

Effect of high pressure on the vibrational modes and the energy gap of ZnP_2

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Abstract. The pressure dependence of the vibrational modes in ZnP_2 has been investigated by Raman Spectroscopy using a diamond anvil cell, up to 150 kbar pressure. The intrachain phosphorus modes exhibit a strong pressure dependence whereas the low frequency Zn-P modes soften very slightly under pressure. For a crystal which is treated as a molecular crystal this is an unexpected result. It is suggested that the behaviour may be due to a buckling of the phosphorus chain, or due to a double bond promotion between P atoms, or a charge transfer under pressure. The shift in the energy gap has also been measured to 100 kbar hydrostatic pressure. There is a small initial blue shift which gradually changes over to a red shift. However the whole shift in 100 kbar is quite small. Combining the $(dE_g/dP)_T$ with the published $(dE_g/dT)_P$ the thermal expansion contribution and the electron-phonon interaction contribution were evaluated. The latter dominates the total $(dE_g/dT)_P$ of ZnP_2 .

Keywords. ZnP_2 ; vibrational modes; high pressure studies; energy gap; Raman spectroscopy.

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1. Introduction

Zinc diphosphide (ZnP_2) and CdP_2 are semiconductors with a gap of about ~ 2 eV. They crystallize in the tetragonal system and belong to the space group (Stalinskii 1972) D_4^4 or D_4^8 . In the structure, the P atoms form helical chains and can be regarded as covalently bonded molecules, whereas the metal atoms weakly interact with the phosphorus as well as with one another. Therefore, ZnP_2 and CdP_2 may be treated as inorganic molecular crystals, but they really are borderline cases.

Several Raman studies have been carried out on them at ambient pressure (Valakh *et al* 1974; Artamonov *et al* 1976, 1979; Gorban *et al* 1978) and the main features of the spectra have been interpreted in terms of concepts generally applied to molecular crystals (Valakh *et al* 1974; Artamonov *et al* 1976). It occurred to us that a Raman study under pressure might reveal some interesting information about the changes in bonding with pressure, viz, whether the molecular aspect is emphasized with increasing pressure. In particular, what happens to the phosphorus chains and to the metal-metal and metal-phosphorus interactions are of much interest. We have investigated in this study the effect of pressure on the energy gap as well as the Raman modes in ZnP_2 . To

The authors felicitate Prof. D S Kothari on his eightieth birthday and dedicate this paper to him on this occasion.

our knowledge, the present investigation represents the first high pressure Raman and optical absorption study on ZnP_2 . The results will be presented and discussed.

2. Experiments and results

High pressure was generated using a gasketed diamond anvil cell (Piermarini and Block 1975) with the standard 4:1 methanol-ethanol mixture as the pressure medium. Pressure was calibrated by the well-known ruby fluorescence technique (Barnett *et al* 1973). For exciting the Raman modes, the 647.1 nm line of the krypton laser was employed at a power level of 30–40 mW. The original ZnP_2 crystals were a millimeter or two in linear dimensions and a millimeter in thickness. Small fragments from these crystals were sliced for mounting in the gasket hole. The crystals were red in colour and were clear and transparent to the 647.1 nm radiation. The Raman measurements were carried out at room temperature using a Spex double monochromator equipped with a conventional photon counting system.

The absorption spectra were taken using a micro-optic set-up similar to the one used in our study of lead tungstates (Jayaraman *et al* 1985). For this, very thin plates were obtained by cleaving with a blade, and the orientation of the plate is believed to be perpendicular to the *c*-axis of the crystal, namely (001). A xenon lamp was used as the continuous light source and a Jarrel Ash half-meter spectrometer recorded the absorption spectrum.

The Raman spectrum of ZnP_2 obtained at very low pressure in the diamond cell is shown in figure 1, along with the spectrum obtained near 100 kbar. In all, 15 Raman peaks were observed at ambient pressure and most of these were pursued as a function of pressure. The pressure dependence of the Raman frequencies are plotted in figure 2. The high frequency Raman peaks in the spectrum have been attributed to the internal

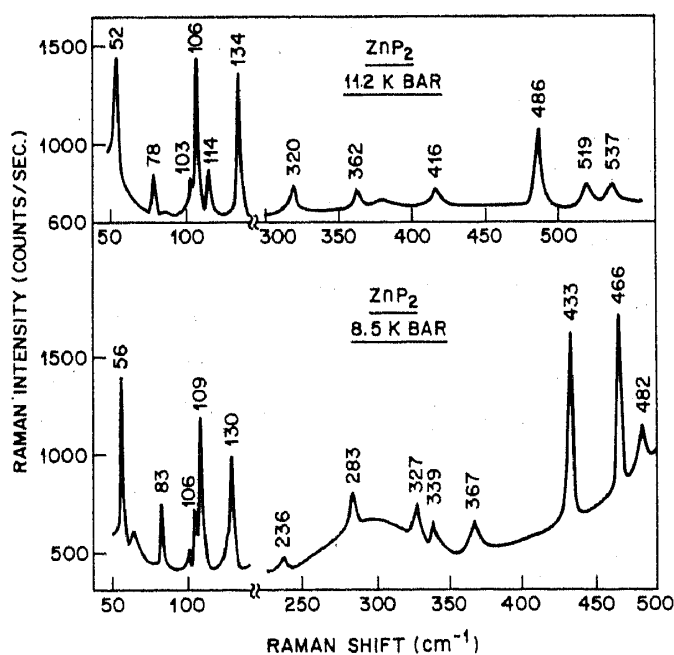


Figure 1. The Raman spectrum of ZnP_2 at 8.5 kbar and 112 kbar.

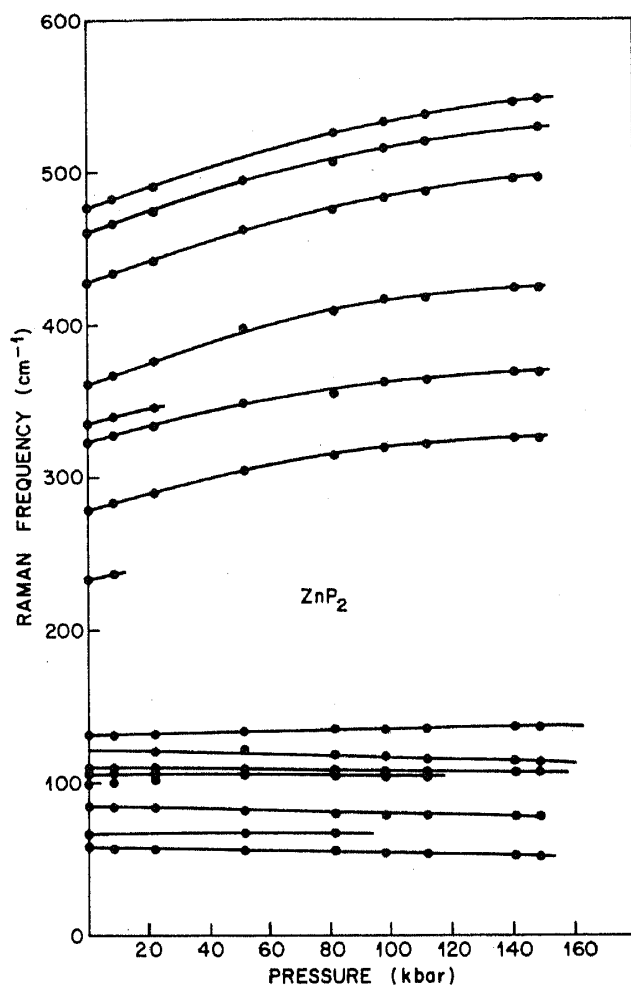


Figure 2. The pressure dependence of the Raman peaks in ZnP_2 . The high frequency modes exhibit large pressure-induced shifts.

vibrations of the phosphorus chain, while the low frequency vibrations are assigned to the Zn-P and Zn-Zn modes. What is remarkable is that the low frequency modes are practically pressure-independent, while the high frequency modes are quite sensitive to pressure. In table 1 the observed frequencies, their pressure dependence and the calculated Grüneisen parameters are listed.

The transmission curve taken in the diamond cell with one of the plates is shown in figure 3(a). The thickness of this plate turned out to be 11μ . The transmission curve shows a periodic variation in intensity (maxima and minima) due to interference effects that are known to occur, when extremely good thin parallel plates are used (see figure 3(a)). Data with two other plates were also taken. By comparing the transmission curves recorded at different pressures under similar conditions of illumination, the pressure variation of the energy gap was obtained and this is shown in figure 3(b). Initially, there is a very small blue shift of the gap ($\sim 0.5 \text{ meV/kbar}$) with pressure and around 40 kbar it turns over to red, gradually.

From the spacing of the interference band $\Delta\lambda$ and the measured thickness l of the thin parallel plate of ZnP_2 , the refractive index n was calculated as ~ 5 ($n = \lambda^2/2\Delta\lambda l$) for $\lambda = 590 \text{ nm}$. This value appears reasonable for wavelengths right near the

Table 1. Pressure dependence of the Raman frequencies and the mode Grüneisen parameters for ZnP₂.

1 bar ω_i	8.5 kbar ω_i	22 kbar ω_i	112 kbar ω_i	$d\omega_i/dP$	γ_i
57	56.5	56	52.5	-0.04	-0.44
66					
84	83	83	78	-0.05	-0.4
105	105	105	103	-0.02	-0.12
109	109	108	106	-0.03	-0.17
129	127	125	114	-0.13	-0.63
129	129.5	131	134	0.05	0.24
278	283	289	320	0.6	1.35
323	327	331	362	0.5	0.97
335	339	345		0.5	0.93
361	367	375	416	0.75	1.3
427	433	441	486	0.75	1.1
460	466	474	519	0.75	1.02
476	482	490	537	0.75	1.0

$\gamma_i = (B/\omega_i) (d\omega_i/dP)$ $B = 627$ kbars obtained from the elastic constants (Llisavskii *et al* 1981).

absorption region. This method can be used to obtain the pressure variation of the refractive index n , if the thickness of the crystal is evaluated at each pressure using the compressibility data.

3. Discussion

3.1 The vibrational mode behaviour

Group theoretical analysis gives the following symmetry types for the vibrational modes of ZnP₂: $9A_1 + 9A_2 + 9B_1 + 9B_2 + 18E$ (Gorban *et al* 1978). The A_1 , B_1 , B_2 and E vibrations are first-order Raman active and the $A_2(z)$ and $E(xy)$ modes are IR active. Our spectra are consistent with what has been reported in the earlier Raman studies (Valakh *et al* 1974; Artamonov *et al* 1976; Gorban *et al* 1978).

In the crystal lattice of ZnP₂ the phosphorus atoms form infinite chains and these lie perpendicular to the c -axis. The unit cell contains four structurally similar but differently oriented segments of P-chains, each containing four atoms and separated from one another by the metal atoms (Gorban *et al* 1978). A comparison of the ZnP₂ and CdP₂ Raman modes has shown that the high frequency vibrations $\nu > 400$ cm⁻¹ are due to the P-P bond frequencies and are therefore the intrachain modes (Valakh *et al* 1974). The low frequency part of the spectrum is attributed to vibrations involving the metal and phosphorus atoms. Hence, in treating the vibrational spectrum the molecular approximation is considered as appropriate for both ZnP₂ and CdP₂. In this case one may expect that the application of high pressure would tighten the weak Zn-P bonds and hardly affect the P-P covalent bond frequencies. The pressure dependence of the phonon frequencies shown in figure 2 clearly demonstrates that the P-P covalent bond frequencies substantially increase with pressure while the low frequency vibrations are hardly affected. This is the opposite of what is expected.

Gorban *et al* (1978) attributed the decrease in the high frequency vibration $\nu > 400$ cm⁻¹ in going from ZnP₂ to CdP₂ to a decrease in the Cd-P bond strength.

This would indicate that an increase in the high frequency vibrations could result from an increase in the metal phosphorus bond strength. However our results do not support this. If at all, the Zn-P bond weakens slightly with pressure, as indicated by the softening of the lowest frequency mode at 57 cm^{-1} with pressure. Therefore the observed increase in the P-P bond strength must be due to other reasons. The possibilities in this connection are (i) that the phosphorus chains buckle under pressure in such a way, decreasing the bond distance in the chain (ii) that a double bonding between the P atoms in the chain is promoted under pressure and (iii) that there is a charge transfer under pressure, in a direction which strengthens the P-P bonds and slightly weakens the Zn-P bonds. The chemistry of phosphorus would be consistent with double bond formation.

3.2 Optical absorption

Sobolov *et al* (1971) proposed a model for the energy band structure of ZnP_2 , based on measurements of the spectral distribution of photoconductivity and edge emission spectra of tetragonal ZnP_2 . In the model, the two lowest-conduction band minima are both indirect and are placed at 1.65 and 1.85 eV respectively from the highest valence band maximum. The direct gap is placed at 2.18 eV. The strong peaks near 2.55 eV are ascribed to direct transitions from valence subbands into the direct conduction band minimum. In our absorption curves it is difficult to see anything corresponding to the indirect gaps at 1.65 and 1.85 eV. The photoconductivity peaks corresponding to these energies reported by Sobolov *et al* are very weak. Therefore it is possible that the indirect absorption is too weak to be observable with thin samples or the above peaks are due to the presence of deep impurity levels and have nothing to do with any band edge. The absorption that we observe is very strong and we believe that it is definitely connected with a direct gap, at 2.18 eV referred to above. The absorption edge shift shown in figure 3(b) exhibits an initial blue shift of small magnitude and gradually changes over to a red shift above 40 kbar. A natural interpretation of this behaviour would be an initially lower direct edge changes over to an indirect edge, at pressures above 40 kbar and the bands cross around this pressure. However, the entire shift with pressure is very small compared to pressure-induced direct edge shifts observed in ZnSe for instance (Ves *et al* 1985).

The temperature dependence of the energy gap in tetragonal ZnP_2 has been measured by Karajamaki *et al* (1980) and these authors report a 250 meV decrease in the gap, in going from 4.2 K to 400 K. The behaviour is similar to that of well-known semiconductors (Varshni 1967). The change of an electronic level with temperature under constant pressure can be written

$$(\partial E_g / \partial T)_P = (V \cdot \partial E_g / \partial V)_T \frac{1}{V} \cdot \partial V / \partial T|_P + (\partial E_g / \partial T)_V \dots \quad (1)$$

The first term in this equation comes from the volume change due to thermal expansion and the second term $(\partial E_g / \partial T)_V$ from electron-phonon interaction. The measured total temperature dependence of tetragonal ZnP_2 is found to be linear with a temperature coefficient of 0.73 meV/K in the range 100 K–400 K, although below 100 K there is a flattening. The thermal shift is indeed very large. Since the pressure-induced shift $(\partial E_g / \partial P)_T$ is very small, the first term can be neglected, which would then indicate that

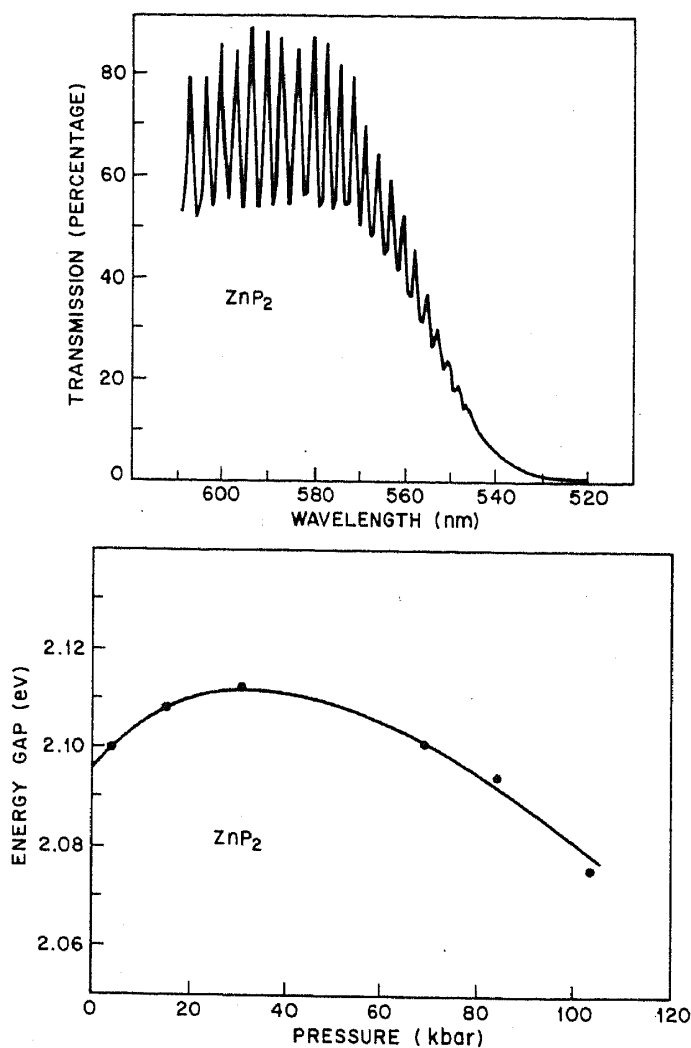


Figure 3. The optical transmission curve (upper) of a thin plate ($11 \mu\text{m}$ in thickness) of ZnP_2 . The periodic variation in the intensity especially in the transparent region is due to interference effect characteristic of a thin perfectly parallel plate. The lower curve is a plot of the shift in the energy gap with pressure. The energy gap was determined from the optical absorption data.

the electron-phonon interaction dominates the total temperature coefficient $(\partial E_g/\partial T)_p$. We believe that the large thermal shift of the electronic level is connected with atomic motions and interband excitations involving phosphorus and its s - p electronic states. The theory of the temperature dependence of the electronic band structure has been discussed by Schluter *et al* (1975) and Allen and Heine (1976). The latter have modified Fan's theory (Fan 1951) to include both intraband and interband self energy terms, and Debye-Waller corrections to the self-energy. Unfortunately, the details of the band structure of tetragonal ZnP_2 are unavailable at the present time and hence further comments and evaluation are not possible.

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