

Pressure dependence of the refractive index in InSe

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Abstract. In this work we report on the pressure dependence of the refractive index of indium selenide (InSe) for polarization perpendicular to the c -axis ($E \perp c$). The refractive index dispersion $n_{\perp}(\omega)$ of InSe has been measured between 0.77 and 1.5 eV for hydrostatic pressures up to 8 GPa and interpreted through a single oscillator Phillips–van Vechten model yielding the electronic refractive index and dielectric function. This model also yields the pressure dependence of the Penn gap in InSe, whose interlayer and intralayer deformation potentials have been obtained and compared with those of the lower energy optical gaps. The possible electronic transitions responsible for the Penn gaps for both polarizations (perpendicular and parallel to the c -axis) in InSe and other III–VI layered materials are also discussed on the basis of recent band structure calculations.

1. Introduction

The pressure dependence of the dielectric function plays a central role in the interpretation of pressure experiment results on other optical, electrical and lattice-dynamical properties in semiconductors. The dielectric function in the low-frequency limit, ϵ_{∞} , and its pressure dependence is used in a number of semiempirical models of semiconductor properties under pressure [1–3].

The III–VI layered materials present an anisotropic structure with layers formed by two chair-deformed sublayers of hexagonal symmetry held together by strong covalent cation–cation bonds directed along the c -axis (perpendicular to the layers) while the bonding between the layers is mainly of van der Waals type. This anisotropy in bonding can be altered by application of pressure because the interlayer and intralayer compressibilities evolve in different ways as pressure is increased. Several works dealing with measurements of the dielectric function in III–VI layered compounds can be found in the literature [4–14].

In most tetrahedral semiconductors, ϵ_{∞} decreases with increasing pressure due to the reduction of the electronic polarizability [15–17]. Nevertheless, in III–VI layered semiconductors, a different behaviour is observed. The static dielectric constant for polarization $E \parallel c$, $\epsilon_{0\parallel}$ increases considerably with pressure in InSe, GaSe and GaS, which has been attributed mainly to the increase of the electronic contribution [18, 19]. This increase has been explained through the pressure decrease of the Penn gap for the

polarization parallel to the c -axis, in accordance with recent LMTO band structure calculations [23]. An increase of the dielectric constant of GaTe with pressure has also been proposed from the pressure dependence of the exciton Rydberg [24]. On the other hand, an increase of $\epsilon_{\infty\perp}$ with pressure has been observed in GaS and GaSe [20–22]. In that case, the electronic polarizability decreases under pressure and the effect has been shown to occur mainly because of the high compressibility of layered materials.

In this paper we report on refractive index measurements for polarization $E \perp c$ in InSe under pressure. Experimental details are given in section 2, and section 3 is devoted to the presentation and discussion of results on the base of a single-oscillator Phillips–van Vechten model and recent band structure calculations [23, 25].

2. Experimental details

Single crystals of γ -InSe were grown by the Bridgman–Stockbarger method. Thin samples were cleaved from the ingot and cut into small pieces (4–20 μm in thickness and $100 \times 100 \mu\text{m}^2$ in size). For the optical measurements under pressure a sample was placed together with a ruby chip into a 200 μm diameter hole drilled on a 60 μm thick Inconel gasket and inserted between the diamond anvils of a membrane-type cell (MDAC) [26]. A 4 : 1 methanol–ethanol mixture was used as pressure-transmitting medium ensuring hydrostatic conditions up to 10 GPa [27] and the pressure was determined from the ruby luminescence linear scale [28].

The transmission spectra of the samples were measured in the MDAC using the sample-in sample-out method [22] up to ~ 10 GPa. In our transmittance measurements white light from a tungsten lamp was chopped at 180 kHz and focused

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onto the sample inside the MDAC as a 25 μm diameter spot. Transmitted light in the spectral range between 0.77 and 1.5 eV was spatially filtered and focused on the entrance slit of a 1 m single-grating spectrometer. The bandwidth was 32 \AA for transmission measurements and 0.5 \AA for the pressure determination from the ruby luminescence. The signal dispersed by the monochromator was detected by a Ge photodiode whose signal was synchronously measured with a lock-in amplifier. All measurements were performed at room temperature with incident non-polarized light propagating in the direction perpendicular to the layers.

The refractive index $n_{\perp}(\omega)$ was measured by analysing the interference fringes of the transmittance spectrum of InSe samples with parallel faces. The effect of the sample tilting has been neglected as pointed out and discussed in [16] and [17]. The interference condition for a maximum in the interference pattern is given by

$$2n(\omega)d = k\lambda_k \quad k = 1, 2, 3, \dots \quad (1)$$

with d the sample thickness, k the order of interference and λ_k the wavelength at the maximum corresponding to that order. Samples around 10 μm in thickness have been selected to obtain a well resolved interference pattern in which the orders of the maxima are small enough to be identified and followed under pressure.

The sample thickness and the order of each maximum at room pressure were obtained from the interference fringe pattern in the transparent region using equation (1) and the known index dispersion $n(\omega)$ at room pressure and temperature [10]. The wavelength shift of each maximum was followed with pressure, allowing the determination of the optical path length $n(P)d(P)$ for each order of interference at each pressure. Finally, the dispersion $n(\omega)$, and consequently $n_{\infty\perp}(P)$, for each pressure can be obtained once the variation of the thickness $d(P)$ is calculated from the compressibility of the sample along the c -axis.

The determination of the refractive index up to 8 GPa in InSe, well above the pressure at which precursor defects of the phase transition appear (7.0 ± 0.5 GPa) [29], was possible thanks to the linear character and inhomogeneous distribution of those defects.

3. Results and discussion

3.1. Refractive index under pressure

Figure 1 shows the transmittance interference fringe patterns of an InSe sample at different pressures. Arrows indicate the representative shift of an interference maximum with pressure. The inset of figure 2 shows the relative variation up to 8 GPa of the optical path $n(P)d(P)$, for two samples, at two photon energies. A 2% decrease of the optical path is observed between room pressure and 6 GPa.

The variation of the thickness $d(P)$ under pressure has been calculated by scaling the room-pressure thickness with a Murnaghan law describing the evolution of the lattice parameter c

$$c(P) = c(0) \left(1 + \frac{B'_0}{B_0} P \right)^{-1/3B'_0} \quad \text{with} \quad B_0 = 1/3\chi_{\parallel} \quad (2)$$

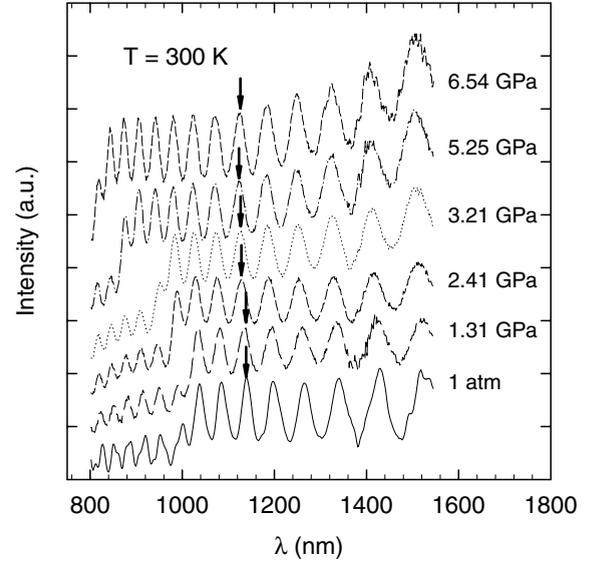


Figure 1. Transmittance spectra of an InSe sample 4 μm thick at several pressures. The thick solid curve indicates the evolution of one order of interference as a function of pressure.

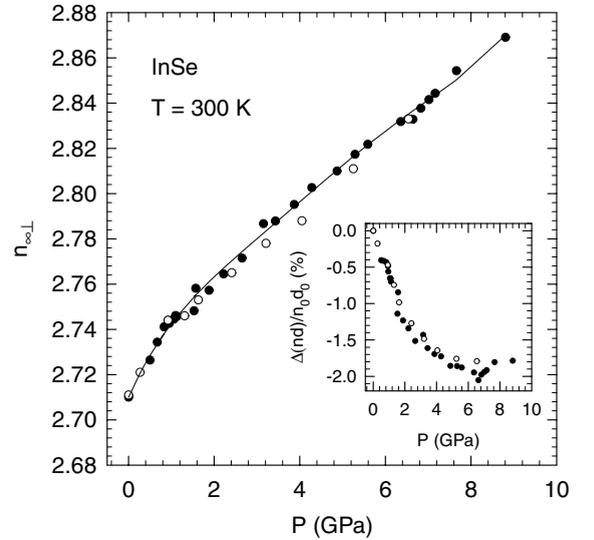


Figure 2. Low-frequency refractive index for polarization perpendicular to the c -axis as a function of pressure. Filled and hollow symbols represent the values of samples of 17 and 4 μm respectively. The value of $n_{\infty\perp}(0) = 2.71$ has been taken from [10]. The inset figure shows the relative variation of the optical path length as a function of pressure measured at the energies of 0.7 eV (filled symbols) and 1.0 eV (hollow symbols) of samples of 17 and 4 μm respectively.

with $c(0) = 24.946$ \AA [30], $B_0 = 15.015$ GPa and $B'_0 = 7.933$. The value of B_0 is calculated from the elastic constants measured by ultrasonic methods [31, 32]. We consider that this method gives a most accurate value for the compressibility parallel to the c -axis at low pressures (with respect to x-ray diffraction). On the other hand, the derivative of the incompressibility modulus B'_0 has been obtained by fitting a Murnaghan equation of state to the high-pressure data ($P > 4$ GPa) of the variation of the c -axis in InSe with pressure, as measured by x-ray diffraction [33].

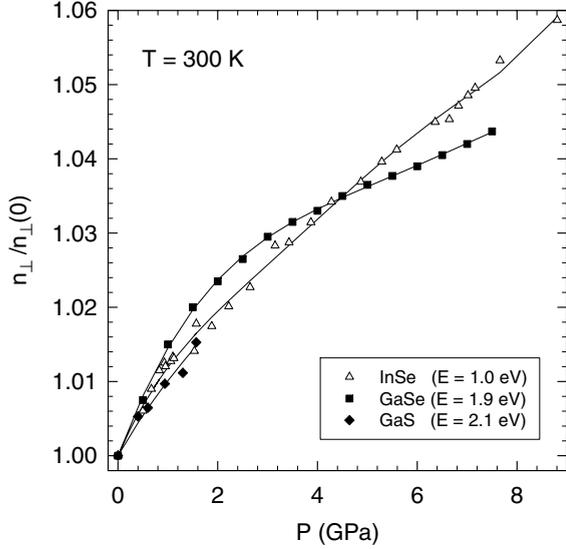


Figure 3. The pressure dependence of the relative refractive index for light polarization perpendicular to the c -axis in InSe (this work), GaSe [22] and GaS [20] measured at energies below the corresponding direct gaps.

From the knowledge of the variation of the thickness with pressure given in equation (2) we obtain the pressure dependence of the electronic refractive index shown in figure 2. For the sake of comparison, we also present in figure 3 the relative variation of the refractive index for light polarization perpendicular to the c -axis in InSe, GaSe and GaS. The data for GaS correspond to the low-pressure phase [20]. Previous results [34] give a steeper variation, as the phase transition occurring at 1.5 GPa was not taken into account [35]. Results of Kuroda *et al* [21] for GaSe are close to those of Gauthier *et al* and have not been represented in figure 2 for the sake of clarity. Table 1 gives the absolute and logarithmic pressure coefficients of the refractive index at room pressure for the three compounds. Table 2 summarizes the dielectric constants in InSe, GaSe and GaS and their pressure coefficients at room pressure as reported in the literature.

3.2. Penn gap under pressure

According to the Phillips–van Vechten semi-empirical model for the dielectric function [1], the electronic contribution to the refractive index at photon energy E , assuming a one-gap model, is given by

$$n_{\perp}^2(E) = 1 + (n_{\perp}^2(0) - 1) \frac{E_0^2}{E_0^2 - E^2} = 1 + \frac{E_p^2}{E_0^2 - E^2} \quad (3)$$

where E_0 is the Penn gap and E_p is the plasma energy, defined by

$$E_p = \hbar\omega_p = \hbar \sqrt{\frac{n_v e^2}{m_0 \epsilon_0}}$$

where n_v is the electron density in the valence band, e and m_0 are the electron charge and mass respectively and ϵ_0 is the vacuum permittivity. A fit of equation (3) to data of the refractive index dispersion at room temperature and

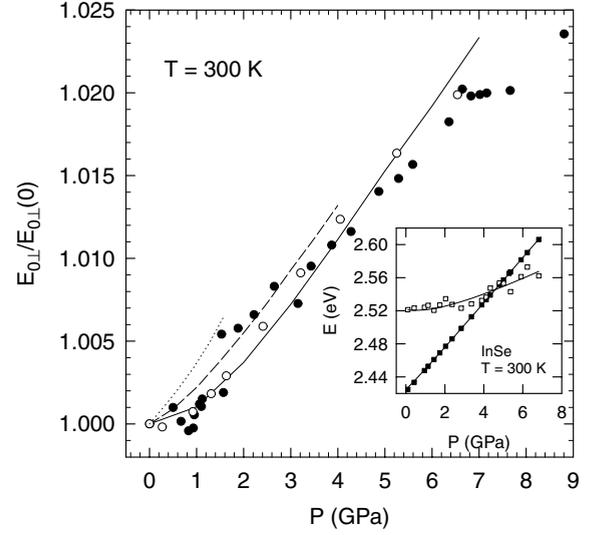


Figure 4. The pressure dependence of the relative Penn gap for polarization $E \perp c$ in InSe for samples of 17 and 4 μm (filled and hollow symbols respectively). Solid and dashed curves represent the evolution of the Penn gap in GaSe, as measured in [21] and [22] respectively, and the dotted curve represents evolution of the Penn gap in GaS calculated by us from data of [20]. The inset figure shows the evolution of the direct gap $Z_3^{1v}-Z_1^{1c}$ (filled symbols) [23, 36] and of the indirect gap $Z_3^{1v}-D^{1/c}$ (hollow symbols) [29, 43] in InSe as a function of pressure. Solid curves represent the fits of the data to equation (6).

pressure [10] yields $E_0 = 4.3$ eV and $E_p = 10.808$ eV for InSe.

The pressure dependence of the Penn gap for polarization $E \perp c$ can be obtained from the pressure dependence of the refractive index and the sample volume through the relation

$$E_0(P) = E_0(0) \sqrt{\frac{V(0) (n_{\infty}^2(0) - 1)}{V(P) (n_{\infty}^2(P) - 1)}}. \quad (4)$$

Figure 4 represents the relative evolution of the Penn gap for polarization $E \perp c$ in InSe as obtained with equation (4), and in the other III–VI compounds, as taken from the literature [20–22]. In the three compounds the Penn gap increases with pressure, which leads to a decrease of the electronic polarizability. This result shows that the increase of the refractive index with pressure in the three compounds is mainly due to the relatively high compressibility of the III–VI layered materials.

Figure 4 also shows a slightly nonlinear pressure variation of the Penn gap at low pressure. In order to explain this nonlinearity, an interlayer and intralayer deformation potential model was proposed by Gauthier *et al* [22]. In such a model, the low-pressure nonlinearities are explained through the strongly nonlinear variation of the interlayer distance. According to this model, the nearly linear behaviour of the Penn gap for polarization $E \perp c$ in InSe and GaSe suggests that the transition or transitions responsible for it are not sensitive to the variation of the interlayer distance.

Our discussion about the possible transitions contributing to the Penn gap for polarization $E \perp c$ in InSe will be based on the available experimental data of the reflectivity and ellipsometry and on the available electronic band structures of

Table 1. The electronic refractive index for polarization $E \perp c$ of III–VI semiconductors and their relative and absolute pressure coefficients at room pressure.

	γ -InSe	ε -GaSe	β -GaS
$\frac{d \ln n_{\infty \perp}}{dP}$ (GPa $^{-1}$)	$1.57(8) \times 10^{-2}$	$1.80(2) \times 10^{-2}$	$1.18(4) \times 10^{-2}$
$n_{\infty \perp}$	2.71 ^a	2.72 ^b	2.51 ^c
$\frac{dn_{\infty \perp}}{dP}$ (GPa $^{-1}$)	$4.3(2) \times 10^{-2}$	$4.90(5) \times 10^{-2}$	$3.0(1) \times 10^{-2}$

^a [10].^b [5].^c [20].**Table 2.** Static and low-frequency dielectric constants and their pressure coefficients in InSe, GaSe and GaS at ambient conditions.

	$\varepsilon_{\infty \perp}$	$\frac{\partial \ln \varepsilon_{\infty \perp}}{\partial P}$ [10 $^{-3}$ GPa $^{-1}$]	$\varepsilon_{\infty \parallel}$	$\frac{\partial \ln \varepsilon_{\infty \parallel}}{\partial P}$ [10 $^{-3}$ GPa $^{-1}$]	$\varepsilon_{0 \perp}$	$\frac{\partial \ln \varepsilon_{0 \perp}}{\partial P}$ [10 $^{-3}$ GPa $^{-1}$]	$\varepsilon_{0 \parallel}$	$\frac{\partial \ln \varepsilon_{0 \parallel}}{\partial P}$ [10 $^{-3}$ GPa $^{-1}$]
γ -InSe	7.34 ^g	31.5 ^h	7.0 ^g	—	10.2 ^j	—	7.6 ^b	120 ^b
ε -GaSe	7.44 ^a	36 ^d , 27 ⁱ	5.76 ^a	—	10.6 ^a	—	6.1 ^b	135 ^b
β -GaS	6.52 ^c	39.2 ^c , 22.6 ⁱ	4.76 ^c	90 ^b	9.7 ^f	—	5.3 ^b	85 ^b

^a [5].^b [19].^c [34].^d [22].^e Calculated from data of [9, 19].^f Calculated from data of [9, 34].^g [10].^h This work.ⁱ [18].

γ -InSe calculated without taking into account the spin–orbit interaction [23, 25]. In what follows, we will introduce a notation for the bands at each high-symmetry point of the Brillouin zone (BZ). Figure 5 shows a scheme of the electronic band structure of γ -InSe calculated by Ulrich through the LMTO-LDA-ASA method [23, 36]. In this figure we note the extrema of each band at the high-symmetry points of the BZ by: (i) the name of the point; (ii) the symmetry of the band at that point; and (iii) the order of the band with respect to the top (bottom) of the valence (conduction) band. The symmetry of the band in the single group notation is denoted as a subscript number or a superscript symbol.

According to group theory [37], the high-symmetry points Γ and Z in InSe belong to the C_{3v}^5 point group; therefore, bands with s and p_z character at Γ and Z belong to the A_1 symmetry and bands with p_x and p_y character belong to the A_3 symmetry. On the other hand, bands with s , p_z or p_y character at D and A (point group C_s) belong to the A' symmetry while bands with p_x character belong to the A'' symmetry. In this sense, the topmost valence band at Z with anion p_z character has Z_1 symmetry and is denoted Z_1^{1v} . The second and third valence bands with anion p_x – p_y character have Z_3 symmetry and are denoted Z_3^{1v} and Z_3^{2v} respectively. On the other hand, the lowest conduction band at Z with cation s character has Z_1 symmetry and is denoted Z_1^{1c} and the second conduction band at Z with cation s – p_z character has Z_1 symmetry and is denoted Z_1^{2c} .

In order to start the discussion of the transitions contributing to the Penn gaps in InSe, we should point out that Penn gaps are usually related to direct allowed transitions with a high joint density of states located at points of the BZ where valence and conduction bands run parallel. According

to band structure calculations [23, 25] such band arrangement is observed around both the D and A points of the BZ in InSe (figure 5) and similarly around M and L points of the BZ in GaSe and GaS [38–40]. On the other hand, a clear difference between the pressure dependences of the Penn gap for both polarizations $E \perp c$ and $E \parallel c$ in the III–VI layered semiconductors has been observed. The positive linear pressure coefficient of the Penn gap for the polarization $E \perp c$ (figure 4) contrasts with the negative nonlinear pressure coefficient of the Penn gap for polarization $E \parallel c$ in InSe (GaSe) at low pressures [19]. In light of these remarks and the fact that the pressure coefficients of the Penn gaps $E_{0 \parallel}$ at room pressure in III–VI layered compounds scale with the variation of the Γ – M indirect gap in GaSe and with the Z_1^{1v} – A^{1c} indirect gap in InSe, we conclude that the Penn gap for polarization $E \parallel c$ in InSe is most probably due to transitions between the upper valence band A^{1v} and the lowest conduction bands A^{1c} and A^{2c} .

The discussion on the transitions contributing to the Penn gap for polarization $E \perp c$ is far more complex. The nonlinear pressure dependences of the Z_1^{1v} – Z_1^{1c} direct transition [29, 41–43] and of the Z_1^{1v} – A^{1c} and Z_1^{1v} – D^{1c} indirect transitions at pressures below 2 GPa [29, 43, 44] contrasts with the linear pressure coefficient of the Z_3^{1v} – Z_1^{1c} and Z_3^{2v} – Z_1^{1c} direct transitions (E'_1 and E_1 direct transitions, in Kuroda's notation [45]) in InSe and other III–VI layered semiconductors [23, 36, 42]. Such different behaviour at low pressures suggests that the variation of the interlayer distance affects drastically the energy of the maximum of the valence band Z_1^{1v} , with predominant anion nonbonding p_z character, and, to a lesser extent, the Z_3^{1v} and Z_3^{2v} valence bands, with anion p_x – p_y character. Therefore, the almost

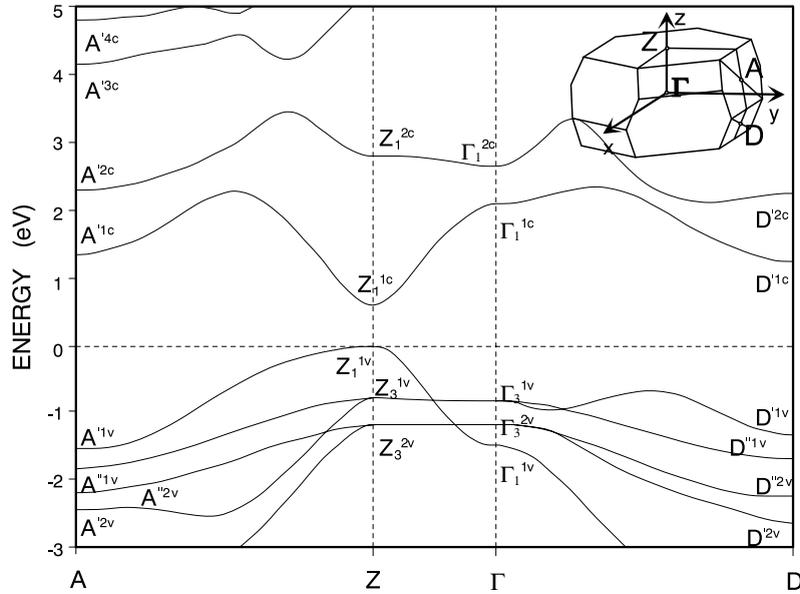


Figure 5. The scalar relativistic electronic band structure of γ -InSe obtained by the LMTO-LDA-ASA method with the BZ of the rhombohedral unit cell (inset) [23, 36].

linear positive pressure coefficient of the Penn gap for polarization $E \perp c$ suggests that the transition or transitions responsible for the behaviour of the Penn gap for polarization $E \perp c$ (i) do not involve the topmost valence band with p_z character, but transitions related to valence bands with anion p_x or p_y mixed character, and (ii) correspond to optical gaps exhibiting positive pressure dependences in InSe. On the other hand, theoretical studies of the electronic band structure in InSe suggest that valence bands with predominant anion p_x character show a small and almost pressure-insensitive energy dispersion along the Z-A and Z-D directions. This feature and the previous experimental results allow for a calculation of the pressure dependences of the different transitions involving anion p_x bands along Z-A and Z-D directions in InSe. Negative pressure coefficients were estimated for the transitions $A''^{1v}-A'^{1c}$ and $A''^{2v}-A'^{1c}$, which are related to the mainly cation p_y character of the A'^{1c} band, thus excluding the assignment of the Penn gap for polarization $E \perp c$ to these latter transitions. Positive pressure coefficients were estimated for transitions related to conduction bands with mainly cation s ($A''^{1v}-A'^{2c}$ and $A''^{2v}-A'^{2c}$) or a mixture of cation $s-p_y$ character ($D''^{1v}-D'^{1c}$ and $D''^{2v}-D'^{1c}$) instead.

The inset of figure 4 shows the pressure dependence of the $Z_3^{1v}-D'^{1c}$ transition (calculated from data of [23, 29] and [43]) and the experimentally measured $Z_3^{1v}-Z_1^{1c}$ transition [23]. Pressure coefficients of these transitions above 2 GPa of 27 meV GPa^{-1} ($Z_3^{1v}-Z_1^{1c}$) and $11.7 \text{ meV GPa}^{-1}$ ($Z_3^{1v}-D'^{1c}$) were obtained. The latter value compares reasonably well with the linear pressure coefficient of the Penn gap for polarization $E \perp c$ in InSe ($13.2 \text{ meV GPa}^{-1}$) unlike those of transitions with the initial state in the upper valence band ($Z_1^{1v}-Z_1^{1c}$, $Z_1^{1v}-D'^{1c}$ and $Z_1^{1v}-A'^{1c}$), which have linear pressure coefficients above 2 GPa of 61, 41 and -22 meV GPa^{-1} respectively [29, 43]. Therefore, we conclude that the Penn gap for polarization $E \perp c$ in InSe is probably related to transitions from valence bands with

Table 3. Compatibility relations between the point group C_{3v} and their subgroups and selection rules at D and A points of the BZ in InSe for $E \perp c$ and $E \parallel c$.

C_{3v}	C_3	$C_{1h} = C_s$
$\Gamma_1 = A_1$	A	A'
$\Gamma_2 = A_2$	A	A''
$\Gamma_3 = E$	E	A' + A''
Final state accessible with:		
Initial state	$E \perp c$ ($E = A' + A''$)	$E \parallel c$ ($A_1 = A'$)
A'	A' + A''	A'
A''	A' + A''	A''

predominant p_x anion character (A'' symmetry) to conduction bands with predominant $s-p_y$ cation character (A' symmetry) at the A and/or D points of the BZ with some contribution from conduction bands with predominant s character. This hypothesis is reasonable in light of available experimental and theoretical studies of the pressure dependence of the electronic band structure of InSe and is compatible with selection rules reported in table 3.

Furthermore, reported reflectivity and ellipsometry spectra in InSe (also in GaSe and GaS) for light with polarization $E \perp c$ show structures, known as E_2 and E_3 , at 3.3 and 4.3 eV respectively (3.65 and 4.9 eV in GaSe and 4.0 and 6.1 eV in GaS) [7, 12, 39, 46–48] in agreement with the features observed in the calculated imaginary part of the dielectric function from band structure calculations [25]. Therefore we propose that transitions around 3.3 eV (4.3 eV) contributing to the Penn gap for polarization $E \perp c$ in InSe are probably $D''^{1v}-D'^{1c}$ ($A''^{1v}-A'^{2c}$). The $D''^{1v}-D'^{2c}$ transition around 4.3 eV is not likely to contribute to the Penn gap for polarization $E \perp c$ in InSe because of the different sign of the curvature of valence and conduction bands for this transition (see figure 5). These conclusions are in agreement with Piacentini *et al* considerations [7], who tentatively attributed

the E_3 structure to transitions between the highest valence band or the lower valence bands with p_x - p_y character and the second group of conduction bands.

Finally we want to note that the similarity of the reflectivity and spectroscopic ellipsometry spectra and the pressure dependences of the Penn gaps for polarization $E \perp c$ in InSe, GaSe and GaS indicates that the Penn gaps in the three materials could be related to similar transitions in the electronic band structure. This means that transitions which could probably contribute to the Penn gap in GaSe and GaS are those between the topmost valence bands with p_x - p_y character and the lowest conduction band with s character, at the L and/or M points of the BZ. In light of band structure calculations, we estimate these transitions to be around 4.9 eV (5.9 eV) in GaSe (GaS), in agreement with values reported for the position of the E_3 peaks.

4. Conclusions

We have measured the pressure dependence of the electronic refractive index and dielectric function for light polarized perpendicular to the c -axis ($E \perp c$) in InSe up to 8 GPa. The electronic refractive index $n(\omega)$ for such polarization in InSe increases with pressure in the whole pressure range studied. A similar trend in the linear room-pressure coefficient of the refractive index is observed in the III–VI layered semiconductors. The pressure dependence of the Penn gap in InSe for polarization $E \perp c$ has been obtained in the framework of a one-gap Phillips–van Vechten model for the dielectric function, showing a behaviour similar to those calculated for GaS and GaSe. Furthermore, the interlayer and intralayer deformation potentials of the Penn gap for polarization $E \perp c$ in InSe obtained in the light of an interlayer and intralayer interaction model have been shown to be similar to those of GaSe.

In light of the available band structure calculations, the selection rules and the pressure dependences of the Penn gaps and of the optical gaps in InSe, we conclude that the Penn gap for polarization $E \perp c$ in III–VI layered materials (i) shows a negligible dependence on the variation of the interlayer distance and (ii) is probably related mainly to transitions from the first valence band with anion p_x or p_x - p_y character to the first conduction band with cation s or s - p_y character essentially, unlike the Penn gap for polarization $E \parallel c$, which is mainly related to transitions between the upper valence band with main anion p_z character and the first conduction band mainly with cation p_y character.

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