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Pressure dependence of the Raman phonon spectrum in 6h-silicon carbide*

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Abstract

The pressure dependence of the first-order Raman spectrum of 6h-SiC has been measured up to 100 kbar with a diamond anvil cell. Since SiC is present in a great number of different polytypes, use has been made of the standard large zone scheme, where all polytypes have a common set of phonon dispersion branches. The linear relationships between phonon energies and relative lattice compression and the corresponding mode-Grüneisen parameters have been calculated. The crystal anisotropy, as expressed by the energy difference between the two TO modes, decreases as the pressure is increased. The "planar acoustic" modes, which correspond to the TA modes at various values of $k \neq 0$ in the Brillouin zone of cubic 3c-SiC, do not appear to shift with pressure and the implications of this behaviour are discussed.

INTRODUCTION

Silicon carbide (SiC) occupies a special position among tetrahedrally coordinated compounds: it is the only IV–IV compound to form stable and long-range ordered structures [1]. Its crystallography is characterized by the phenomenon of polytypism, i.e. the fact that new structures of the same material are formed from simple structural units by alteration of their sequence.

All SiC structures consist of a single basic unit, a plane of tetrahedra arbitrarily chosen either as SiC_4 or CSi_4. Figure 1 illustrates how different polytypic structures arise when these parallel planes are stacked in different ways; for the second neighbours of each, say, carbon atom there are two types of configuration: a hexagonal configuration, *h*, like that of atom B in the sequence $A\alpha B\beta A\alpha$ (ABA for short) and a cubic configuration, *k*, like that of atom B in the sequence ABC. The spacings between the Si–C planes that are linked by A–α type bonds are 3/4 *b*, those linked by γ–A type bonds are 1/4 *b*, where *b* is the distance between C planes [2].

A SiC polytype is represented by the number of double layers (i.e. Si–C

*Dedicated to the memory of Professor George Wilkinson.

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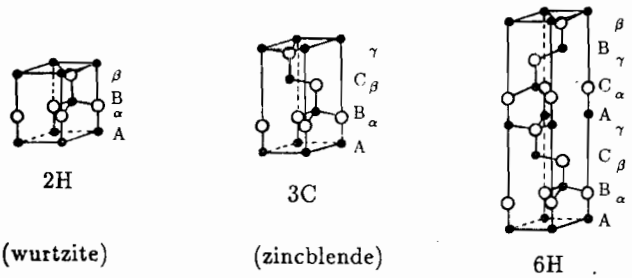

Fig. 1. Three polytypes of SiC. The position of C atoms (small solid circles) is represented by Latin letters and that of Si atoms (large open circles) by Greek letters (after ref. 2).

planes) in the unit cell, which has added to it the letters h, r or c to specify the lattice symmetry indicating a hexagonal, rhombohedral or cubic cell, thus the symbol 6h, for example, represents a structure with six double layers in the primitive hexagonal unit cell. Clearly, by varying the sequence of the stacking planes A, B, C and its length, a great number of different structures is possible, e.g.: AB (2h), ABC (3c), ABCACB (6h), ABACBCACBABCBAC (15r) etc. and SiC is known to exist in nearly 170 different polytypes [3].

Since the difference between all polytypes is only an order of stacking we expect the small structural differences to produce correspondingly only small differences in most physical properties. In particular, the phonon density of states of all polytypes is expected to be similar in many respects. The difficulty of having different numbers of atoms per unit cell, hence different numbers of phonon branches in the Brillouin zone (BZ) for each different polytype is removed by using, for all polytypes, a standard large zone (LZ), which extends in the axial direction to $N\pi/c$, where N is the number of layers in the polytype stacking sequence and c is the length of the unit cell (proportional to N). This LZ has 3 "acoustic" and 3 "optic" branches for any polytype [4].

In the case of 3c-SiC the large zone is the real Brillouin zone itself, while in the case of 6h-SiC, which has 12 atoms per unit cell and the same space group C_{6v}^4 ($P6_3mc$) as wurtzite, the large zone is six times larger than the real BZ, i.e. it extends to $6\pi/c$.

Since $2\pi/c$ is a reciprocal lattice vector, the pseudomomentum vectors $q=0$, $2\pi/c$, $4\pi/c$, $6\pi/c$ are all equivalent to $q=0$ in the Brillouin zone. Thus if we define $x=(q/q_{max})$, the values of x accessible to Raman scattering measurements in 6h-SiC are $x=0$, 0.33, 0.67 and 1 [5].

The optic modes at $x=0$, in which the Si and C sub-lattices vibrate against each other, should appear strongly in the Raman spectra compared with the $x\neq 0$ modes, which are expected to be weaker because their polarizabilities result from the very small Si or C site differences, a distant neighbour effect. These modes have anisotropic intracell motion along or perpendicular to the

TABLE 1

Distribution and symmetry of 6h-SiC phonon modes in the large zone

Branch	$x=0$	$x=0.33$	$x=0.67$	$x=1$
Longitudinal optic	E_{1l}			
Transverse optic (1)	E_{1t}			
Transverse optic (2)	A_1			
Axial optic				
Planar optic		$2B_1$(F)	$2A_1$	B_1(F)
Axial acoustic		$2E_2$	$2E_1$	E_2
Planar acoustic		$2B_1$(F)	$2A_1$	B_1(F)
		$2E_2$	$2E_1$	E_2

B_1 modes are forbidden (F). For the LO and TO modes the assignments of representations are valid only for the propagation direction $\theta=90°$ with respect to the c-axis. For $\theta=0°$ the LO mode has A_1 symmetry and the TO mode is degenerate with E_1 (or $2E_{1t}$) symmetry. For intermediate values of θ the LO and TO_2 modes have mixed (A_1+E_1) symmetry. (After Feldman et al. [5]).

c-axis, i.e. of the bond-stretching or bond-bending type and are therefore usually described as "axial" or "planar" [4].

Table 1 (after Feldman et al. [5]) summarizes the type and symmetry of the Raman accessible modes for 6h-SiC. There are double sets of representation for $x=0.33$ and $x=0.67$ because of the energy discontinuities at these internal boundaries.

In this experiment we have investigated the pressure dependence, up to 100 kbar, of the first order Raman spectrum in 6h-SiC.

Previous Raman and pressure work on SiC was done by Mitra et al. [6], (probably on 3c-SiC) up to 10 kbar, and by Olego and co-workers [7,8] on 3c-SiC up to 225 kbar. Feldman and co-workers [5,9] measured the first order Raman spectrum of the polytypes 4h, 6h, 15r and 21r at zero pressure, which made the dispersion branches of the phonon density of states in the large zone, common to all polytypes, accessible to Raman investigation at the points $x=0$, 0.29, 0.33, 0.4, 0.5, 0.57, 0.67, 0.87 and 1.

To our knowledge, this is the first experimental work on the pressure dependence of the SiC Raman phonon spectrum done on a hexagonal polytype. Further similar work on the 4h, 15r and 21r polytypes would allow a more extensive mapping of the pressure induced changes in the phonon dispersion curves along the axis of the large zone, but already our data for $x=0$, 0.33, 0.67 and 1 allow a fairly clear picture to be obtained.

EXPERIMENTAL DETAILS

The 6h-SiC sample used in this experiment came from a thin n-doped single crystal plate. The crystal, which was weakly transparent and of a pale green colour, was broken into small pieces and a tiny fragment, suitable to fit into

the 100 μm hole of the hardened stainless steel gasket in the diamond anvil cell (DAC), was chosen. A small ruby chip was also inserted in the gasket hole to act as a pressure calibrant and finally the hole was filled with a 4:1 methanol–ethanol mixture as the hydrostatic pressure transmitting medium.

Details of the DAC used in this experiment, which was entirely designed and constructed in our laboratory, and of the rather unusual optical system coupling the focussed laser beam to the cell and the emerging scattered light to the spectrometer are available elsewhere [10]. Briefly, the exciting light was focussed onto the sample with a numerical aperture of 0.4 and with an estimated spot size of less than 5 μm; the scattered light was collected in a back-scattering geometry and focussed onto the entrance slit of the double monochromator of a Spex Ramalog 5 system. A cooled photomultiplier and photon counter were used to analyse the dispersed light as it was scanned across the exit slit of the monochromator.

Nearly all the Raman spectra were excited with the 4880 Å line of an Ar^+ ion gas laser; a few times, when plasma lines were interfering with spectral bands, the 5145 Å line was used.

The sample temperature was frequently monitored by measuring the relative intensities of the Stokes and anti-Stokes bands of the planar "acoustic" mode centred at 149 cm^{-1}. A temperature of 310 ± 10K was recorded throughout the experiment.

RESULTS AND DISCUSSION

The first order Raman spectrum is shown in Figs. 2–6 with some of the fast-shifting bands displayed at two different pressures.

The LO band appears, surprisingly, rather wide and presents a certain de-

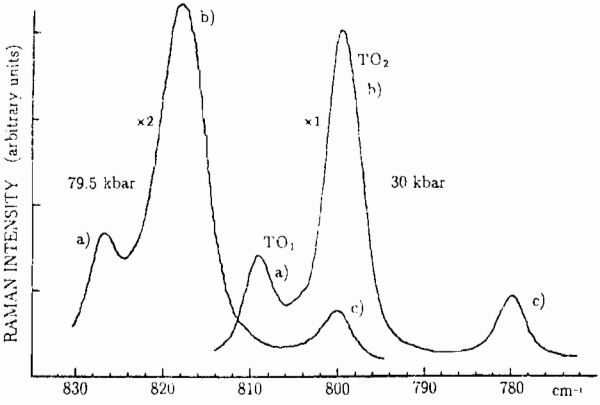

Fig. 2. Portion of Raman spectrum showing: (a), TO_1 mode; (b), TO_2 mode; (c), planar optic mode ($x=1$), at two different pressures.

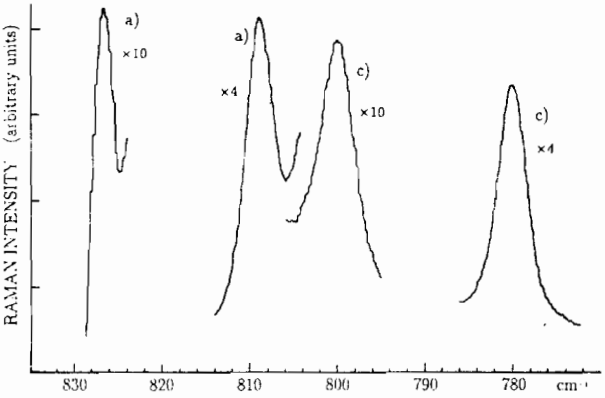

Fig. 3. Portions of Raman spectrum showing: (a), TO_1 mode; (c), planar optic mode ($x=1$), measured with increased gains with respect to Fig. 2.

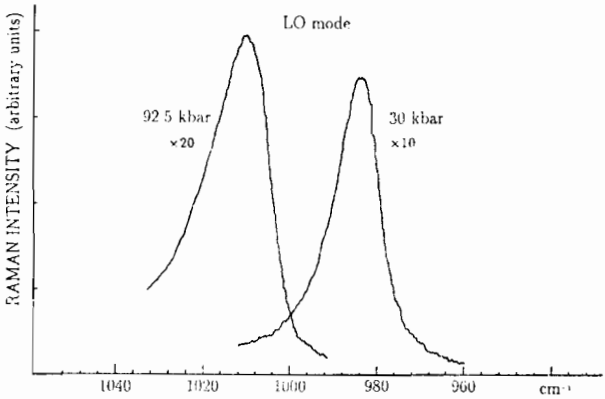

Fig. 4. Portion of Raman spectrum showing the LO mode at two different pressures.

gree of asymmetry. This is probably a consequence of the nitrogen doping in our sample [11]. The strongest band corresponds to the TO mode of A_1 symmetry (TO_2), while the TO mode of E_1 symmetry (TO_1) is rather weak in comparison (Figs. 2 and 3).

As shown by Feldman et al. [5], the frequency of the optic modes at $x=0$ depends on the angle of propagation, θ, of the phonons with respect to the crystal axis, c. They reported a decrease in frequency from 970 cm^{-1} to 964 cm^{-1} for the LO mode and an increase from 788 cm^{-1} to 797 cm^{-1} for the TO_2 mode as θ varied from 90° to 0°, whereas the TO_1 band remained centred at 797 cm^{-1} independently of θ. The fact that the two TO modes become degenerate for $\theta=0°$ is hardly surprising considering that the c-axis of 6h-SiC cor-

responds to the [111] direction of cubic 3c-SiC, which also has a TO mode energy of 797 cm^{-1} [8].

Our results are consistent with an angle of propagation $\theta = 90°$. All the remaining modes, i.e. those at $x \neq 0$, whose atomic vibrations can only be parallel or perpendicular (axial or planar) to the c-axis, have no frequency dependence on the angle of propagation.

As mentioned in the introduction, the energy discontinuities within the large zone are responsible for the splitting of all folded modes at $x = 0.33$ and $x = 0.67$ into a doublet structure. The doublets of the allowed "acoustic" modes are shown in Figs. 5b, 6b and 6c. The axial optic mode ($x = 0.67$), centred at 888 cm^{-1} at zero pressure, was too weak to be resolved (Fig. 5a), while the planar

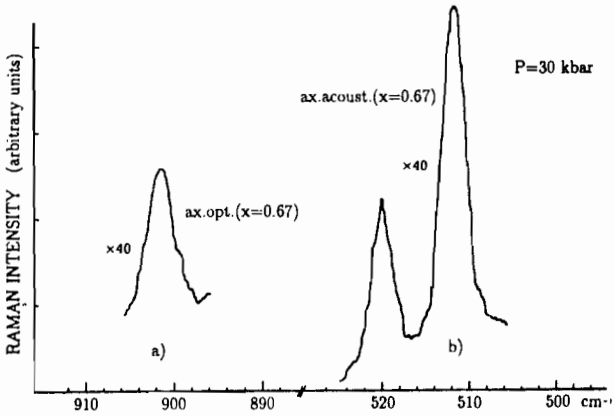

Fig. 5. Portions of Raman spectrum showing: (a), axial optic mode ($x = 0.67$); (b), axial acoustic mode ($x = 0.67$), measured at a pressure of 30 kbar.

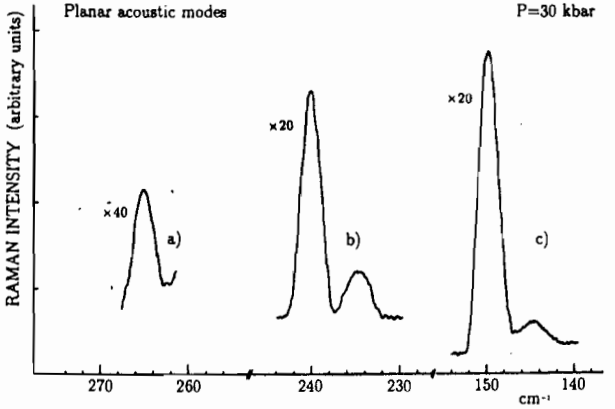

Fig. 6. Portions of Raman spectrum showing the planar acoustic modes at: (a), $x = 1$; (b), $x = 0.67$; (c), $x = 0.33$, measured at a pressure of 30 kbar.

optic ($x=0.33$) expected at 788 cm^{-1} was obscured by the strong TO_2 band and the planar optic ($x=0.67$) was not observed.

The remaining two allowed modes are the planar optic at $x=1$ shown in Figs. 2 and 3 and the planar acoustic at $x=1$ (Fig. 6a).

We used Murnaghan's equation of state to relate the measured pressure to the corresponding change in volume, V [12]

$$\frac{V}{V_o}=\left(\frac{B_o'}{B_o}p+1\right)^{-1/B_o'} \tag{1}$$

where p is the pressure, V_o is the volume of the unit cell at ambient pressure and room temperature, B_o the bulk modulus and B_o' its derivative with respect to p.

There are very few experimental measurements of B_o reported in the literature. Ultrasonic measurements by Carnahan [13] and by Schreiber and Soga [14] on pressure-sintered α-SiC (extrapolated to zero porosity) give 2250 kbar and 2302 kbar, respectively. Yean and Reiter [15] estimated (not experimentally measured, as reported in some literature) 2240 kbar, while Tolpygo [16] obtained the value 2110 kbar from the theoretical calculation of the elastic constants. Various theoretical models of the structural and high-pressure properties of SiC give $B_o=2500$ kbar [17], 2160 kbar [18], 2120 kbar [19], 2340 kbar [20].

To our knowledge there are no reports of measurements of B_o' in the literature. Theoretical models give the values: $B_o'=3.7$ [19], 3.2 [21], 3.5 [17].

As a working hypothesis, we set $B_o'=3.5$, which is the average of the theoretical predictions, and $B_o=2250$ kbar, which at least has some support from experiment.

When the measured phonon energies of the 6h-SiC bands were plotted against a scale linear in $\Delta V/V_o$, the solid lines shown in Figs. 7–9 were obtained as least-squares fits to the experimental points. The upper scale, which is non-linear in p in view of eqn. (1), shows the pressure dependence.

The least-squares fits for all the bands investigated and the corresponding Grüneisen parameters, $\gamma_i=-\partial\ln\omega_i/\partial\ln V$, which can be directly obtained from the coefficients of the linear equations, are summarized in Table 2.

Of the bands with a doublet structure we only analysed the stronger component. At zero pressure the weaker components are centred at approximately 513, 234 and 145 cm^{-1} and, as the pressure is increased, their separations from their main components remain constant to within the accuracy of these measurements.

The frequency difference between the TO_1 and TO_2 modes for $\theta=90°$ gives a measure of the crystal anisotropy. As mentioned in the introduction, if the structure beyond second neighbours is disregarded, each layer in the stacking sequence may then be considered to lie in a small hexagonal (h) or cubic (k)

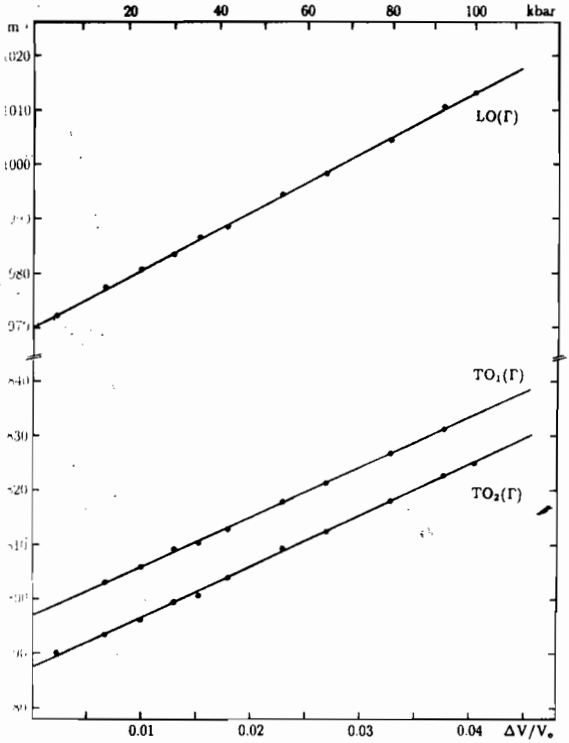

Fig. 7. Frequency dependence of the LO (Γ) mode and TO (Γ) modes on relative lattice compression (linear lower scale) and pressure (non-linear upper scale).

vironment, e.g. the layer B is *h* in the sequence ABA, but *k* in the sequence ABC, therefore 3c-SiC (ABC) is *kkk*, i.e. it has a 0% hexagonality, while 6h-SiC (ABCACB) is $(hkk)_2$ or 33% hexagonal (see Fig. 1), and other polytypes ave:

1r: $h=28.5\%$	with $\omega(TO_1)-\omega(TO_2)$ (Δ)	=	8.6 cm^{-1}
5r: $h=40\%$	Δ	=	12.1 cm^{-1}
4h: $h=50\%$	Δ	=	14.8 cm^{-1}

here the Δ values are those obtained by Feldman et al. [9].

There is a good linear relationship between these (TO_1-TO_2) frequency ifferences and the percentage *h*, as shown in Fig. 10, where our value for 6h f 9.7 cm^{-1} at zero pressure has been added to the results of Feldman et al.

As the pressure is increased, this separation decreases until it reaches the alue 8.6 cm^{-1} at 100 kbar suggesting that 6h becomes less anisotropic as a esult of compression. The linearity of the zero pressure data shown in Fig. 10

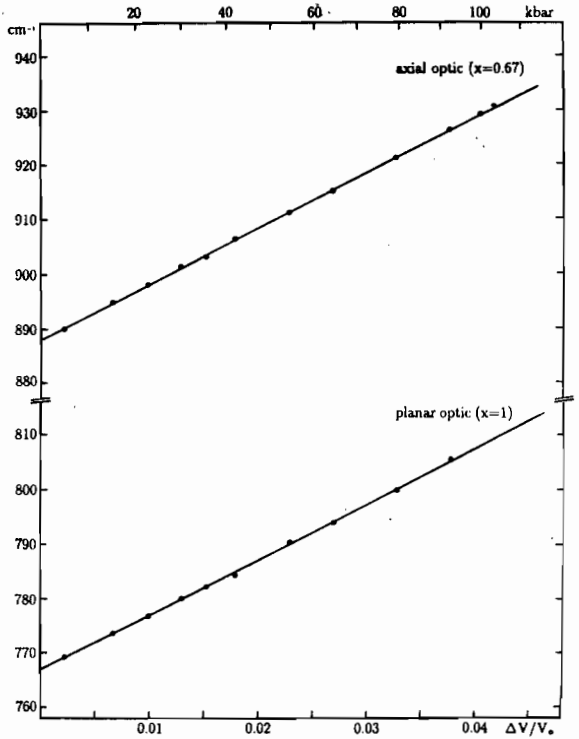

Fig. 8. Frequency dependence of the axial optic mode ($x=0.67$) and planar optic mode ($x=1$) on relative lattice compression (linear lower scale) and pressure (non-linear upper scale).

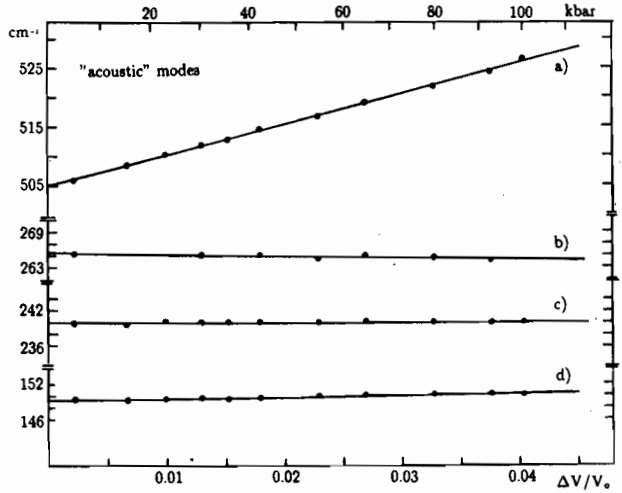

Fig. 9. Frequency dependence of the "acoustic" modes on relative lattice compression (linear lower scale) and pressure (upper non-linear scale): (a), axial ($x=0.67$); (b), planar ($x=1$); (c), planar ($x=0.67$); (d), planar ($x=0.33$).

TABLE 2

Least-squares fits of the dependence of phonon energies on relative lattice compression and corresponding Grüneisen parameters

Phonon mode	ω_i (cm^{-1})	γ_i
LO (Γ)	$(970.1 \pm 0.3) + (1062 \pm 12)\ \Delta V/V_o$	1.09 ± 0.01
TO_1 (Γ)	$(796.9 \pm 0.2) + (910 \pm 9)\ \Delta V/V_o$	1.14 ± 0.01
TO_2 (Γ)	$(787.2 \pm 0.3) + (937 \pm 14)\ \Delta V/V_o$	1.19 ± 0.02
Axial optic ($x=0.67$)	$(888.0 \pm 0.1) + (1017 \pm 7)\ \Delta V/V_o$	1.15 ± 0.01
Planar optic ($x=1$)	$(766.7 \pm 0.2) + (1023 \pm 9)\ \Delta V/V_o$	1.33 ± 0.01
Axial acoust. ($x=0.67$)	$(505.0 \pm 0.1) + (522 \pm 5)\ \Delta V/V_o$	1.03 ± 0.01
Plan. acoust. ($x=0.33$)	$(149.3 \pm 0.1) + (28 \pm 3)\ \Delta V/V_o$	0.19 ± 0.02
Plan. acoust. ($x=0.67$)	$(239.9 \pm 0.1) + (8 \pm 5)\ \Delta V/V_o$	0.03 ± 0.02
Plan. acoust. ($x=1$)	$(265.5 \pm 0.2) - (31 \pm 9)\ \Delta V/V_o$	-0.12 ± 0.03

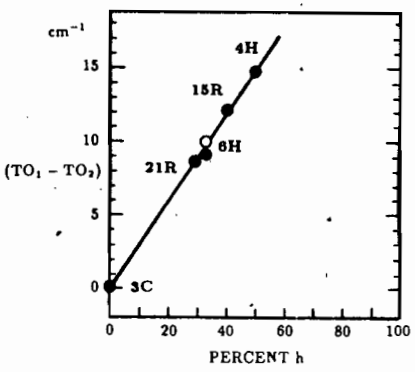

Fig. 10. Correlation of $\omega(TO_1) - \omega(TO_2)$ with "percent h": the filled circles represent the values obtained by Feldman et al. [9]; the open circle represents the result obtained in this work.

also suggests that probably all polytypes would be less anisotropic at higher pressures.

Of particular interest is the behaviour with pressure of the planar acoustic modes. With the exception of diamond and possibly of CuI, the mode Grüneisen parameters, γ, for the BZ boundary TA phonons in most tetrahedrally coordinated semiconductors are negative. The available data for these materials show that negative γ values apply to a rather large set of these TA modes covering most of the BZ boundary and extending $\approx \frac{1}{3}$ into the zone [22].

However, as can be seen from Fig. 9 and Table 2, the planar acoustic modes of 6h-SiC appear to be almost totally unresponsive to the effect of pressure over the whole width of the large zone.

At $x=0.33$ there is still a very small shift towards higher frequencies, while at $x=0.67$ there is no evidence of shift. At $x=1$ there is some evidence of a very

small softening of the mode, but the value of the Grüneisen parameter $\gamma = -0.12$ is still very small compared with the negative γ values of the TA zone boundary modes of the other tetrahedral semiconductors [22].

The planar acoustic mode at $x = 1$ corresponds, for all polytypes, to intracell vibrations of the shear type in which each double layer (i.e. the Si and C planes separated by $\frac{1}{4}b$) move as single solid unit 180° out of phase with respect to the adjacent layers. It is this kind of motion that will ultimately be responsible for inducing phase transitions to different polytype structures. However, the small negative value of its γ, indicating only a small weakening with pressure of the force constants between layers, suggests that any phase transition in 6h-SiC will require much greater pressures than those achieved in this experiment.

Our results differ from those obtained by Olego and Cardona [7] from the second order Raman spectrum of 3c-SiC, where the frequency shift of the TA(L) mode was derived from the shift of a combination band interpreted as TO(L)+TA(L) and a value of $\gamma = -0.43 \pm 0.08$ was found. They also derived $\gamma = -0.17 \pm 0.04$ for the LA(L) mode, in contrast with our result of $\gamma = 1.03 \pm 0.01$ for the axial acoustic mode of 6h-SiC at $x = 0.67$ in the large zone. Unfortunately, the axial acoustic mode is not Raman active for $x = 1$ in 6h-SiC, but it seems most unlikely that the γ-value would change so dramatically between $x = 0.67$ and $x = 1$. Thus we feel bound to question the findings of Olego and Cardona [7] for these bands.

SUMMARY

In this work we have investigated the hydrostatic pressure dependence of the first order Raman spectrum of 6h-SiC up to 100 kbar using a new diamond anvil cell of our own design.

The cell performed quite well and throughout the whole pressure cycle we obtained good Raman spectra of the phonon bands, including most of those belonging to extremely weak modes. From these measurements we derived the linear relationships between phonon energies and relative lattice compression and we calculated the corresponding mode-Grüneisen parameters.

The large zone scheme was used to present the phonon energies of this polytype, and their dependence on pressure, as points belonging to a set of dispersion curves common to all SiC polytypes, including the 3c cubic polytype, in which the large zone coincides with the Brillouin zone.

An interesting finding of this work was the unusual behaviour with pressure of the "acoustic" modes, which further confirms that SiC occupies a singular position amongst tetrahedrally coordinated semiconductors.

At the time of writing we are planning to extend our investigations of the pressure dependence of SiC to a number of other polytypes, so as to obtain a more comprehensive mapping of the phonon dispersion curves in the large

zone, and also to increase the pressure range well above the 100 kbar upper limit reached in this experiment.

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