

Higher order elastic constants and generalized Gruneisen parameters of elastic waves and low temperature thermal expansion of gadolinium

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Abstract. Expressions for the higher order elastic constants are derived 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 gadolinium. The higher order elastic constants are used to find out the generalized Gruneisen parameters of the elastic waves propagating in different directions in gadolinium. 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.

Keywords. Elasticity; elastic constants; thermal expansion.

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1. Introduction

Higher order elastic constants is a measure of the anharmonicity of a solid. 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 six SOEC's, ten TOEC's, and nineteen FOEC's 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 gadolinium. The first order pressure derivatives of the second order elastic constants of a crystal are evaluated. The second order pressure derivatives are obtained as a function of the second, third and fourth order elastic constants. Using the finite strain theory of Muranaghan [2] the expressions for the second pressure derivatives of the effective SOEC of a hexagonal solid have been derived in terms of the 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 gadolinium. These elastic constants are also used to find the low temperature limit of the thermal expansion coefficients of gadolinium.

Gadolinium has importance as a rare earth material of a hexagonal close-packed structure. This metal shows interesting thermal expansion characteristics at low temperatures. The lattice constants of gadolinium are $D = a = 3.63$ AU and $C = 5.78$ AU and the density of the crystal is 7.89 g/cc. The second order elastic

constants of gadolinium have been experimentally determined by Fisher and Dever [4] and their pressure derivatives by Fisher *et al* [5]. The third order elastic constants are reported by Menon and Ramji Rao [6] using Keatings approach.

2. Theory

2.1 Higher order elastic constants of gadolinium

Interactions between atoms only up to the second nearest neighbours of gadolinium are considered. The position coordinates of the two non-equivalent atoms in the unit cell are

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

Here P is the axial ratio c/a ; c and a are the unit cell distances. The PE/unit cell is

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

Here I atoms are the six nearest neighbours of the same type in the basal plane and the J atoms are the six nearest non-equivalent neighbours out of the basal plane. The components of interatomic vector R after deformation is 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} which is given as

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

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

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

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

$$\begin{aligned} \phi = & \phi_0 + k_2 \left[\sum_I [\Delta R^2(I)]^2 + \sum_J [\Delta R^2(J)]^2 \right] \\ & + k_3 \left[\sum_I [\Delta R^2(I)]^3 + \sum_J [\Delta R^2(J)]^3 \right] \\ & + k_4 \left[\sum_I [\Delta R^2(I)]^4 + \sum_J [\Delta R^2(J)]^4 \right]. \end{aligned} \quad (1)$$

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Here k_2 is the harmonic parameter 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-Jones potential is given by

$$\phi = -a/r^m + b/r^n.$$

For this potential K_2 , K_3 and K_4 are calculated as

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

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

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

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

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

Ramanand *et al* [7] have shown that to evaluate 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.,

$$\begin{aligned} \bar{W}_x &= [-D/2\sqrt{3}][\eta_{yy} - \eta_{xx}] + [D/2\sqrt{3}][\eta_{yy}^2 - \eta_{xx}^2] \\ &\quad + [\sqrt{3}p^2D/4][\eta_{zz}(\eta_{yy} - \eta_{xx})], \\ \bar{W}_y &= [-D/\sqrt{3}]\eta_{xy} + D/\sqrt{3}[\eta_{xy}(\eta_{yy} + \eta_{xx})] + [\sqrt{3}p^2D/2][\eta_{xy}\eta_{zz}], \\ \bar{W}_z &= 0. \end{aligned} \quad (2)$$

Substituting the value of W_i from (2) to (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

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

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

$$\begin{aligned}
 C_{1111} &= [\{4390/9\}D^8/V_a]K_4 + [\{4D^6/V_a\}]K_3 - [\{143/6\}D^4/V_a]K_2 \\
 C_{1112} &= [\{1474/9\}D^8/V_a]K_4 + [\{23/6\}D^6/V_a]K_3 \\
 C_{1113} &= [\{24/9\}D^8p^2/V_a]K_4 + [3D^6p^2/V_a]K_3 - [\{12/6\}D^4p^2/V_a]K_2 \\
 C_{1122} &= [\{502/9\}D^8/V_a]K_4 - [\{4/3\}D^6/V_a]K_3 + [\{11/2\}D^4/V_a]K_2 \\
 C_{1123} &= [\{24/9\}D^8p^2/V_a]K_4 - [D^6p^2/V_a]K_3 + [6D^4p^2/V_a]K_2 \\
 C_{1133} &= [4D^8p^4/V_a]K_4 + [\{3/2\}D^6p^4/V_a]K_3 - [3D^4p^4/V_a]K_2 \\
 C_{1144} &= C_{1244} = C_{1255} = [\{24/9\}D^8p^2/V_a]K_4 - [D^6p^2/V_a]K_3 \\
 C_{1155} &= [\{24/9\}D^8p^2/V_a]K_4 + [3D^6p^2/V_a]K_3 \\
 C_{1166} &= [\{1461/9\}D^8/V_a]K_4 + [\{2/3\}D^6/V_a]K_3 + [\{25/18\}D^4/V_a]K_2 \\
 C_{1233} &= [4D^8p^4/V_a]K_4 - [\{3/2\}D^6p^4/V_a]K_3 + [3D^4p^4/V_a]K_2 \\
 C_{1333} &= C_{3344} = [6D^8p^6/V_a]K_4 \\
 C_{1344} &= [4D^8p^4/V_a]K_4 + [\{3/2\}D^6p^4/V_a]K_3 \\
 C_{1355} &= [4D^8p^4/V_a]K_4 - [\{3/2\}D^6p^4/V_a]K_3 \\
 C_{2223} &= [\{24/9\}D^8p^2/V_a]K_4 + [3D^6p^2/V_a]K_3 - [6D^4p^2/V_a]K_2 \\
 C_{3333} &= [9D^8p^4/V_a]K_4 \\
 C_{4444} &= [6D^8p^4/V_a]K_4 \tag{4}
 \end{aligned}$$

$$\begin{aligned}
 C_{111} &= [\{1099/10\}D^6/V_a]K_3 + [\{23/3\}D^4/V_a]K_2 \\
 C_{112} &= [\{83/5\}D^6/V_a]K_3 - [\{7/5\}D^4/V_a]K_2 \\
 C_{113} &= [\{5/3\}D^6p^2/V_a]K_3 + [D^4p^2/V_a]K_2 \\
 C_{123} &= [\{7/5\}D^6p^2/V_a]K_3 - [D^4p^2/V_a]K_2 \\
 C_{133} &= [\{16/5\}D^6p^4/V_a]K_3 \\
 C_{344} &= [3D^6p^4/V_a]K_3 \\
 C_{144} &= [2D^6p^2/V_a]K_3 \\
 C_{155} &= [\{4/3\}D^6p^2/V_a]K_3 \\
 C_{222} &= [\{175/2\}D^6/V_a]K_3 + [\{39/5\}D^4/V_a]K_2 \\
 C_{333} &= [\{9/2\}D^6p^6/V_a]K_3 \tag{5}
 \end{aligned}$$

$$\begin{aligned}
 C_{11} &= [\{167/8\}D^4/V_a]K_2 \\
 C_{12} &= [\{41/8\}D^4/V_a]K_2 \\
 C_{13} &= [\{5/3\}D^4p^2/V_a]K_2 \\
 C_{33} &= [3D^4p^4/V_a]K_2 \\
 C_{44} &= [2D^4p^2/V_a]K_2 \\
 C_{66} &= \frac{1}{2}(C_{11} - C_{12}) \tag{6}
 \end{aligned}$$

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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 gadolinium.

2.2 Low temperature thermal expansion of gadolinium

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

$$\gamma'_j(\theta, \phi) = -\frac{1}{v_j(\theta, \phi)} \frac{\partial v_j(\theta, \phi)}{\delta \epsilon'},$$

$$\gamma''_j(\theta, \phi) = -\frac{1}{v_j(\theta, \phi)} \frac{\partial v_j(\theta, \phi)}{\delta \epsilon''},$$

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 in the direction the 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

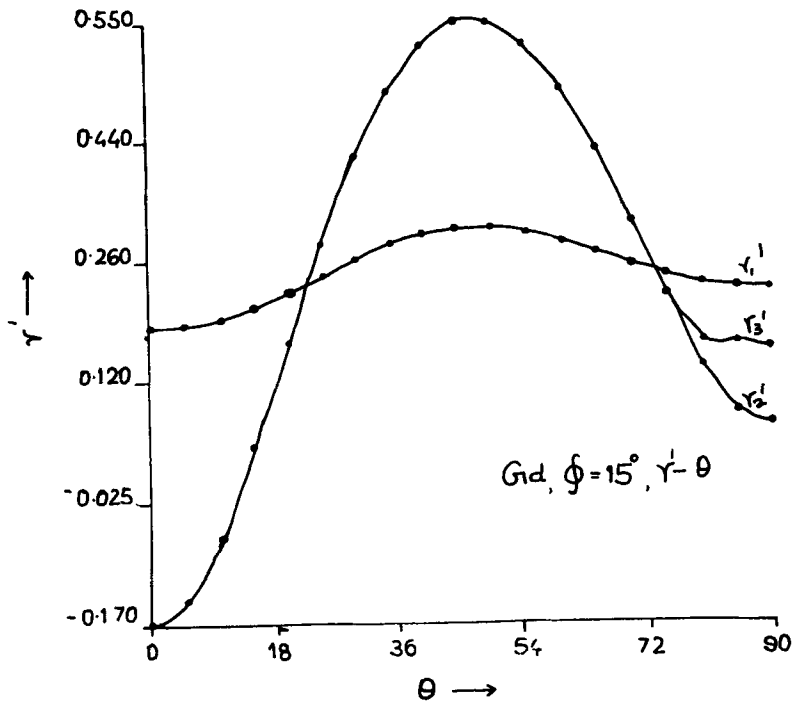


Figure 1A. Variation of generalized GP's γ' with θ for azimuthal angle $\phi = 15^\circ$ in gadolinium.

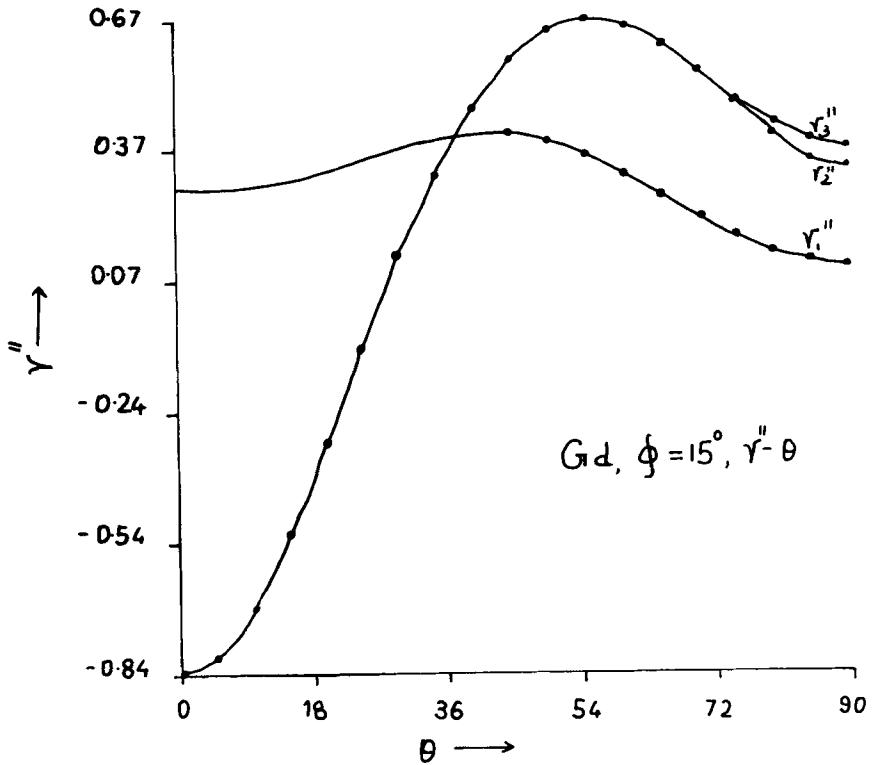


Figure 1B. Variation of generalized GP's γ'' with θ for azimuthal angle $\phi = 15^\circ$ in gadolinium.

unique axis. These generalized Gruneisen parameters can be calculated from the second and third order elastic constants of a solid as shown below by Ramji Rao and Srinivasan [8]. Using the second and third order elastic constants of gadolinium 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 coefficient of an uniaxial crystal is given by

$$\begin{aligned}
 V\alpha_{\parallel} &= [2S_{13}\gamma'(T) + S_{33}\gamma''(T)]C_v(T), \\
 V\alpha_{\perp} &= [(S_{11} + S_{12})\gamma'(T) + S_{13}\gamma''(T)]C_v(T).
 \end{aligned}
 \tag{7}$$

Here V is the molar volume, 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 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

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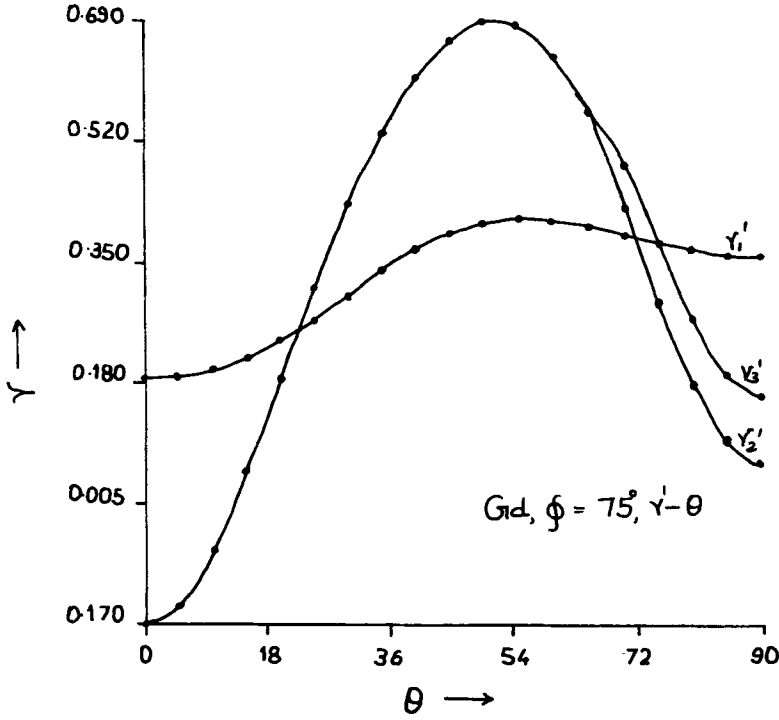


Figure 2A. Variation of generalized GP's γ_j' with θ for azimuthal angle $\phi = 75^\circ$ in gadolinium.

$\gamma_j''(\theta, \phi)$, these limits are defined by

$$\gamma_0' = \left[\sum_{j=1}^3 \int v_j^{-3}(\theta, \phi) \gamma_j'(\theta, \phi) d\Omega \right] / \left[\sum_{j=1}^3 \int v_j^{-3}(\theta, \phi) d\Omega \right],$$

$$\gamma_0'' = \left[\sum_{j=1}^3 \int v_j^{-3}(\theta, \phi) \gamma_j''(\theta, \phi) d\Omega \right] / \left[\sum_{j=1}^3 \int v_j^{-3}(\theta, \phi) d\Omega \right]. \quad (8)$$

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 were 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

$$\gamma_{\perp}^{\text{Br}}(0) = [(S_{11} + S_{12})\gamma_0' + S_{13}\gamma_0''] / \chi_{\text{iso}},$$

$$\gamma_{\parallel}^{\text{Br}}(0) = [2S_{13}\gamma_0' + S_{33}\gamma_0''] / \chi_{\text{iso}}.$$

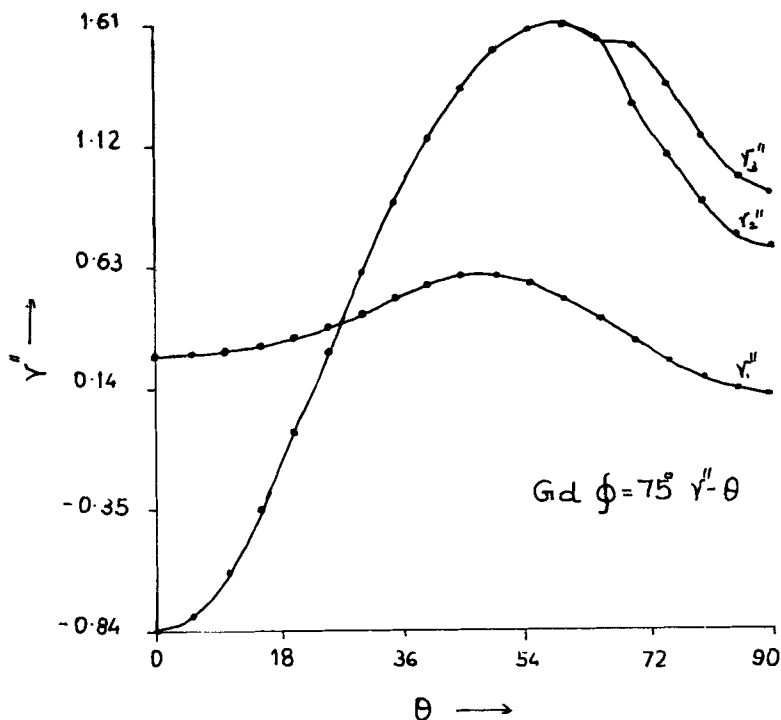


Figure 2B. Variation of generalized GP's γ'' with θ for azimuthal angle $\phi = 75^\circ$ in gadolinium.

Here S_{11} , S_{33} , S_{12} and 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

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

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Table 1. Second order elastic constants in 10^{10} N/m^2 and first pressure derivative of gadolinium.

C_{ij}	Calculated values	Experimental values	dC_{ij}/dp	Calculated values	Experimental values
C_{11}	7.22	6.67	dC_{11}/dp	3.69	3.018
C_{12}	1.77	2.5	dC_{12}/dp	1.967	2.26
C_{13}	1.406	2.13	dC_{13}/dp	1.472	—
C_{33}	6.68	7.19	dC_{33}/dp	7.061	5.726
C_{44}	1.75	2.07	dC_{44}/dp	1.708	0.185
C_{66}	2.769	2.08	dC_{66}/dp	0.8912	0.377

Table 2. Third order elastic constants of gadolinium in 10^{10} N/m^2 .

C_{ijk}	Calculated values	Reported values
C_{111}	-50.25	-50.3
C_{112}	-15.27	-13.3
C_{113}	-1.15	-0.4
C_{133}	-9.92	-9.7
C_{123}	-4.73	-6.3
C_{344}	-9.3	-9.7
C_{333}	-74.72	-76.2
C_{222}	-63.79	-55.2
C_{144}	-3.85	-3.9
C_{155}	-2.56	-2.0

3. Results and discussion

Values of second order elastic constants C_{11} and C_{33} are used to evaluate the harmonic parameter K_2 . Third order elastic constants of Menon and Rao [6] are used to evaluate the anharmonic parameter K_3 . These SOEC's and first pressure derivatives are given in table 1. These are compared with the experimental SOEC values [4] and first pressure derivatives [5]. The TOEC's are given in table 2. These values are compared with the other reported theoretical values of Menon and Rao [6]. The value of m and n [10,11], are so chosen to give a satisfactory agreement to the reported TOEC of gadolinium. The value of k_2 , m and n are used to evaluate the anharmonic parameter k_4 .

The calculated fourth order elastic constants of gadolinium are given 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 gadolinium. These values are given in table 4. The magnitude of C_{11}^2 and C_{33}^2 is quite large indicating that phase change would occur in this metal when subjected to high pressure. This is confirmed by the experimental evidence. The occurrence of phase change in gadolinium at 25 kbar from hexagonal to orthorhombic structure was reported by Robinson *et al* [12]. The value of Gruneisen coefficients $\gamma'_0 = 0.258$ and $\gamma''_0 = 0.641$ for gadolinium. The Brugger gammas are calculated as

$$\gamma_{\perp}^{\text{Br}}(0) = 0.131, \quad \gamma_{\parallel}^{\text{Br}}(0) = -0.0069.$$

Table 3. Fourth order elastic constants of gadolinium in 10^{10}N/m^2 ($m = 5.74$, $m = 1.42$).

C_{ijkl}	Calculated values
C_{1111}	287.189
C_{1112}	102.99
C_{1113}	-12.12
C_{1122}	37.053
C_{1123}	11.302
C_{1133}	1.735
C_{1144}	6.046
C_{1155}	-1.305
C_{1166}	99.322
C_{1233}	29.555
C_{1244}	6.046
C_{1255}	6.046
C_{1333}	59.33
C_{1344}	22.92
C_{1355}	8.36
C_{2223}	-6.901
C_{3333}	224.99
C_{4444}	23.46
C_{3344}	59.33

Table 4. Second pressure derivatives of gadolinium in $10^{10}\text{m}^2/\text{N}$.

d^2C_{ij}/dp^2	Calculated values
d^2C_{11}/dp^2	0.7417
d^2C_{12}/dp^2	1.984
d^2C_{13}/dp^2	1.0604
d^2C_{33}/dp^2	-0.79
d^2C_{44}/dp^2	-0.247
d^2C_{66}/dp^2	-0.6989

Table 5. Low temperature limit of gadolinium.

	Present calculation	Reported value [6]
γ_L	0.2547	0.383

The low temperature limit of the Gruneisen gamma is obtained as 0.2547. This is compared with the available reported value and is given 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 0K for this crystal. The variation of γ with θ for different value of ϕ is shown. The anisotropy in all the 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 0.131 and -0.0069 which suggests that the anisotropy in thermal expansion along the c-axis is more pronounced than that along the ab plane.

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