Pramāṇa, Vol. 8, No. 5, 1977, pp. 402-407. © Printed in India.

Anharmonic force constants of GaSb from the measured third order elastic constants at 300° K

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MS received 13 August 1976; after revision 9 February 1977

Abstract. The third-order elastic constants of single crystal GaSb are determined using ultrasonic pulse interferometer at 10 MHz. The constants at 300°K, in units of 10^{11} N.m.$^{-2}$, are

$C_{111} = -4{\cdot}75 \pm 0{\cdot}06$ $\quad$ $C_{144} = +0{\cdot}50 \pm 0{\cdot}25$
$C_{112} = -3{\cdot}08 \pm 0{\cdot}02$ $\quad$ $C_{166} = -2{\cdot}16 \pm 0{\cdot}13$
$C_{123} = -0{\cdot}44 \pm 0{\cdot}29$ $\quad$ $C_{456} = -0{\cdot}25 \pm 0{\cdot}15$

These constants are used to evaluate the three anharmonic first and second neighbour force constants based on modified Keating's model. The constants are (in units of 10^{11} N.m^{-2}) $\gamma = -2{\cdot}406$; $\delta = 0{\cdot}407$; $\epsilon = -0{\cdot}222$.

Keywords. Third-order elastic constants; GaSb; ultrasonic pulse interferometer; anharmonic force constants.

1. Introduction

The interatomic forces which bond a solid are mainly responsible for the elastic properties of solids. The second order elastic constants (SOEC) are mainly related to harmonic forces while higher order elastic constants to the anharmonic forces, the major contribution to the anharmonicity arising from the third-order elastic constants (TOEC). The TOEC can be determined from the study of changes in ultrasonic wave velocity under applied static stress (Thurston and Brugger 1964). A complete set of TOEC has been determined for a number of metallic crystals and for a very few semiconducting crystals. In the case of intermetallic semiconducting compounds, the constants are available only for GaAs (Drabble and Brammer 1966, McSkimin and Andreatch 1967) and InSb (Drabble and Brammer 1967). In this communication, we present in detail the experimental determination of independent TOEC of GaSb at 300° K. A brief report of these measurements has already been published (Raja and Reddy 1976). These are obtained using an ultrasonic interferometer at 10 MHz. The results are utilised in evaluating the three anharmonic first and second neighbour force constants on the basis of modified form of Keating's model (1966 *b*).

2.1. *Sample preparation*

The gallium antimonide single crystal was in the form of a cylindrical ingot with its growth direction nearly parallel to ⟨110⟩. A cube of approximately 1 cm side

was cut with (001), (110) and (1$\bar{1}$0) external faces. The orientation were held to well with in $\frac{1}{2}°$ by careful hand lapping and polishing. Enough care was taken to obtain the surface finish and the parallelism of sample faces to minimise the error in measured velocity. From the electrical conductivity and the Hall effect measurements, the resistivity and the charge carrier density of this *n*-type sample were found to be 2×10^{-4} ohm-m and 2×10^{23} donors/m^3 respectively. The electrical resistivity was low enough to assure zero field propagation conditions for this piezoelectric material (Huston and White 1962). Gallium antimonide belongs to cubic zinc blende structure with point group $\bar{4}$ 3 m and is characterized by six independent TOEC.

2.2. *Ultrasonic velocity measurement*

A pulsed ultrasonic interferometer at 10 MHz was employed to measure the transit times of longitudinal and shear waves. Gold plated *x*- and *y*-cut quartz transducers of fundamental frequency 10 MHz were employed to excite longitudinal and shear waves respectively. Phenyl salycilate (salol) gave a good bonding at the room temperature. The pulsed interferometer employed is the one already described (Sarma 1972, Sarma and Reddy 1972) which works on the principle of Williams and Lamb (1958). The method takes into account the effect of transducers and coupling film on the measured velocities. With this system, relative changes in velocity could be measured to a few parts per million.

3. Results and Discussion

The TOEC were computed from the uniaxial stress derivatives determined from the variation of 'natural' wave velocity W with applied uniaxial stress P (Thurston and Brugger 1964). The details of the directions of propagation, polarisation and applied stress for the experiments performed are shown in table 1 along with the uniaxial stress derivatives obtained. Thurston and Brugger (1964) have developed expressions for these stress derivatives in terms of SOEC and TOEC. The six stress derivatives of the modes propagated along ⟨1$\bar{1}$0⟩ direction were utilised to

Table 1. Uniaxial stress derivatives of GaSb at 300° K.

Experiment No.	Propagation direction	Polarisation direction	Stress direction	$\frac{\partial}{\partial P}(\rho_0 W^2)_{P=0}$
1	1$\bar{1}$0	1$\bar{1}$0	110	$+0{\cdot}60 \pm 0{\cdot}05$
2	1$\bar{1}$0	110	110	$-0{\cdot}74 \pm 0{\cdot}06$
3	1$\bar{1}$0	001	110	$-0{\cdot}02 \pm 0{\cdot}03$
4	1$\bar{1}$0	1$\bar{1}$0	001	$-2{\cdot}54 \pm 0{\cdot}09$
5	1$\bar{1}$0	110	001	$+1{\cdot}92 \pm 0{\cdot}05$
6	1$\bar{1}$0	001	001	$+1{\cdot}23 \pm 0{\cdot}03$
7	001	001	110	$+1{\cdot}86 \pm 0{\cdot}08$
8	001	110	110	$-0{\cdot}84 \pm 0{\cdot}06$
9	001	1$\bar{1}$0	110	$-0{\cdot}42 \pm 0{\cdot}07$

deduce the six independent TOEC by computer programming. These are presented in table 2 along with the associated errors. To make a cross check, the computed TOEC were substituted in the explicit relations of Thurston and Brugger for ⟨001⟩ propagation to evaluate $(\rho_0\omega^2)'_{p=0}$ and the resulting stress derivatives agreed very closely with the experimental ones. Here ρ_0 is the density of the crystal in the unstressed state. McSkimin *et al* (1968) have measured the hydrostatic pressure derivatives of GaSb. From their data certain combinations of TOEC are calculated and compared with those obtained from the present measurements. The agreement, as seen in table 3, appears to be good.

3.1. *Evaluation of anharmonic force constants*

Keating (1966 *a*, *b*) has derived expressions for SOEC and TOEC of diamond-like crystals by taking short-range interactions up to second neighbours. The basis of the method is to compare microscopic and macroscopic expressions for strain energy density and obtain relations for SOEC and TOEC in terms of harmonic and anharmonic force constants. The microscopic strain energy density, considering only cubic terms in strain, is given by (Keating 1966 *b*).

$$
\begin{aligned}
U = &\left[\frac{(\gamma^1 - \delta^1 + 3\epsilon^1)}{3} + \frac{(\alpha + 3\beta)}{2a}\right] \cdot (e_1^3 + e_2^3 + e_3^3) \\
&+ 2(\gamma^1 + 3\delta^1 - \epsilon^1)\, e_1 e_2 e_3 + \left[\left(\gamma^1 - \delta^1 + \frac{\epsilon^1}{3}\right) + \frac{(\alpha - \beta)}{2a}\right] \\
&\times [e_1^2 (e_2 + e_3) + e_2^2 (e_3 + e_1) + e_3^2 (e_1 + e_2)] \\
&+ 2\gamma^1 (1 - s)^3 e_4 e_5 e_6 + \left[\gamma^1 (1 - s)^2 + \delta^1 (1 + s)^2\right. \\
&\left. + \tfrac{1}{3}\epsilon^1 (1 + s)(3s - 1) + \frac{s^2 (\alpha - \beta)}{2a}\right] \cdot (e_1 e_4^2 + e_2 e_5^2 + e_3 e_6^2) \\
&+ \left[\gamma^1 (1 - s)^2 - \delta^1 (1 + s)^2 + \tfrac{1}{3}\epsilon^1 (1 + s)(3 - s) + \frac{s^2 (\alpha - \beta)}{2a}\right] \\
&[e_1 (e_5^2 + e_6^2) + e_2 (e_6^2 + e_4^2) + e_3^2 (e_4^2 + e_5^2)] \qquad (3.1)
\end{aligned}
$$

Here, α is the nearest neighbour central interaction and β is second-neighbour noncentral interaction and γ^1, δ^1 and ϵ^1 are constants representing anharmonic

Table 2. Third-order elastic constants of GaSb at 300° K

Constants	Experimental (in units of 10^{11} N.m^{-2})	Derived from force constant
C_{111}	−4·75±0·06	−4·78
C_{112}	−3·08±0·02	−3·03
C_{123}	−0·44±0·29	−0·47
C_{144}	+0·50±0·25	+0·56
C_{166}	−2·16±0·13	−2·15
C_{456}	−0·25±0·15	−0·13

Table 3. Comparison of combinations of TOEC obtained from hydrostatic and uniaxial measurements.

Combination	Uniaxial (in units of 10^{11} N.m^{-2})	Hydrostatic
$C_{111} + 2C_{112}$	−10·91	−10·92
$C_{123} + 2C_{112}$	− 6·60	− 6·56
$C_{144} + 2C_{166}$	− 3·82	− 3·83

interactions. γ^1 is purely first neighbour third-order force constant, and δ and ϵ are the two second neighbour noncentral force constants; s and a are internal strain parameter and the lattice parameter respectively. Comparing eq. (3.1) with the well-known macroscopic strain energy density expression (Brugger 1964), expressions for SOEC and TOEC were obtained for diamond-like crystals. But in the case of zinc blende structure crystals, long range electrostatic interaction also contribute to SOEC and TOEC. In addition, in the case of non-primitive lattices with ions not at the center of symmetry, there is electrostatic contribution to internal strain parameter s. Gerlich (1973) has extended Keating's theory to zinc blende structure crystals, taking into account the electrostatic contributions worked out by Fuller and Naimon (1972). The final expressions for SOEC and TOEC are

$$C_{11} = \frac{\alpha + 3\beta}{a} - 4{\cdot}053\,\frac{Z^2e^2}{a^4} \tag{3.2}$$

$$C_{12} = \frac{\alpha - \beta}{a} - 5{\cdot}538\,\frac{Z^2e^2}{a^4} \tag{3.3}$$

$$C_{44} = \left[\frac{\alpha + \beta}{a} - 5{\cdot}538\,\frac{Z^2e^2}{a^4}\right] - \left[\frac{\alpha + \beta}{a} - 4.189\,\frac{Z^2e^2}{a^4}\right] \tag{3.4}$$

$$C_{111} = \gamma - \delta + 9\epsilon + 17{\cdot}207\,\frac{Z^2e^2}{a^4} \tag{3.5}$$

$$C_{112} = \gamma - \delta + \epsilon + 1{\cdot}531\,\frac{Z^2e^2}{a^4} \tag{3.6}$$

$$C_{123} = \gamma + 3\delta - 3\epsilon + 24{\cdot}633\,\frac{Z^2e^2}{a^4} \tag{3.7}$$

$$C_{144} = \gamma\,(1 - s)^2 + \delta\,(1 + s)^2 + \epsilon\,(1 + s)\,(3s - 1) + \frac{(\alpha - \beta)}{a}\,.\,s^2 + [24{\cdot}633 - 33{\cdot}526\,s + 0{\cdot}820s^2]\,\frac{Z^2e^2}{a^4} \tag{3.8}$$

$$C_{166} = \gamma\,(1 - s)^2 - \delta\,(1 + s)^2 + \epsilon\,(1 + s)(3 - s) + \frac{(\alpha - \beta)}{a}\,.\,s^2 + [1{\cdot}531 - 33{\cdot}526s + 10{\cdot}026s^2]\,\frac{Z^2e^2}{a^4} \tag{3.9}$$

$$C_{456} = \gamma\,(1 - s)^3 + [24{\cdot}633 - 50{\cdot}288s + 42{\cdot}753s^2 - 19{\cdot}203s^3]\,\frac{Z^2e^2}{a^4} \tag{3.10}$$

Table 4. Anharmonic force constants of GaSb (in units of 10^{11} N.m^{-2})

Author	γ	δ	ϵ
Present study	−2·406	0·407	−0·222
Gerlich	−2·402	0·340	−0·253

where

$$s = \frac{(\alpha - \beta)/a - 10{\cdot}058\left(\frac{Z^2e^2}{a_4}\right)}{(\alpha + \beta)/a - 4{\cdot}189\left(\frac{Z^2e^2}{a^4}\right)} \tag{3.11}$$

and

$$\gamma = 2\gamma^1,\ \delta = 2\delta^1 \text{ and } \epsilon = 2/3\epsilon^1$$

where e is the electronic charge and Z is the effective charge. Z is calculated using Martin's (1970) method and the value is 0·33. The constants α and β are evaluated from the measured SOEC, namely $C_{11} = 8{\cdot}850$; $C_{12} = 4{\cdot}034$; $C_{44} = 4{\cdot}320$ in units of 10^{10} N.m^{-2}, and the effective charge, Z. They turn out to be $\alpha = 32{\cdot}63$ N.m^{-1} and $\beta = 7{\cdot}32$ N.m^{-1}. The three anharmonic force constants γ, δ and ϵ are computed by double precision linear least square fit from the measured TOEC employing the six equations (3.5) to (3.10) using IBM 370 computer. In the absence of independent TOEC, Gerlich (1973) has evaluated these three constants from the three hydrostatic pressure derivatives obtained by McSkimin *et al* (1968). The present values are compared with that of Gerlich in table 4. The agreement is good in spite of the fact that the experimental data used in both the approaches are different. It is seen that the anharmonic first neighbour central force constant γ is larger in magnitude than δ and ϵ which indicates that the most of the anharmonicity is due to first neighbour shell-shell interactions. This dominant nearest neighbour central interaction accounts for general negative sign of TOEC.

Acknowledgements

One of the authors (VS) wishes to thank CSIR for the award of a fellowship. His thanks are also due to V P N Sarma and B P N Reddy for valuable suggestions.

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