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Low-temperature Grüneisen gamma of II–VI semicoductor ZnS

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Abstract The theoretical study of low-temperature lattice thermal expansion of the II–VI semiconductor ZnS is attempted. The generalized Grüneisen gammas of the elastic waves propagating in different directions with respect to the [001] crystallographic axis of ZnS are calculated using the second- and third-order elastic constants. The values of mode Grüneisen gammas γ_j are determined and found generally positive except from γ_2 at $\theta = 25°$ to $\theta = 65°$. The low-temperature limit of the Grüneisen gamma $\bar{\gamma}$ is determined and compared with experimental values. Using this $\bar{\gamma}$, we calculated the Brugger gamma γ^{Br} and hence the low-temperature volume lattice thermal expansion γ_L. It is expected that the volume expansion is positive down to absolute zero for ZnS.

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Introduction

The thermal expansion of large gap semiconductors attained a great deal of interest in recent years [1–4]. Technological and theoretical interest in II–VI compounds and their alloys is due to its potential application in electro-optical and electro-acoustical devices. ZnS is a prototype II–VI semiconductor and its cubic phase, which occurs naturally as a mineral has been called the zinc blende structure. This structure consists of two interpenetrating fcc sublattices, which are displaced from each other by one quarter of a body diagonal. One fcc sublattice is made up entirely of S atoms and the other entirely of Zn atoms. Unlike the crystal structure of elemental semiconductors, the compound II–VI semiconductors exhibit a certain deviation from inversion symmetry. The conventional cell is a cube with lattice parameter $a = 0.541$ nm containing eight atoms. The present study aims at the determination of thermal expansion and the Grüneisen gammas of the semiconducting compound ZnS. We have calculated the generalized isothermal Grüneisen gammas γ_j for acoustic modes. This is affected by means of the determination of the third-order elastic constants of ZnS. The expression for finding out the mode Grüneisen gamma for ZnS is obtained from the effective second-order elastic constants. The expressions for elastic constants are derived for the point group $\bar{4}3$ m symmetry and are used to obtain the mode Grüneisen gammas of ZnS.

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Third-order elastic constants of ZnS

Third-order elastic constants quantify the lowest order anharmonic properties of solids such as thermal expansion, temperature and pressure dependence of the elastic constants and the interactions of acoustic and thermal phonons. Potential energy can be expanded as a Taylor's series involving co-ordinate derivatives as follows

$$\phi = \phi_0 + O'\phi(r)\left\{\sum_l \Delta R^2(l)\right\} + \frac{1}{2}O''\phi(r) \left\{\sum_l \left[\Delta R^2(l)\right]^2\right\} + \frac{1}{6}O'''\phi(r)\left\{\sum_l \left[\Delta R^2(l)\right]^3\right\} + \ldots \quad (1)$$

where l refers to the nearest neighbours. O', O'', O''' are the first-,second-and third-order coordinate derivatives of the potential function, and

$$\Delta R^2\begin{pmatrix} L & L' \\ \mu & \mu' \end{pmatrix} = \left[R'\begin{pmatrix} L & L' \\ \mu & \mu' \end{pmatrix} \bullet R'\begin{pmatrix} L & L' \\ \mu & \mu' \end{pmatrix} - R\begin{pmatrix} L & L' \\ \mu & \mu' \end{pmatrix} \bullet R\begin{pmatrix} L & L' \\ \mu & \mu' \end{pmatrix}\right] \quad (2)$$

where $R'\begin{pmatrix} L & L' \\ \mu & \mu' \end{pmatrix}$ is the vector distance of atom μ in the Lth cell of the strained lattice and $R\begin{pmatrix} L & L' \\ \mu & \mu' \end{pmatrix}$ is the corresponding vector in the unstrained position. The strain energy computed is compared with the lattice energy expression from continuum model approximation

$$U = U_0 + \frac{1}{2}\sum_{ijkl} C_{ijkl}\eta_{ij}\eta_{kl} + \frac{1}{6}\sum_{ijklmn} C_{ij,kl,mn}\eta_{ij}\eta_{kl}\eta_{mn} \quad (3)$$

to get the second- and third-order elastic constants. We have calculated the second- and third-order elastic constants of ZnS [5] using the finite deformation theory of Murnaghan [6] where the elastic stress is nonlinear with elastic strain. The higher order elastic constants of ZnS are obtained by assuming Lennard–Jones type of interatomic potential. The values obtained are generally in agreement with the reported values. We obtain the Grüneisen gammas of semiconductor ZnS using quasi-harmonic approximation by making use of the second- and third-order elastic constants of ZnS from reference [5].

Low-temperature thermal expansion of ZnS

The linear thermal expansion coefficients denoted by α can be expressed as

$$V\alpha = \left[(S_{11} + 2S_{12})\bar{\gamma}(T)\right]C_V = \gamma^{\mathrm{Br}}C_v\chi_{\mathrm{iso}} \quad (4)$$

Here S_{ij} are the elastic compliance coefficients, V is the molar volume is the molar Volume, C_V is the molar specific heat in the T^3 region, and χ_{iso} is the isothermal compressibility. $\bar{\gamma}(T)$ are the low-temperature limits of the effective Grüneisen gamma. γ^{Br} which is the average or effective Grüneisen gamma in the notation of Brugger [7]. The effective Grüneisen gamma can be defined as

$$\bar{\gamma}(T) = \left[\sum_{qj}\gamma(q,j)C_V(q,j)\right]\left[\sum_{qj}C_V(q,j)\right]^{-1} \quad (5)$$

This effective Grüneisen gamma is weighed averages of the generalized Grüneisen gammas $\gamma(q, j)$. q is the wave vector and j is the polarization index. C_V (q, j) is the contribution of a single normal mode of frequency ω, wave vector q, and polarization index j to the specific heat of the lattice $\gamma(q, j)$ is given by

$$\gamma(q,j) = -\frac{\partial \log\omega(q,j)}{\partial\varepsilon} \quad (6)$$

where ϵ is the uniform volume strain. Here, instead of choosing arbitrary strain components in defining Grüneisen gammas, we choose such strain that leave the symmetry of the crystal unchanged. Here we use the Lagrangian strain parameter η_{ij}, which are in place of volume change, are selected such that $i = j$ (where $i = j = 1,2,3$), in the quasi-harmonic approximation. At low temperatures, the Grüneisen gammas of the elastic wave frequencies determine the anisotropy thermal expansion of the crystal, and the effective Grüneisen gamma becomes

$$\bar{\gamma}(0) = \left[\int\sum_{J=1}^{3}\gamma_j(\theta,\phi)V_j^{-3}(\theta,\phi)d\Omega\right]^{-1} \quad (7)$$

Here V_j (θ,ϕ) is the wave velocity of elastic wave of polarization index j, propagating in the direction (θ,ϕ). γ_j is the Grüneisen gammas of the acoustic mode. The Grüneisen gammas for the acoustic modes can be calculated using the second- and third-order elastic constants and hence the low temperature limit of Grüneisen gamma can be obtained from the procedure of Jayachandran and Menon [8]. In cubic crystal, it is assumed that Grüneisen gammas and acoustic wave velocities depend only on θ and are independent of the azimuth ϕ. The average effective Grüneisen function in the notations of Brugger and Fritz in Eq. 4 is expressed as

$$\gamma^{\mathrm{Br}} = [(S_{11} + 2S_{12})\bar{\gamma}]\chi_{\mathrm{iso}}^{-1} \quad (8)$$

The Mode Grüneisen Gammas of ZnS

The general Thurston and Brugger equation for wave propagation is [9]

$$\rho_0\omega^2 U_i = 4\pi^2 \sum_{kjl} U_j Y_l Y_k \left[C_{ik,jl} + \sum_{mn} \varepsilon_{mn} \left(C_{ik,jl,mn} + C_{ik,nl}\delta_{mj} + C_{nk,jl}\delta_{ml} + C_{kl,mn}\delta_{ij} \right) \right] \quad (9)$$

Here Y_i's are the components of the arbitary direction through which the wave is propagating and U_j's are the components of displacement. ω is the angular frequency and ρ_0 is the density of the crystal in the unstrained state. The $C_{ij,kl}$ and $C_{kl,mn}$ values are the second- and third-order elastic constants, respectively. From the elements of the secular determinant formed by the coefficient of U_i's, the expressions for the effective second-order elastic constant in terms of the strain component ϵ are obtained as

$$C'_{11} = \varepsilon/3(2C_{112} + 2C_{12} + C_{11} + 3C_{11}) + C_{11} \quad (10a)$$

$$C'_{12} = \varepsilon/3(2C_{112} + 2C_{123} - C_{11}) + C_{12} \quad (10b)$$

$$C'_{44} = \varepsilon/3(2C_{155} + C_{144} + C_{11} + 2C_{12} + 2C_{44}) + C_{44} \quad (10c)$$

Here the C_{ij} and C_{ijk} are, respectively, the second- and third-order elastic stiffness constants in Voigt's notations.

The general expressions for Grüneisen gammas from the deteminantal Eq. 9 is

$$\gamma = (-1/2\bar{X}_j) \left[\frac{\bar{X}_j \frac{\partial(A+B)}{\partial\varepsilon} - \frac{\partial(AB-C^2)}{\partial\varepsilon}}{2\bar{X}_j - (\bar{A}_0 + \bar{B}_0)} \right] \quad (11)$$

where

$$A = C'_{11}\mathrm{Sin}^2\theta + C'_{44}\mathrm{Cos}^2\theta \quad (12a)$$

$$B = C'_{44}\mathrm{Sin}^2\theta + C'_{11}\mathrm{Cos}^2\theta \quad (12b)$$

$$C = \mathrm{Sin}\theta\mathrm{Cos}\theta\left(C'_{12} + C'_{44}\right) \quad (12c)$$

and

$$X_j = \rho_0 V_j^2(\theta, \phi) \quad (12)$$

Table 1 Third-order elastic constants of ZnS in GPa along with the reported values

$C_{111} = -609.53$	$C_{123} = -4.72$	$C_{155} = -300$
$C_{112} = -307.14$	$C_{144} = -4.03$	$C_{456} = -9.89$

Ref. [5]

Here we make use of the reported values [5] of C_{ij} and C_{ijk} (given in Table 1) by the same authors for the calculation of γ_j. Fig. 1 gives the plot of the generalized Grüneisen gammas γ_j for acoustic modes as a function of angle θ, which the direction of propagation makes with the [001] crystallographic axis. The calculated value of the low-temperature limit of the effective Grüneisen gamma $\bar{\gamma}_j(0)$ from Eq. 7 for ZnS is 0.32. Now from Eq. 8 the γ^{Br} can be evaluated as 0.11. The low-temperature volume lattice thermal expansion (in terms of the Grüneisen gammas) $\gamma_{\mathrm{L}} = 3\gamma^{\mathrm{Br}}$ is 0.33. Figure 2 gives the plot of the generalized Grüneisen gammas ($_j$ for acoustic modes as a function of $\rho_0 v^2$, the velocity of propagation in different directions.

Discussion

The theory of low-temperature thermal expansion has been used to determine the mode gammas and low-temperature limit of the lattice mode Grüneisen gamma in the wide gap semiconductor ZnS. The mode Grüneisen gammas of the acoustic modes in different wave propagation directions have been calculated and are given in Fig.1, which show slight anisotropy in the acoustic wave directions. The low-temperature limit of the Grüneisen gamma of the ZnS crystal obtained in the present calculation is 0.32. Smith and White [10] measured the thermal expansion in a three terminal capacitance dilatometer from 2 K up to about 33 K.

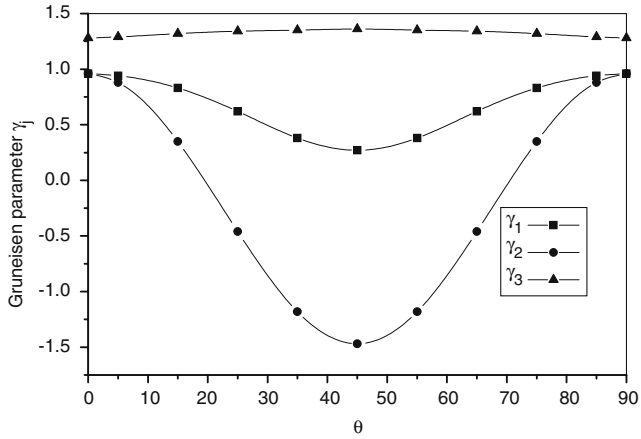

Fig. 1 Variation of the generalized Grüneisen parameters γ_j (θ) as a function of θ for ZnS

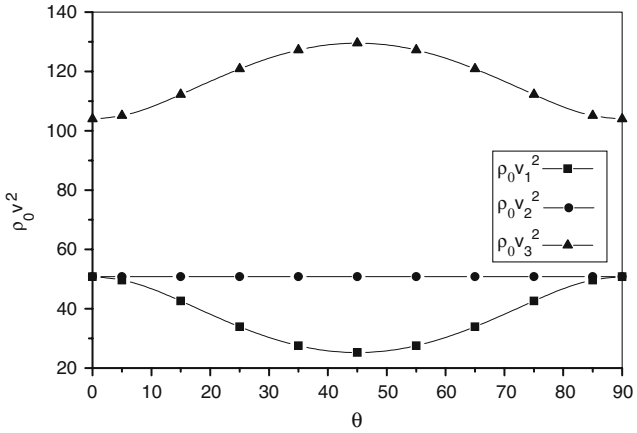

Fig. 2 Variation of $\rho_0 V^2$ as a function of θ for ZnS

They have also measured the change in length relative to the material of dilatometer cell using silicon for calibration below 35 K. But for below 15 K they calculated the α values based upon elastic constants. They have reported two independent series of calibrations of the cell. According to Smith and White [10], these results differ from earlier calibrations and such shifts are presumed to be due to long term changes in the mechanical and physical characteristics associated with the construction of the cell. The limiting values for the Grüneisen gamma γ_0^{th} calculated using the equation $\gamma_0^{\text{th}} = \frac{3\alpha V B_s}{C_p}$ where C_p is the molar heat capacity at constant pressure, V is the molar volume and B_s is the adiabatic bulk moduli. They obtain the limiting value for Grüneisen gamma γ_0^{th} as –0.14. The present value of low-temperature limit of mode gamma 0.32 shows deviation from their experimental gamma [10]. However, the low-temperature limit of mode gamma for ZnS using earlier experimental results for specific heat, thermal expansion and elastic constants by Yates et al. [11] is above –1 from graph. According to Yates et al., it is difficult to offer many comments due to the restricted temperature range over which it was possible to calculate γ.

The variation of mode Grüneisen gamma γ_j for the acoustic branches of elastic waves as a function of angle θ, which the direction of propagation makes with the [001] crystal axis for ZnS, is shown in Fig. 1. All the γ_1 and γ_3 values are positive. The γ_2 values for angles ranging from 25° to 65° are negative. This is suggestive of a possible phase change as these modes can trigger a structural phase transition. The acoustic mode γ_1 assumes a maximum value of 0.96, both at $\theta = 0°$ and at $\theta = 90°$ to the axis of the crystal and a minimum of 0.27 when the direction of propagation makes 45° to the crystal axis. The other acoustic mode γ_2 possesses the maximum value 0.96 when the direction of propagation of the wave is along and perpendicular to the direction of crystal axis. γ_3 attains a maximum value of 1.36 when $\theta = 450°$. The corresponding minimum value of γ_2 and γ_3 for ZnS are –1.47 and 1.28 at different angles of θ. The low temperature volume lattice thermal expansion γ_L for ZnS is obtained as 0.33 from the value of Brugger gamma.

Conclusion

The mode Grüneisen gammas of ZnS for different acoustic wave propagation direction have been calculated .The results show that the thermal expansion anisotropy of the material is less for various acoustic modes. The average Grüneisen function γ^{Br} is 0.11. The Grüneisen gammas provide insight into the more or less isotropic nature of thermal expansion in ZnS. The theory followed here to calculate Grüneisen gammas along various crystal directions is applicable to other zinc blende structures as well.

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