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Band-to-Band and Band-to-Acceptor Photoluminescence Studies in InSe under Pressure

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We report on photoluminescence (PL) measurements under pressure on p-type N-doped InSe at 10 K and on n-type Si-doped InSe at room temperature. Low-temperature PL of N-doped InSe is dominated by a band-to-acceptor peak. From the pressure dependence of the ionization energy of the N related shallow acceptor, the pressure change of the hole effective mass is estimated through the Gerlach-Pollmann model for hydrogenic levels in uniaxial crystals and discussed in the framework of a $\mathbf{k} \cdot \mathbf{p}$ model. Room temperature PL in Si-doped InSe is dominated by a band-to-band peak exhibiting a pressure shift in agreement with previous works. This PL peak has been measured up to 7 GPa and a steep reversible decrease of its intensity has been observed above 4 GPa. This decrease has been interpreted as a supplementary evidence of a direct-to-indirect gap crossover, already observed in other layered semiconductors.

1. Introduction

The optical properties of gallium and indium selenides (GaSe, InSe) under pressure have been widely investigated, mainly the pressure dependence of the fundamental band gap and some higher direct transitions [1 to 3]. A direct-to-indirect gap crossover has been observed in GaSe and GaTe [4, 5]. However, as regards InSe the only evidence of this crossover is given by the broadening of the free exciton absorption peak above 1 GPa [3].

There is a number of papers dealing with photoluminescence (PL) measurements on as-grown and doped InSe [6, 7], but to our knowledge no work has been done in order to study its pressure dependence. Nitrogen behaves as a shallow acceptor in InSe. This shallow acceptor shows a band-to-acceptor PL peak (BA) at low temperature. The binding energy of the acceptor level is determined experimentally, giving a good estimation of the hole effective mass tensor using the Gerlach-Pollmann model [6]. On the other side, silicon (Si) doped InSe is grown with a high crystal quality allowing the observation of a quite intense band-to-band PL peak (BB) at room temperature [7]. In this paper, we study the pressure dependence of both band-to-band and band-to-acceptor PL peaks in order to get supplementary information about the structure of the valence and conduction bands on the light of recent band structure calculations [2, 8].

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2. Experimental

InSe single crystals were grown by the Bridgman method. Impurities have been added in the synthesis process as InN and SiSe compounds in the melt. Samples of about 100×100 μm^2 in size and 15 to 50 μm in thicknesses were cleaved from the ingot and placed together with a ruby chip into a hole of 250 μm diameter in a gasket and inserted between the diamonds of a DAC. Pressure calibration was done using the pressure shift of the ruby R_1 fluorescence line. Low temperature PL measurements at 10 K were performed in the reflection configuration by exciting the sample inside a helium-flow cryostat with the 488 nm line of a Ar^+ laser. Condensed helium was used as pressure-transmitting medium. The luminescence light was dispersed through a monochromator and detected with a liquid-nitrogen-cooled Ge detector. Room temperature PL measurements were carried out both in the transmission and reflection configurations by exciting with a He–Ne laser (632 nm). A 4:1 methanol–ethanol mixture was used as pressure-transmiting medium. The luminescence light was dispersed through a monochromator and detected with a Si photodiode.

3. Results and Discussion

3.1 Low temperature luminescence of N-doped InSe under pressure

Fig. 1 shows the evolution of the PL spectra of N-doped InSe at 10 K for different pressures. The plot at 1 atm shows the band-to-acceptor peak at 1.289 eV and its one-phonon replica at 1.264 eV. The ionization energy of the acceptor is obtained by comparing our data with the experimental data of the fundamental gap of Goñi et al. [3]. The pressure variation of the ionization energy of N-doped InSe as deduced from the band-to-acceptor PL peak maximum is shown in Fig. 3a. The ionization energy is

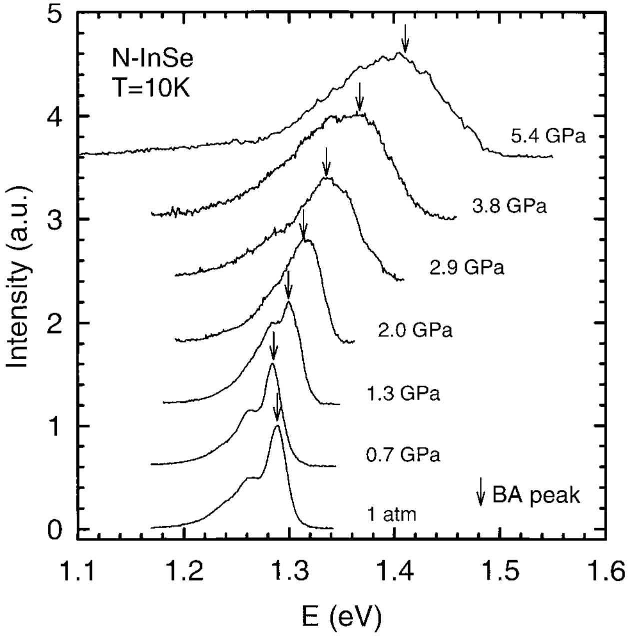

Fig. 1. PL spectra (intensity in arb. units) of N-doped InSe at 10 K and different pressures. The spectra have been normalized to unity and shifted in intensity. The band-to-acceptor peak (BA) is indicated by an arrow showing the pressure behaviour. The shoulder at 1.264 eV shown in the spectrum at 1 atm is the one-phonon replica of the acceptor

roughly constant at low pressure and increases with pressure above 1.5 GPa. The intensity of the BA peak decreases with increasing pressure. This quenching process is fully reversible. According to the Gerlach-Pollmann model for hydrogenic levels in uniaxial crystals [9], the ionization energy of the acceptor is related to the components of hole effective mass ($m_{\mathrm{h}\perp}$, $m_{\mathrm{h}\|}$) and dielectric constant ($\varepsilon_{0\perp}$, $\varepsilon_{0\|}$) tensors through the following equation:

$$E_{nlm}(\alpha) = -\frac{1}{n^2}\frac{R_\infty m_{\mathrm{h}\perp}}{\varepsilon_{0\perp}\varepsilon_{0\|}}\, Z^2_{l|m|}(\alpha)\,, \tag{1}$$

where R_∞ is the Rydberg energy, $Z(\alpha)$ is the effective charge, $\alpha = 1 - A$ is the anisotropy parameter, and $A = m_{\mathrm{h}\perp}\varepsilon_{0\perp}/m_{\mathrm{h}\|}\varepsilon_{0\|}$ is the anisotropy ratio. On this assumption, the hole effective mass tensor was determined experimentally at ambient pressure in [6], being $m_{\mathrm{h}\perp} = 0.73m_0$ and $m_{\mathrm{h}\|} = 0.17m_0$. In order to explain the change of the ionization energy under pressure we should point out that both components of the dielectric constant $\varepsilon_{0\perp}$ and $\varepsilon_{0\|}$ increase with pressure in InSe [10, 11], especially $\varepsilon_{0\|}$, which results in an increase of the effective charge through the decrease of the parameter A [11]. As the effective charge is a slowly varying function of α, its effect is not enough for overcompensating the increase of the dielectric constants under pressure; thus, an increase of $m_{\mathrm{h}\perp}$ has to be invoked in order to explain both stages of the acceptor ionization energy. In order to propose a $\mathbf{k}\cdot\mathbf{p}$ model for the hole effective mass behaviour, we must take into account the character of the bands. These bands were obtained by LMTO-ASA-LDA calculations [12] and they lead us to the following considerations: (i) the fundamental transition from the uppermost valence band (Se p_z) to the lowest conduction band (In s), located at the Z point of the BZ, is allowed uniquely for polarization parallel to the c-axis (matrix element $|P|^2$); (ii) the only transitions to the uppermost valence band allowed for polarization perpendicular to the c-axis are those from the lower lying Se $\mathrm{p}_x - \mathrm{p}_y$ valence bands (at energies E_a and E_c taken from the uppermost valence band and with $|Q|^2$ as matrix element) or from upper In $\mathrm{p}_x - \mathrm{p}_y$ conduction bands (at energies E_d and E_h above the uppermost valence band with $|R|^2$ as matrix element). With these assumptions, the $\mathbf{k}\cdot\mathbf{p}$ model yields

$$\frac{m_0}{m_{\mathrm{h}\perp}} = 1 + \left\{\frac{1}{E_\mathrm{a}} + \frac{1}{E_\mathrm{c}}\right\}\frac{2\,|Q|^2}{m_0} - \left\{\frac{1}{E_\mathrm{d}} + \frac{1}{E_\mathrm{h}}\right\}\frac{2\,|R|^2}{m_0}\,, \tag{2}$$

$$\frac{m_0}{m_{\mathrm{h}\|}} = -\frac{1}{E_\mathrm{g}}\frac{2\,|P|^2}{m_0}\,. \tag{3}$$

In this model, $m_{\mathrm{h}\|}$ changes under pressure proportionally to the direct bandgap E_g, which shows a strong nonlinear behaviour [1, 2, 5]. As regards $m_{\mathrm{h}\perp}$, its absolute value at ambient pressure is of the order of m_0. It means that the positive component in eq. (2) compensates a part of the negative contribution, which accounts for the negative curvature of the topmost valence band. As regards the In $\mathrm{p}_x - \mathrm{p}_y$ conduction bands at the Z point of the Brillouin zone, they are expected to shift up in energy under pressure in accordance with LMTO calculations. Consequently, E_d and E_h are expected to increase monotonically with pressure, resulting in a decrease of the negative part of eq. (2). On the other hand, E_a and E_c slightly increase in the pressure range below 1 GPa ($E_\mathrm{a} = E_1' - E_\mathrm{A}$, $E_\mathrm{c} = E_1 - E_\mathrm{A}$ in Ulrich's notation [2]). This would partly compensate the effect of the negative term. However, E_a and E_c decrease with increasing pressure above 1 GPa and both terms in eq. (2) tend to cancel, thus, increasing the absolute value of the hole effective mass. This model appears to be coherent with the evolution of the acceptor ionization energy given in Fig. 3a.

3.2 Room temperature luminescence of Si-doped InSe under pressure

Fig. 2 shows the band-to-band PL room temperature (RT) spectra of Si-doped InSe at different pressures. Our data for the pressure dependence of the energy of the band-to-band peak is in good agreement with the experimental data at RT given in [2] for the direct band gap. The intensity of the BB PL peak versus pressure is shown in Fig. 3b. The PL intensity remains nearly constant at low pressure and decreases exponentially above 4.5 GPa. The abrupt decrease in intensity is interpreted as evidence of the direct-to-indirect gap crossover. In order to explain the behaviour of the luminescence intensity we have considered that the BB luminescence intensity is proportional to the photoexcited electron concentration in the conduction band minimum (at the Z point of the Brillouin zone). The energy difference between this minimum and the one associated to the indirect gap decreases linearly under pressure [5]. As a consequence, photoexcited carriers are redistributed between both minima [13]. As no trace of indirect PL has been observed at this excitation rate, we assume that the intensity decreases with pressure due to change of the ratio between the electron population in the Z minimum and that of the indirect minimum. Thus, if we assume that the minimum of

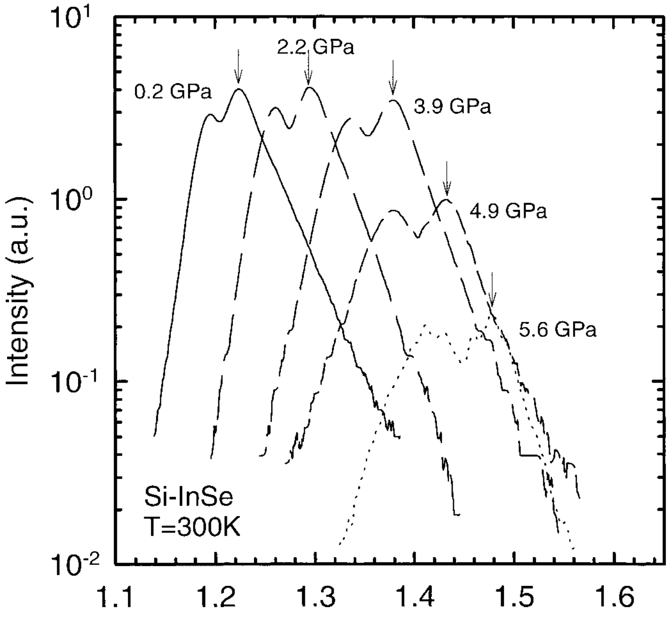

Fig. 2. Experimental transmitted PL spectra of Si-doped InSe at 300 K and different pressures. The BB peak (at 1.22 eV at 1 atm) is depicted with an arrow at each curve. The other peak originates from self-absorption inside the sample and is negligible with respect to the BB peak when the correction of self-absorption is taken into account

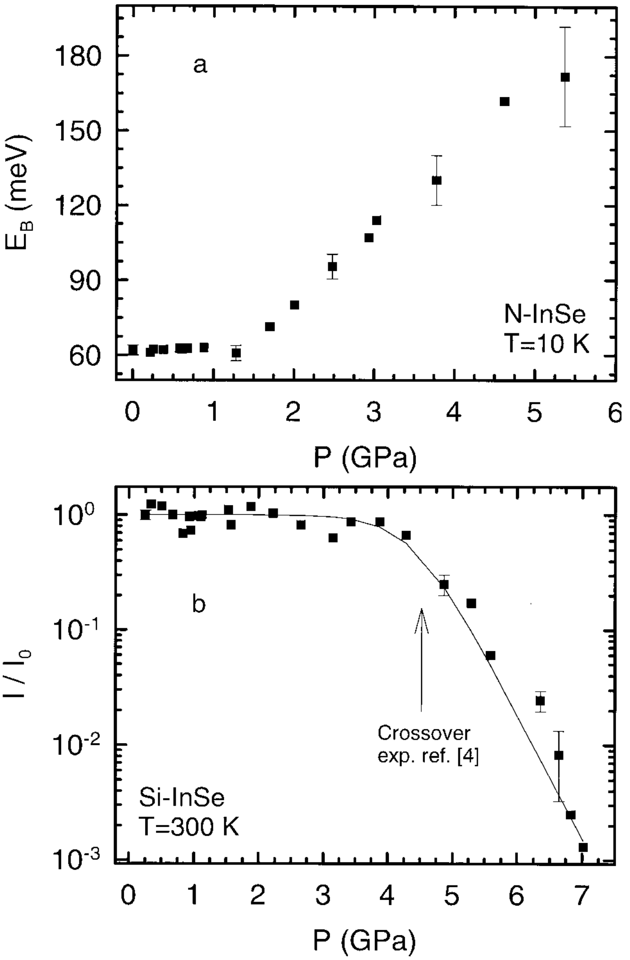

Fig. 3. a) Binding energy of N acceptor in InSe versus pressure at 10 K. An increase of the hole effective mass under pressure must be invoked in order to account for the increase of the ionization energy above 1.5 GPa. b) Normalized PL intensity of BB peak in Si-doped InSe versus pressure at 300 K. The solid line corresponds to the fit of eq. (4) to the experimental data. The pressure at which the direct-to-indirect gap crossover occurred was measured by optical absorption in InSe in [5], and is indicated by an arrow

the conduction band related with the indirect gap is located at the A point of the Brillouin zone, the PL intensity as a function of pressure would be given by the following equation:

$$\frac{I(P)}{I(0)} = \left[1 + M\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{Z}}}\right)^{3/2} \exp\left(-\frac{(\Delta E_{\mathrm{AZ}} - \beta P)}{k_{\mathrm{B}}T}\right)\right]^{-1}, \tag{4}$$

where $I(P)/I(0)$ is the normalized intensity at a given pressure with respect to that at ambient pressure, M is the number of equivalent minima related to the indirect gap in InSe, m_{Z} and m_{A} are the electron effective masses in the Z and A minima, respectively, ΔE_{AZ} is the difference in energy between the two minima at ambient pressure and β is the absolute value of the pressure coefficient of this energy difference. In equation (4), the pressure dependence of both the radiative and non-radiative lifetimes is neglected.

From transport and absorption measurements under pressure in InSe and $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{Se}$ [5, 14], the values of $\Delta E_{\mathrm{AZ}} = (0.32 \pm 0.02)$ eV and $\beta = (75 \pm 15)$ meV/GPa have been obtained. The number of equivalent secondary minima is $M = 3$. A fit of equation (4) to the experimental results yields $m_A = (0.75 \pm 0.05)\, m_Z$, and the calculated intensity fairly reproduces the actual dependence of the PL intensity in spite of the simplicity of the model. We must point out that the fit is sensitive to the effective mass ratio only in the pressure range around the crossover. Consequently, the value of m_A should be considered as a rough estimation. This value could be refined within this simple model once the change under pressure of radiative and non-radiative lifetimes involved in the radiative process be measured.

4. Conclusions

We have performed PL measurements of InSe under pressure at 10 K and at room temperature. An estimation of the pressure dependence of the ionization energy of the nitrogen acceptor has been obtained. Using the Gerlach-Pollman model for uniaxial crystals, this energy is related to the dielectric constant and the hole effective mass of the host. An increase of the hole effective mass of the topmost valence band with pressure is invoked to explain the increase of the acceptor binding energy.

A new evidence of the direct-to-indirect gap crossover in InSe has been observed from the intensity decrease of photoluminescence under pressure. This crossover, which was predicted by LMTO calculations for InSe, has been observed experimentally in absorption measurements of InSe and $In_{1-x}Ga_xSe$ at a similar pressure.

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