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Raman and absorption spectroscopy of InP under high pressure

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Abstract. Raman and absorption measurements on three samples of InP are measured in a diamond-anvil cell at room temperature for pressures up to the phase transition. This occurs progressively between 90 and 99 kbar for all three samples, with a highest band-gap energy of 2.01 eV. The results from this work are compared with previous results in the literature. Correlation of the maximum shift of the Raman signal and of the band gap with the phase transition pressure are used to distinguish real differences from experimental error. In this way the phase transition pressure is found to range from 90 kbar to more than 105 kbar. We find consistent pressure coefficients for the band gap energy of $8.2 \text{ meV kbar}^{-1}$, for the longitudinal optical (LO) phonon energy of $0.56 \pm 0.02 \text{ cm}^{-1} \text{ kbar}^{-1}$ and for the transverse optical (TO) of $0.63 \pm 0.02 \text{ cm}^{-1} \text{ kbar}^{-1}$. The mode-specific Grüneisen parameters are $\gamma_{LO} = 1.19 \pm 0.04$ and $\gamma_{TO} = 1.52 \pm 0.05$.

Several investigations of InP under hydrostatic pressure have been reported since the development of diamond-anvil high-pressure cells (DACs) made optical spectroscopy under high pressure an accurate, quantitative technique. Raman (Trommer *et al* 1980), absorption (Müller *et al* 1980, Kobayashi *et al* 1986) and photoluminescence (Müller *et al* 1980, Menoni *et al* 1986, Leroux 1989, Tozer *et al* 1988, Ernst *et al* 1996) spectroscopy have been used to obtain the pressure dependence of the phonon frequencies and the band gap, and the phase transition pressure. Significant variation in these parameters is observed. The purpose of the present work is to correlate the phase transition pressure with the values of the optical band gap and Raman shift at the phase transition in order to distinguish between scatter due to experimental error and scatter due to sample-to-sample variation.

The energy of the photoluminescence of a bulk specimen of InP varies with crystal purity and with the nature of residual defects. The Raman and absorption spectra are more nearly invariant properties of InP and therefore, more appropriate for this study. Moreover, they permit measurement at 300 K, which guarantees more nearly hydrostatic conditions in the pressure cell than cryogenic temperatures. We used a miniature diamond-anvil cell system (Dunstan and Scherrer 1989); the cell was loaded with argon as the pressure medium (Spain and Dunstan 1989), and ruby was used for pressure calibration. A Renishaw Raman microscope was used to obtain both Raman and absorption spectra from the sample as well as the ruby photoluminescence at pressures up to the phase transition. White light was introduced behind the diamonds for the absorption spectra. The advantage of this system is that the microscope is confocal, so that masking should not be required within the pressure

cell. While masking is feasible (Kobayashi *et al* 1986, Leong *et al* 1992, Lindner *et al* 1992) it creates added technical difficulties. However, absorption spectra were still difficult to obtain and reliable data up to the phase transition were obtained from only one sample.

There is a wide variation in the phase transition pressures reported in the literature. Reported values include 96 kbar (Kobayashi *et al* 1986), 100 kbar (Trommer *et al* 1980, Müller *et al* 1980), 103 kbar (Leroux 1989), 106.5 kbar (Tozer *et al* 1988), 108 kbar (Menoni and Spain 1987), 110 kbar (Ernst *et al* 1996) and 120 kbar (Menoni *et al* 1986) while all three of our samples went black and lost the Raman spectrum in the range 97–99 kbar. There has long been debate about how reproducible the phase transition pressure should be (for a discussion see Besson *et al* 1991); there is also considerable scope for error in its determination in a diamond-anvil cell due to errors in pressure calibration, non-hydrostatic strains, etc. Comparison of the values of the band gap and of the Raman shift and intensity at the phase transition are used here to resolve this question.

1. Raman spectroscopy

1.1. Phase transition pressure

Three samples of InP were used in separate pressure runs. One was taken from a recent S-doped InP wafer; the other two were from ten-year-old wafers of unknown provenance. Raman spectra were recorded at pressures from ambient to the phase transition; data at the higher pressures are shown in figure 1 together with the data from Trommer *et al* (1980) for comparison. We find the ambient pressure LO phonon energy to be $341.5 \pm 0.3 \text{ cm}^{-1}$, three wavenumbers lower than Trommer *et al*, consequently, we plot here the shifts with pressure rather than the absolute values. The heavy curve in the figure is the linear fit to lattice constant reported by Trommer *et al*, converted to pressure using the Murnaghan (1944) equation of state

$$\Delta\omega(P) = \omega(P) - \omega_0 = \frac{d\omega}{d \ln a_0} \left(-1 + \left[1 + \frac{B'P}{B} \right]^{-1/3B'} \right) \quad (1)$$

with the values used by Trommer *et al* of bulk modulus $B = 725 \text{ kbar}$, its pressure derivative $B' = 4.67$, and $-d\omega/d \ln a_0 = 1280 \text{ cm}^{-1}$ for the LO phonon and $-d\omega_0/d \ln a_0 = 1380 \text{ cm}^{-1}$ for the TO phonon. The two lighter curves are fits to our data with different values of $d\omega_0/d \ln a_0$ but all other parameters are kept the same. Agreement with the results of Trommer *et al* is well within experimental error.

The Raman signal was weak at low pressures and became much stronger when the band gap was greater than the laser photon energy. The Raman intensity was then stable up to 90 kbar. At the highest pressures, as shown in figure 2, the Raman signal weakened significantly, to the point where in two of the three runs the TO phonon disappeared before the LO. Visual inspection of the samples showed some blackening at this stage, and the phase transition may be presumed to have started—that is, parts of the sample may have become metallic. Figure 2 shows that the LO Raman intensity decreased exponentially from 90 to 99 kbar in all three samples, and that good agreement was observed between the data from the three samples. No Raman signal was observed at pressures above 99 kbar in any of the three samples.

The data of figures 1 and 2 together implies that the scatter in phase transition pressure determined from our three data sets and that of Trommer *et al* is not due to errors in pressure calibration, nor to sample-to-sample variation, but to the estimation of the completion of the transition during the quenching of the Raman intensity in figure 2. This estimate will

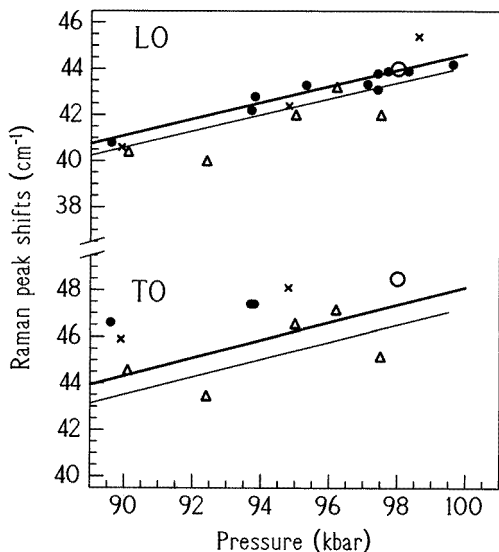


Figure 1. Raman peak positions observed at higher pressures. The three samples yielded the data sets shown as the points ● and × from the old wafer and Δ from the new InP:S wafer. The other two points ○ are the final data points of Trommer *et al* (1980). The heavy curves show the fits of Trommer *et al* to their data, using equation (1). The two light curves are the fits to our own data using the same equation and parameter values.

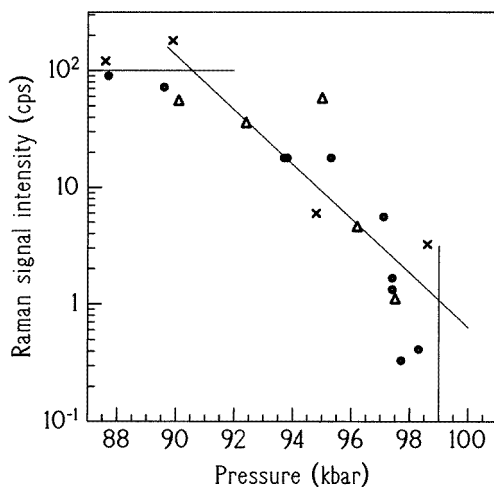


Figure 2. Raman LO peak intensities plotted against pressure. The symbols (●, × and Δ) correspond to the same data sets as in figure 1. The straight lines are guides to the eye, to indicate how the phase transition may be taken to start at 91 kbar and be complete at 99 kbar.

vary from run to run, because it is not possible to obtain exactly reproducible pressure increments in a DAC, and because the Raman intensity shows random variation between successive pressures. This is presumably because the laser focus has to be moved from the sample to the ruby, to measure the pressure, and back to measure the Raman. When the final data point occurs at a lower Raman shift than the previous one (as it does here

in the data shown in figure 1 by triangles), it is not clear if this is due to random error in pressure and peak position determination or, as Leroux (1989) proposes, because a partial phase transition reduces the hydrostatic pressure in other parts of the sample. In this case, it is not clear if the phase transition pressure should be taken at the final or the penultimate data point. There are, therefore, two key points to note about the data in figures 1 and 2. The first is that the relationship between Raman frequency shift and pressure is the same in all three of our runs and in the experiment of Trommer *et al* (1980); it follows that the differences in the phase transition pressures are not due to errors in the pressure calibration. The second key point is the progressive quenching of the Raman intensity in figure 2. We conclude, from the Raman data, that the phase transition in InP begins at 90–91 kbar and is essentially complete at 99 kbar.

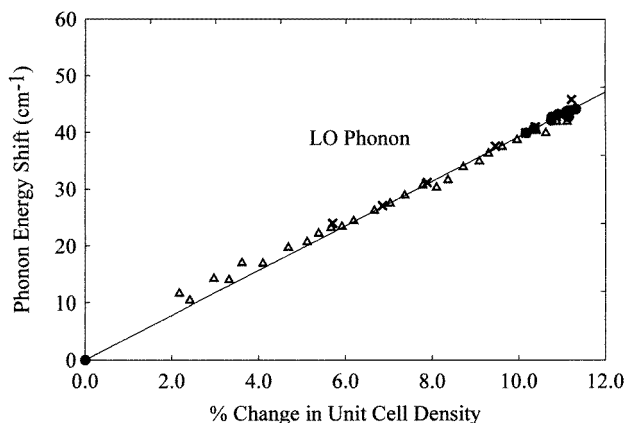


Figure 3. The LO phonon peak shifts are plotted against the relative change in density of the crystal, calculated from equation (2). The symbols (●, × and △) correspond to the same data sets as in figure 1. The curve is a least squares linear fit with a slope of 393 cm^{-1} .

1.2. Pressure coefficients and Grüneisen parameters

In most of our data the TO phonon peak is weak and relatively inaccurately determined, and we consider first the pressure dependence of the LO peak. In agreement with Trommer *et al* (1980), it is sublinear with pressure and linear (within error) when plotted against lattice constant. Using the same B and B' , we find a gradient $d\omega/d \ln a_0$ of 1265 cm^{-1} , which compares well with the value of Trommer *et al* of 1280 cm^{-1} . Using the recommended values of $B = 723 \text{ kbar}$ and $B' = 4.5$ (Prins and Dunstan 1991), we obtain 1250 cm^{-1} , which is not very different. However, figure 3 shows our LO data plotted not against lattice constant, but against the density of the crystal ρ , calculated from the Murnaghan (1944) equation using $B = 723 \text{ kbar}$ and $B' = 4.5$. Again a linear fit is appropriate so that we may write

$$\Delta\omega(P) = \omega(P) - \omega_0 = \frac{d\omega}{d \ln \rho} \left(-1 + \left[1 + \frac{B'P}{B} \right]^{1/B'} \right) \quad (2)$$

and now the gradient $d\omega/d \ln \rho$ is 393.0 cm^{-1} , significantly less than a third of $-d\omega/d \ln a_0$.

We have shown elsewhere (Prins *et al* 1996) that a parabolic fit to pressure of a quantity which varies linearly with lattice constant gives parabolic fitting parameters which vary with

the pressure range of the experiment and therefore, do not provide a satisfactory description of the physical parameters. We conclude that the linear pressure coefficient is best described as $-3^{-1}B^{-1}d/d \ln a_0$ or as $B^{-1}d/d \ln \rho$, with no good theoretical reason to choose between the linear fit to lattice constant or the linear fit to pressure. Evaluating these two quantities, we obtain $0.581 \text{ cm}^{-1} \text{ kbar}^{-1}$ from the lattice constant fit and $0.544 \text{ cm}^{-1} \text{ kbar}^{-1}$ from the density fit of figure 3. These are to be compared with the values of $0.54 \text{ cm}^{-1} \text{ kbar}^{-1}$ reported by Trommer *et al* from their parabolic fit to pressure, and $0.588 \text{ cm}^{-1} \text{ kbar}^{-1}$ from their linear fit to lattice constant—i.e. $1280 \text{ cm}^{-1}/(3 \times 725 \text{ kbar})$. Plainly, the major source of uncertainty in the linear pressure coefficient is not the accuracy of the experiments, but the choice of fitting procedures. Given the lack of any good theoretical reason to choose between the fit to lattice constant and the fit to density, we can only give $0.56 \pm 0.02 \text{ cm}^{-1} \text{ kbar}^{-1}$ as the linear pressure coefficient of the LO phonon.

For the TO phonon, we obtain 1355 cm^{-1} from a linear fit to lattice constant using the parameter values of Trommer *et al* to be compared with their value of 1380 cm^{-1} . Using $B = 723 \text{ kbar}$ and $B' = 4.5$, the lattice constant fit gives 1345 cm^{-1} and the density fit gives 1281 cm^{-1} . However, our TO phonon peaks were weak and difficult to measure accurately. We prefer, therefore, to compare our LO–TO splittings with those reported by Trommer *et al*. Our data are plotted in figure 4 and seen to be in reasonable agreement with the parabolic fit Trommer *et al* made to their LO–TO splittings. A linear least-squares fit to our data gives a rate of change of splitting with lattice constant of -145 cm^{-1} , implying a gradient for the TO phonon of $d\omega/d \ln a_0 = (1265 + 145) \text{ cm}^{-1} = 1410 \text{ cm}^{-1}$. This implies a linear pressure coefficient of $0.650 \text{ cm}^{-1} \text{ kbar}^{-1}$, to be compared with the values of $0.58 \text{ cm}^{-1} \text{ kbar}^{-1}$ reported by Trommer *et al* from their parabolic fit against pressure and $0.634 \text{ cm}^{-1} \text{ kbar}^{-1}$ from their fit to lattice constant. Similarly, we obtain $(393 + 46) \text{ cm}^{-1}/723 \text{ kbar}$, i.e. $0.607 \text{ cm}^{-1} \text{ kbar}^{-1}$, from our density fit and therefore give $0.63 \pm 0.02 \text{ cm}^{-1} \text{ kbar}^{-1}$ as the linear pressure coefficient of the TO phonon.

The mode-specific Grüneisen parameter is defined as

$$\gamma = \frac{d \ln \omega}{d \ln V} = \frac{B}{\omega} \frac{d\omega}{dP} \quad (3)$$

so the pressure coefficients we give for the LO and TO phonons correspond to $\gamma_{LO} = 1.19 \pm 0.04$ and $\gamma_{TO} = 1.52 \pm 0.05$. Finally, this corresponds to a difference in the Grüneisen parameters of $\gamma_{TO} - \gamma_{LO} = 0.33 \pm 0.01$, to compare with the misprinted value of 0.20 ± 0.05 given by Trommer *et al* (1980) and their actual value of 0.28.

2. Absorption spectroscopy

The other authors who have reported the phase transition pressure have monitored not the Raman shift but the band gap as a function of pressure. In order to compare our result with theirs, we measure the band gap using absorption spectroscopy. Because the samples are about $20 \mu\text{m}$ thick, we measure the wavelength at which transmission becomes detectable, corresponding to an absorption coefficient of about 1000 cm^{-1} . This is not quite the band gap, but correction is straightforward (see later). Uncorrected data for one sample are plotted in figure 5 together with a linear fit to the change in lattice constant, i.e.

$$E_g(P) = E_0 + 3\Xi \left(-1 + \left[1 + \frac{B'P}{B} \right]^{-1/3B'} \right) \quad (4)$$

using $B = 723 \text{ kbar}$, $B' = 4.5$ and fitting for the deformation potential $\Xi = -6.64 \text{ eV}$. The linear pressure coefficient from the fit is $-\Xi/B = 9.18 \text{ meV kbar}^{-1}$, in fair agreement

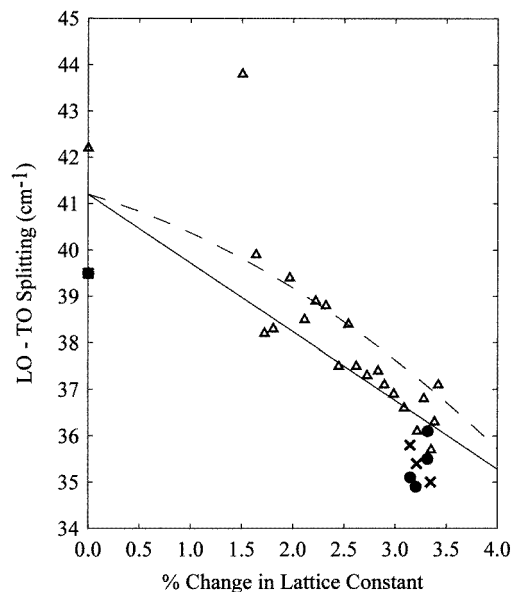


Figure 4. The LO-TO splitting is plotted against relative change in lattice constant. The symbols (●, × and Δ) correspond to the same data sets as in figure 1. The full curve is a least squares linear fit with a slope of 147 cm^{-1} . The broken curve is the parabolic fit given by Trommer *et al* (1980).

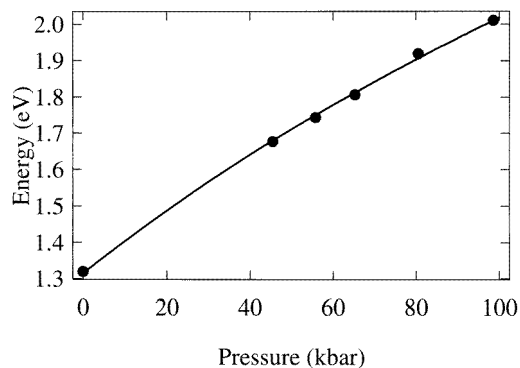


Figure 5. The position of the absorption edge is plotted against pressure. The curve is a fit using equation (4) and the parameters are given in the text.

with the literature values which range from $7.5 \text{ meV kbar}^{-1}$ (Menoni *et al* 1986) to $8.4 \text{ meV kbar}^{-1}$ (Müller *et al* 1980) and $9.3 \text{ meV kbar}^{-1}$ (from the data of Kobayashi *et al* (1986)). Note, however, that fitting to the change in density rather than lattice constant gives $\Xi = -6.18 \text{ eV}$ and a pressure coefficient of $-\Xi/B = 8.55 \text{ meV kbar}^{-1}$.

The band gap at the phase transition was 2.01 eV . This result is plotted together with data from the literature in figure 6. Since different authors have measured the band gap in different ways and under different conditions, the data require correction before a comparison can be made. For example, our own data require correction for the low absorption coefficient used; since we obtain a band gap of 1.32 eV at ambient pressure compared with the

established value of 1.344 eV (Poerschke and Madelung 1991). The easiest way to handle these corrections is to plot, not the band gap itself, but its reported increase from ambient pressure to the phase transition pressure, $\Delta E(P_t)$; our value is thus 690 meV. For the data in the literature, we take the measured shift directly from the authors' data, when possible, and we also compare this with the equation they use to fit the data. The absorption of Kobayashi *et al* (1986) was recorded at low temperature, 77 K and shows a shift of 653 meV from ambient pressure to their highest data point. This is in exact agreement with the value from their $aP_t + bP_t^2$. Agreement is less satisfactory in other cases; the largest discrepancy being found in the results of Menoni *et al* (1986) where the experimental shift was 650 meV while their $aP_t + bP_t^2$ gave 707 meV. Inspection of their data shows an S-shaped behaviour with little shift from 0–8 kbar and also little shift at the highest pressure. For our purposes, it is the experimental shift which is most directly comparable and so in figure 6 we plot the experimental rather than fitted shifts. The data of Ernst *et al* (1996) are not presented over the full pressure range, and their sample was degenerately doped. However, they identify the band gap at 106 kbar at 2.027 eV in a photoluminescence spectrum taken at 8 K. From this, we estimate 2.044 eV at their phase transition pressure of 110 kbar, giving a shift of 611 meV from the low-temperature band gap of 1.434 eV, or about 685 meV if we include the band gap renormalization due to the doping and estimated by Ernst *et al* to be 75 meV.

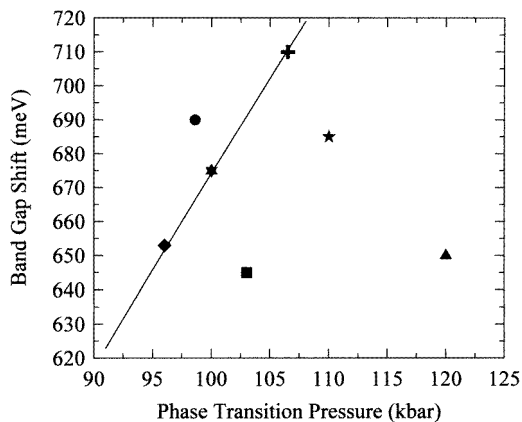


Figure 6. The maximum shifts of the band gap from its ambient pressure value plotted against the reported phase transition pressures. The data come from: \blacklozenge , Kobayashi *et al* (1986); \bullet , this work; \star , Müller *et al* (1980); \blacksquare , Leroux (1989); $+$, Tozer *et al* (1988); \star , Ernst *et al* (1996); and \blacktriangle , Menoni *et al* (1986). The full curve is the proposed best estimate of $E_g(P)$ as discussed in the text.

In figure 6, the full curve is the band gap as a function of pressure, $E_g(P)$, calculated using a density deformation potential $\Xi = -5.94$ eV and the Murnaghan equation of state to relate pressure and density with the bulk modulus $B = 723$ kbar and its pressure derivative $B' = 4.5$. The value of Ξ has been chosen to give excellent agreement with three of the data points. One more data point is in reasonable agreement with the full curve (our own from this work), lying within 3 or 4 kbar, while the remaining three data points are in more or less severe disagreement. This fit gives a linear pressure coefficient of $-\Xi/B = 8.22$ meV kbar $^{-1}$.

3. Discussion

Both the Raman and the band-gap data confirm that the phase transition pressure in InP is variable and usually measured accurately. Errors in pressure calibration are not unexpected in a high-pressure experiment but are very hard to assess. The plot here of the maximum shift of the band gap against the phase transition pressure provides an excellent test of the data, and enables us to give both a reliable assessment of P_t and a more reliable value of the deformation potential Ξ . The latter in turn gives a reliable value of the pressure coefficient of the band gap of $\Xi/B = 8.22 \text{ meV kbar}^{-1}$;—we have shown elsewhere that this is a more accurate description than the conventional parabolic fitting parameters a and b (Prins *et al* 1996), and we have given a density deformation potential because Frogley *et al* (1998) have shown that results from different workers for $E_g(P)$ in GaAs can only be reconciled by assuming that the band gap varies linearly with density, rather than with volume or lattice constant.

The analysis also illustrates the value of doing two or more independent measurements on the sample in the same experiment as a control on the pressure calibration and to permit a direct comparison with the data of other workers. Had all the workers reported, for example, the Raman shift at the phase transition as well as the pressure, the comparison of the various data sets would have been facilitated. Optical measurements such as photoluminescence vary too much from sample-to-sample to serve in this way as a standard. Raman spectroscopy, however, is eminently suitable. The fundamental phonon frequencies and their pressure dependence can scarcely vary from one sample to another, and the Raman signal is easy to obtain at all pressures up to the phase transition.

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