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Pressure and volume dependence of the LO–TO phonons in InAs

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Abstract. The pressure dependence of the LO-TO phonons in InAs has been investigated by Raman scattering using the diamond anvil cell. Indium arsenide transforms, presumably to the rock-salt structure at 70 ± 1 kbar. The mode Grüneisen parameters for the LO-TO phonons are $\gamma_{LO} = 0{\cdot}99 \pm 0{\cdot}03$, $\gamma_{TO} = 1{\cdot}2 \pm 0{\cdot}03$ respectively. The effective charge, e_T^*, for InAs decreases slightly with pressure and this trend is in accordance with the behaviour of other III-V zinc blende structured semiconductors: The structural phase transition is discussed in the light of theoretical calculations for phase stability of III-V compounds, as well as recent high pressure x-ray diffraction studies.

Keywords. LO-TO phonons; indium arsenide; pressure dependence; Raman scattering; diamond anvil cell; Grüneisen parameters.

1. Introduction

With the development of the diamond anvil cell for Raman scattering measurements (Weinstein and Piermarini 1975; Jayaraman 1983), the pressure dependence of the LO-TO phonon frequency, as well as the peaks in the second order Raman spectrum have been investigated in many III-V compounds, in recent years (Weinstein and Piermarini 1975; Trommer *et al* 1980). Trommer *et al* (1980) have reported on the pressure dependence of the phonon spectrum of InP up to its phase transition pressure of 100 kbar. In this study we have investigated the effect of pressure on the LO-TO phonon frequencies in InAs up to the phase transition pressure. The results are presented and discussed in this paper.

2. Experimental

Samples of InAs for Raman scattering studies were prepared from semiconductor grade single crystal material. Samples parallel to the (110) plane were easily obtained by cleaving, but samples parallel to (100) and (111) had to be prepared from oriented crystal plates by grinding, polishing and chemically etching them to thin platelets. Typically, the samples for Raman studies were 50–100 μ in linear dimensions and 30–50 μ in thickness.

For pressure generation a diamond anvil cell (Piermarini and Block 1975) was employed and the pressure was calibrated using the ruby fluorescence technique (Barnett *et al* 1973). For pressure medium a 4:1 methanol-ethanol mixture was used. Raman spectra were obtained with a Spex double monochromator, equipped with a

conventional phonon counting system. For excitation the 4880 Å line from an argon ion laser was used. The laser power was 100 mW.

3. Results

The LO-TO peaks are shown in figure 1 at atmospheric pressure and at about 50 kbar. We could not get any second order spectrum of the sample (Carles *et al* 1980) in the diamond cell. In figure 2 the pressure and volume dependences of the LO and TO phonons are plotted. With the sample parallel to the (110), only the TO phonon can be seen, whereas in the (100) orientation the LO phonon is seen. With the (111) oriented samples both LO and TO can be seen. These are in accordance with the expected orientation dependence of the LO-TO phonon intensity, on the scattering geometry. However, in the diamond cell measurements no polarization studies were attempted. The TO linewidth became sharper in the high pressure spectra; the half-width decreased from about 10 wavenumbers at low pressures to about 4 wavenumbers at the high pressure end. This may be due to the annealing of residual stresses on the surface with pressure.

Above 70 kbar the LO and the TO phonons abruptly disappear and the sample reflectively for the exciting laser line increases, as judged by the focussed spot on the slit of the spectrometer. The disappearance of the phonon and the change in the reflectance is due to a first-order phase transition in InAs to a metallic state, which is known to occur near 70 kbar from earlier resistivity measurements (Pitt and Vyas 1973).

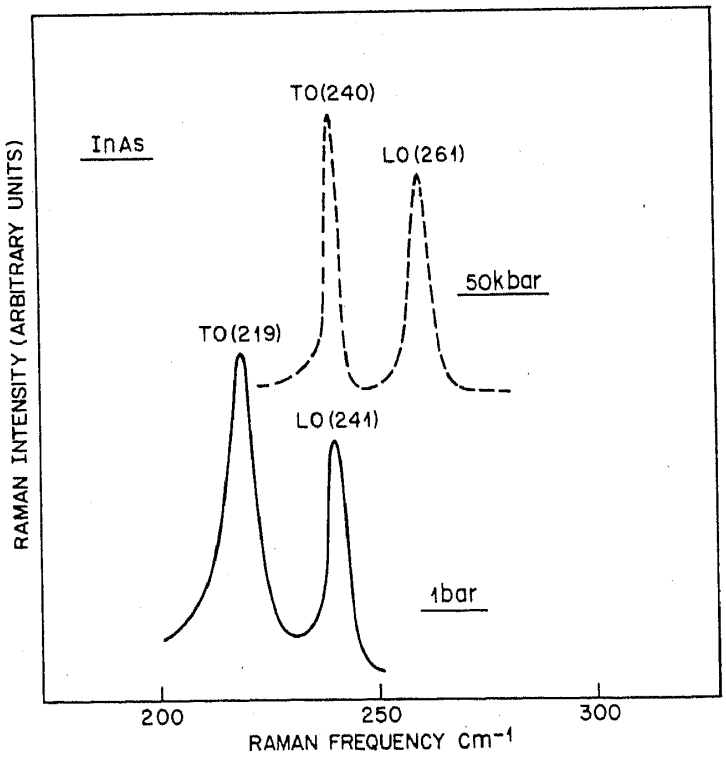

Figure 1. The LO-TO phonons in InAs at ambient pressure and at a pressure of 50 kbar.

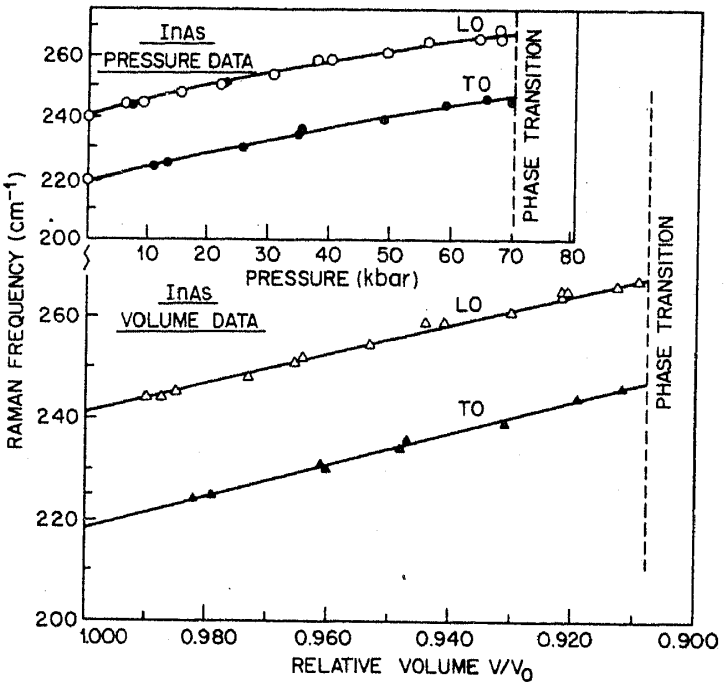

Figure 2. A plot of the LO-TO phonon frequency against pressure (top) and against relative volume (bottom). The dotted line indicates the disappearance of the phonons and the phase transition.

4. Discussion

Using the bulk modulus of $B_0 = 580$ kbar obtained from the elastic constant data (Kunc 1973), we get for the mode Grüneisen parameter $\gamma_{TO} = 1{\cdot}2 \pm 0{\cdot}03$ and $\gamma_{LO} = 0{\cdot}99 \pm 0{\cdot}03$ for the TO and LO phonon respectively. These values are in line with the systematics observed for the other III-V compounds (Trommer *et al* 1980). For InP, $\gamma_{TO} = 1{\cdot}44 \pm 0{\cdot}92$ and $\gamma_{LO} = 1{\cdot}24 \pm 0{\cdot}02$; for GaP, $1{\cdot}09 \pm 0{\cdot}03$ and $0{\cdot}95 \pm 0{\cdot}02$ and for GaAs, $1{\cdot}39 \pm 0{\cdot}02$ and $1{\cdot}23 \pm 0{\cdot}02$, respectively (Trommer *et al* 1980).

The pressure dependence of the LO and TO phonons is sublinear but becomes linear when plotted against volume, which are shown in figure 2. For figure 2 (bottom) the volume data for InAs was computed with the Birch equation of state, using B_0 of 580 kbar and B_0' of 4·5. The latter value was assumed after comparing the measured B_0' for materials belonging to the family. For InP, Trommer *et al* (1980) assumed a B_0' of 4·67 which is the same as the value reported for GaAs. The pressure volume curve thus obtained is shown in figure 3.

The pressure dependence of the Born's dynamical transverse charge can be calculated as a function of pressure, to ascertain charge transfer under pressure, from the LO-TO splitting (Harrison 1980). The Born's transverse charge (e_T^*) is related to the LO-TO splitting through the expression:

$$e_T^{*2} = \frac{MV\varepsilon_1(\omega_{LO}^2 - \omega_{TO}^2)}{4\pi e^2},$$

Where M is the reduced mass per atom, V is the volume per atom and ε_1 is the IR dielectric constant. The e_T^* was calculated for several pressures from the measured

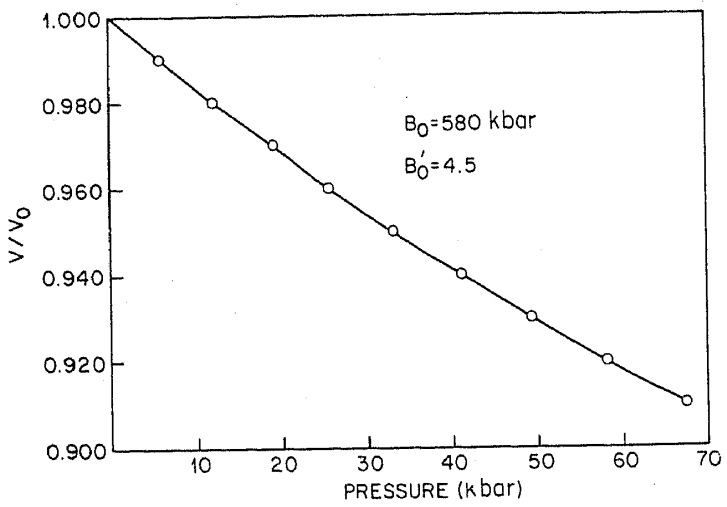

Figure 3. Pressure-volume relationship for InAs obtained from the Birch-equation of state.

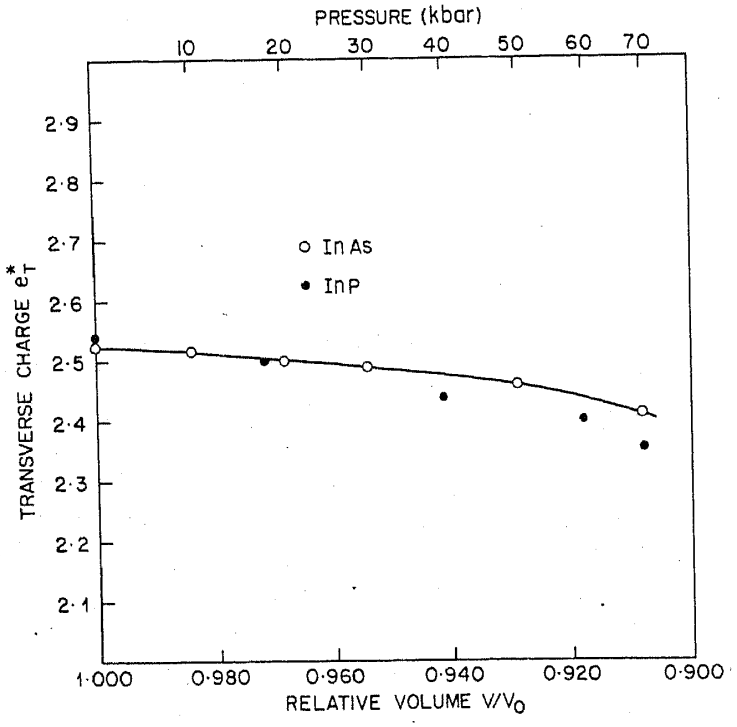

Figure 4. Born's transverse charge plotted against relative volume. The pressure scale is on top. The filled circles are the data points for InP.

splitting and $\varepsilon_1 = 12{\cdot}3$ (Harrison 1980). The latter was assumed to be pressure-independent. The effective charge, e_T^*, is plotted in figure 4. The charge decreases slightly with pressure and this is in accordance with the behaviour observed in other III-V compounds. In figure 4 the open circles are the e_T^* values of Trommer *et al* (1980) for InP shown for the purpose of comparison. The decrease in e_T^* with pressure for InAs is a factor of two smaller than for InP; see for instance at about 70 kbar.

4.1 *High pressure phase*

The occurrence of a pressure-induced phase transition to the metallic state in InAs was first reported by Minomura and Drickamer (1962) from high pressure resistivity measurements and the transition pressure was stated by them as 84 kbar. In a high pressure x-ray diffraction study Jamieson (1963) reported the structure of the high pressure phase of InAs as rock-salt type. Pitt and Vyas (1973) carried out another resistivity measurement on InAs and reported the metallic transition at 69 ± 2 kbar. From the positive temperature coefficient of resistivity they concluded that the high pressure phase was metallic. In the present Raman study the phonons were seen at 70 kbar, but they disappeared abruptly at 71·5 kbar. Hence we place the transition pressure at 70 ± 1 kbar which is in good agreement with the pressure of transition reported by Pitt and Vyas (1973). It should be noted here that the pressure medium was strictly hydrostatic in the present experiment and hence no shear forces could influence the transition.

Earlier theoretical investigations on the stability of tetrahedrally-coordinated diamond-zinc blende $A^N B^{8-N}$ type (Phillips 1971; van Vechten 1973) crystals under pressure have established that ionicity has a controlling influence on the crystal structure of AB compounds. The transition pressures and volumes ΔV for the covalent-ionic and covalent-metallic transitions were calculated from their Gibb's energies. Phillips (1971) has proposed the ionicity criterion for structural stability as follows: If f_i (Phillips ionicity) is between $0{\cdot}3 \leqslant f_i \leqslant 0{\cdot}78$ the tetrahedrally-coordinated structure is stable at ambient pressure, but the crystal would transform under pressure to the rock-salt structure. If, on the other hand, $f_i \leqslant 0{\cdot}3$ the transformation would be to the white-tin (β–Sn) or to an orthorhombic structure. More recently Froyen and Cohen (1983) investigated the structural stability of a number of III-V compound semiconductors under pressure, by calculating the total energies in the zinc-blende, rock-salt, β–Sn and NiAs structures as a function of volume using the pseudopotential method. From the results of these calculations they conclude that the rock-salt and NiAs phases would be favoured for the Al compounds at high pressure, while in Ga compounds it could be β–Sn, NiAs, or the rock-salt structure, for they are all close in energy. The band structure calculations reveal that the rock-salt phase would be metallic in all of them, just as the β–Sn and NiAs would be.

Recent high pressure x-ray diffraction studies with the diamond cell have shown that the high pressure crystallography of the III-V (Yu *et al* 1978; Baublitz and Ruoff 1982) compounds is not quite as simple as was previously believed. Thus the metallic phase of GaAs appears to possess an orthorhombic structure, while that of GaP surprisingly appears to be β-Sn. The high pressure phase of AlP has been indexed on the basis of rock-salt structure, although the x-ray diffraction line intensities are not consistent with the latter structure. The high pressure phase of AlSb (Yu *et al* 1978) has recently been reported to have the rock-salt structure, contrary to Jamieson's (1963) findings of a β–Sn structure. Thus the structure of the high pressure metallic phases of III-V compounds is still indefinite. In view of this, both InAs and InP need reinvestigation by high pressure x-ray diffraction. It would also be instructive to carry out total energy calculations for all the indium compounds (InP, InAs and InSb). The high pressure phases of both InAs and InP appear to be metallic. If indeed the rock-salt structure for them is confirmed, their metallic character would not appear to be inconsistent, for Froyen and Cohen (1983) have already shown that the electronic structure of the rock-salt phases of Al and Ga compounds is all metallic.

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