High-pressure elastic properties of gallium phosphide

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The pressure dependence of the elastic constants C_{ij} of GaP have been measured up to 15 GPa in a diamond anvil cell. Brillouin backscattering experiments along the principal crystallographic directions yielded four combinations of elastic constants from which the three independent C_{ij} were extracted. Above 15 GPa the closure of the energy band gap prevents the detection of the signal. [S0163-1829(99)04827-4]

I. INTRODUCTION

Like many III-V semiconductors, gallium phosphide crystallizes in the cubic zinc-blende structure ($F\bar{4}3m$ space group). In this structure, the atoms are tetrahedrally bonded to their nearest neighbors through covalent bonds. Under pressure, the cubic phase is destabilized, and a transition to a tetragonal metallic phase occurs. At room temperature, this transition takes place in the 20-GPa range.

The properties of the zinc-blende phase as a function of pressure have been studied by Raman scattering up to 13.5 GPa,[1–5] fundamental absorption,[6] refractive index measurements,[7] and a combined x-ray diffraction-x-ray absorption spectroscopy experiment.[8] The transition to the metallic phase was first observed in resistivity measurements,[9,10] and then by x-ray diffraction.[11–13]

The elastic properties were studied under hydrostatic and uniaxial pressures up to about 0.14 GPa using ultrasonics.[14] From such a study, the second- and third-order elastic moduli were deduced, and hence the bulk modulus B and its pressure derivative B'.

In the present paper we present the pressure dependence of the second-order elastic moduli of GaP up to 15 GPa measured by Brillouin scattering in a diamond anvil cell.

Section II of this paper is devoted to a brief presentation of the experimental techniques used, as well as to details of the data analysis. The results obtained for GaP are presented and discussed in Sec. III.

II. EXPERIMENT AND BACKGROUND

The Brillouin scattering technique has been extensively described in the literature.[15,16] The 514.5-nm argon ion laser line with a single longitudinal mode was used with an input power of about 150 mW. In the present study, we used a 5 +4 tandem Fabry-Perot interferometer. The diamond anvil cell was of the Block-Piermarini type,[17] and hence all experiments were restricted to the backscattering geometry. In this geometry, the shift (in cm^{-1}) of the scattered radiation is given by

$$\Delta\sigma = 2nv/\lambda c, \tag{1}$$

where n is the refractive index of the medium, λ the wavelength of the incident radiation (in cm), c the velocity of light, and v the velocity of sound in the medium. Experiments were performed with three different directions of phonon propagation: [100], [110], and [111]. Longitudinal modes are observed for all three propagation directions,[18] additionally a transverse mode is also observed for the [111] direction.[18] The combinations of elastic moduli involved in these experiments are summarized in Table I. Argon was used as a pressure transmitting medium in all our experiments, and the pressure was measured from the shift of the R_l luminescence peak of a ruby microsphere, using the quasihydrostatic scale.[19]

In order to deduce the sound velocity from Eq. (1), it is necessary to know the pressure dependence of the refractive index. We used the determination of Ref. 7, i.e.,

$$n(\lambda,P) = n(\lambda) + \left(\frac{\partial n(\lambda,P)}{\partial P}\right)_\lambda P + \left(\frac{\partial^2 n(\lambda,P)}{\partial P^2}\right)_\lambda P^2, \tag{2}$$

TABLE I. Combination of elastic moduli involved in the various propagation directions explored.

Propagation direction	Polarization	Combination of elastic moduli
[100]	L	C_{11}
[110]	L	$(C_{11}+C_{12}+2C_{44})/2$
[111]	L	$(C_{11}+2C_{12}+4C_{44})/3$
[111]	T	$(C_{11}-C_{12}+C_{44})/3$

TABLE II. Ambient condition elastic moduli and bulk modulus (in GPa) obtained by different authors.

C_{11}	C_{12}	C_{44}	B	Ref.
141.2±0.3	62.5±0.3	70.5±0.1	88.8±1	Weil (Ref. 20)
141.4	64	70.3	89.8	Boyle (Ref. 21)
141.1±3.8	62.6±2.5	70.3±1.2	88.8±6	Yamada (Ref. 22)
145.1	61.1	71.6	89.1	Pesin (Ref. 23)
137.5	59.4	72.2	85.4	Gehrlich (Ref. 24)
140.5	62.0	70.3	88.1	Yoğurtçu (Ref. 14)
146.1±0.9	63.6±1.2	69.9±0.8	91.1±5	Present work

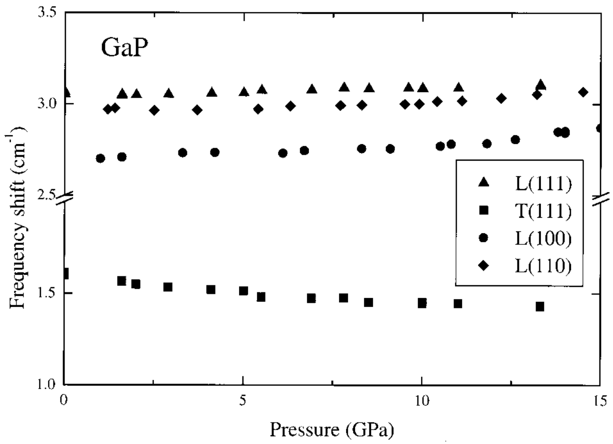

FIG. 1. Pressure dependence of the measured acoustic mode frequencies. Triangles, rhombs, and circles represent the longitudinal phonon propagating along the [111], [110], and [100] directions; squares correspond to the TA along [111].

with $n=3.532$, $\partial n/\partial P=-0.029\,\mathrm{GPa}^{-1}$, and $\partial^2 n/\partial P^2=0.001\,\mathrm{GPa}^{-2}$ for $\lambda=514.5\,\mathrm{nm}$.

The elastic moduli are related to the sound velocity through

$$v^2=\frac{1}{\rho}F(C_{ij}), \tag{3}$$

where ρ is the density, and $F(C_{ij})$ is a function of the elastic moduli that depends on the propagation and polarization directions. The values we have used for the density were obtained from the equation of state measured by extended x-ray-absorption fine structure (EXAFS),[8] i.e.,

$$\rho=\rho_0\left(1+\frac{B'P}{B_0}\right)^{1/B'}, \tag{4}$$

where $\rho_0=4138\,\mathrm{kg/m}^3$ is the density at $P=0$, $B_0=87.4\,\mathrm{GPa}$ the bulk modulus at $P=0$ and $B'=4.5$ (Ref. 8).

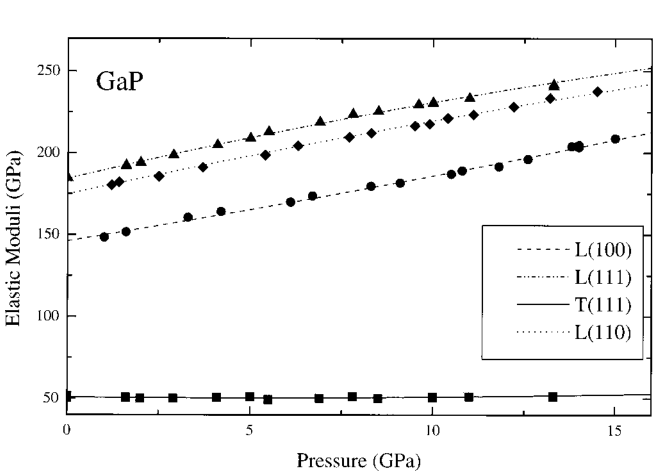

FIG. 2. Pressure dependence of the various combinations of C_{ij}'s obtained in this study. The symbols are the experimental results and the lines are the fits described in the text.

TABLE III. Coefficients of the quadratic least squares fit of the elastic moduli. [See Eq. (5).]

Elastic modulus	q (GPa)	r	t (GPa^{-1})
C_{11}	146.1 ± 0.9	3.7 ± 0.3	0.03 ± 0.02
C_{12}	63.6 ± 1.2	4.9 ± 0.4	-0.06 ± 0.03
C_{44}	69.9 ± 0.8	0.6 ± 0.3	-0.03 ± 0.02

III. RESULTS AND DISCUSSION

The values of the elastic moduli at ambient pressure are given in Table II and compared with previous determinations;[20–24] overall, there is good agreement for all the C_{ij} including the bulk modulus which, for a cubic crystal, is given by $B=(C_{11}+2C_{12})/3$.

In Fig. 1, we present the frequency shift as a function of pressure measured for the various orientations. The triangles, rhombs, circles, and squares represent the frequency shift due to the longitudinal mode propagating along the [111], [110], [100] directions and the transverse mode along the [111] direction, respectively. From these data the pressure dependence of the sound velocities is deduced using Eqs. (1) and (2). The various combinations of elastic moduli are then extracted using Eqs. (3) and (4) and Table I. The full lines in Fig. 2 were obtained by a simultaneous least squares fit to all four data sets in which each of the three independent constants (C_{11}, C_{12}, and C_{44}) were assumed to be of the form

$$C_{ij}(P)=q+rP+tP^2. \tag{5}$$

The values obtained for the individual C_{ij} are summarized in Table III and plotted in Fig. 3 together with the resulting bulk modulus and $(C_{11}-C_{12})/2$.

In Table IV, we listed the pressure derivative of various elastic moduli determined in this work and in previous investigations.[14,24,25] Although there is qualitative agreement between our values and previous determinations, the discrepancies lie slightly outside the estimated errors. These discrepancies may be due to the much larger pressure range covered in the present investigation compared to that covered in the earlier ultrasonic experiments. It is interesting to

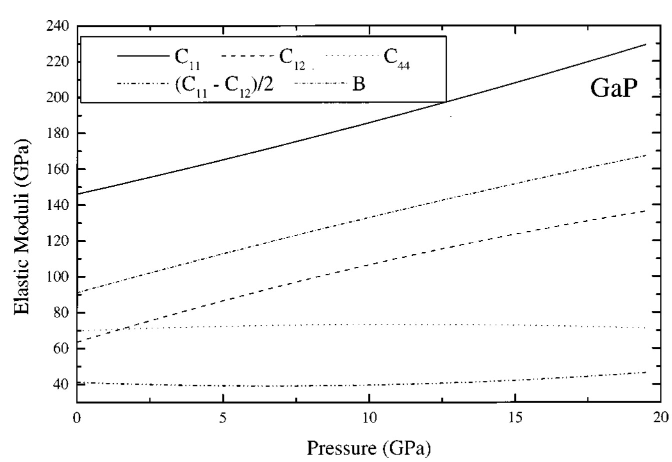

FIG. 3. C_{ij} obtained by fitting the Brillouin data in Fig. 2.

TABLE IV. Pressure derivative of elastic moduli.

	Present work	Ref. 25	Ref. 24	Ref. 14	Ref. 8
$\partial C_{11}/\partial P$	3.7 ± 0.3	5.0 ± 0.2	5.40 ± 0.22	4.77 ± 0.15	
$\partial C_{12}/\partial P$	4.9 ± 0.04	5.0 ± 0.2	5.93 ± 0.36	4.79 ± 0.16	
$\partial C_{44}/\partial P$	0.6 ± 0.3	1.1 ± 0.1	1.24 ± 0.012	0.92 ± 0.03	
$\partial(C_{11}-C_{12})/2\partial P$	-0.6 ± 0.4	-0.04 ± 0.02	-0.088 ± 0.003	-0.03 ± 0.007	
$B'=\partial B/\partial P$	4.5 ± 0.4	5.0	5.75	4.79	4.5

note, however, that our value of B' is in excellent agreement with the value obtained in Ref. 8 by EXAFS over a similar pressure range.

Recalling that C_{44} and $(C_{11}-C_{12})/2$ represent the extrema of the transverse moduli in a cubic crystal, the results in Fig. 3 show no evidence that a soft acoustic mode is responsible for the phase transition which occurs at ~20 GPa.

In an attempt to understand the mechanism of the pressure-induced phase transition in many group IV and III-V crystals, Yoğurtçu, Miller, and Saunders proposed that the transition occurs when $C'=(C_{11}-C_{12})/2B$ decreases to approximately 0.2: it was also further suggested that the decrease is due to a softening of the shear mode. Although our present results can be extrapolated to yield $C'=0.2$ at ~25 GPa, quite close to the observed transition, they do not support the idea of a soft shear acoustic branch.

IV. CONCLUSIONS

Using Brillouin scattering we have determined the pressure dependence of the three independent elastic constants of GaP up to 15 GPa; close to the previously reported phase transition. Although the material exhibits somewhat unusual pressure independent shear moduli, there is no evidence for a soft acoustic branch being responsible for the phase transition.

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