

Higher Order Elastic Constants and Generalized Gruneisen Parameters of Elastic Waves and Low Temperature Thermal Expansion of Titanium

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Received May 30, 1996; in revised form November 15, 1996; accepted November 18, 1996

The expressions for the 19 fourth order elastic constants, 10 third order elastic constants, and 6 second order elastic constants of a solid are derived using the method of homogenous deformation with interactions extending up to second neighbors using the sublattice displacements to the second degree in strains. These expressions are used to obtain the higher order elastic constants and their pressure derivatives in titanium. Titanium belongs to the hexagonal class of crystals. The higher order elastic constants are used to find the generalized Gruneisen parameters of the elastic waves propagating in different directions in titanium. The Brugger gammas are evaluated and the low temperature limit of the Gruneisen gamma is obtained. The results are compared with the available reported values. © 1997 Academic Press

INTRODUCTION

Higher order elastic constants are a measure of the anharmonicity of a solid. Higher order elastic constants determine the anharmonic properties of solids, such as thermal expansion, temperature and pressure dependence of elastic constants, and interactions of acoustic and thermal phonons. The hexagonal system has 6 second order elastic constants (SOEC), 10 third order elastic constants (TOEC), and 19 fourth order elastic constants (FOEC). In this paper the expressions for the 6 SOECs, 10 TOECs, and 19 FOECs have been derived using the method of homogenous deformation of Born and Huang (1). These expressions are used to evaluate the higher order elastic constants of titanium. First order pressure derivatives of the second order elastic constants of a crystal are evaluated. Second order pressure derivatives are obtained as a function of second order, third order, and fourth order elastic constants. Using the finite

strain theory of Murnaghan (2), the expressions for second pressure derivatives of the effective SOEC of a hexagonal solid have been derived in terms of second, third, and fourth order elastic constants by Ramji Rao and Padmaja (3). These expressions are used in this paper to obtain the second pressure derivatives of titanium. These elastic constants are also used to find the low temperature limit of the thermal expansion coefficients of titanium. Titanium belongs to group IV A of the periodic table. Titanium crystallises in hexagonal close packed structure at atmospheric pressures and low temperatures. It undergoes phase transformation from the hcp to the bcc structure at high temperatures.

The cell parameters of titanium are $D = a = 2.95 \text{ \AA}$ and $c = 4.686 \text{ \AA}$ and the density of the crystal is 4.54 g cm^{-3} . Second order elastic constants of titanium have been experimentally determined by Fisher and Renken (4) and their pressure derivatives by Fisher and Manghnani (5). The third order elastic constants are reported by Ramji Rao and Menon (6) using Keating's approach.

HIGHER ORDER ELASTIC CONSTANTS OF TITANIUM

Interactions between atoms only up to second nearest neighbors of titanium are considered. The position coordinates of the two nonequivalent atoms in the unit cell are

$$R \begin{pmatrix} 0 \\ 1 \end{pmatrix} = D[0, 0, 0], \quad R \begin{pmatrix} 0 \\ 1 \end{pmatrix} = D[1/2\sqrt{3}, 1/2, p/2].$$

Here p is the axial ratio c/a ; c and a are the unit cell distances.

The potential energy/unit cell is

$$\phi = \sum_{I=1}^6 \phi R(I) + \sum_{J=1}^6 \phi R(J).$$

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Here I atoms are the six nearest neighbors of the same type in the basal plane and the J atoms are the six nearest nonequivalent neighbors out of the basal plane. The components of the interatomic vector R after deformation are given by

$$R'_i(I) = R_i(I) + \sum_I \varepsilon_{ij} R_j(I)$$

$$R'_i(J) = R_i(J) + \sum_J \varepsilon_{ij} R_j(J) + W_i.$$

Here ε_{ij} is the deformation parameter related to the macroscopic Lagrangian strain η_{ij} by

$$\eta_{ij} = \frac{1}{2} \left(\varepsilon_{ij} + \varepsilon_{ji} + \sum_k \varepsilon_{ki} \varepsilon_{kj} \right),$$

and \bar{W}_i are the internal displacements given by

$$\bar{W}_i = W_i + \sum_j \varepsilon_{ji} \bar{W}_j.$$

Potential energy can be expanded in powers of changes in the squares of vector distances $R(I)$ and $R(J)$ as

$$\begin{aligned} \phi = \phi_0 + K_2 & \left[\sum_I [\Delta R^2(I)]^2 + \sum_J [\Delta R^2(J)]^2 \right] \\ + K_3 & \left[\sum_I [\Delta R^2(I)]^3 + \sum_J [\Delta R^2(J)]^3 \right] \quad [1] \\ + K_4 & \left[\sum_I [\Delta R^2(I)]^4 + \sum_J [\Delta R^2(J)]^4 \right]. \end{aligned}$$

Here K_2 is the harmonic parameter and K_3 and K_4 are the third and fourth order anharmonic parameters, which are defined as

$$K_2 = \frac{1}{2!} \left[\frac{\delta^2 \phi(r)}{\delta (r^2)^2} \right]$$

$$K_3 = \frac{1}{3!} \left[\frac{\delta^3 \phi(r)}{\delta (r^2)^3} \right]$$

$$K_4 = \frac{1}{4!} \left[\frac{\delta^4 \phi(r)}{\delta (r^2)^4} \right].$$

The term $[\delta \phi(r)/\delta (r^2)]$ does not exist, as the derivatives are calculated in the equilibrium configuration. The Lennard-Jonnes potential is given by

$$\phi = \frac{-a}{r^m} + \frac{b}{r^n}.$$

For this potential K_2 , K_3 , and K_4 are calculated as

$$K_2 = 1/4(\eta M/D^2)$$

$$K_3 = -K_2/6D^2(m+n+6)$$

$$K_4 = K_2/48D^4[(m+n)(m+n+12) - mn + 44]$$

$$\eta = nb(n-m)/2MD^{n+2},$$

where M is the mass of the atom and $D = a$ is the nearest neighbor distance in the basal plane.

Ramanand *et al.* (7) have shown that to evaluate the FOEC of an hcp lattice it is enough to obtain the sublattice displacements up to second degree in strain. The internal displacements W_i can be obtained in terms of the Lagrangian strain by minimizing the strain energy with respect to W_i ; i.e.

$$\bar{W}_x = [-D/2\sqrt{3}][\eta_{yy} - \eta_{xx}] + [D/2\sqrt{3}][\eta_{yy}^2 - \eta_{xx}^2]$$

$$+ [\sqrt{3}p^2D/4][\eta_{zz}(\eta_{yy} - \eta_{xx})]$$

$$\bar{W}_y = [-D/\sqrt{3}]\eta_{xy} + D/\sqrt{3}[\eta_{xy}(\eta_{yy} + \eta_{xx})] \quad [2]$$

$$+ [\sqrt{3}p^2D/2][\eta_{xy}\eta_{zz}]$$

$$\bar{W}_z = 0.$$

Substituting the value of W_i from Eq. [1] we get the expressions for energy/unit volume of the undeformed state. The resulting expression is compared with that of the elastic energy density:

$$\begin{aligned} U = \frac{1}{2!} \sum_{ijkl} C_{ijkl} \eta_{ij} \eta_{kl} + \frac{1}{3!} \sum_{ijklmn} C_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn} \\ + \frac{1}{4!} \sum_{ijklmnop} C_{ijklmnop} \eta_{ij} \eta_{kl} \eta_{mn} \eta_{op} + \dots \end{aligned} \quad [3]$$

We get the expressions for the fourth, third, and second order elastic constants as

$$C_{1111} = [\{4390/9\} D^8/V_a] K_4 + [\{4D^6/V_a\}] K_3$$

$$- [\{143/6\} D^4/V_a] K_2$$

$$C_{1112} = [\{1474/9\} D^8/V_a] K_4 + [\{23/6\} D^6/V_a] K_3$$

$$C_{1113} = [\{24/9\} D^8p^2/V_a] K_4 + [\{3D^6p^2/V_a\}] K_3$$

$$- [\{12/6\} D^4p^2/V_a] K_2$$

$$C_{1122} = [\{502/9\}D^8/V_a]K_4 - [\{4/3\}D^6/V_a]K_3 \\ + [\{11/2\}D^4/V_a]K_2$$

$$C_{1123} = [\{24/9\}D^8p^2/V_a]K_4 - [D^6p^2/V_a]K_3 \\ + [6D^4p^2/V_a]K_2$$

$$C_{1133} = [4D^8p^4/V_a]K_4 - [\{3/2\}D^6p^2/V_a]K_3 \\ - [3D^4p^4/V_a]K_2$$

$$C_{1144} = C_{1244} = C_{1255} \\ = [\{24/9\}D^8p^2/V_a]K_4 - [D^6p^2/V_a]K_3$$

$$C_{1155} = [\{24/9\}D^8p^2/V_a]K_4 + [3D^6p^2/V_a]K_3$$

$$C_{1166} = [\{1461/9\}D^8/V_a]K_4 + [\{2/3\}D^6/V_a]K_3 \\ + [\{25/18\}D^4/V_a]K_2$$

$$C_{1233} = [4D^8p^4/V_a]K_4 - [\{3/2\}D^6p^4/V_a]K_3 \\ + [3D^4p^4/V_a]K_2$$

$$C_{1333} = C_{3344} = [6D^8p^6/V_a]K_4$$

$$C_{1344} = [4D^8p^4/V_a]K_4 + [\{3/2\}D^6p^4/V_a]K_3$$

$$C_{1355} = [4D^8p^4/V_a]K_4 - [\{3/2\}D^6p^4/V_a]K_3$$

$$C_{2223} = [\{24/9\}D^8p^2/V_a]K_4 + [3D^6p^2/V_a]K_3 \\ - [6D^4p^2/V_a]K_2$$

$$C_{3333} = [9D^8p^4/V_a]K_4$$

$$C_{4444} = [6D^8p^4/V_a]K_4 \quad [4]$$

$$C_{111} = [\{1099/10\}D^6/V_a]K_3 + [\{23/3\}D^4/V_a]K_2$$

$$C_{112} = [\{83/5\}D^6/V_a]K_3 - [\{7/5\}D^4/V_a]K_2$$

$$C_{113} = [\{5/3\}D^6p^2/V_a]K_3 + [D^4p^2/V_a]K_2$$

$$C_{123} = [\{7/5\}D^6p^2/V_a]K_3 - [D^4p^2/V_a]K_2$$

$$C_{133} = [\{16/5\}D^6p^4/V_a]K_3$$

$$C_{344} = [3D^6p^4/V_a]K_3$$

$$C_{144} = [2D^6p^2/V_a]K_3$$

$$C_{155} = [\{4/3\}D^6p^2/V_a]K_3$$

$$C_{222} = [\{175/2\}D^6/V_a]K_3 + [\{39/5\}D^4/V_a]K_2$$

$$C_{333} = [\{9/2\}D^6p^6/V_a]K_3 \quad [5]$$

$$C_{11} = [\{167/8\}D^4/V_a]K_2 \quad C_{12} = [\{41/8\}D^4/V_a]K_2$$

$$C_{13} = [\{5/3\}D^4p^2/V_a]K_2 \quad C_{33} = [3D^4p^4/V_a]K_2$$

$$C_{44} = [2D^4p^2/V_a]K_2 \quad C_{66} = \frac{1}{2}(C_{11} - C_{12}) \quad [6]$$

where $V_a = \sqrt{3/2}pD^3$ is the volume of the unit cell. These expressions are used to evaluate the fourth, third, and second order elastic constants of titanium.

LOW TEMPERATURE THERMAL EXPANSION OF TITANIUM

Uniaxial crystals are characterized by two principal linear expansion coefficients, $\alpha_{||}$, parallel to the unique axis, and α_{\perp} , perpendicular to the unique axis. The behavior of these expansion coefficients at low temperature is governed by two generalized Gruneisen parameters $\gamma_j(\theta, \phi)$, defined as

$$\gamma_j'(\theta, \phi) = -\frac{1}{v_j(\theta, \phi)} \frac{\partial v_j(\theta, \phi)}{\partial \varepsilon'}$$

$$\gamma_j''(\theta, \phi) = -\frac{1}{v_j(\theta, \phi)} \frac{\partial v_j''(\theta, \phi)}{\partial \varepsilon''}$$

where $v_j(\theta, \phi)$ is the velocity of the elastic waves travelling in a direction (θ, ϕ) , j is the polarization index of the wave, θ is the angle the direction of wave propagation makes with the hexagonal axis, ϕ is the azimuthal angle, ε' is a uniform areal strain perpendicular to the unique axis, and ε'' is a uniform longitudinal strain parallel to the unique axis. These generalized Gruneisen parameters can be calculated from the second and third order elastic constants of a solid as shown by Ramji Rao and Srinivasan (8). Using the second and third order elastic constants of titanium the elastic wave velocities $v_j(\theta, \phi)$, the generalized Gruneisen parameters $\gamma_j'(\theta, \phi)$ and $\gamma_j''(\theta, \phi)$ for different values of θ and ϕ at intervals of 5° for θ and ϕ ranging from 0 to 90° are calculated. The calculations were made on a computer using the programming language FORTRAN.

The linear thermal expansion coefficients of a uniaxial crystal are given by

$$V\alpha_{||} = [2S_{13}\gamma'(T) + S_{33}\gamma''(T)]C_v(T)$$

$$V\alpha_{\perp} = [(S_{11} + S_{12})\gamma'(T) + S_{13}\gamma''(T)]C_v(T). \quad [7]$$

Here V is the molar volume, the S_{ij} are the elastic compliance coefficients, and $C_v(T)$ is the molar specific heat at temperature T . $\gamma'(T)$ and $\gamma''(T)$ are the effective Gruneisen functions, being the weighted averages of the Gruneisen functions of all the normal modes of the crystal. At very low temperatures, the effective Gruneisen parameters are determined by the mode gammas of the elastic waves and $\gamma'(T)$ and $\gamma''(T)$ attain limiting values γ'_0 and γ''_0 . In terms of $v_j(\theta, \phi)$, $\gamma_j'(\theta, \phi)$, and $\gamma_j''(\theta, \phi)$, these limits are defined by

$$\gamma'_0 = \frac{\sum_{j=1}^3 \int v_j^{-3}(\theta, \phi) \gamma_j'(\theta, \phi) d\Omega}{\sum_{j=1}^3 \int v_j^{-3}(\theta, \phi) d\Omega}$$

$$\gamma''_0 = \frac{\sum_{j=1}^3 \int v_j^{-3}(\theta, \phi) \gamma''_j(\theta, \phi) d\Omega}{\sum_{j=1}^3 \int v_j^{-3}(\theta, \phi) d\Omega}. \quad [8]$$

The integration is over the entire solid angle. We have obtained the values of γ'_0 and γ''_0 by numerical integration over the solid angle. The integral was evaluated by dividing θ and ϕ into intervals of 5° and the values are obtained.

Brugger and Fritz (9) have defined the functions

$$\gamma_{\perp}^{\text{Br}} = V\alpha_{\perp}/C_v\chi_{\text{iso}}$$

$$\gamma_{\parallel}^{\text{Br}} = V\alpha_{\parallel}/C_v\chi_{\text{iso}}$$

where χ_{iso} is the isothermal compressibility. Combining [7] and [8] the low temperature limits of the Brugger gammas are given by

$$\gamma_{\perp}^{\text{Br}}(0) = [(S_{11} + S_{12})\gamma'_0 + S_{13}\gamma''_0]/\chi_{\text{iso}}$$

$$\gamma_{\parallel}^{\text{Br}}(0) = [2S_{13}\gamma'_0 + S_{33}\gamma''_0]/\chi_{\text{iso}}.$$

Here S_{11} , S_{33} , S_{12} , S_{13} are given by

$$S_{11} = \frac{C_{11}C_{33} - C_{13}^2}{(C_{12} - C_{11})[2C_{13}^2 - C_{33}(C_{11} + C_{12})]}$$

$$S_{33} = \frac{C_{11} + C_{12}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}$$

$$S_{12} = \frac{C_{13}^2 - C_{12}C_{33}}{C_{13}}$$

$$S_{13} = \frac{C_{13}}{2C_{13}^2 - C_{33}(C_{11} + C_{12})}$$

and

$$\chi_{\text{iso}} = 2[S_{11} + S_{12} + S_{13}] + 2S_{13} + S_{33}.$$

Using the values of γ'_0 and γ''_0 we get $\gamma_{\perp}^{\text{Br}}(0)$ and $\gamma_{\parallel}^{\text{Br}}(0)$. Using these two values the low temperature limit γ_{L} of a hexagonal metal can be calculated using the formula

$$\gamma_{\text{L}} = 2\gamma_{\perp}^{\text{Br}}(0) + \gamma_{\parallel}^{\text{Br}}(0).$$

RESULTS AND DISCUSSION

Values of second order elastic constants C_{11} and C_{33} by Fisher and Renken (4) are used to evaluate the harmonic parameter K_2 and the third order elastic constants of Ramji Rao and Menon (6) are used to evaluate the anharmonic parameter K_3 using the expressions [5] and [6]. The values

TABLE 1
Second Order Elastic Constants in 10^{10} N/m² and First Pressure Derivatives of Titanium

C_{ij}	Calc values	Exptl values	dC_{ij}/dp	Calc values	Exptl values
C_{11}	17.33	16.24	dC_{11}/dp	3.55	5.01
C_{12}	4.84	9.2	dC_{12}/dp	1.069	4.11
C_{13}	3.96	6.96	dC_{13}/dp	1.772	—
C_{33}	18.03	18.07	dC_{33}/dp	6.336	4.88
C_{44}	4.34	4.67	dC_{44}/dp	0.593	0.52
C_{66}	6.72	3.52	dC_{66}/dp	1.745	0.45

of K_2 and K_3 are used to obtain the SOECs and TOECs of titanium using the derived expressions. The pressure derivatives of the SOECs of titanium are also evaluated. These evaluated SOECs and first pressure derivatives are collected in Table 1. These are compared with the experimental SOEC values (4) and first pressure derivatives (5). The evaluated TOECs are collected in Table 2. These values are compared with the other reported theoretical values of Ramji Rao and Menon (6). The values of m and n (10, 11), are chosen to give satisfactory agreement to the reported TOEC of titanium. The values of K_2 , m , and n are used to evaluate the anharmonic parameter K_4 . Thus the values obtained for K_2 , K_3 , and K_4 are used in Eq. [14] to get the fourth order elastic constant of titanium. The calculated fourth order elastic constants of titanium are collected in Table 3. C_{1111} and C_{3333} have large magnitude. The large difference in magnitude of C_{1111} and C_{3333} indicates the higher order elastic anisotropy in the crystal. These higher order elastic constants are used to evaluate the second pressure derivatives of titanium. These values are collected in Table 4. The magnitude of d^2C_{11}/dp^2 and d^2C_{33}/dp^2 are quite large, indicating that phase change from hcp to bcc structure would occur in this metal at a high temperature of 1155 °K (4). The values of Gruneisen coefficients are

TABLE 2
Third Order Elastic Constants of Titanium in 10^{10} N/m²

C_{ijk}	Calc values	Exptl values
C_{111}	− 134.78	− 135.8
C_{112}	− 38.29	− 110.5
C_{113}	− 3.23	− 1.7
C_{133}	− 35.99	− 38.3
C_{123}	− 10.59	− 16.21
C_{344}	− 38.3	− 33.17
C_{333}	− 161.7	− 161.5
C_{222}	− 230.6	− 189.57
C_{144}	− 11.28	− 26.3
C_{155}	− 5.93	11.7

TABLE 3
Fourth Order Elastic Constants of Titanium in 10^{10} N/m²
($m=1, n=5$)

C_{ijkl}	Calc values
C_{1111}	1280.6
C_{1112}	442.55
C_{1113}	-21.42
C_{1122}	156.69
C_{1123}	34.54
C_{1133}	34.95
C_{1144}	22.5
C_{1155}	4.668
C_{1166}	435.39
C_{1233}	101.62
C_{1244}	22.5
C_{1255}	22.5
C_{1333}	258.44
C_{1344}	85.161
C_{1355}	51.416
C_{2223}	-8.377
C_{3333}	978.69
C_{4444}	102.43
C_{3344}	258.44

$\gamma'_0 = 0.548$ and $\gamma''_0 = 0.972$ for titanium. The Brugger gammas are calculated as

$$\gamma_{\perp}^{Br}(0) = 0.27, \quad \gamma_{\parallel}^{Br}(0) = 0.002.$$

TABLE 4
Second Pressure Derivatives of Titanium in 10^{-10} m²/N

d^2C_{ii}/dp^2	Calc values
d^2C_{11}/dp^2	1.4425
d^2C_{12}/dp^2	1.2973
d^2C_{13}/dp^2	0.7086
d^2C_{33}/dp^2	1.624
d^2C_{44}/dp^2	0.2191
d^2C_{66}/dp^2	0.4542

TABLE 5
Low Temperature Limit of γ_L in Titanium

	Present calculation	Exptl value (8)	Reported value (6)
γ_{\perp}	0.5489	1 ± 0.5	0.78

The low temperature limit of the Gruneisen gamma is obtained as 0.5489. This is compared with the available reported value in Table 5.

The low temperature limit of the Gruneisen gamma is positive and so we expect the volume expansion to be positive down to OK for this crystal. The variation of γ with θ for different value of ϕ ($\phi = 15^\circ, 35^\circ, 75^\circ$) is shown in Figs. 1A, 1B, 2A, 2B, 3A, and 3B. The anisotropy in all the

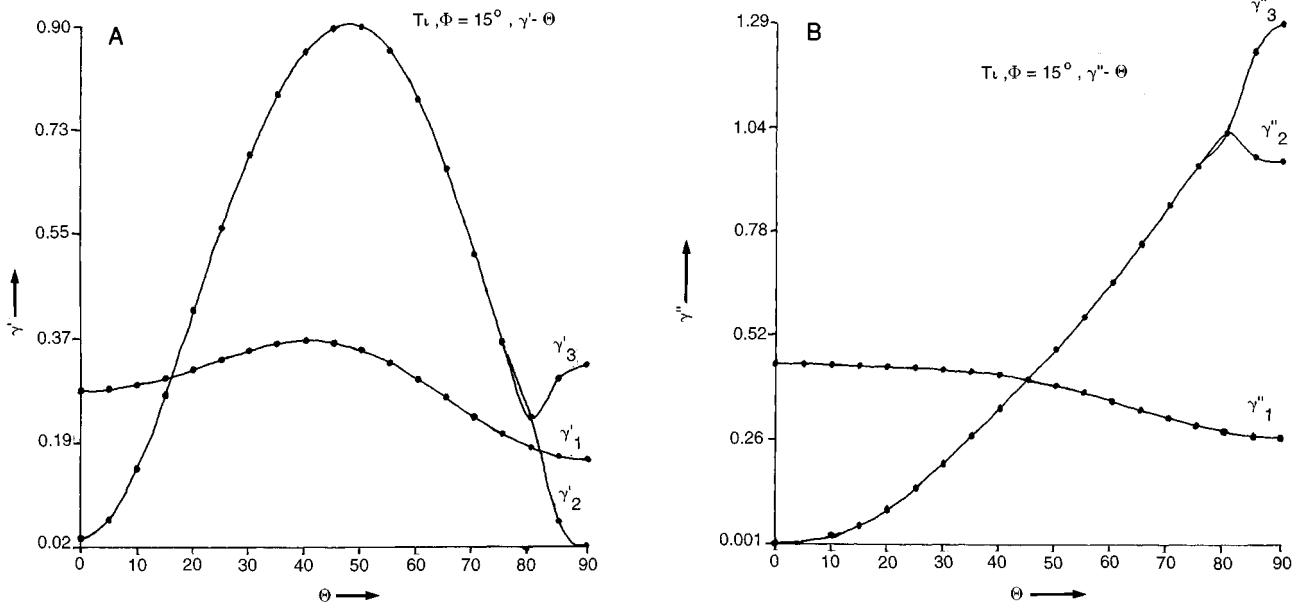


FIG. 1. Variation of the Generalized Gruneisen Parameters γ' (A) and γ'' (B) as a Function of θ for the Azimuthal Angle $\phi = 15^\circ$ in Titanium.

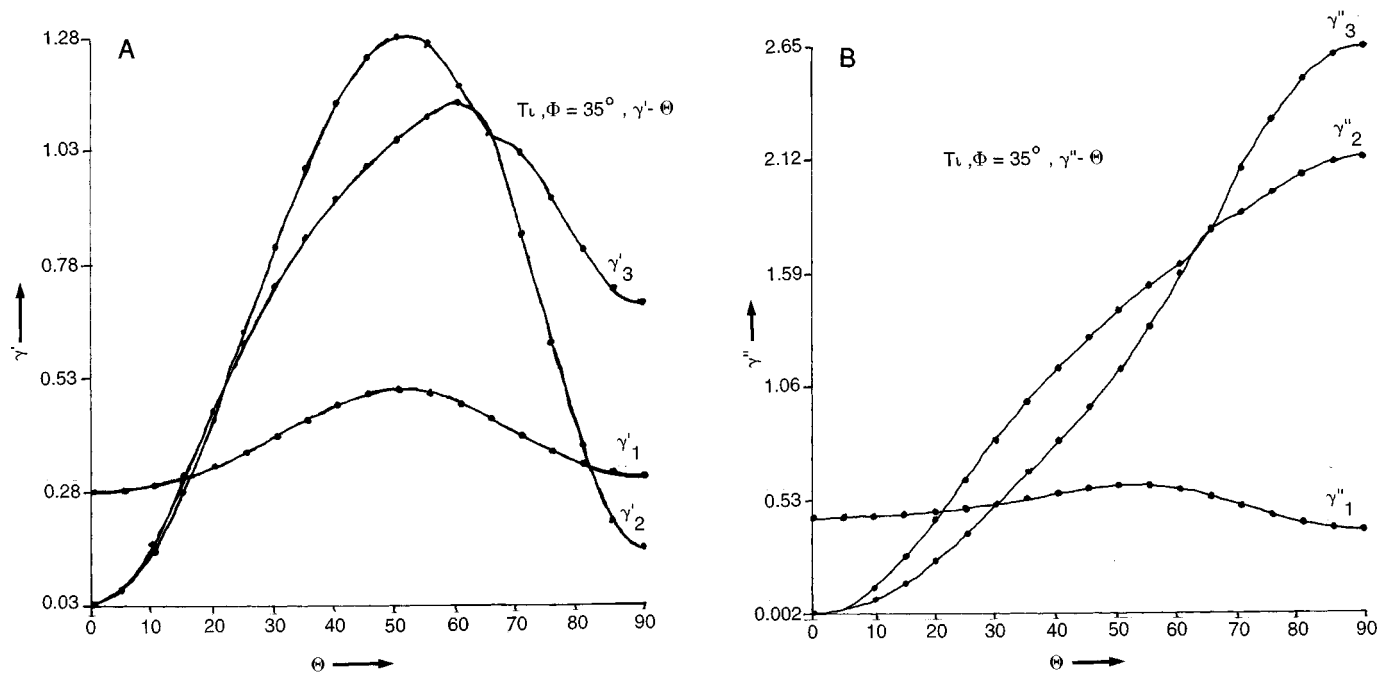


FIG. 2. Variation of the Generalized Gruneisen Parameters γ' (A) and γ'' (B) as a Function of θ for the Azimuthal Angle $\phi = 35^\circ$ in Titanium.

graphs of γ vs θ accounts for the pronounced anharmonicity of the solid in certain specific directions. The average Gruneisen function, $\gamma_{\perp}^{\text{Br}}$ and $\gamma_{\parallel}^{\text{Br}}$ are 0.27 and 0.002,

respectively. This suggests that the anisotropy in thermal expansion along the c -axis is more pronounced than that along the ab plane.

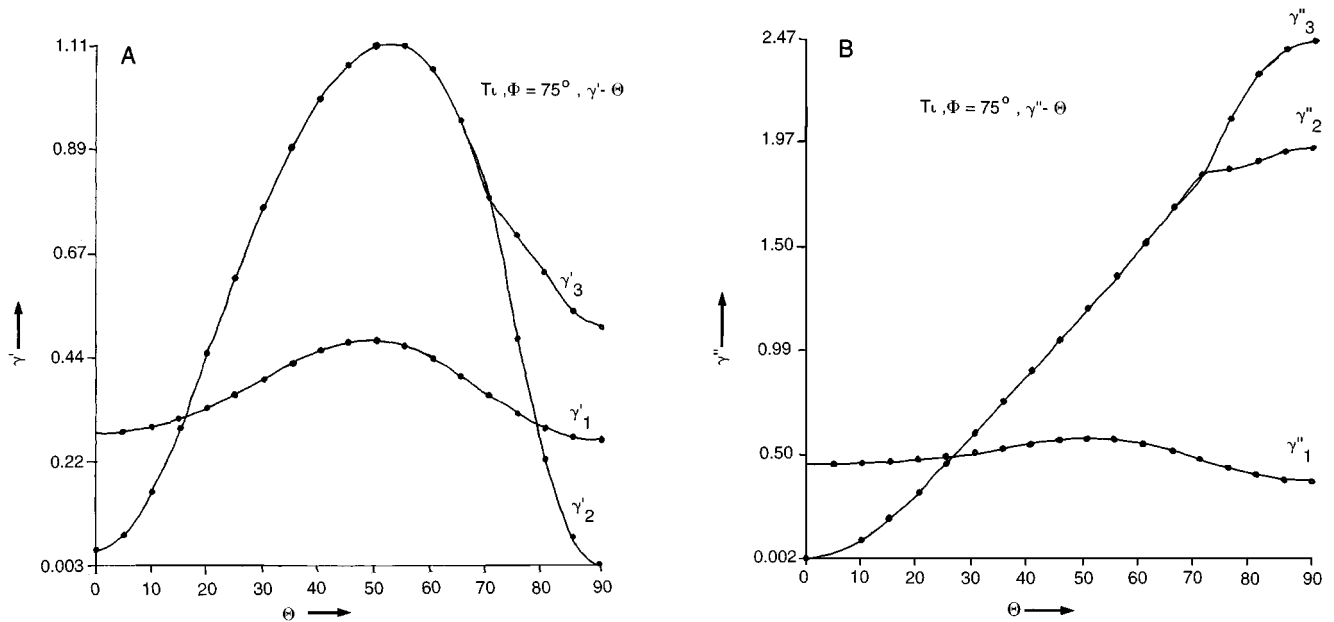


FIG. 3. Variation of the Generalized Gruneisen Parameters γ' (A) and γ'' (B) as a Function of θ for the Azimuthal Angle $\phi = 75^\circ$ in Titanium.

ACKNOWLEDGMENTS

Thanks are offered to Dr. N. V. Eldhose, M. G. University, for stimulating discussions. In addition, we thank Mr. P. C. Joseph for his assistance in computing the program.

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