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Direct to Indirect Crossover in III–VI Layered Compounds and Alloys under Pressure

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The pressure dependence of the optical absorption edge of $In_{1-x}Ga_xSe$ ($0 < x < 0.2$) and GaTe has been investigated in order to determine the direct to indirect crossover pressure and the energy difference between the absolute and subsidiary minima of the conduction band at ambient pressure. In the $In_{1-x}Ga_xSe$ alloy, the crossover pressure decreases with increasing Ga proportion. For InSe, from the extrapolation to $x = 0$ the band crossover is found to occur at 4.3 GPa and the subsidiary minimum of the conduction band is located, at ambient pressure, (0.32 ± 0.02) eV above the absolute minimum. In addition, the energy difference between the conduction band minima is shown to decrease linearly with pressure, in agreement with previous transport results in InSe and optical results in GaSe. As regards GaTe, the behaviour of the absorption edge is similar to that of the other III–VI compounds, which suggests that, in spite of the different crystal structure, the electronic states close to the band-gap have the same character.

1. Introduction

III–VI layered semiconductors are of particular interest due to their potential applications to optical nonlinear and bistable devices [1]. Pressure experiments contribute to a better understanding of their electronic properties through the tuning of the degree of the anisotropy of the chemical bonds in these semiconductors. The pressure effects in the optical properties of GaSe [2] and InSe [3] have been investigated in the last decade. In these studies, it was observed that the direct band-gap energy (E_{gd}) follows a strongly nonlinear dependence with pressure, decreasing up to around 1 GPa and then increasing. On the opposite, the indirect band-gap energy (E_{gi}) in GaSe was found to decrease monotonically with increasing pressure. In InSe, E_{gi} and its pressure dependence have not been properly determined yet. However, transport measurements give an accurate measurement of the energy difference between the conduction band minima under compression [4]. Regarding GaTe, up to now, no work has been done to understand the evolution of its absorption edge under pressure. In this paper we present measurements of the absorption edge under compression for $In_{1-x}Ga_xSe$ ($0 < x < 0.2$) and GaTe. The pressure dependence of both band-gaps has been determined from the experimental data by using the Elliott-Toyozawa model [5, 6] for the direct absorption edge and a simple quadratic model for the indirect edge.

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2. Experimental

All the measurements were carried out in a membrane diamond anvil cell (MDAC) at room temperature. The samples were prepared with dimensions of $100 \times 100 \times 30\ \mu m^3$ for $In_{1-x}Ga_xSe$ and $100 \times 100 \times 6.1\ \mu m^3$ for GaTe. The larger faces were parallel to the layer plane. They were placed together with ruby chips in a 200 μm diameter hole drilled on a 60 μm thick Inconel gasket. A 4:1 methanol–ethanol mixture was used as pressure-transmitting medium to ensure hydrostatic conditions. The pressure was measured from the shift of the R_1 line of the ruby fluorescence. The optical source was a tungsten lamp chopped at 180 kHz. The light from the lamp was collimated and focused on a DAC and the transmitted light was again collimated and focused on the entrance slit of a THR1000 Jovin-Ivon monochromator. The detector was a Si photodiode whose signal was synchronously measured with a lock-in amplifier. The transmittance was measured using the sample-in sample-out method. Stray light was measured in the high absorption region of the sample, and the minimum transmitted intensity was subtracted from every spectrum. Then a correction was made to the experimental transmittance by adjusting it to the theoretical value at the region were the sample is transparent to light. Finally, the absorption coefficient (α) was calculated taking into account the corrected transmittance, the thickness and the reflectivity of the sample.

3. Results and Discussion

We have studied five samples of $In_{1-x}Ga_xSe$ with different proportions of Ga. Fig. 1 shows several spectra at different pressures measured in a sample of $In_{0.84}Ga_{0.16}Se$. For this Ga proportion an exciton maximum can be seen in the absorption edge at ambient pressure (AP). However, with increasing pressure it broadens and disappears at around 1.6 GPa. As expected, the pressure change of the absorption spectra ex-

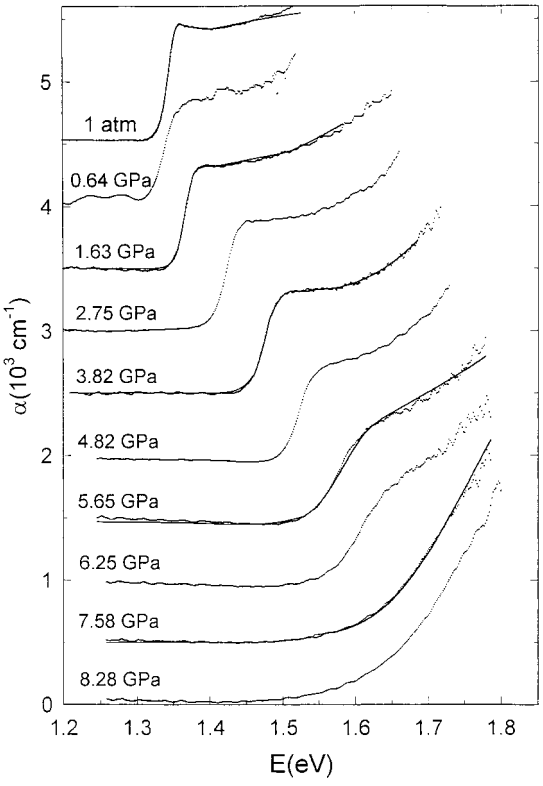

Fig. 1. Experimental absorption coefficient for $In_{0.84}Ga_{0.16}Se$ under pressure at $T = 300$ K (points). The curves are shifted 500 cm^{-1} for clarity. Pressure is indicated in the figure. Solid lines represent the fits

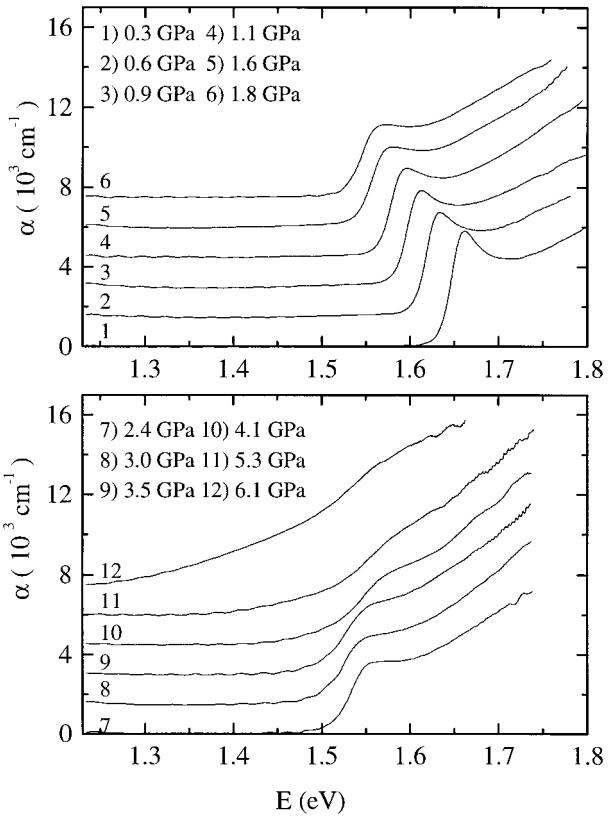

Fig. 2. Experimental absorption coefficient for GaTe under pressure at $T = 300$ K

hibits a behaviour intermediate between that of InSe and that of GaSe. The absorption edge first shifts towards low energies, up to a pressure that increases with the Ga content, and then shifts towards high energies. Above 7 GPa the spectra shift again to lower energies. At low pressures the spectra have the typical shape of a direct transition. With increasing pressure, from the shape of the absorption curves, no dramatic changes can be seen up to 4.8 GPa. However, above this pressure, the shape of the absorption edge becomes smoother, a low-energy absorption tail appears, and the spectra evolve to the typical shape of an indirect transition. Fig. 2 shows the evolution of the absorption edge of GaTe under compression. The exciton structure is clearly observable up to 1.8 GPa and shifts to lower energies up to 3 GPa. The low energy tail appears above 2.4 GPa and also shifts to lower energies under compression.

In order to analyze the spectra, both direct and indirect processes have beem taken into account. As a first approximation, the direct and indirect absorption can be simply added to obtain the total absorption [2]. Since the early works of Elliot [5] and Toyozawa [6], it is well known that the interaction between the electron and the hole enhances the optical absorption and introduces a sequence of hydrogenic levels located below the band-gap. The electron–lattice interaction broadens the exciton lines and the step-like absorption edge of the exciton continuum and band-to-band transitions. This model, has been satisfactorily applied to III–VI semiconductors by different authors

[2, 3, 7]. According to it, the absorption coefficient is given by

$$\alpha(E) = \frac{C_0 R^{1/2}}{E} \left\{ \sum_{m=1}^{\infty} \frac{2R}{m^3} L(E_m - E) + \int_{E_{gd}}^{\infty} \frac{dE'}{\sqrt{1 + \exp\left(-2\pi \sqrt{\frac{R}{E' - E_{gd}}}\right)}} L(E' - E_{gd}) \right\}$$

with

$$C_0 = \frac{4\pi^2 (2\mu)^{3/2} e^2 |M_R|^2}{nc\hbar^2 m_0^2} \tag{1}$$

and

$$E_m = E_0 - R/m^2 , \tag{2}$$

where R is the Rydberg energy, μ the exciton reduced mass, m_0 the free electron mass, n the refractive index, M_R the matrix element for electron–photon interaction, E_m the energy of the m-th exciton line, respectively and E_{gd} the energy of the direct gap. $L(x)$ is a line shape function depending on the strength of the exciton–lattice coupling: a Lorentzian function for weak coupling or a Gaussian for strong coupling [6]. The indirect absorption contribution was described through the usual quadratic equation for an

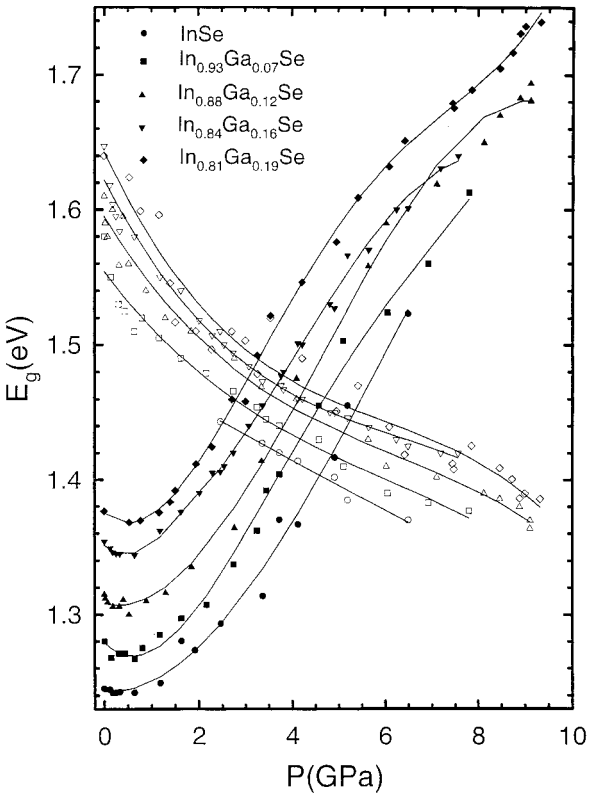

Fig. 3. Pressure dependence of E_{gd} (full symbols) and E_{gi} (open symbols) for the five samples of $In_{1-x}Ga_xSe$. Solid lines are only a guideline to the eye

indirect edge [8], neglecting the phonon-absorption contribution because it could not be measured on such thin samples.

For $In_{1-x}Ga_xSe$ a Lorentzian lineshape gives better account to the spectra, in agreement with previous results for InSe and GaSe. In the case of GaTe, the much larger width of exciton peak reveals a stronger exciton–phonon coupling and, coherently, a Gaussian lineshape fits better the experimental results. The empirical rule proposed in [7] was used to relate the width of the exciton lines (Γ_m) and that of the continuum (Γ_C). Using C, Γ_1, Γ_C, R, E_{gd} and E_{gi} as fitting parameters, we have fitted equation (1) to the experimental spectra at each pressure in all the samples.

Fig. 3 shows the direct and indirect bandgaps as a function of pressure for $In_{1-x}Ga_xSe$. The direct gap follows a nonlinear dependence on pressure, with a minimum that moves from 0.5 to 0.7 GPa as x increases from 0 to 0.2. This shift of the minimum gap to higher pressures is consistent with the fact that the minimum occurs at 0.5 GPa for InSe and at 1.3 GPa for GaSe [9]. In all the samples, but in InSe, the indirect band-gap and its pressure dependence could be determined in the whole pressure range. Obviously, it could be better determined for pressures above 4.8 GPa when it is unambiguously separated from the direct edge. The pressure dependence of E_{gi} is also nonlinear, as in GaSe, and the pressure coefficient is negative in the whole pressure range. It is remarkable that the pressure dependence of the gap difference $E_{gd} - E_{gi}$ is fairly linear for all the samples in the explored pressure range. The pressure coefficient $d(E_{gd} - E_{gi})/dP$ changes from -80 meV/GPa for $x = 0.07$ to -94 meV/GPa for $x = 0.19$. Fitting the overall results of E_{gi} as a function of x at different pressures we can extrapolate its value for InSe. From this fit, the difference between the indirect band-gap and the direct one of InSe as a function of pressure (P) is given by

$$E_{gi} - E_{gd} = (330 \pm 20)\ \text{meV} - (76 \pm 15\ \text{meV/GPa})\ P\,. \tag{3}$$

At ambient pressure the indirect band-gap is located 330 meV above the direct band-gap and the direct to indirect crossover occurs at 4.3 GPa. Both results are coherent with those deduced from transport measurements [4].

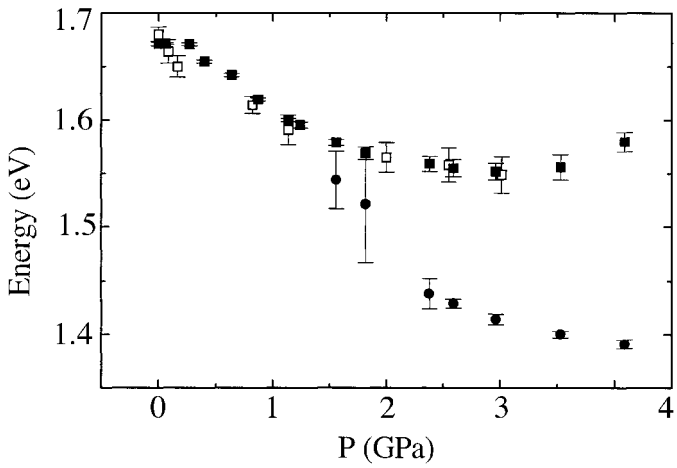

Fig. 4. Variation of the direct and indirect band-gap of GaTe under pressure. The squares and circles represent values of the direct and indirect band-gap, respectively. Full and open symbols correspond to two different samples

Fig. 4 gives the pressure dependence of both direct and indirect band-gap in GaTe. The most remarkable difference with respect to the other III–VI semiconductors is the fact that the minimum value of E_{gd} occurs at a much higher pressure (2.9 GPa). Coherently, the pressure coefficient at low pressure, $dE_{gd}/dP = (-85.7 \pm 0.4)$ meV/GPa, is higher (in absolute value) than that of InSe and GaSe. On the other hand, in the pressure range where the indirect band-gap could be determined, its behaviour is similar to that of GaSe and InSe, with a pressure coefficient that decreases (in absolute value) with increasing pressure. The direct to indirect crossover occurs at about 1.2 GPa. If one assumes a linear dependence on pressure of the difference $E_{gd} - E_{gi}$, the indirect edge at AP would be (1.76 ± 0.04) eV. The fact that, in spite of the different crystal structure, the behaviour of both transitions is similar to that of the other III–VI semiconductors indicates that the electronic states close to the band-gap have the same character. It seems reasonable to assume that, as in GaSe and InSe, the uppermost valence band has mainly Te p_z antibonding character and the lowest conduction band has Ga s antibonding character. The nonlinear behaviour of the direct transition would be due to the stronger sensibility of Te p_z states to the interlayer distances, which makes the top of the valence band to move up in energy quicker than the bottom of the conduction band in the first stages of compression in which the interlayer distances decrease quicker than the intralayer ones. The pressure dependence of the direct gap can be accounted for in terms of intra and interlayer deformation potentials, as proposed in references for GaSe and InSe. In relative terms, i.e. dividing the deformation potential by the band gap at AP, it turns out that in GaTe the intralayer deformation potential is fairly of the same order as in those materials, but the interlayer deformation potential is more than double that of GaSe and InSe. This can be attributed to the tilt of Te p_z orbitals with respect to the layer plane and its larger extent with respect to Se p_z orbitals.

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