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Localization behavior of donor-related complexes in InP under hydrostatic pressure

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We report a direct observation of the dependence of the localization energy of D^0X and D^0h complexes as a function of the mass ratio σ. This has been done for indium phosphide, using hydrostatic pressure at low temperature. After a comparative study of the pressure dependence of D^0X and D^0h from photoluminescence data collected at liquid-helium temperature we find an increase of the localization energy with the pressure for both complexes, but with different slopes. This allowed us to achieve an understanding concerning the mass-ratio dependence of these two types of complexes, which is believed to be helpful for the theoretical calculations of many-body problems.

I. GENERAL CONSIDERATIONS

Experimental investigations of the influence of hydrostatic pressure on the optical properties of semiconductors have attracted special interest for years. Hydrostatic pressure preserves the crystal symmetry but alters its electronic properties via changes in interatomic distances.[1,2] Photoluminescence measurements performed at low temperature can give quantitative information concerning the electronic states of the crystal under pressure.[3] Particularly accurate results along this line can be obtained in some cases, when the photoluminescence spectrum of the crystal is sufficiently rich to select several types of excitons (free and bound ones). In this paper we concentrate on the behavior of shallow donor bound excitons in direct-band-gap III-V compounds under hydrostatic pressure and at liquid-helium temperature.

From the theoretical point of view, it is well known that, in the simplest model, the total energy of a neutral-donor–bound-exciton complex (D^0X) or neutral-donor–bound-hole (D^0h) is a monotonically increasing function of the effective-mass ratio $\sigma = m_e^*/m_h^*$. But, the localization energy of such complexes does not need to be monotonic in σ. Indeed some very complicated effects such as central cell corrections, electron-hole exchange interactions, etc., can have notable influence on the binding energies.[4]

The results of the theoretical predictions are in remarkable discrepancy.[4] As a consequence, new experimental help has been anticipated for a long time. Hydrostatic pressure changes the mass ratio σ and consequently changes the localization energy of the excitons bound to these complexes. Thus it is of value to study these phenomena by using hydrostatic pressure.

II. EXPERIMENTAL RESULTS

We report the experimental results obtained with reflectivity and luminescence measurements inside and outside our pressure cell at liquid-helium temperature. A Unipress copper beryllium pressure cell has been used here; it is described in an earlier paper.[5] It enables us to work at up to 8 kbar at low temperature.

We have shown on Fig. 1 both the reflectivity spectrum (top of the figure) and the luminescence pattern (bottom of the figure) collected at pumped liquid-helium temperature. The sample was a very-high-purity InP epitaxial layer grown by vapor-phase epitaxy (VPE) at the Royal Signal and Radar Establishments ($n \sim 10^{13}$ cm^{-3} and $\mu_n = 80\,000$ $cm^2/V\,s$ at 77 K). Both spectra obtained under atmospheric pressure conditions reflect the quality of the sample: we resolve the $n = 1,2,3$ exciton-polariton states and four rotational levels for the bound hole in the case of the neutral-donor–bound-exciton complex (D^0X). We also resolve the fine structure of the neutral-acceptor–bound-exciton complex (A^0X) which lies on the lowest-energy side. This A^0X complex consists of two holes and one electron while the D^0X complex consists of two electrons and one hole. Two weak transitions labeled D^+X and D^0h, respectively, correspond to the trapping of

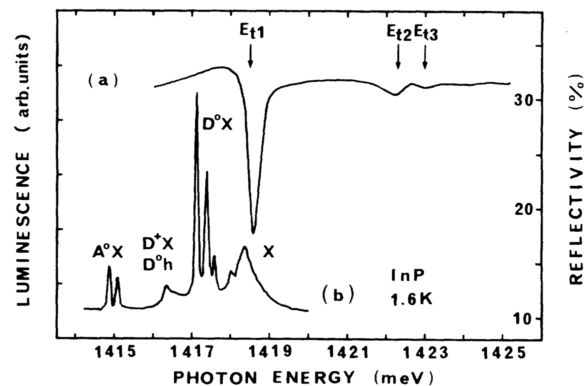

FIG. 1. (a) A typical reflectivity spectrum of indium phosphide obtained at pumped-liquid-helium temperature and atmospheric pressure. We observe the three low-energy exciton-polariton structures clearly. We have plotted the energies corresponding to the transverse polariton obtained from a numerical fit of the reflectivity spectrum, using the method detailed in Ref. 11. (b) The corresponding near band-edge luminescence showing the free-exciton–polariton luminescence (X), the series of recombination lines corresponding to the donor bound complex (D^0X, D^+X, D^0h), and the exciton bound to the residual effective-mass acceptor (A^0X).

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an exciton to an ionized donor and to the recombination of a hole trapped by a neutral donor. Details concerning these bound excitons can be found in the work of Skolnick and Dean.[6] In summary, we have simultaneously in the same spectrum, several types of bound excitons; since both the valence-band states and the conduction-band state behave differently with the pressure,[2] some different behaviors are expected for each type of bound exciton when the crystal is pressed.

In Fig. 2 is displayed one typical luminescence spectrum obtained under hydrostatic pressure conditions in the cell. We clearly resolve three transitions which are identified as due to the recombination emission of the neutral-donor–hole and the neutral-donor–exciton complexes, D^0h and D^0X, and the ground state of the free-exciton–polariton system (X). From the relative intensities of the D^0h and D^0X lines we can estimate the true temperature of the sample[7] to be about 8 K. The D^0h and D^+X structures are always very close in indium phosphide ($\sim$0.1 meV). A careful examination of these two complexes under an electric field has been made by Skolnick and Dean.[8] Upon increasing the field strength, the D^+X structure quickly disappears; in other words, D^+X ionizes more easily than D^0h does. In the present situation, given the 8 K temperature in the (D^0h, D^+X) system, D^0h is predominant.

For the study of this phenomenon, our experimental resolution is better than the previous findings[9,10] in diamond anvil cells when argon is used as the pressure-transmitting medium. The corresponding reflectivity spectrum is inserted just above the luminescence pattern. This enables us to obtain the correct energy of the transverse exciton polariton after a fit of the experimental reflectivity spectrum for each pressure in the whole range of pressure.[11]

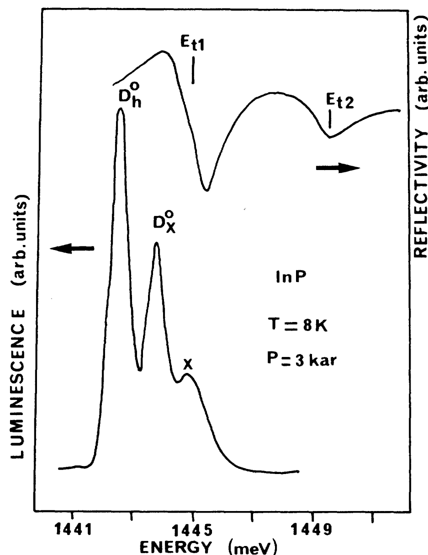

FIG. 2. A typical luminescence spectrum (bottom of the figure) collected in our pressure cell for a pressure of 3 kbar. The corresponding reflectivity spectrum (top of the figure) enables us to estimate accurately the energy of the ground state of the exciton polariton and then to identify the high-energy transition of the luminescence spectrum with the free exciton. Lower in energy we find the envelope of the ground state of the exciton bound to a neutral donor (D^0X) and the recombination line corresponding with the trapping of a hole to a neutral donor. The true sample temperature is estimated to be about 8 K.

Comparing both atmospheric and hydrostatic pressure we observe a broadening of our data, which arises from the increase of the temperature from 2 to 8 K, and from a small nonhydrostatic component in the strain field. Careful analysis of the $n=1$ exciton polariton in light of the uniaxial stress measurements of Mathieu *et al.*[12] permits us to estimate the shear component of the stress. It is always less than 100 bars. The D^0X lines is broader than at 2 K and we only resolve the envelope of the fine structure of this complex.

The accurate energy position of D^0h, D^0X, and X have been obtained after a fitting of the luminescence spectra using a set of Gaussian functions. We observe a small decrease of the D^0h-D^0X splitting with the pressure. This behavior is illustrated in Fig. 3. From a least-mean-square fit of our experimental findings we find a decrease of the splitting of $\sim$0.57 meV/Mbar. Such a decrease arises from the change of both electron and hole effective mass under pressure.

III. EFFECTS OF THE PRESSURE ON THE EXCITONIC STATES OF INP

Keeping the crystal symmetry, hydrostatic pressure changes the band structure and provides a shift of the energy levels and a decrease of the band bendings (in the range of the pressure of this work, indium phosphide does not undergo a phase transition nor a direct-indirect change of the fundamental energy gap.[13] This has already been theoretically established quantitatively. In the $\mathbf{k}\cdot\mathbf{p}$ perturbation scheme, the effective mass of both the conduction electron and valence-band hole can be derived from the band structure of the material. Roughly speaking, both of them are proportional to the fundamental gap and inversely proportional to the matrix element of the kinetic momentum.[14] The pressure coefficients of the band gap can be correctly measured with great accuracy from the energy of the transverse exciton polariton obtained

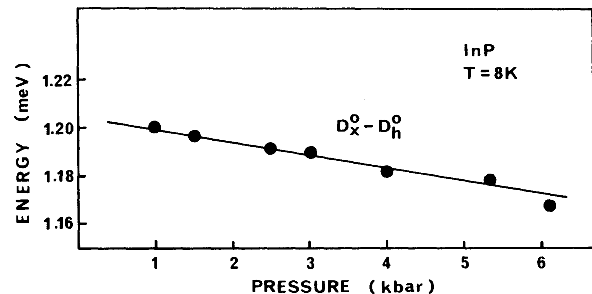

FIG. 3. Plot of the experimental energy difference between the D^0X and D^0h transitions, as a function of the pressure (solid circles) and a plot of the results of the numerical investigation (solid line).

after a quantitative fit of the reflectivity of the sample, collected in the whole range of pressure of interest.[11] The variation of the matrix element of the momentum is relatively small and can be obtained from scaling relations.[15–17] Then one can calculate the pressure dependence of both the electron and hole effective masses. In the case of InP some experimental measurements have shown a significant change of the electron effective mass (0.62%/kbar) (Ref. 18) and a smaller variation of the hole mass (0.08%/kbar) (Ref. 19) in agreement with the theoretical prediction. This results in a change of σ in such a way that the localization energy of the complexes studied in this paper are significantly changed under pressure. The last point we have to take into account concerns the slight decrease of the macroscopic dielectric constant under pressure. In the case of InP, since there are no experimental results reported, we have taken the theoretical value of Ref. 17: $(1/\epsilon)(d\epsilon/dp) \sim -0.1\%$/kbar, which is comparable with the measurement of Samara[20] for GaAs, $\sim -0.17\%$/kbar.

IV. DATA ANALYSIS

The quantitative investigation of these experimental results requires knowledge of the behavior of the localization energy of these complexes as a function of the mass ratio between the electron and the hole. Although many theoretical calculations have been performed since the original estimate of Hopfield,[21] there are some remarkable discrepancies between the different methods and the different authors, especially for the D^0X complex. We first focus on the D^0h complex. From the very accurate calculation performed by Skettrup *et al.*,[22] we obtain a value of -0.8 for $\delta(E(D^0h)/E_d)/\delta\sigma$ in the case of InP, where $m_e^* = 0.08 m_0$ and $m_h^* = 0.85 m_0$.[23] Here, $E(D^0h)$ and E_d denote the localization energy of the D^0h complex and the binding energy of the neutral donor, respectively. It should be noted that Fig. 1 of the original paper of Skettrup *et al.*[22] is valid for D^0h but not for D^+X. The localization of this latter complex can be obtained using Eq. (5) of Ref. 22.

Second, concerning the D^0X complex, most calculations exhibit a decrease of the localization energy with decreasing σ in the neighborhood of $\sigma = 0.1$. Following the recent investigations performed by Wunsche *et al.*,[24] Chang and McGill,[25] Stébé and Munschy,[26] and Adamowski *et al.*,[27] we consider a coefficient $(\delta/\delta\sigma)[E(D^0X)/E_d]$ of -0.4.

Now the difference between the pressure coefficients of the localization energy of the D^0X and D^0h complexes becomes

$$\Delta = \frac{d}{dp}[E(D^0h) - E(D^0X)]$$
$$= \frac{d\sigma}{dP} E_d \left[\frac{\delta}{\delta\sigma}\left[\frac{E(D^0h)}{E_d}\right] - \frac{\delta}{\delta\sigma}\left[\frac{E(D^0X)}{E_d}\right]\right]$$
$$+ [E(D^0h) - E(D^0X)] \frac{d}{dP}(\ln E_d) .$$

In the case of InP, where $E_d = 7.1$ meV and $E(D^0X) - E(D^0h) = 1.2$ meV under atmospheric pressure conditions at 8 K, we calculate a value of -0.6 meV/Mbar for Δ; a value in close agreement with the experimental one given in Sec. II ($\Delta_{\text{expt}} = -0.57$ meV/Mbar).

V. CONCLUSION

We have studied the change in the localization energy of the D^0X and D^0h complexes in the tetrahedral direct-band-gap semiconductor indium phosphide. Our experimental finding, a decrease of the D^0X-D^0h energy separation with hydrostatic pressure, has led us to a critical examination of the theoretical calculations of the localization energy for these two types of complexes as a function of the mass ratio σ. It appears that the binding energy of an exciton to a neutral donor is a decreasing function of the mass ratio $\sigma = m_e^*/m_h^*$ in the range of σ values characteristic of standard cubic direct-band-gap semiconductors.

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