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The carrier contribution to the elastic constants in small-gap materials

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We present a simple theoretical analysis of the carrier contribution to the second and third order elastic constants in nonparabolic materials on the basis of an electron dispersion law by taking into account various anisotropies of the energy band structure within the framework of $k \cdot p$ formalism. It is found that the carrier contributions to the elastic constants in n -Cd₃As₂, InSb, InAs, GaAs, Hg_{1-x}Cd_xTe, and lattice matched In_{1-x}Ga_xAs_yP_{1-y} increase with the increase of carrier degeneracy in different manners which, depend on the material parameters and band structure. A relationship between the said contributions and the thermoelectric power has been derived for materials obeying arbitrary dispersion laws in the presence of a classically large magnetic field. Our analysis is based on the derivation of a more generalized band structure of the materials which agrees well with the relationship suggested. It is also observed that the second and third order elastic constants increase with the decrease of alloy composition for ternary and quaternary compounds, respectively. The corresponding well-known results for degenerate wide-gap materials can be derived as special cases of our generalized analysis. © 1998 American Institute of Physics. [S0021-8979(98)08101-8]

I. INTRODUCTION

Considerable attention has been paid in recent years to the study of the band structure dependence of various electronic properties of nonparabolic compounds.¹ Theoretical analyses of the carrier contribution to the second and third order elastic constants in lead chalcogenides and heavily doped semiconductors have been reported in the literature.² These reports show that the said contribution depends on the density-of-states function. The purpose of the present article is to carry out an investigation of the carrier contributions to the elastic constants in tetragonal, ternary, quaternary, and III-V compounds. The present analysis is based on $k \cdot p$ formalism and takes into account the different anisotropies in the energy band spectra. The tetragonal compounds have important applications in nonlinear optics and in light emitting diodes.³ Rowe and Shay have explained the observed splitting and symmetry properties of the conduction and valence bands of these compounds by using the quasicubic model⁴ of the band structure. It has been shown that the s -like conduction band is singly degenerate for these compounds. Also, the dispersion relation of the conduction electrons in these tetragonal materials was derived by Kildal⁵ taking into account the crystal potential. In his analysis Kildal assumed that the momentum matrix element and the spin-orbit splitting parameters are isotropic in tetragonal compounds. But the experimental results show that these assumptions are not true. In the present article the different anisotropies in the energy band spectra are taken into account to make the analysis a generalized one. A theoretical investigation of the carrier contribution to the elastic constants in tetragonal compounds is presented in Sec. II A.

The carrier contribution to the elastic constants in III-V materials has been obtained as a special case of our generalized analysis and is presented in Sec. II B. The well-known

results for materials having parabolic energy bands under certain limiting conditions can also be obtained from the above study. A relationship between the thermoelectric power in the presence of a classically large magnetic field (an easily measurable experimental quantity) and the carrier contribution to the elastic constants has been derived for materials obeying arbitrary dispersion laws and is presented in sec. II C. The effects of doping and alloy composition on the said contribution have also been studied in materials such as n -Cd₃As₂, InSb, InAs, GaAs, Hg_{1-x}Cd_xTe, and lattice matched In_{1-x}Ga_xAs_yP_{1-y}.

II. THEORETICAL BACKGROUND

A. Formulations of the carrier contributions to the second and third order elastic constants in tetragonal materials

The form of the $k \cdot p$ matrix for the above class of compounds can be written as

$$H = \begin{bmatrix} H_1 & H_2 \\ H_2^+ & H_1 \end{bmatrix}, \quad (1)$$

where

$$H_1 = \begin{bmatrix} E_0 & P_{11}k_z & 0 & 0 \\ P_{11}k_z & -(\delta + \frac{1}{3}\Delta_{11}) & (\sqrt{2}\Delta_{\perp}/3) & 0 \\ 0 & (\sqrt{2}\Delta_{\perp}/3) & -\frac{2}{3}\Delta_{11} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix},$$

$$H_2 = \begin{bmatrix} 0 & 0 & f_{,-} & f_{,+} \\ 0 & 0 & 0 & 0 \\ -f_{,-} & 0 & 0 & 0 \\ f_{,+} & 0 & 0 & 0 \end{bmatrix},$$

in which E_0 is the band gap, P_{11} and P_{\perp} are the momentum-matrix elements parallel and perpendicular to the direction of the c axis, respectively, δ is the crystal-field splitting constant, Δ_{11} and Δ_{\perp} are the spin-orbit splitting parameters parallel and perpendicular to the direction of the c axis, respectively, $f_{\pm, -} = (P_{\perp}/\sqrt{2})(k_x \pm ik_y)$ and $i = \sqrt{-1}$. Diagonalizing the above matrix, the generalized electron energy spectrum in the bulk specimen of the tetragonal compounds can be expressed as

$$\gamma(E) = f_1(E)k_s^2 + f_2(E)k_z^2, \quad (2a)$$

where $\gamma(E) = \{E(E+E_0)[(E+E_0)(E+E_0+\Delta_{11}) + \delta(E+E_0+\frac{1}{3}\Delta_{11})] + (2/9)E(E+E_0)(\Delta_{11}^2 - \Delta_{\perp}^2)\}$, $k_s^2 = k_x^2 + k_y^2$, $f_1(E) = \{\hbar^2 E_0(E_0 + \Delta_{\perp}) \cdot [2m_{\perp}^*(E_0 + \frac{2}{3}\Delta_{\perp})]^{-1}\} \cdot [\delta(E+E_0 + \frac{1}{3}\Delta_{11}) + (E+E_0)(E+E_0 + \frac{2}{3}\Delta_{11}) + \frac{2}{9}(\Delta_{11}^2 - \Delta_{\perp}^2)]$, $f_2(E) = \{\hbar^2 E_0(E_0 + \Delta_{11}) \cdot [2m_{11}^*(E_0 + \frac{2}{3}\Delta_{11})]^{-1}\} \cdot [(E+E_0)(E+E_0 + \frac{2}{3}\Delta_{11})]$, where E is the electron energy measured from the edge of the conduction band, $\hbar = h/2\pi$ where h is the Planck constant, and m_{11}^* and m_{\perp}^* are the effective masses of the electron at the edge of the conduction band parallel and perpendicular to the direction of the c axis, respectively. The expression of the density-of-states function is obtained from Eq. (2a) and is given by

$$N(E) = (3\pi^2)^{-1} [\gamma(E)]^{3/2} [f_1(E)\sqrt{f_2(E)}]^{-1} \cdot \{[3\gamma'(E)/2\gamma(E)] - [f_1'(E)]/[f_1(E)] - [f_2'(E)]/[2f_2(E)]\}, \quad (2b)$$

where the primes denote the differentiation with respect to E . Using Eq. (2b), the electron concentration can be written as

$$n_0 = (3\pi^2)^{-1} [B_0(E_F) + C(E_F)], \quad (3)$$

where $B_0(E_F) = [\gamma(E_F)]^{3/2} [f_1(E_F)\sqrt{f_2(E_F)}]^{-1}$, E_F is the Fermi energy measured from the edge of the conduction band,

$$C(E_F) = \sum_{r=1}^S \nabla_r [B_0(E_F)],$$

r is the set of real positive integer whose upper limit is S , $\nabla_r = 2(k_B T)^{2r} (1 - 2^{1-2r}) \zeta(2r) d^{2r}/dE_F^{2r}$, k_B is the Boltzmann constant, T is the temperature and $\zeta(2r)$ is the zeta function of order $2r$.

The carrier contributions to the second and third order elastic constants can be expressed as²

$$\Delta C_{44} = (-G_0^2/9)(\partial n_0/\partial E_F) \quad (4a)$$

and

$$\Delta C_{456} = (G_0^3/27)(\partial^2 n_0/\partial E_F^2), \quad (4b)$$

where G_0 is the deformation potential constant.

Combining Eqs. (3), (4a), and (4b) we get

$$\Delta C_{44} = (-G_0^2/27\pi^2)[B_0'(E_F) + C'(E_F)] \quad (5)$$

and

$$\Delta C_{456} = (G_0^3/81\pi^2)[B_0''(E_F) + C''(E_F)], \quad (6)$$

where the single and double primes denote, respectively, the first and second order differentiations with respect to E_F .

B. Formulations of ΔC_{44} and ΔC_{456} for III-V materials

Under the conditions $\Delta_{11} = \Delta_{\perp} = \Delta$ (the isotropic spin-orbit splitting parameter), $\delta = 0$ and $m_{11}^* = m_{\perp}^* = m^*$ (the isotropic effective mass of the electron at the edge of the conduction band), Eq. (2a) assumes the form

$$\frac{\hbar^2 k^2}{2m^*} = \frac{E(E+E_0)(E+E_0+\Delta)(E_0+(2/3)\Delta)}{E_0(E_0+\Delta)(E+E_0+(2/3)\Delta)}. \quad (7)$$

The above equation is the well-known three-band Kane model⁶ which is a valid model for studying the electronic properties of III-V materials. The electronic properties of n -InAs, and ternary and quaternary compounds can also be studied by using the above model because the spin-orbit splitting of the valence bands in these compounds is of the order of the band gap. Thus the expressions for n_0 , ΔC_{44} , and ΔC_{456} are given by

$$n_0 = (2m^*/\hbar^2)^{3/2} (3\pi^2)^{-1} [U(E_F) + V(E_F)], \quad (8)$$

$$\Delta C_{44} = [-G_0^2(2m^*/\hbar^2)^{3/2}/27\pi^2][U'(E_F) + V'(E_F)], \quad (9a)$$

and

$$\Delta C_{456} = [G_0^3(2m^*/\hbar^2)^{3/2}/81\pi^2][U''(E_F) + V''(E_F)], \quad (9b)$$

where

$$U(E_F) = \left(\frac{E_F(E_F+E_0)(E_F+E_0+\Delta)(E_0+(2/3)\Delta)}{E_0(E_0+\Delta)(E_F+E_0+(2/3)\Delta)} \right)^{3/2}$$

and

$$V(E_F) = \sum_{r=1}^S \nabla_r [U(E_F)].$$

Under the condition $\Delta \gg E_0$ or $\Delta \ll E_0$, Eq. (7) becomes

$$E(1 + \alpha E) = (\hbar^2 k^2/2m^*), \quad \alpha = (E_0)^{-1}, \quad (10)$$

which is two-band Kane model.⁶ Thus the expressions for n_0 , ΔC_{44} , and ΔC_{456} can be written as

$$n_0 = (3\pi^2)^{-1} (2m^*/\hbar^2)^{3/2} [C_2(E_F) + C_3(E_F)], \quad (11)$$

$$\Delta C_{44} = (-G_0^2/27\pi^2)(2m^*/\hbar^2)^{3/2} [C_2'(E_F) + C_3'(E_F)], \quad (12a)$$

and

$$\Delta C_{456} = (G_0^3/81\pi^2)(2m^*/\hbar^2)^{3/2} [C_2''(E_F) + C_3''(E_F)], \quad (12b)$$

where $C_2(E_F) = [E_F(1 + \alpha E_F)]^{3/2}$ and

$$C_3(E_F) = \sum_{r=1}^S \nabla_r [C_2(E_F)].$$

In the case of wide-gap materials $\alpha \rightarrow 0$ and therefore the expression for n_0 , ΔC_{44} , and ΔC_{456} can be written as

$$n_0 = N_c F_{1/2}(\eta), \quad (13)$$

$$\Delta C_{44} = (-G_0^2 N_c / 9 k_B T) [F_{-1/2}(\eta)], \quad (14)$$

and

$$\Delta C_{456} = (G_0^3 N_c / 27 (k_B T)^2) [F_{-3/2}(\eta)], \quad (15a)$$

where $F_j(\eta)$ is the one-parameter Fermi-Dirac integral of the order given by⁷

$$F_j(\eta) = (\overline{|j+1|})^{-1} \int_0^\infty [1 + \exp(x - \eta)]^{-1} x^j dx, \quad (15b)$$

for $j > -1$,

or for all j , analytically continued as a complex contour integr around the negative real axis as

$$F_j(\eta) = (\overline{|-j/2\pi\sqrt{-1|})} \int_{(+\infty)}^{(-\infty)} [1 + \exp(-x - \eta)]^{-1} (x^j) dx. \quad (15c)$$

C. Derivation of the relation between the carrier contribution to the elastic constants and the thermoelectric power for materials obeying arbitrary dispersion laws in the presence of a classically large magnetic field

It is well known that in the presence of a classically large magnetic field the density-of-states function is not changed.⁸ Thus the thermoelectric power becomes independent of scattering mechanisms and is determined only by the dispersion laws. The magnitude of the thermoelectric power can be written as⁹

$$L_0 = (1/e T n_0) \int_{-\infty}^{\infty} [\phi(E)(E - E_F)] (-\partial f_0 / \partial E) dE, \quad (16)$$

where $\phi(E)$ is the total number of states and f_0 is the Fermi-Dirac function. Following Tsilkovski,⁸ the thermoelectric power under the condition of carrier degeneracy is given by

$$L_0 = (\pi^2 k_B^2 T / 3 e n_0) (\partial n_0 / \partial E_F). \quad (17)$$

Using Eqs. (17), (4a), and (4b) we get

$$\Delta C_{44} = -n_0 G_0^2 L_0 e / (3 \pi^2 k_B^2 T) \quad (18)$$

and

$$\Delta C_{456} = (G_0^3 e n_0 L_0^2 / 3 \pi^4 k_B^3 T) [1 + (n_0 / L_0) (\partial L_0 / \partial n_0)]. \quad (19)$$

The whole mathematical background may be summarized as follows. We have obtained the expressions for ΔC_{44} and ΔC_{456} in tetragonal, ternary, quaternary, and III-V compounds by using appropriate carrier energy spectra. The results of the three-band and the two-band Kane models are obtained as special cases of our generalized analysis. The Kane type band models are being used extensively to describe the energy band structures of ternary, quaternary, and III-V materials. The dispersion relations reduce to those of wide-gap materials under certain limiting conditions. The expressions for ΔC_{44} and ΔC_{456} which have been obtained by using the above models reduce to the well-known results given by Eqs. (14) and (15a). Thus the expressions for ΔC_{44} and ΔC_{456} in wide-band gap materials can be obtained from the generalized expressions for tetragonal and III-V com-

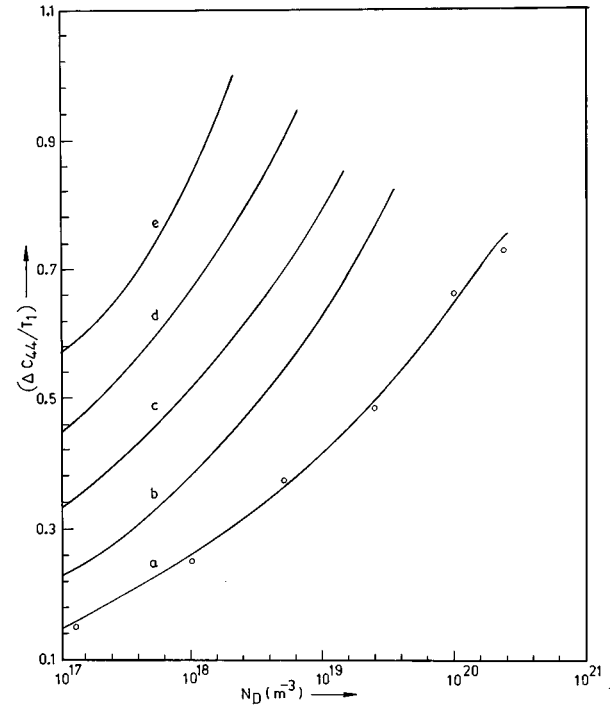


FIG. 1. Plot of the normalized ΔC_{44} vs N_D in n -Cd₃As₂ in accordance with (a) our proposed dispersion law, (b) $\delta=0$, (c) three-band Kane model, (d) two-band Kane model, and (e) wide band-gap model. The circular points have been drawn by using Eq. (18) and the experimental values of L_0 given in Ref. 1.

pounds. We have also formulated the relationship between the carrier contribution to the elastic constants and the thermoelectric power in the presence of a classically large magnetic field (an easily measurable experimental quantity).

III. RESULTS AND DISCUSSION

Theoretical analysis shows that the prior determination of the Fermi energy (E_F) is necessary for the evaluation of ΔC_{44} and ΔC_{456} as functions of the donor concentration N_D . The following expression⁶ is used to determine E_F :

$$n_0 = \left[1 + 2 \exp\left(\frac{E_F - E_d}{k_B T}\right) \right]^{-1} (N_D - N_a), \quad (20)$$

where E_d is the energy of the donor state and N_a is the acceptor concentration. The value of E_F is obtained from Eq. (20) because n_0 depends on band structure. The expressions for n_0 have been derived in Secs. II A and II B of this article for materials having different band structures. Figures 1(a) and 2(a) show, respectively, the plots of normalized $\Delta C_{44}(\Delta C_{44}/T_1, T_1 = -G_0^2 n_0 / 9 k_B T)$ and the normalized $\Delta C_{456}(\Delta C_{456}/T_2, T_2 = G_0^3 n_0 / 27 k_B^2 T^2)$ as functions of N_D for n -Cd₃As₂ according to our generalized model. The material parameters given in Table I(a) have been used in Eqs. (3), (5), (6), and (20) to plot Figs. 1(a) and 2(a). Figures 1(b) and 2(b) correspond to $\delta=0$ and thus show the influence of crystal-field splitting on ΔC_{44} and ΔC_{456} , respectively. Figures 1(c) and 2(c) which correspond to degenerate three-band Kane model are obtained from Eqs. (8), (9a), (9b), and (20) for $\Delta=0.35$ eV and $m^* = 0.035 m_0$. Figures 1(d) and 2(d)

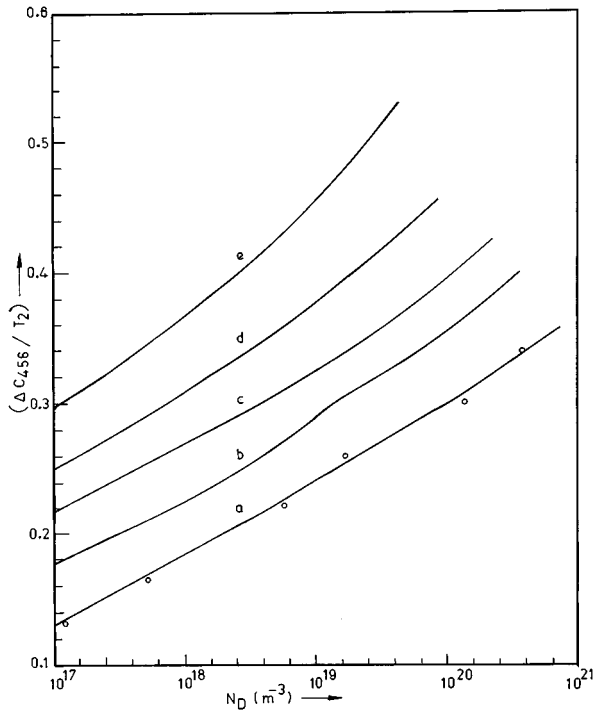


FIG. 2. Plot of the normalized ΔC_{456} vs N_D in n - Cd_3As_2 for all the cases in Fig. 1. The circular points have been obtained by using Eq. (19) and the experimental values of L_0 given in Ref. 1.

which correspond to the two-band Kane model are obtained from Eqs. (11), (12a), (12b), and (20). Similarly Figs. 1(e) and 2(e) which correspond to the wide-band gap model are obtained from Eqs. (13), (14), (15a), and (20). Figures 1 and 2 (circular points) are plotted by using the experimental results of L_0^1 and the Eqs. (18) and (19). The circular points in Figs. 1(a) and 2(a) show that our generalized model is in

TABLE I. Values of the materials parameters (after Refs. 6, 10–12) for (a) n - Cd_3As_2 , (b) InSb, (c) InAs, (d) GaAs, (e) $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, and (f) lattice matched $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ at $T=4.2$ K.

(a)
$E_g = 0.095$ eV, $\Delta_{11} = 0.24$ eV, $\Delta_{\perp} = 0.29$ eV, $m_{11}^* = 0.03m_0$, $\Delta_{\perp} = 0.06m_0$ $\delta = 0.085$ eV, $N_a = 5 \times 10^{14}$ m^{-3} , $E_d = 4.5$ meV, and $G_0 = 15$ eV for Cd_3As_2
(b)
$E_g = 0.24$ eV, $m^* = 0.0145m_0$, $\Delta = 0.9$ eV, $E_d = 3.4$ meV, $N_a = 5 \times 10^{14}$ m^{-3} , and $G_0 = 14$ eV for InSb
(c)
$E_g = 0.36$ eV, $m^* = 0.026m_0$, $\Delta = 0.43$ eV, $E_d = 4$ meV, $N_a = 3 \times 10^{14}$ m^{-3} , and $G_0 = 13$ eV for InAs
(d)
$E_g = 1.55$ eV, $m^* = 0.667m_0$, $\Delta = 0.35$ eV, $E_d = 4.2$ meV, $N_a = 4 \times 10^{14}$ m^{-3} , and $G_0 = 10$ eV for GaAs
(e)
$E_g = [-0.302 + 1.93x + 5.25 \times 10^4 T(1-2x) - 0.810x^2 + 0.83x^3]$ eV, $m^* = 3\hbar^2/4P^2$, $P^2 = (\hbar^2/2m_0)(18+3x)$, $\Delta = [0.63 + 0.24x - 0.27x^2]$ eV, $E_d = 5.7$ meV, $N_a = 4.3 \times 10^{14}$ m^{-3} , and $G_0 = 15$ eV for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$
(f)
$E_g = (1.337 - 0.73y + 13y^2)$ eV, $m^* = (0.080 - 0.039y)m_0$, $\Delta = (0.114$ $+ 0.26y - 0.22y^2)$ eV, $N_a = 10^{14}$ m^{-3} , $E_d = 6.1$ meV, $G_0 = 14$ eV and $y = (0.1896 - 0.4052x)(0.1896 + 0.123x)^{-1}$ for $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ lattice matched to InP.

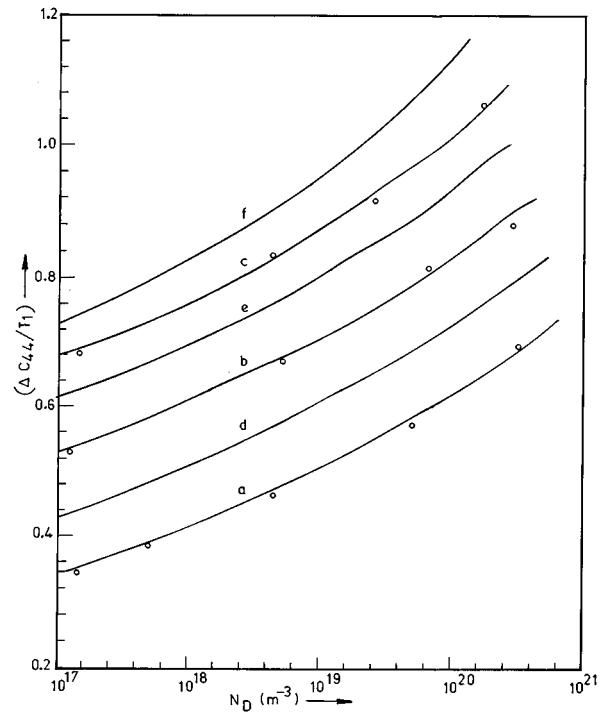


FIG. 3. Plot of the normalized ΔC_{44} vs N_D in n -InSb, InAs, and n -GaAs as shown by curves (a), (b), and (c) for the three-band Kane model, respectively. Plots (d), (e), and (f) exhibit the same dependences in accordance with the two-band Kane model. The circular points have been obtained by using Eq. (18) and the experimental values of L_0 given in Ref. 6.

close agreement with the suggested relationship. Thus the electron dispersion relation law given in Eq. (2a) accurately describes the band model for tetragonal compounds. Figure 1(a) shows that ΔC_{44} for tetragonal materials increases monotonically with increasing N_D . Further, it is observed that the values of ΔC_{44} for a given value of N_D are lowered when the effect of the crystal-field splitting parameter is taken into account in our generalized band model. The curves of Figs. 1(c), 1(d), and 1(e) which correspond to the three-band Kane model, two-band Kane model, and wide-band gap model, respectively, indicate clearly that the values of ΔC_{44} for tetragonal materials depend strongly on the band models. Figures 3(a)–3(c) show the plots of $(\Delta C_{44}/T_1)$ vs N_D for n -InSb, InAs, and n -GaAs, respectively, corresponding to the three-band Kane model. Figures 3(d)–3(f) show similar plots corresponding to the two-band Kane model. It is evident from Figs. 3(a), 3(f), 4(a), and 4(f), respectively, that the values of ΔC_{44} and ΔC_{456} are greater in accordance with the two-band Kane model for the whole range of N_D under consideration. Thus the spin-orbit splitting parameter (Δ) leads to a lowering of the values of ΔC_{44} for III–V materials. Although the three-band Kane model as given by Eq. (7) is an accurate model for III–V compounds, several authors have used the simplified two-band Kane model as given by Eq. (10) to study the electronic properties of these compounds under the inequalities $\Delta \gg E_g$ or $\Delta \ll E_g$. It is observed from Fig. 5 that ΔC_{44} decreases monotonically with increasing alloy composition x for both the ternary n - $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy and the quaternary lattice matched $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ alloy. The numerical values of ΔC_{44} in

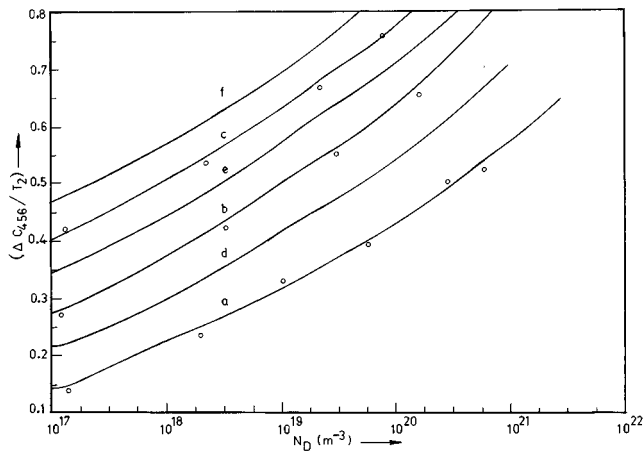


FIG. 4. Plots of the normalized ΔC_{456} vs N_D in n -InSb, n -InAs, and n -GaAs for all the cases in Fig. 3. The circular points have been obtained by using Eq. (19) and the experimental values of L_0 given in Ref. 6.

ternary alloys are greater than those in quaternary alloys for the whole range of alloy compositions under consideration. Our numerical computation is valid for $x > 0.17$ in case of the n - $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy system because the band gap of the alloy becomes negative for $x < 0.17$. It is further observed that the rate of increase of ΔC_{456} with N_D and the rate of decrease of ΔC_{456} with alloy composition are both slower (Figs. 2, 4, and 6) as compared to the corresponding rates of ΔC_{44} . This is because the differentiation of a monotonic increasing function decreases its curvature.

Our present analysis shows that the elastic constants ΔC_{44} and ΔC_{456} vary widely for different tetragonal and optoelectronic compounds which obey different electron dispersion laws. This may be verified experimentally in the following way. The magnitudes of ΔC_{44} and ΔC_{456} as functions of N_D can be determined experimentally from the

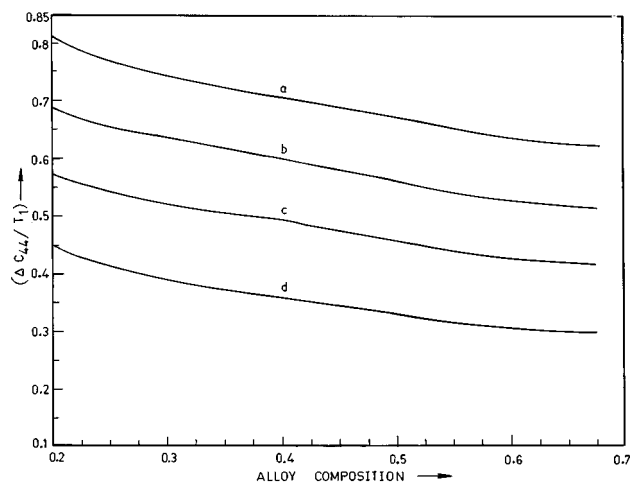


FIG. 5. Plots of the normalized ΔC_{44} as function of alloy composition in n - $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ lattice matched to InP in accordance with the three-band Kane model, shown by curves (a) and (b), respectively. Plots (c) and (d) exhibit the same dependences in accordance with two-band Kane model.

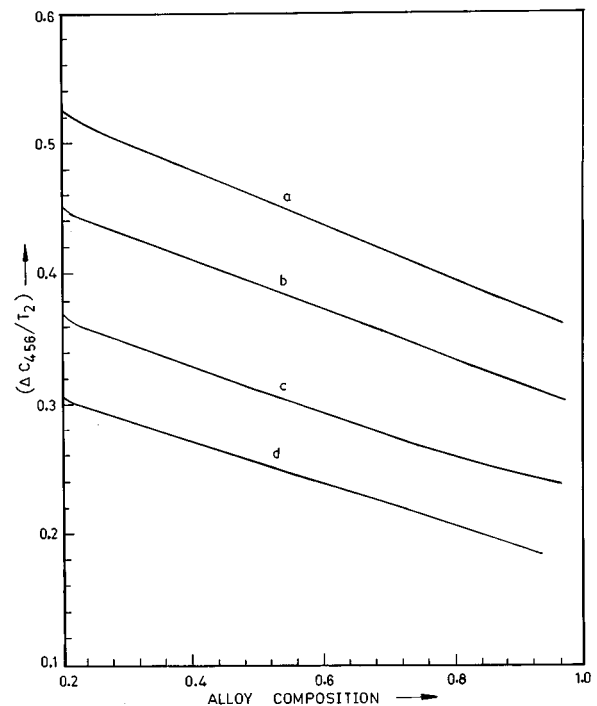


FIG. 6. Plots of the normalized ΔC_{456} as function of alloy composition in n - $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ lattice matched to InP for all the cases in Fig. 5.

velocity of sound which involves the shear mode as a function of N_D .

An important feature of the present work is that the influence of energy band models on ΔC_{44} and ΔC_{456} can be determined in various types of tetragonal and optoelectronic materials. Our simplified analysis can also be applied to different materials by using the appropriate sets of energy band parameters. The numerical values of ΔC_{44} and ΔC_{456} would be different for different nonparabolic materials, but the nature of the variations of ΔC_{44} and ΔC_{456} with N_D would be similar to those with alloy composition. Thus the analysis presented in this article exhibits the basic qualitative features of ΔC_{44} and ΔC_{456} for nonparabolic compounds. This theory can also be used to determine n_0 as a function of the Fermi energy and temperature which, in turn, determines various transport coefficients of compound semiconductors.

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