbf{k}\cdot\mathbf{r}} + \alpha_{\mathbf{k}}^{\pm} e^{i\mathbf{k}'\cdot\mathbf{r}}) / [1 + (\alpha_{\mathbf{k}}^{\pm})^2]^{1/2}$$

where

$$\alpha_{\mathbf{k}}^{\pm} \equiv \frac{1}{2} E_g / (E_{\mathbf{k}}^{\pm} - E_{\mathbf{k}'}^0) \quad (3)$$

$$E_{\mathbf{k}}^0 \equiv (\hbar^2/2m)k^2, \quad \mathbf{k}' \equiv \mathbf{k} - 2K_F \hat{k}$$

Here, E is the electron energy, \mathbf{k} is the wave vector, \mathbf{K}_F is the Fermi wave vector and α represents an averaged Jones boundary [12]. The electron energy E as a function of wave vector k for an isotropic three-dimensional free electron model is plotted in Fig. 1. This model of placing the energy gap above the Fermi surface was first suggested by Callaway [11] in his investigation of the correlation energy of electrons.

Fig. 2 shows the density of states vs. the energy and describes the treatment of the Penn model. The dashed line represents Callaway's model and the solid line represents the Penn model. According to the Penn model, the states from the energy gap are removed and piled up at the top of the valence band and the bottom of the conduction band [10]. The resulting graph is thus asymptotic.

Based on this model, Penn describes the dielectric function as:

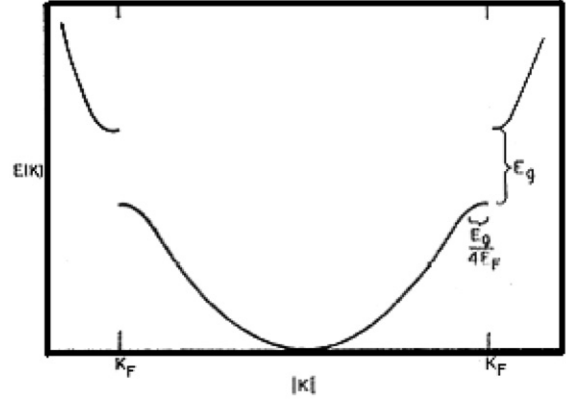


Fig. 1. Electron energy as a function of k for isotropic three-dimensional nearly free electron model [10].

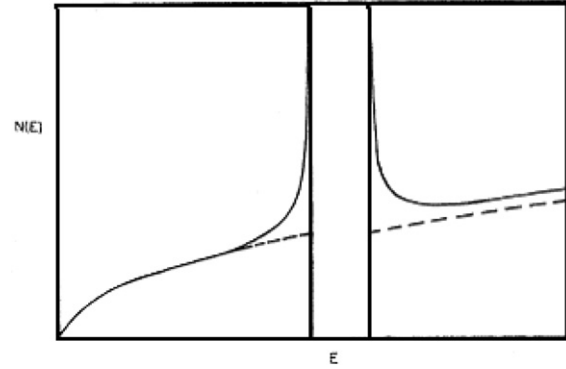


Fig. 2. Density of states vs. energy. The solid curve represents the three-dimensional nearly free electron model while the dashed curve represents Callaway's model [10].

$$\epsilon(\mathbf{q}) = 1 + \frac{8\pi e^2}{q^2} \left[\sum_{\mathbf{k}} N_{\mathbf{k}} (1 - N_{\mathbf{k}+\mathbf{q}}) \frac{|\langle \mathbf{k} | e^{-i\mathbf{q}\cdot\mathbf{r}} | \mathbf{k} + \mathbf{q} \rangle|^2}{E_{\mathbf{k}+\mathbf{q}}^+ - E_{\mathbf{k}}^-} + \sum_{\mathbf{k}} N_{\mathbf{k}} (1 - N_{\mathbf{k}'}) \frac{|\langle \mathbf{k} | e^{-i\mathbf{q}\cdot\mathbf{r}} | \mathbf{k}' \rangle|^2}{E_{\mathbf{k}'}^+ - E_{\mathbf{k}}^-} \right] \quad (4)$$

In this equation, $\mathbf{k}' = \mathbf{k} + \mathbf{q} - (2K_F)(\mathbf{k} + \mathbf{q})/|\mathbf{k} + \mathbf{q}|$ where \mathbf{K} is the reciprocal lattice vector and \mathbf{q} is a wave number. N is the occupation number for the states \mathbf{k} and $\mathbf{k} + \mathbf{q}$. e is the electronic charge. If the Brillouin zone is divided into sections, then the dielectric function can be written as:

$$\epsilon(\mathbf{q}) = 1 + \frac{8\pi e^2}{q^2} \sum_{\mathbf{k}i} \delta_{\mathbf{k}}^i \frac{|M_i|^2}{E_i} \quad (5)$$

where $\delta_{\mathbf{k}}^i = 1$ when k is in the i region and 0 otherwise. M_i is the matrix element. For the specific case when $q = 0$,

$$\epsilon(0) \approx 1 + (\hbar\omega_p/E_0)^2 + [1 - (E_g/E_F/4) + ((E_g/E_F)^2 + 48)] \quad (6)$$

where ω_p is the plasma frequency and E_F is the Fermi energy. The expression in the brackets is nearly equal to 1 for materials with band gaps in the commonly occurring range where $(E_g/E_F) = 0.3$ [12]. Since the most significant varia-

tion occurs in the expression before the square brackets, (5) can be written as,

$$\varepsilon(0) \approx 1 + (\hbar\omega_p/E_0)^2 \cdot S_0 \quad (7)$$

where S_0 represents the quantity in brackets in Eq. (6). Penn approximates S_0 to be nearly 1, thereby neglecting the smaller quantities of E_g/E_F . The dielectric function is thus:

$$\varepsilon(0) \approx 1 + (\hbar\omega_p/E_0)^2 \quad (8)$$

Grimes and Cowley [12] found a more accurate value of S_0 . In their investigation, Grimes and Cowley found that the value of S_0 is only weakly dependent on the band gap and that a value of 0.62 is a fairly good representation of S_0 . Thus, with this slightly more accurate value for S_0 , the energy gap can be determined by using appropriate values of the dielectric constant.

In the Penn model, the dielectric constant was found to have reasonable values for small values of wave number (\mathbf{q}). This model is quite simplistic in design, though it accounts for the formation of standing waves near the Brillouin zone. It does not consider the degeneracy that may occur in the Brillouin zone. In spite of the simplicity of the Penn model, the mere isotropy of the system allows the model to be applied to a liquid or amorphous semiconductor.

3. Ravindra relation

The Ravindra relation, which was initially proposed empirically [13] was shown to be an approximation [14] of the Penn model [10]. One feature common to all the semiconductor band structures is that the valence and conduction bands are more or less parallel to each other at least along the symmetry directions. This formed the basis for Gupta and Ravindra [14] to define:

$$E_p = E_g + K \quad (9)$$

Using Eq. (9) in the Penn model in Eq. (8) and considering the situation for which $E_g/K < 1$, Gupta and Ravindra arrived at an expression for the refractive index:

$$n = K_1 - K_2E_g + K_3E_g^2 - K_4E_g^3 \quad (10)$$

where the values of K are calculated by Gupta and Ravindra [14] and the higher values are neglected since they are too small to be considered. Eq. (10) then reduces to a form:

$$n = 4.16 - 1.12E_g + 0.31E_g^2 - 0.08E_g^3 \quad (11)$$

The oscillator model from Wemple [15] defines the dielectric constant as: $\varepsilon = 1 + E_d/E_0$ where ε is the real part of the complex dielectric constant, E_d is the oscillator strength and E_0 is the average energy gap which is approximately equal to the Penn energy gap, E_p .

Performing a similar treatment with the dielectric function in the optical region, they [14] show a similar equation for the refractive index with the constants evaluated,

$$n = 4.16 - 0.85E_g \quad (12)$$

Other forms of the Ravindra relation include a variation of the relation with respect to temperature and pressure [16]:

$$\frac{dn}{dT} = -0.62 \frac{dE_g}{dT} \quad (13)$$

$$\frac{dn}{dp} = -0.62 \frac{dE_g}{dp} \quad (14)$$

3.1. Moss relation and its implications

It is perhaps noteworthy to mention that other optical properties of semiconductors are merely integral relations to the energy gap and refractive index. Moss [9] pointed out that the absorption edge can be calculated using the refractive index. Moss [9] showed that the refractive index and absorption edge are related by:

$$n - 1 = \frac{1}{2\pi^2} \times \int \left(K \frac{d\lambda}{1 - \frac{z^2}{\lambda_c^2}} \right) \quad (15)$$

which for long wavelengths at zero frequency becomes,

$$n - 1 = \frac{1}{2\pi^2} \times \int K d\lambda \quad (16)$$

Here, K is the absorption coefficient and λ_c is the wavelength corresponding to the absorption edge. This function is integrated over the wavelength rather than energy. This expression shows that the long wavelength refractive index is determined simply by the total area under the curve of absorption coefficient vs. wavelength – it is independent of the absorption spectrum [18]. As a result, if a certain level of absorption persists over a given energy interval – as it occurs where absorption is due to transitions between two allowed energy bands – then, the 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 larger n [9].

Moss [9] provided an illustration of this relation in his paper. This analysis shows that much of the refractive index originates from narrow bands of intense absorptions. The absorption occurs at wavelengths below $1 \mu\text{m}$ which corresponds to the very short wavelength compared to the absorption edge.

With these observations, Moss concluded that the narrow absorption band of semiconductors in the UV region is the factor which determines the refractive index. Two conclusions followed from this assumption: (1) the relation between the energy gap and UV oscillator frequency are factors in determining the relationship between the refractive index and the long wavelength absorption edge; (2) any modifications of the absorption edge that do not vary at the same time are not expected to produce a change in the refractive index.

Moss compared his relation with the Ravindra relation [9]. The Ravindra relation predicts no results of indices

beyond 4.1. However, very reliable infrared materials, such as PbSe and PbSnTe, do exist at refractive indices of 4.7 and 7.0 respectively. The Moss formula, however, closely estimates these values with the formula: $n^4 E_g = 108$ eV where the constant has been revised. This formula yields refractive indices of 4.6 for PbSe and 6.03 for PbSnTe. For low refractive indices, the Ravindra relation predicts impractical results. It predicts that the refractive index will become zero when the energy gap is 6.6 eV. The Moss formula on the other hand requires that the energy gap be infinity for the same result. For the index to be unity, the Ravindra relation predicts the energy gap to be 5 eV. However, there exist materials which exceed this value. The Moss relation requires that the energy gap should be greater than 100 eV to obtain a refractive index of 1. This is much larger than the refractive index of any material.

In a theoretical derivation of optical polarizability, Finkenrath [17] described a treatment in the transitions from the valence band to the conduction band. These transitions are represented by differential oscillator densities that occur at distributed resonant frequencies. The combined polarizabilities are summed and replaced by an integral over the relevant frequencies. These differential oscillators are identified through the wave number and occupation probability based on spherical energy surfaces. The result of this study showed that $(\epsilon_{\text{eff}} - 1)^2 E_g$ is a complex expression that is basically constant. From this expression, one can see that neglecting unity compared to the dielectric constant gives the Moss relation. According to Finkenrath's estimate, the average value of the constant is nearly 95 eV. These observations are made for direct interband transitions. It must be understood that, if the transitions are not direct, then deviations could arise from ignoring the transitions from other bands and the varying densities of states and the matrix elements.

Moss [9] thus showed the interrelations between the refractive index and the absorption. He showed that the important factor that determines the index is the frequency of the UV absorption peak. Reasonable values for the refractive index can be found using the model of a single classical oscillator at this frequency. The relation between the refractive index and the absorption edge band energy arises from the comparative nature of the band edge and the resonance energy. Assuming a constant energy difference, a relation similar to the linear Ravindra relation can be obtained. However, the Ravindra relation is shown to have a few shortcomings at high and low index values. The Moss relation out performs the Ravindra relation in these areas and is further supported by formal theory from Finkenrath. From the different semiconductors known, one can understand that a relationship between refractive index and energy gap, or for that matter, other optical constants that are integrally related, can only be general and approximate at best. From Moss [9], it is seen that where the Ravindra relation fails, the Moss relation holds approximately true.

4. Alternate approaches and interpretations

Further relations were developed as a modification or addition to the Moss and Ravindra relations. While the Moss formula is limited by the structure of the material, the Ravindra relation is restricted by the refractive index. From the Ravindra relation, the refractive index cannot be greater than a value of 4.1, which corresponds to an energy gap of 6.587 eV. In an effort to broaden the application of these two concepts, several authors have presented variations of the Moss and Ravindra relations.

In 1992, a relation similar to the Moss relation was proposed by Reddy and Anjaneyulu [19]. According to their formula, the relation is:

$$E_g e^n = 36.3 \quad (17)$$

This relation holds true for energy gaps greater than 0 eV.

Reddy and Ahammed [20] proposed an empirical relation that was a modification of the Moss formula [18]

$$n^4 (E_g - 0.365) = 154 \quad (18)$$

This relation was proposed to overcome some of the drawbacks of the Moss relation. However, it is not valid when the energy gap is less than 0.36 eV nor does it hold for infrared materials such as lead salts and InSb.

Further derivations based on the Moss and Ravindra relations include approaches by Herve and Vandamme [21]. They separated the semiconductors into a covalently bonded group and ionically bonded group. For a covalently bonded crystal, the dielectric function is:

$$\epsilon(\omega) = 1 + 4\pi Nq^2 / [m(\omega_0^2 - \omega^2)] \quad (19)$$

where N is the density of valence electrons, m the rest mass and ω_0 the UV resonance frequency. Eq. (19) describes the dielectric constant for elements like Si and Ge. For the case of binary compounds such as NaCl or GaAs, the dielectric function needs to account for the ionic bonding. Thus the dielectric function in an ionic diatomic lattice is,

$$\epsilon'(\omega) = \epsilon'(\omega_{\text{op}}) + \Omega_p^2 / (\omega_T^2 - \omega^2) \quad (20)$$

where Ω_p is similar to the plasma frequency for ions and ω_T is the infrared resonance frequency. To account for materials in the optical range, $\omega_T < \omega_{\text{op}} < \omega_0$, Herve and Vandamme proposed,

$$n = [\epsilon'(\omega_{\text{op}})]^{1/2} = n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2} \quad (21)$$

where A is the hydrogen ionization energy ≈ 13.6 eV and B is 3.47 eV. Herve and Vandamme based this equation on oscillatory theory, assuming the UV resonance energy has a constant difference with band gap energy,

$$h\omega_0 = E_g + B \quad (22)$$

Herve and Vandamme claim that their model provides the lowest deviation for III–V, I–VII and chalcopyrites. This

model is accurate for most materials used in optoelectronic device structures and high band gap materials. Yet it does not explain the behavior of the IV–VI group.

In the Moss, Ravindra and Herve and Vandamme relations, the variation of the energy gap with temperature leads to three relations. By differentiating their relation with respect to temperature, we arrive at:

$$\frac{dn}{dT} = -\frac{13.6^2}{n(E_g + B)^3} \times \left(\frac{dE_g}{dT} + B_1 \right) \quad (23)$$

where $B_1 = \frac{dB}{dT}$ Allowing, $E_g + B = \sqrt{\frac{13.6^2}{n^2} - 1}$,

$$\frac{1}{n} \frac{dn}{dT} = -\frac{(n^2 - 1)^{3/2}}{13.6n^2(E_g + B)^3} \times \left(\frac{dE_g}{dT} + B_1 \right) \quad (24)$$

Similarly, the Moss and Ravindra relations were differentiated to arrive at temperature coefficient for the energy gap.

A few values of (dE_g/dT) and (dn/dT) calculated using this relation for some semiconductors are given in Table 1.

In conducting this study, Herve and Vandamme [22] found two particular temperature dependences. Generally, the energy gap and temperature are inversely proportional for most semiconductors, that is, as T increases, the energy gap decreases, and, as a result, the refractive index increases. This occurs in diamond and similar structures. On the other hand, infrared detector materials including the lead sulphide, lead selenide and lead telluride exhibit a positive temperature coefficient of energy gap and negative refractive index temperature dependence.

Herve and Vandamme [22] found that the Moss relation showed the strongest deviation at lower energy gaps (<1.43 eV), as shown in Fig. 3. Above this value, the Moss relation provides results closest to the experimental values.

Calculations made with the Ravindra relation show more accurate estimations for energy band gap values less than 1.43 eV. These results deviate at energy gaps greater than 1.43 eV. Herve and Vandamme found that their model presents the best results below the specified energy gap and is quite close to the experimental results above 1.43 eV.

Table 1

Energy gap, its temperature coefficient and refractive index temperature dependence for some semiconductors as calculated by the Herve Vandamme equation [22]

| Material | E_g (eV) | dE_g/dT (eV K ⁻¹) | $(dn/dT)/n$ (K ⁻¹) |
|----------|------------|---------------------------------|--------------------------------|
| InSb | 0.18 | -2.8×10^{-4} | 6.9×10^{-5} |
| PbSe | 0.278 | $+5.1 \times 10^{-4}$ | -2.1×10^{-4} |
| Ge | 0.67 | -3.7×10^{-4} | 6.9×10^{-5} |
| GaSb | 0.75 | -3.7×10^{-4} | 8.2×10^{-5} |
| Si | 1.1 | -2.8×10^{-4} | 4.0×10^{-5} |
| InP | 1.35 | 2.9×10^{-4} | 2.7×10^{-5} |
| GaAs | 1.43 | -3.9×10^{-4} | 4.5×10^{-5} |
| AlAs | 2.15 | -4.0×10^{-4} | 4.6×10^{-5} |
| AlP | 2.41 | -3.7×10^{-4} | 3.6×10^{-5} |
| SiC | 2.86 | 3.3×10^{-4} | 2.9×10^{-5} |
| GaN | 3.5 | -4.8×10^{-4} | 2.6×10^{-5} |
| C | 5.48 | -5.0×10^{-5} | 4.0×10^{-6} |

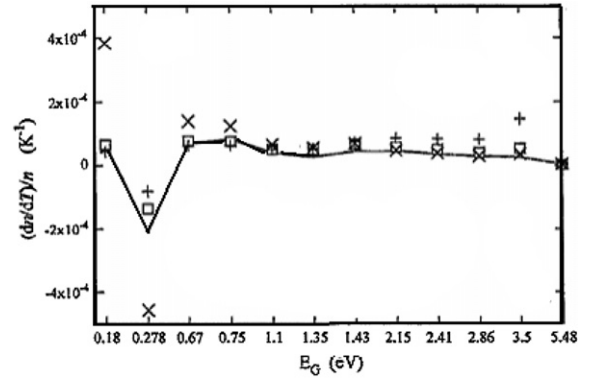


Fig. 3. Temperature coefficient of refractive index vs. energy band gap. The solid line represents the experimental results. The cross (x) represent the differentiated Moss formula, the (+) represent the differentiated Ravindra formula and the open squares (□) represent the Herve Vandamme model [22].

5. Case studies of applications to condensed matter physics

5.1. IR detector materials

One application of the energy gap–refractive index relation helps to determine the strontium composition in PbSe and lead-alkaline-earth-chalcogenide materials ($Pb_{1-x}Sr_xSe$ [23]). The compounds are notably used in mid infrared (mid-IR) lasers and mid-IR/ultraviolet (UV) detectors. The energy gap and refractive indices of these materials depend on the strontium composition. Majumdar et al. [23] sought to determine the electronic and optical properties of the ternary compound for Sr compositions. PbSe has a direct band gap at 0.3 eV, at the L point of the Brillouin zone [23]. Contrastingly, SrSe has a wide indirect band gap between the X – Γ bands of the Brillouin zone. As the amount of Sr in $Pb_{1-x}Sr_xSe$ increases, the band gap changes from narrow and direct to wide and indirect. Majumdar et al. have determined the composition at which this change takes place.

In their experiment [23], the transmission spectra measured from the epitaxial layers of $Pb_{1-x}Sr_xSe$ were used to calculate the refractive index and the absorption coefficient. The refractive index was approximated from odd interference peaks in the long wavelength region, which is below the energy gap. This approximated value was then fitted with the experimental curve from which the true refractive index and absorption coefficient were determined. The refractive index of $Pb_{1-x}Sr_xSe$ was calculated and was found to be in the range of 4.8–2.04 for room temperature and for a strontium composition of 0–1 at a wavelength of 4 μ m. Similarly, SrSe has a refractive index of 2.04 at room temperature and at a wavelength of 4 μ m. This is shown in Fig. 4.

From Fig. 4, the refractive index of PbSe shows a negative temperature coefficient while SrSe shows a positive coefficient. When the composition is nearly $Pb_{0.82}Sr_{0.18}Se$, the refractive index at the specified wavelength is

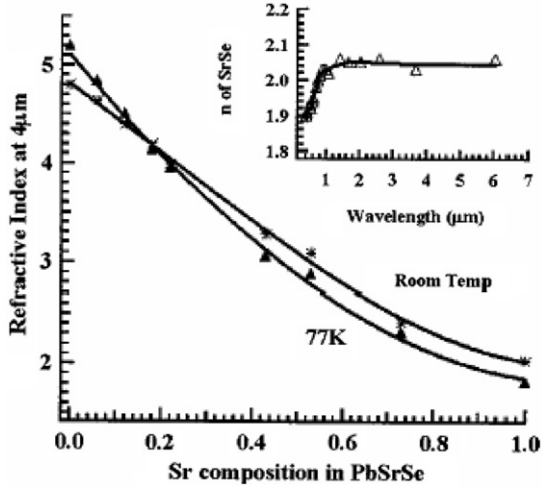


Fig. 4. Refractive index of $Pb_{1-x}Sr_xSe$ for different strontium compositions at room temperature and liquid nitrogen temperature (77 K) at a wavelength of $4 \mu m$. Inset shows refractive index of SrSe at 77 K [23].

independent of temperature in the measured range. The slope of the curvature of the absorption coefficient changes dramatically with the increase of Sr in the compound. Such a change in curvature of the absorption coefficient represents a change in band gap.

The absorption coefficients for direct and indirect transitions are calculated as follows:

$$\alpha_{\text{direct}} = \frac{A}{(hv)^{1/2}} (hv - E_g)^{1/2} \quad (25)$$

$$\alpha_{\text{indirect}} = \frac{B}{hv} (hv - E_g \pm E_p)^2$$

Here, A and B are constants, hv is the photon energy and E_p is the phonon energy. The phonon energy is much lower than the energy band gap and so is neglected. These equations only hold true in the region where the photon energy is greater than the energy band gap. Taking the second derivative of the absorption coefficient (α) (25) with respect to the photon energy yields,

$$\frac{d^2\alpha_{\text{direct}}}{d(hv)^2} = \frac{-AE_g}{4} \{4(hv)^3 - 3(hv)^2E_g\} \{(hv)^4 - (hv)^3E_g\}^{-3/2}, \quad (26)$$

which is negative for $hv > E_g$ and,

$$\frac{d^2\alpha_{\text{indirect}}}{d(hv)^2} = 2 \frac{BE_g^2}{(hv)^3} \quad (27)$$

which is positive for $hv > E_g$. As the absorption coefficient changes from negative to positive, the band gap changes from direct to indirect due to the increase in strontium composition [23]. Fig. 5 shows the direct and indirect band gap plotted against the strontium composition at 77 K for $Pb_{1-x}Sr_xSe$.

The following equations were found to describe the best fit for the curve of the calculated direct and indirect band gap energies:

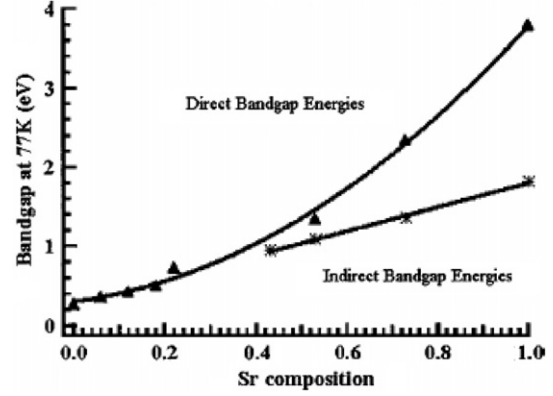


Fig. 5. Direct and indirect band gap energies for $Pb_{1-x}Sr_xSe$ at different compositions of strontium at 77 K [23].

$$E_{\text{gdirect}} = 0.278 + 1.356x + 1.040x^2 + 1.144x^3 \quad (\text{eV}) \quad (28)$$

$$E_{\text{gindirect}} = 0.29 + 1.527x \quad (\text{eV})$$

As can be seen, the direct band gap shows a dependence on a polynomial function of the strontium composition (x) while the indirect band gap is linear in nature with respect to the strontium composition. In this experiment, Majumdar et al. found the indirect band gap of SrSe at 77 K to be 1.82 eV and the direct band gap to be 3.81 eV. For PbSe, the direct band gap occurred at 0.278 eV at 77 K. Majumdar et al. assumed that the lowest indirect band gap energy for all strontium compositions (0.43–1) occurs at similar bands which separate linearly as the amount of strontium increases. This occurs as the indirect band gap of $Pb_{1-x}Sr_xSe$ changes linearly with the strontium composition. When the indirect band gap energy curve of lower Sr composition is extrapolated, the direct energy band gap curve crosses at $x \sim 0.2$. This suggests that at $x \sim 0.2 - 1$, the lowest energy band gap of $Pb_{1-x}Sr_xSe$ is direct.

Majumdar et al. have thus, determined the refractive indices and direct and indirect band gaps of $Pb_{1-x}Sr_xSe$ for strontium compositions ranging from 0 to 1. Using the data obtained in this experiment, it would be possible to aid further development of optoelectronic devices based on $Pb_{1-x}Sr_xSe$.

5.2. HgZnTe (MZT)

Ali Omar and El-Akkad [24] performed a study on the optical parameters of mercury zinc telluride (MZT) in solid solution. MZT is a direct band gap material with an energy gap between -0.15 and 2.20 eV depending on the composition ratio. An equation describing the energy gap is,

$$E_g = a_0 + a_1x^{1/2} + a_2x + a_3x^2 + a_4x^3 \quad (\text{eV}) \quad (29)$$

The best fit was found to be,

$$E_g = -0.1016 + 1.978x + 0.3144x^2 \quad (30)$$

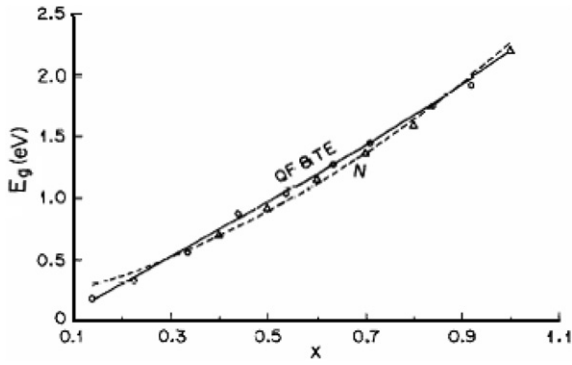


Fig. 6. E_g vs. percent composition. TE refers to the energy gap equation (29) and QF refers to the best fit equation (30). N refers to the ternary solution equation (32) [24].

where x represents the percent composition. According to Nag [25], an empirical formula illustrating the dependency of energy gap on percent composition is given by,

$$E_g = (a - b\bar{Z})^2 \tag{31}$$

where a and b depend on the semiconductor group. When this formula is applied to the ternary solution, $E_g(x)$ becomes:

$$E_g(x) = 0.15 + 0.8637x + 1.245x^2 \text{ (eV)} \tag{32}$$

Fig. 6 describes the results of Eqs. (29)–(32).

Relating the energy gap to the refractive index, Ali Omar and El-Akkad refer to the Ravindra relation. With reference to the best fit, this equation is:

$$n = 4.036 - 1.127x - 0.262x^2 \tag{33}$$

In the range of $0 \leq x \leq 1$ the quadratic approximation is

$$n_{CM} = 3.84 - 1.56x + 0.428x^2 \tag{34}$$

From graphical illustrations of the refractive index vs. percent composition, as in Fig. 7, the refractive index is seen to decrease with x .

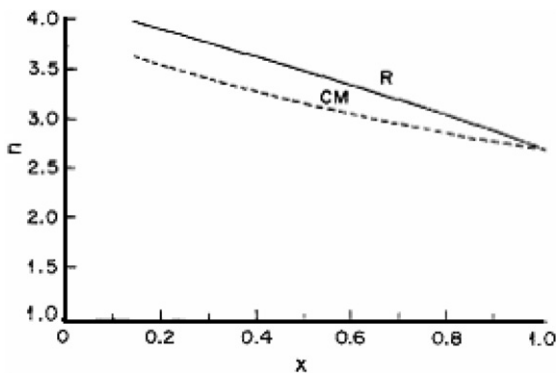


Fig. 7. Refractive index vs. composition ratio. R refers to refractive index with respect to best fit, CM refers to the quadratic approximation [24].

Studying the relation between these parameters, composition and E_g for MZT allows for an understanding and use of the material for IR detectors and solar cells.

5.3. GaN

Bourissa [26] performed a study on the pressure dependence of optoelectronic properties of GaN in the zinc-blende structure. The refractive index was calculated at different pressures with the Moss, Ravindra and Herve Vandamme relations. On a graph of the band lineup vs. pressure, the conduction band minimum is seen to increase with the increase in pressure at Γ yet it is seen to decrease at X . The valence band maximum decreases at Γ (Fig. 8).

The lowest direct energy gap increases with increasing pressure while the indirect gap is seen to have a smaller dependence on pressure. As a result, the direct band gap of zinc-blende GaN cannot be expected to crossover to indirect behavior in the pressure range studied (Fig. 9).

The dependency of band gap on pressure can be represented by,

$$E = a^* + b^* \left(\frac{\Delta a}{a_0} \right) + c^* \left(\frac{\Delta a}{a_0} \right)^2 \tag{35}$$

where $\Delta a = a_p + a_0$ and a_p and a_0 are lattice constants at pressure p and zero pressure. Applying this to the equation describing least square fit, namely,

$$E(p) = E(0) = \frac{dE(p)}{dp} p \tag{36}$$

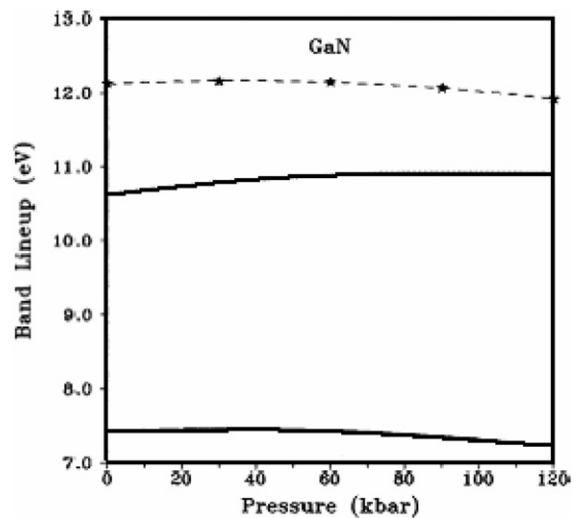


Fig. 8. Band lineup in eV vs. pressure in (kbar). The valence band maximum Γ is indicated by (—) while the conduction band Γ is indicated (\cdots). ($-\star-$) indicates the conduction band X bottom [26].

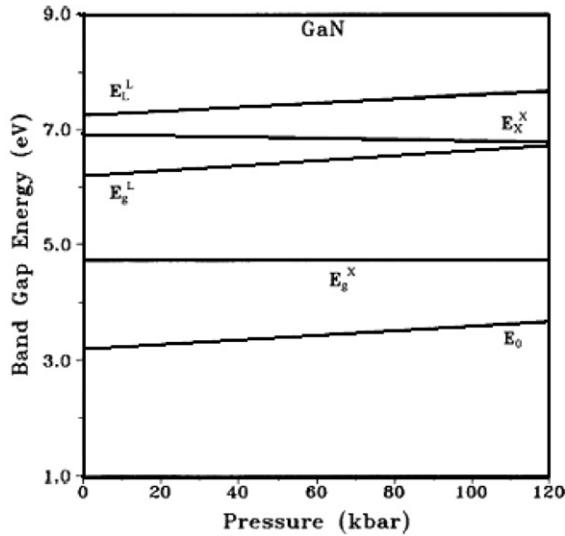


Fig. 9. Direct and indirect band gaps of GaN as a function of pressure in (kbar) [26].

is then,

$$\begin{aligned}
 E_0 &= 3.2 - 23.83 \left(\frac{\Delta a}{a_0} \right) + 195.62 \left(\frac{\Delta a}{a_0} \right)^2 \\
 E_x^x &= 6.91 + 3.24 \left(\frac{\Delta a}{a_0} \right) - 240.65 \left(\frac{\Delta a}{a_0} \right)^2 \\
 E_L^L &= 7.23 - 23.60 \left(\frac{\Delta a}{a_0} \right) + 106.10 \left(\frac{\Delta a}{a_0} \right)^2 \\
 E_g^x &= 4.70 - 0.16 \left(\frac{\Delta a}{a_0} \right) + 1.22 \left(\frac{\Delta a}{a_0} \right)^2 \\
 E_g^L &= 6.20 - 25.48 \left(\frac{\Delta a}{a_0} \right) + 166.76 \left(\frac{\Delta a}{a_0} \right)^2
 \end{aligned} \quad (37)$$

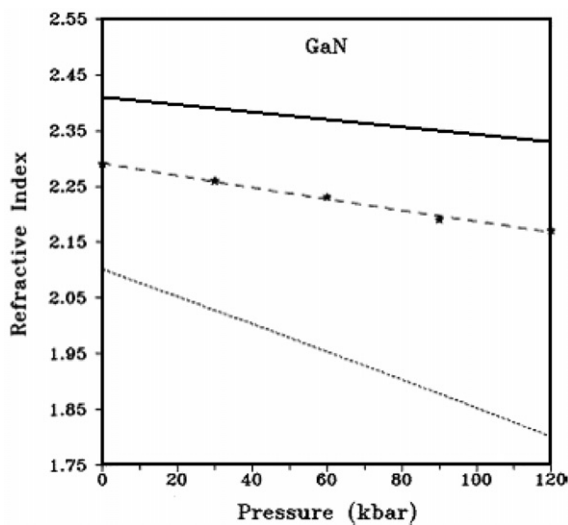


Fig. 10. Refractive index as a function of pressure for GaN. (—) indicates Moss relation, (···) represents Ravindra relation and (-★-) is the Herve Vandamme relation [26].

Table 2

Refractive indices at zero pressure and the first pressure derivative for GaN [26]

| Model | n | $\frac{dn}{dp}$ (10^{-3} kbar $^{-1}$) |
|-----------------------------|-------|--|
| Moss relation | 2.41 | -0.67 |
| Ravindra et al. relation | 2.10 | -2.40 |
| Herve and Vandamme relation | -2.29 | -1.13 |

These dependencies show a non-linear behavior. From Fig. 9, the valence band width is shown to increase with pressure. This can be attributed perhaps to decreasing ionicity under hydrostatic compression which is typical of semiconductors.

The refractive index obtained by the three models is also plotted as a function of pressure in Fig. 10.

In Fig. 10, the refractive index is seen to decrease linearly with respect to increasing pressure, as opposed to the energy gap which shows the opposite behavior. It can be concluded that for GaN and other III–V compounds, the smaller the energy band gap, the larger the refractive index.

In Table 2 are the refractive indices at zero pressure and the first pressure derivative. The refractive index obtained by the Moss relation shows a large difference when compared with the Ravindra and Herve Vandamme relations. Since no known experimental data has been published on the refractive index of GaN, Bourissa calculated the index using $\epsilon_\infty = n^2$. The results of the refractive index for the three relations were 5.81, 4.41 and 5.24 respectively.

Compared to the experimental value of 5.15 for the dielectric constant obtained by Yu et al. [27], the value 5.24 as obtained by the Herve Vandamme relation is a better result. However, the value of the dielectric function of 5.8, theoretically calculated by Zheng et al. [28] is almost in agreement with the Moss relation.

The pressure derivative of the refractive index is another significant parameter which explains pressure induced distortion. The first pressure derivative calculated through the Ravindra relation indicates a greater effect of applied hydrostatic pressure to the refractive index. Results of calculations show that the pressure derivative is negative and this appears to be the trend among the III–V group. However, a study by Johanssen et al. [29] shows a direct linear relation between refractive index and increase in pressure. Thus, it is believed that ionicity of the material plays a significant role in determining the magnitude and sign of the pressure coefficient of refractive index.

6. Conclusions

The various energy gap–refractive index relations and their applications to semiconductors have been summarized in the above study. The analysis examines the contributions of Moss, Penn, Finkenrath, Wemple and Ravindra. Applications of these relations to IR detector materials such as $\text{Pb}_{1-x}\text{Sr}_x\text{Se}$ and $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ and UV detector material such as GaN have been discussed.

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