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HIGH DENSITY PHOTOLUMINESCENCE INDUCED BY LASER PULSE EXCITATION IN InSe UNDER PRESSURE

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We report on high density photoluminescence (HDPL) measurements in undoped indium selenide under pressure at 300 K. Direct electron-hole plasma (DEHP) stimulated emission, induced by high density excitation, has been observed in InSe from room pressure up to 5.1 GPa. Spontaneous and stimulated emission bands observed in the spectra have been analyzed within the framework of the band gap renormalization theory (BGR) in a multi-valley scenario. The pressure coefficients of the spontaneous and stimulated emission bands have led us to attribute these bands to transitions from different minima in the conduction band, which show different renormalization energies determined by the effective masses and electron densities in each valley. Under high excitation, the direct to indirect crossover is shown to occur at a lower pressure than that observed in absorption measurements, as a result of the different renormalization energies of each transition.

Keywords: Indium selenide; indium chalcogenides; layered materials; photoluminescence; hydrostatic pressure; diamond anvil cell

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I. INTRODUCTION

Indium selenide belongs to the III – VI layered semiconductor family. This semiconductor is specially suitable for the test of the band gap renormalization theory (BGR) in a multivalley scenario [1] because of its relatively simple band structure and the small energy differences between the minima in the lowest conduction band. A large number of experiments on nonlinear properties, stimulated emission and optical gain in the III – VI layered compounds are reported in literature [2, 3]. However, there exists no agreement on the nature of the different emission bands and renormalizations energies observed under high excitation conditions in these materials. In this paper we report on high density photoluminescence (HDPL) experiments in InSe under pressure. These experiments can throw some light on the problem because pressure changes the relative energy of the conduction band valleys and, consequently, the photoexcited electron distribution among them.

II. EXPERIMENTAL PROCEDURE

γ-InSe single crystals were grown by the Bridgman method from a $In_{1.05}Se_{0.95}$ melt. Samples were cleaved from the ingot and cut into pieces 10 μm thick and $100 \times 100\ \mu m^2$ in size. In this experiment, a piece was placed together with a ruby chip into a hole drilled on a Inconel gasket inside a diamond anvil cell (DAC). A 4 : 1 methanol – ethanol mixture was used as pressure-transmitting medium ensuring hydrostatic conditions up to 10 GPa [4]. The pressure was determined from the shift of the ruby photoluminescence (PL) line excited by an Ar ion laser beam focussed with a microscopic objective onto the DAC [5].

The PL spectra of InSe at 300 K under pressure were measured using the transmission configuration up to ~ 7 GPa. The whole sample was excited by a 10 ns frequency doubled Nd:YAG pulsed laser with no focussing lenses. A spatial filtering system, consisting of a $20\times$ microscope objective and a pin-hole, was used to select HDPL signal coming from a 30 μm diameter spot of the excited central region of the sample. The HDPL signal was focussed on the entrance slit of a 1 m single-grating monochromator. The spectral bandwidth was set to

5 nm for HDPL measurements and 0.05 nm for the pressure determination from the ruby PL. The HDPL signal, dispersed by the monochromator, was detected by an ultrafast Si photodiode and a box-car system synchronized with the repetition frequency of the laser (10 Hz).

Typical excitation fluencies of $3.5\,\mathrm{mJ/cm^2}$ per pulse were used, resulting in a photon flux of $10^{24}\,\mathrm{cm^{-2}s^{-1}}$ at the pulse maximum. For an absorption coefficient of $10^4\,\mathrm{cm^{-1}}$ and a carrier lifetime of 10 ns, the maximum photoexcited carriers density was estimated to be $1-2\cdot10^{20}\,\mathrm{cm^{-3}}$.

III. RESULTS AND DISCUSSION

Figure 1 shows the evolution of the square root of the HDPL spectra in InSe at 300 K under high hydrostatic pressure up to 5.4 GPa. Below

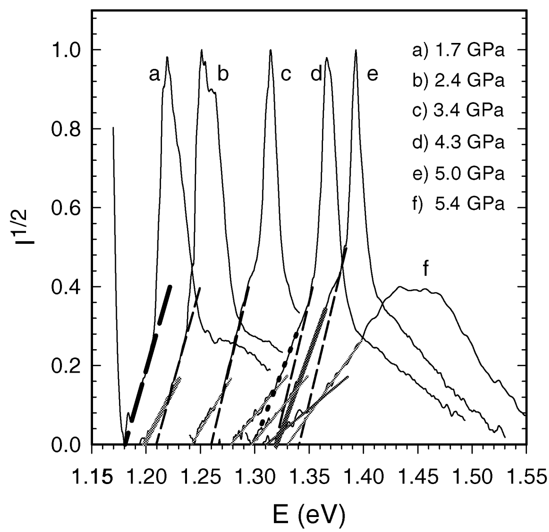

FIGURE 1 HDPL spectra in InSe at room temperature as a function of pressure. The square root of the PL intensity is represented in the y axis. A stimulated emission line dominates the spectra. A straight line can be extrapolated from the low energy tail of the HDPL spectra up to 1.7 GPa. A new straight line with different slope can be extrapolated together with the first one from 2.4 GPa upwards. A third line can be extrapolated above 5.0 GPa, but the first one and the stimulated emission are no longer seen.

1.7 GPa the emission spectra consist of three components, exhibiting different laser intensity dependence and decay behaviour: (i) a broad spontaneous emission band at the energy of the direct gap (1.25 eV), (ii) a stimulated emission line at some 60 meV below the direct gap and (iii) a spontaneous emission band with a low energy tail, located at the same energy as the stimulated emission line and partially hidden by it. We attribute the first band to the band-to-band direct transition already observed in low-density PL measurements (LDPL). The second and third components are attributed to stimulated and spontaneous emission of the direct band-to-band transition at the renormalized direct gap energy. The renormalization energy is determined by the exchange and correlation interaction in the direct electron-hole plasma (DEHP) generated at high excitation conditions. The stimulated DEHP line is observed up to 5.1 GPa with almost constant intensity. The full width at half maximum (FWHM) of this line exhibits a maximum at 2.4 GPa. No stimulated PL from the direct gap was observed above 5.3 GPa.

The low energy tail is due to carrier collision broadening of the spontaneous DEHP emission band. This broadening is of lorentzian type, which yields a straight line when the squared root of the PL intensity is plotted *versus* the photon energy. The extrapolation of this line to zero yields an energy with the same pressure coefficient as the direct gap.

Above 1.7 GPa, a new straight line can be extrapolated from the low energy tail of the spectrum, at lower energy and with a different slope with respect to that of the DEHP. The pressure coefficient of this line is positive but lower than that of the direct gap. Above 5 GPa, another straight line at the low energy tail is observed, showing a negative pressure coefficient. The appearance of this new line is followed by the quenching of the DEHP bands. The pressure coefficients of the two low energy tails (with respect to the Z direct emission bands) are -21 ± 2 meV/GPa and -76 ± 5 meV/GPa. These pressure coefficients correspond to those observed for the Z-D and Z-A indirect gaps in absorption measurements under pressure (with respect to the Z direct absorption edge). This fact, together with the spectral dependence on the squared photon energy, leads us to identify them as spontaneous emission bands from Z-D and Z-A indirect electron-hole plasmas (IEHP). These plasmas exist certainly at lower pressures but are more clearly observed above 1.7 and 4.3 GPa respectively, due to the pressure-induced direct-to-indirect crossovers.

This assignment is also supported by the fact that the intensity of the stimulated DEHP line is barely affected by the Z-D crossover, but strongly affected by the Z-A crossover. A similar effect was observed in LDPL experiments with the InSe samples from the same ingot. The LDPL intensity of the direct band-to-band transition at 300 K is almost constant up to 4 GPa, shows a progressive and reversible quenching above this pressure and is observed up to 7 GPa. This effect was proposed to be a consequence of the Z-A crossover, and attributed to the presence of a deep trap associated to the A minima of the conduction band [6]. This trap moves quickly towards the centre of the gap under pressure and creates a non-radiative recombination channel that is more effective than direct radiative recombination. It is reasonable to attribute the quenching of the stimulated emission line in InSe above 5 GPa to the same process. Under high excitation conditions, the higher effective mass in the A minima results in a higher BGR and makes the Z-A crossover to occur at a lower pressure. As a consequence, the DEHP stimulated emission is effectively quenched at a lower pressure with respect to spontaneous emission at low density excitation.

Figure 2 shows the pressure evolution of the energies of the spontaneous and stimulated emission bands as observed in HDPL measurements. In this figure, these bands are compared to the pressure evolution of the energy gaps Z, Z-D and Z-A. If the zone-edge phonon involved in the Z-D indirect transition has an energy of some 25 meV, the D minima of the InSe conduction band, at room conditions, are estimated to be 70 meV above the absolute minimum (at the Z point), in agreement with the estimation obtained from optical absorption measurements in InSe and $In_{1-x}Ga_xSe$ ($x < 0.2$) under pressure [7].

The information about the electronic band structure of InSe provided by HDPL measurements agrees with the electronic band structure picture obtained by recent pseudopotentials and LMTO calculations [8, 9] and supports previous analysis of the optical absorption coefficient of InSe and $In_{1-x}Ga_xSe$. According to these results, the following model can be proposed: (i) the conduction band structure of InSe has the Z minimum located 70 meV below the D

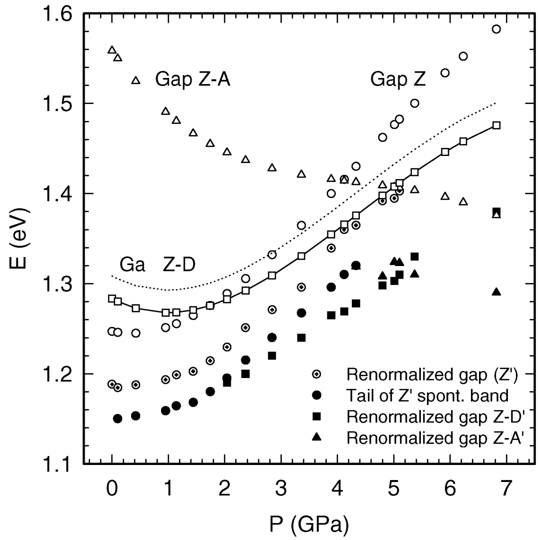

FIGURE 2 Pressure dependence of the spontaneous and stimulated emission bands deduced from HDPL spectra and those of the Z, Z-D and Z-A energy gaps. Full symbols represent the energies of the renormalized direct and indirect gaps extrapolated from the low energy tail of the spontaneous emission bands. Dotted symbols indicate the position of the renormalized direct gap obtained from the stimulated emission band. Empty symbols indicate the energies of the Z, Z-D and Z-A edges. The dotted line indicate the position of the Z-D gap if a 25 meV zone-edge phonon assist the indirect transition.

minima and 300 meV below the A minima, (ii) the pressure coefficients of the gaps above 2 GPa are 61, 41 and – 22 meV/GPa for the Z direct gap and Z-D and Z-A indirect gaps respectively. This scheme indicates that the lowest conduction band structure of InSe resembles that of GaAs, with the Z, D and A minima in InSe corresponding to the Γ, L and X minima in GaAs [10]. This correspondence also applies to the pressure behaviour of each minimum above 2 GPa, once the nonlinear effects in InSe become negligible as a consequence of the increase of the incompressibility of the interlayer space. It must be outlined that this correspondence reveals a deeper similarity in the character of the electronic states in each minimum (mainly *s* of the cation in the Z point, mainly p_y of the cation in the A point and a mixture of both in the D point).

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