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Pressure dependence of the direct absorption edge of InP

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The variation of the lowest direct absorption edge of InP with pressure has been measured at room temperature with a diamond anvil cell for pressures up to the phase transition (100 kbar). Both transmission and luminescence techniques were used. The gap varies sublinearly with pressure but linearly with lattice constant: the gap deformation potential so obtained is $a = -6.35 \pm 0.05$ eV. This result is discussed in the light of theoretical calculations. The observed luminescence intensity remains nearly constant as a function of pressure up to 90 kbar. At this pressure the efficiency begins to decrease thus signaling the crossing of the Γ and X conduction-band minima which we estimate to occur at 104 ± 1 kbar. The pressure coefficient of the Γ-X indirect gap is found to be $-(3 \pm 1) \times 10^{-6}$ eV/bar.

I. INTRODUCTION

The diamond anvil cell is an instrument particularly suited to perform absorption,[1] luminescence,[2] and light-scattering measurements[3] under high hydrostatic pressures. Recent transmission measurements at room temperature on[1] GaAs and[4] Ge for pressures up to the phase transition (180 kbar for GaAs, 105 kbar for Ge) yield a sublinear dependence of the gap energy E_0 on pressure. The fit with quadratic expressions yields for the linear coefficient at low pressures values significantly higher than obtained in previous measurements with conventional large-volume high-pressure cells (typically up to $\sim$10 kbar). The results obtained with absorption measurements for GaAs have been confirmed by means of luminescence and resonant Raman scattering also in a diamond anvil cell.[2,5]

The nonlinearity mentioned above is due, in part, to the nonlinearity in the equation of state at high pressures. When E_0 is plotted as a function of the change in lattice constant $\Delta a/a_0$ using the corresponding equation of state, nonlinearity is considerably reduced but still a sublinear behavior remains. The theoretical interpretation of this remaining nonlinearity, an important parameter in the theory of the electron–two-phonon interaction, presents some difficulties.[1,4,5]

In an attempt to investigate the systematics of the linear and nonlinear pressure coefficients of the E_0 gap ($\Gamma_{15} \rightarrow \Gamma_1$) of zinc-blende- and diamond-type semiconductors we have performed absorption and luminescence measurements on InP at room temperature up to the phase transition (101 kbar). The E_0 gap of this material also exhibits a sublinear variation with pressure [initial slope $(8.4 \pm 0.2) \times 10^{-6}$ eV/bar]. The conversion from pressure to lattice constant is hampered by the lack of exact knowledge of the pressure derivative of the bulk modulus B_0'. Taking for this parameter the same value as measured for GaAs (see previous paper[3]) we find, within experimental error, a linear variation of E_0 vs $\Delta a/a_0$. The deformation potential so determined is $a = (-6.1 \pm 0.2)$ eV considerably smaller in magnitude than that found for GaAs (-9.77 eV) and for Ge (-12.6 eV). We conclude that a decreases rapidly with increasing ionicity.

It has been recently shown[2] that the luminescence efficiency of GaAs decreases rapidly for pressures above 30 kbar as a result of the crossing of the Γ and the X conduction-band minima: the lowest gap becomes indirect. Similar effect is expected for InP but at higher pressures (the Γ-X separation is larger for InP than for GaAs).[6] We observe a decrease in the luminescence intensity starting at 95 kbar. By fitting this decrease with a theoretical expression we find that the crossing between the Γ and the X points occurs at 104 ± 1 kbar. Further, the linear pressure coefficient for the X point is found to be $-(3 \pm 1) \times 10^{-6}$ eV/bar. This leads to an X-Γ separation at $p = 0$ of (1.0 ± 0.2) eV.

II. EXPERIMENTAL AND RESULTS

The samples were prepared by lapping and polishing a piece of n-type single crystal ($N_D \simeq 5 \times 10^{15}$ cm^{-3}) down to a thickness of 20 μm. The sample was then broken into small pieces and a piece suitable to fit into the 200-μm hole of the pres-

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sure cell gasket was chosen under the microscope.

Typical absorption spectra for various pressures are shown in Fig. 1. As band edge E_0 we defined the saturation value of the excitonic absorption indicated by arrows in Fig. 1. These saturation values actually are somewhat lower than the excitonic step for the relatively thick samples used (20 μm). A comparison with previous work,[1,4] however, suggests that the error committed by this somewhat improper definition is small.

The experiments were performed at room temperature. The spectra were corrected for spectral response of the monochromator-multiplier unit and the absorption coefficient $\alpha=-(1/d)\ln I/I_0$ was determined. For transmission measurements a 150-W halogen lamp was used as a source. The optical setup consisted of an achromatic microscope lens system focusing an iris diaphragm down to 40 μm. The magnified image of the illuminated spot was guided into a double monochromator, suitably apertured by a second diaphragm to block any scattered light around the sample. The minimum detectable transmissivity was found to be of the order of 10^{-5}. A nitrogen-cooled S1 photomultiplier, in connection with a photon counting system, improved the signal-to-noise ratio. The pressure was monitored by the fluorescence shift of a small ruby chip, placed together with the sample crystal into the pressure chamber.[6,7]

The experimental setup for the luminescence measurements was similar to that described in the previous paper for Raman work. The photoluminescence was excited by the 514-nm line of an Ar^+ laser. Its power was kept as low as 40 mW so as to minimize heating. Figure 2 represents typical luminescence spectra at various pressures, characterized by a single emission band. The maximum of the intensity of the spectra, corrected for the throughput of the spectrometer, was taken as the direct gap E_0. With increasing pressure the luminescence peak is shifted to higher energies, in agreement with the data of Fig. 1.

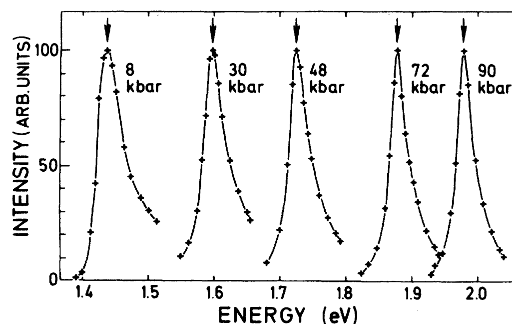

FIG. 2. Typical luminescence spectra of InP at several pressures and room temperature.

The energy of the direct gap as a function of pressure, obtained from both luminescence as well as transmission measurements, is plotted in Fig. 3. A least-squares fit exhibits a sublinearity reported also for GaAs and Ge, yielding for the linear and quadratic pressure coefficients

$$E=E_0+\alpha p+\beta p^2 ,$$

where $\alpha=(8.4\pm0.2)\times10^{-6}$ eV/bar and $\beta=-(1.8\pm0.3)\times10^{-11}$ eV/bar^2.

The quadratic pressure dependence of E_0 can be accounted for by nonlinearities in the elastic bulk modulus: plotted versus the variation of the lattice constant by using Murnaghan's equation [Eq. (1) of the previous paper], however, the band gap can be represented by the linear relation relation (see Fig. 4)

$$E=E_0+3a(\Delta a/a_0) ,$$

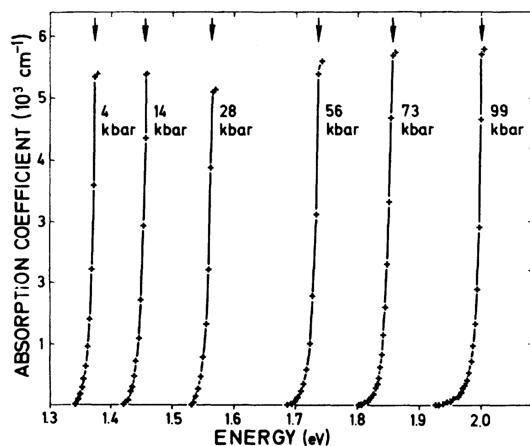

FIG. 1. Typical absorption spectra of InP at several pressures and room temperature.

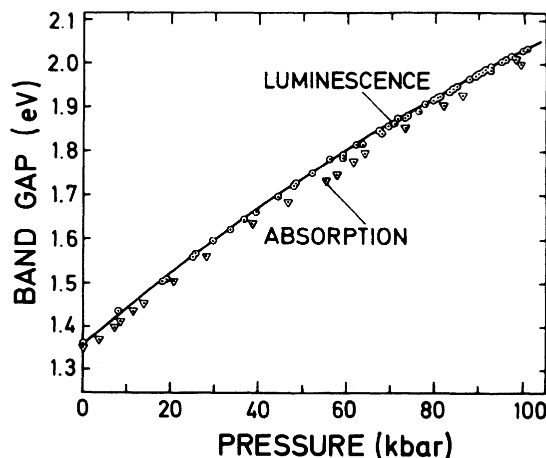

FIG. 3. Band gap E_0 of InP at room temperature vs pressure as obtained from absorption (∇) and luminescence ($\odot$) measurements. The solid line represents a least-squares fit to the *luminescence* data.

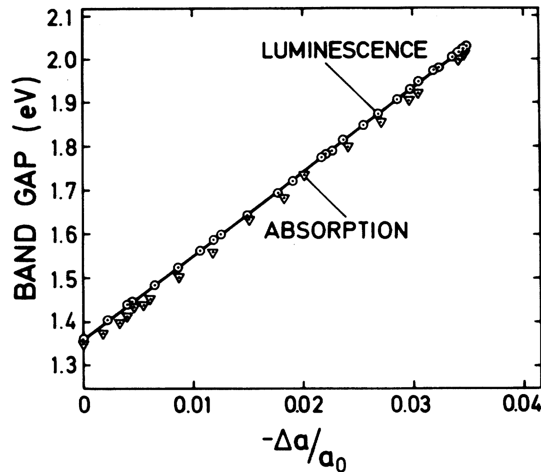

FIG. 4. Band gap E_0 of InP at room temperature vs pressure as obtained from absorption (▽) and luminescence (⊙) measurements. The solid line represents a least-squares fit to the *luminescence* data.

with $a = (-6.35 \pm 0.05)$ eV.

The III-V compounds undergo a metallic first-order phase transition under high pressure. As a consequence the crystals turn opaque and the photoluminescence is totally quenched. In InP, this phase transition occurs at 101.5 ± 0.5 kbar. The luminescence intensity, which shows only a slight variation at lower pressures, decreases significantly already above ~90 kbar, well below the pressure of the phase transition (see Fig. 5). This decrease was found to be reversible with pressure during several cycles up to 100 kbar, as indicated by the numbers in Fig. 5. Therefore the decrease of the luminescence intensity cannot be attributed to partially induced phase transitions in the sample due to an inhomogeneous pressure distribution in the cell. The luminescence decrease, however, can be interpreted in terms of a crossing of the Γ and X minima whose pressure coefficients should be of opposite signs, in a manner similar to the effect reported by Yu and Welber[2] for GaAs: the lowest gap, direct at low pressures, becomes indirect at high pressures. From a least-squares fit of the experimental points of Fig. 5 in this region the pressure coefficient of the Γ-X indirect gap can be inferred.[2] (Caution: because of a camelback structure the conduction minimum may not be exactly at X but may occur along Δ, close to X as in GaP. This is irrelevant for our further reasoning.)

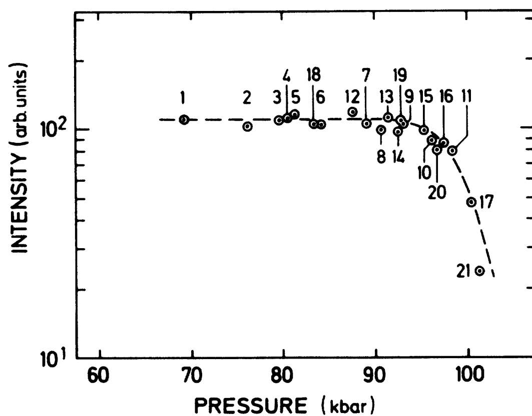

FIG. 5. Luminescence intensity vs pressure in InP. The numbers attached to the experimental points indicate the sequence in which the data were taken. The solid curve is a fit with Eq. (1).

III. DISCUSSION

We have listed in Table I the deformation potential a obtained for InP in the present experiments together with the results of similar determinations using diamond anvil cells for Ge,[4] GaAs, and ZnTe.[8] The experimental values of a show a clear trend to decrease with increasing polarity (the polarities α_P according to Harrison and Ciraci[9] are also listed in Table I). The various theoretical calculations of a listed in Table I also reproduce the trend of decreasing a with decreasing polarity. The most pictorial explanation of this effect is obtained with the so called dielectric theory.[10] In this phenomenological approach there is a contribution to the energy gap of the form $(V_2^2 + V_3^2)^{1/2}$ [see Eq. (9) of preceding paper], which increases with increasing α_P. The assumption made in the previous paper, that V_3 is not affected by hydrostatic stress, leads automatically to a decrease in a with increasing V_3 (i.e., polarity).

Standard pseudopotential calculations[11] also reproduce the trend of decreasing a with increasing polarity. We have performed such calculations for InP using empirical pseudopotential form factors. The form factors of Cohen and Heine[12] were used for zero pressure and about 60 plane waves were included in the calculation of the band structure. The dominating pressure dependence of the energy gap results from two effects: (i) the volume dependence of the form factors through their normalization to the unit cell of the crystal, and (ii) the form factors in the stressed crystal are needed at different wave vectors compared to zero pressure.[13]

In order to obtain the form factors at all wave vectors we interpolated the values given in Table XVI of Ref. 12 with a cubic spline. These tables contain also a cutoff value for the atomic form factors which is the second zero of the pseudopotential as a function of wave vector and occurs between $q = 2k_F$ and $3k_F$. This cutoff does not enter the band structure calculation for zero pressure but influences rather critically

TABLE I. Experimental values of the deformation potential $a = dE_0/3da$ (eV) obtained at room temperature for several tetrahedral semiconductors with diamond anvil cells. Also values of a calculated by several authors and polarities α_p according to Harrison.

	Ge	GaAs	InP	ZnTe
a	-12.5[a]	-9.77[b]	-6.35[c]	-5.8[d]
			-6.7[i]	
	-12.2[e]	-9.95[e]	-8.7[e]	-4.1[e]
	-10.75[f]	-8.23[f]	-6.9[f]	-4.1[f]
			-10[g]	
			-6[h]	
α_p	0	0.50	0.58	0.72

[a]Experimental, Ref. 4.
[b]Experimental, Ref. 1.
[c]Experimental, present work.
[d]Experimental, Ref. 8.
[e]Calculated, Ref. 9.
[f]Calculated, Ref. 10.
[g]Calculated, with Cohen and Heine pseudopotential as described in text.
[h]Calculated with Cohen and Heine pseudopotential modified as to lower the q of the second zero of the In pseudopotential by 5%.
[i]R. A. Bendoryus and A. Yu Shileika, Sov. Phys. Semicond. 6, 1042 (1972).

the deformation potential of the E_0 gap. When the cutoff wave vectors of Cohen and Heine are used ($q_{\mathrm{In}}^c = 2.23$, $q_{\mathrm{P}}^c = 2.14$), which were obtained simply by extrapolation of the form factors used in the band calculation, one obtains $a = -9$ eV, 50% larger in magnitude than observed experimentally. The deformation potential of the Γ-X indirect gap is thereby predicted to be $\mathcal{E}_1(x_{1c}) = -1$ eV in disagreement with the data (see Table II). A shift of q_{In}^c and q_{P}^c by the same amount to slightly smaller wave vectors, namely, $q_{\mathrm{In}}^c = 2.13$ and $q_{\mathrm{P}}^c = 1.99$ has the following effect: (i) The deformation potential $\mathcal{E}_1(x_{1c})$ becomes smaller and thus closer to experiment. We find $a = -6.0$ eV in quite good agreement with the experimental results. This change in a is produced mainly by the decrease in q_{In}^c. (ii) The deformation potential $\mathcal{E}_1(X)$ becomes slightly negative, also in agreement with the observed trend. We obtain $(X_{1c}) = 2.26 + 3\mathcal{E}_1 \Delta a/a$, with $\mathcal{E}_1(X_{1c}) = +2.1$ eV. (iii) We also calculated the change of the splitting of LO and TO modes with pressure (i.e., of the dynamical charge e_T^*) (see previous paper) and get better agreement with experiment. We see that the deformation potentials provide a sensitive means for determining the

TABLE II. Experimental deformation potentials $\mathcal{E}_1(X_{1c})$ (in eV) the X indirect gaps of several theoretical semiconductors. Also, results of theoretical calculations.

InP	GaP	AlSb	Si	GaAs
$+2.2$[a]	$+1.6$[b]	$+2.2$[c]	$+1.6$[d]	$+2.0$[e]
$+2.1$[f]	$+0.7$[g]	$+0.6$[g]	$+0.1$[g]	$+0.6$[g]
$+0.7$[g]	$+1.5$[h]	-0.3[h]	-0.3[h]	-1.1[h]
-1.3[h]				

[a]Present work, experimental.
[b]Reference 14.
[c]L. D. Laude, M. Cardona, and F. H. Pollak, Phys. Rev. B 1, 1436 (1970).
[d]B. Welber, C. K. Kim, M. Cardona, and S. Rodriguez, Solid State Commun. 17, 102 (1975).
[e]Calculated, this work.
[f]Present work, calculated.
[g]Reference 10.
[h]Reference 8.

whole $v(q)$ curve, a conclusion which was reached previously.[9] Table II lists the hydrostatic strain coefficients of the Γ_{15}-X_{1c} indirect gap $\mathcal{E}_1(X_{1c})$ obtained for InP and other tetrahedral semiconductors together with the results of theoretical calculations. We should point out that the calculation performed as described above yields a completely linear dependence of E_0 and $\Delta a/a_0$ in the range of our measurements and in agreement with them. Unpublished work[8] for ZnTe indicates that the existence of a sublinear or supralinear dependence is related very critically to the type of equation of state used: the Murnaghan equation yields a slightly sublinear dependence while Bridgman's equation of state for ZnTe yield slight supralinearity. In view of the crude assumption made for the derivative of the bulk modulus B_0' in the analysis of the InP data, we believe that the question of the linearity is not completely settled. A survey of existing data, however, seems to indicate that the nonlinearity in E_0 vs $\Delta a/a_0$ decreases with increasing polarity.

The decrease of luminescence intensity at high pressures shown in Fig. 5 is attributed to electron transfer from the Γ_1 minimum of the conduction band to X_{1c}, where radiative recombination must be indirect and thus very weak. The observed decrease can be fitted with the expression[2]

$$I(p) = I_0(1 + A\exp\{B_c[a - \mathcal{E}_1(X_{1c})](p - p_0)/kT\})^{-1} , \quad (1)$$

$$A = 6(m_{\parallel X} m_{\perp X}^2 / m_\Gamma^3)^{1/2} \tau_\Gamma / \tau_{nX} ,$$

where p_0 is the pressure at which the Γ and X minima become degenerate; $m_{\parallel X}$, $m_{\perp X}$, and m_T are longitudinal and transverse masses at X_{1c} and the mass at Γ_1, respectively; τ_Γ is the radiative lifetime at Γ and τ_{nX} is the nonradiative one at X; and B_0 is the bulk modulus.[15] We assume a camel-back type of minimum near X_{1c} so as to obtain in A the degeneracy factor of 6. The small range of pressure with decreasing luminescence intensity available before the phase transition severely limits the quality of the fit. For A we took a value of 8, very close to that found for GaAs ($A = 7$). From the fit we obtain $p_0 = 104$ kbar and $\mathcal{E}_1(X_{1c}) = +2.2$ eV.

We list in Table II the deformation potentials $\mathcal{E}_1(X)$ as obtained experimentally and theoretically for a number of tetrahedral semiconductors. The theoretical values scatter widely and some of them even have a sign opposite to the experimental one. They are, however, all quite small in magnitude, in agreement with experiments. These small values result from cancelling terms in the calculations and thus are very sensitive to the parameters of the calculation, such as the pseudopotential cutoffs mentioned above.

The separation between the Γ and X conduction minima at $p = 0$ can now be obtained by extrapolating the pressure dependence for the Γ-X_{1c} gap (assumed linear) and that of the direct gap (taken as quadratic). We find $E(X_{1c}) - E(\Gamma_1) = 1.0 \pm 0.2$ eV at zero pressure. Our pseudopotential calculation yields 0.68 eV for this difference while other experimental work[16] gives ~0.8 eV.

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[1] B. Welber, M. Cardona, C. K. Kim, and S. Rodriguez, Phys. Rev. B 12, 5729 (1975).
[2] P. Y. Yu and B. Welber, Solid State Commun. 25, 209 (1978).
[3] R. Trommer, H. Müller, M. Cardona, and P. Vogl, Phys. Rev. B 21, 4869 (1980) preceding paper.
[4] B. Welber, M. Cardona, Y. F. Tsay, and B. Bendow, Phys. Rev. B 15, 875 (1977).
[5] Y. F. Tsay and B. Bendow, Phys. Rev. B 14, 2681 (1976).
[6] J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. 44, 1 (1973).
[7] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. 46, 2774 (1975).
[8] A. de Losanne and B. A. Weinstein (private communication).
[9] W. A. Harrison and S. Ciraci, Phys. Rev. B 10, 1516 (1969).
[10] D. L. Camphausen, G. A. Neville Connel, and W. Paul, Phys. Rev. Lett. 26, 184 (1971).
[11] Y. F. Tsay, S. S. Mitra, and B. Bendow, Phys. Rev. B 10, 1476 (1974).
[12] M. L. Cohen and V. Heine, in *Solid State Physics*, Vol. 24, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), p. 37.
[13] M. Cardona, in *Atomic Structure and Properties of Solids*, edited by E. Burstein (Academic, New York, 1972), p. 539.
[14] R. G. Humphreys, U. Rössler, and M. Cardona, Phys. Rev. B 18, 5590 (1978).
[15] R. M. Martin, Phys. Rev. B 1, 4006 (1970).
[16] T. Kobayashi, T. Kimura, K. Yamamoto, and K. Abe, *Physics of Semiconductors, 1978*, edited by B. L. H. Wilson (The Institute of Physics, Bristol and London, 1979), p. 351.