PHYSICAL REVIEW B VOLUME 39, NUMBER 1 1 JANUARY 1989

Structural phase transition and high-pressure elastic behavior of III-V semiconductors

R. K. Singh and Sadhna Singh
School of Physics, Bhopal University, Bhopal 462 026, India
and Centre for Science and Technology Development Studies, Bhopal 462 016, India

(Received 19 April 1988)

We have expressed the Gibbs free energy for III-V compound semiconductors as a function of pressure and charge transfer through three-body interactions. The lattice energy in it has been represented by a three-body potential consisting of the long-range Coulomb and three-body interactions, and the short-range van der Waals attraction and overlap repulsion, effective up to the second-neighbor ions. We have depicted the phase diagrams and found that the abrupt volume collapses at the phase-transition pressures agree fairly well with the observed data. The phase-transition pressures (17.0, 4.0, 17.1, 18.0, 1.0, and 11.0 GPa) obtained by us are in close agreement with the experimental data (18.5, 6.7, 22.0, 8.4, 2.2, and 10.8 GPa) for almost all the semiconductors (GaAs, GaSb, GaP, InAs, InSb, and InP) under consideration. The elastic stiffness constants (C_{11}) have been found to increase with pressure while the shear moduli $(C_{11}-C_{12})/2$ and C_{44} decrease with it, and this feature is consistent with the experimental observations.

I. INTRODUCTION

Recent progress in refinements in the diamond anvil technique[1-3] has led to increased interest in the study of the high-pressure behavior of materials. These studies have revealed that the materials often exhibit new and interesting phase transitions and novel elastic behavior under pressure. In recent years, the tetrahedrally coordinated $A^{N}B^{8-N}$ compounds have been found to undergo semiconductor (zincblende)–ionic(NaCl)–metallic(β-Sn) phase transitions at elevated pressures.[1-12] A survey of literature has revealed that theoretical predictions of the phase-transition pressure in III-V semiconductors have been satisfactorily done by means of the pseudopotential total energy[4-6] (PTE) and valence force field[7,8] (VFF) approaches. The latter approach has been used by Miller *et al.*[7,8] for predicting the phase-transition and anharmonic properties of HgTe (Ref. 7) and HgSe.[8] Using the PTE approach, Froyen and Cohen[4] have computed the structural properties of AlP, AlAs, GaP, and GaAs and excluded the compounds with heavier elements, like In and Sb for which they felt the necessity of the relativistic corrections.[6] According to Zhang and Cohen,[6] although the PTE approach has given impressive agreement between theory and experiment for the group IV elements, it has revealed notable discrepancies[4] for these four III-V semiconductors. Later on, Chelikowsky[5] and Zhang and Cohen[6] (ZC) have applied PTE method to compute the phase-transition pressures for all the III-V compound semiconductors. The agreements in transition pressures between pseudopotential theory and experiments obtained by Zhang and Cohen[6] are very good for some of the heavier compounds and experimentally well determined high-pressure structures. The pseudopotential theory employed by Chelikowsky[5] has also satisfactorily predicted the observed pressures for phase-transitions from zincblende-rocksalt-metallic (β-Sn) structures. However, both the authors[5,6] have concluded that rocksalt structure is preferred as the ionicity (or charge transfer) is increased in materials.

Motivated from this remark[6,7] and the versatility of three-body potential (TBP) approach of Singh and coworkers[13,14] for the successful description of the phase-transition and high-pressure behavior of alkali halides and divalent metal oxides, we thought it pertinent to express the well-known Gibbs free energy ($G=U+PV-TS$) as a function of the pressure and charge transfer through three-body interactions at 0 K. For this purpose, we have represented the lattice energy (U) by a three-body potential energy.[14]

It has been found that the agreements between the experimental and our theoretical results on the phase-transition pressures for III-V semiconductors are reasonably good and comparable with those obtained by other theoretical workers.[5,6] Besides, we have calculated their pressure induced percentage volume collapses $[\Delta V(P_t)/V(0)]$ which have shown considerable agreement with their available experimental data.[2,6]

As the study of elastic behavior under pressure is well known to provide useful information about changes in the nature of the covalent and ionic forces induced in the crystal as it is subjected to the phase-transformation, we, therefore, have calculated the pressure variations of the combinations of the second-order elastic constants C_{11}, C_{44}, $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$, and $\frac{1}{2}(C_{11}-C_{12})$. These variations have followed systematic trends identical to those as revealed by the experiments in the cases of HgTe (Ref. 7) and HgSe.[8] Our results on the ratio of shear to bulk (B_t) moduli at the phase-transition pressure have been found to satisfy the modified Born stability criterion[7-9] for III-V semiconductors.

The essentials of the present theory are given in Sec. II. The methods of computations for the results on phase-transition and anharmonic properties are presented in Sec. III. The discussions along with the conclusion are given in Sec. IV.

TABLE I. Values of the *vdW* coefficients of III-V semiconductors (c_{ij} in units of 10^{-79} J m^6 and d_{ij} in units of 10^{-99} J m^8).

Solid	c_{+-}	c_{++}	c_{--}	d_{+-}	d_{++}	d_{--}	C	D
GaAs	214	49	1193	183	16	1062	1403	882
GaSb	315	54	2345	221	18	2133	2284	1175
GaP	163	48	749	124	15	741	1014	603
InAs	671	401	1208	490	205	1077	3565	2160
InSb	956	431	2286	748	227	2067	5200	3341
InP	494	372	721	387	189	704	2569	1690

II. ESSENTIAL THEORY

It is well known that the stability of a particular lattice structure is achieved at the minimum value for the Gibbs free energy ($G=U+PV-TS$). Here, U is the internal energy which at 0 K is equivalent to lattice energy. S is the vibrational entropy at absolute temperature T. At 0 K and pressure P, the Gibbs free energy is given by

$$G_{B3}(r)=U_{B3}(r)+3.08r^3P \tag{1}$$

for the zinc-blende ($B3$, real) structure and

$$G_{B1}(r')=U_{B1}(r')2r'^3P \tag{2}$$

for the rocksalt ($B1$, hypothetical) structure. Here, the abbreviations $U_{B3}(r)$ and $U_{B1}(r')$ stand for the ZB and RS lattice energies considered to consist of the long-range Coulomb and three-body interactions[15] and the short-range van der Waals[14] and overlap repulsion effective up to the second-neighbor ions. Their relevant expressions are given by

$$\begin{aligned}U_{B3}(r)=&-\frac{\alpha_m e^2Z^2}{r}-\frac{4\alpha_m e^2Zf(r)}{r}-\frac{C}{r^6}-\frac{D}{r^8}\\&+4\beta_{ij}b\exp[(r_j+r_j-r)/\rho]\\&+6\beta_{ii}b\exp[(2r_i-r)/\rho]\\&+6\beta_{jj}b\exp[(2r_j-r)/\rho]\ ,\end{aligned} \tag{3}$$

$$\begin{aligned}U_{B1}(r')=&-\frac{\alpha'_m e^2Z^2}{r'}-\frac{6\alpha'_m e^2Zf(r')}{r'}-\frac{C'}{r'^6}-\frac{D'}{r'^8}\\&+6\beta_{ij}b\exp[(r_i+r_j-r')/\rho]\\&+6\beta_{ii}b\exp[(2r_i-r')/\rho]\\&+6\beta_{jj}b\exp[(2r_j-r')/\rho]\ ,\end{aligned} \tag{4}$$

with α_m and α'_m as the Madelung constants for ZB and RS structures, respectively. $C(C')$ and $D(D')$ are the overall van der Waals coefficients of $B3(B1)$ phases. β_{ij} $(i,j,=1,2)$ are the Pauling coefficients. Ze is the ionic charge, $b(\rho)$ are the range (hardness) parameters. $r(r')$ are the nearest-neighbor separations for $ZB(RS)$ structures. $f(r)$ is the three-body force parameter.[15] $r_i(r_j)$ are the ionic radii of ions $i(j)$.

III. COMPUTATIONS AND RESULTS

The model potential TBP described above for the $ZB(B3)$ and $RS(B1)$ phases contains three model parameters, namely the range, hardness, and three-body-force parameters $[b,\rho,f(r)]$. Their values have been determined by using the expressions for any two of the following elastic constants:[16]

$$C_{11}=(e^2/4a^4)\{0.2477Z[Z+8f(r)]+(A_1+2B_1)/3+(A_2+B_2)/2+5.8243af'(r)\}\ , \tag{5}$$

$$C_{12}=(e^2/4a^4)\{-2.6458Z[Z+8f(r)]+(A_1+4B_1)/3+(A_2-5B_2)/4+5.8243af'(r)\}\ , \tag{6}$$

$$C_{44}=(e^2/4a^4)\left[-0.123Z[Z+8f(r)]+(A_1+2B_1)/3+(A_2+3B_2)/4-\frac{1}{\nabla}\{-7.539\,12Z[Z+8f(r)]\}+(A_1-B_1)\right]\ , \tag{7}$$

TABLE II. Input data for III-V semiconductors. The elastic constants (C_{ij}) are in units of 10^{10} nm^{-2}.

Solids	a (10^{-1} nm)	r_i (10^{-1} nm)	r_j (10^{-1} nm)	C_{11}	C_{12}	C_{44}
GaAs	2.825	1.26	1.18	11.81	5.23	5.92
GaSb	3.060	1.26	1.36	8.84	4.03	4.32
GaP	2.725	1.26	1.10	14.12	6.25	7.05
InAs	3.020	1.44	1.18	8.53	4.53	3.96
InSb	3.240	1.44	1.36	6.67	3.65	3.02
InP	2.930	1.44	1.10	10.22	5.76	4.60

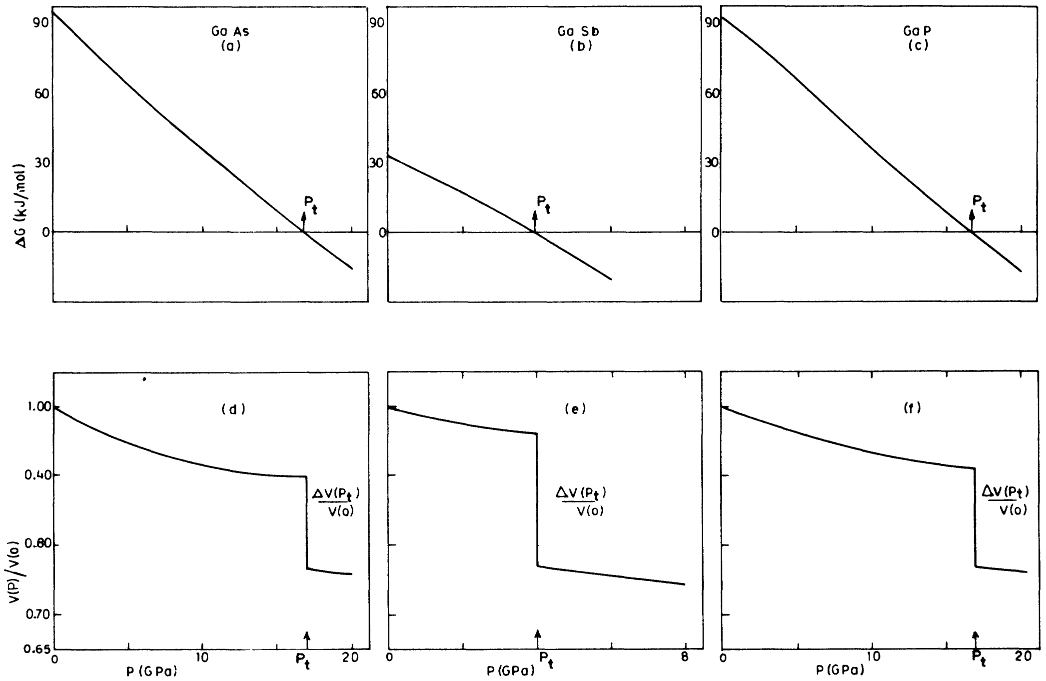

FIG. 1. The variation of Gibbs free energy difference (ΔG) with pressure (P) for GaAs, GaSb, and GaP, respectively, shown in (a), (b), and (c). The phase diagrams of GaAs, GaSb, and GaP, respectively, shown in (d), (e), and (f).

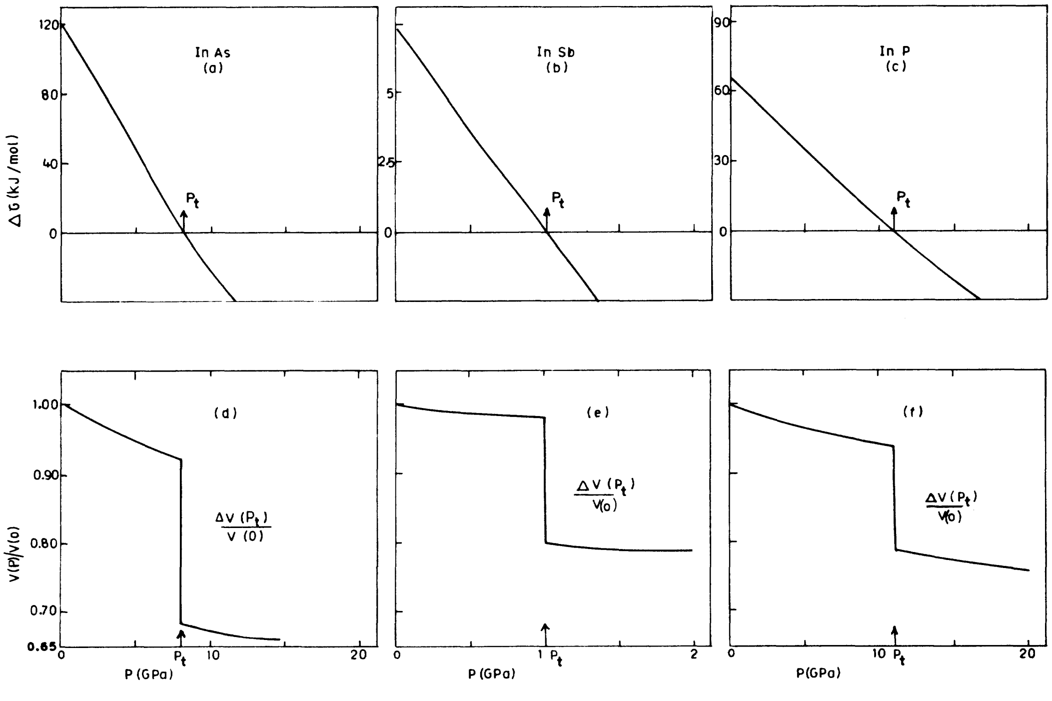

FIG. 2. The variation of Gibbs free energy difference (ΔG) with pressure (P) for InAs, InSb, and InP, respectively, shown in (a), (b), and (c). The phase diagrams of InAs, InSb, and InP, respectively, shown in (d), (e), and (f).

TABLE III. Model parameters of III-V semiconductors.

Solids	ρ (10^{-1} nm)	b (10^{-19} J)	$f(r)$
GaAs	0.365	2.07	−0.22
GaSb	0.357	1.80	−0.22
GaP	0.352	1.94	−0.23
InAs	0.386	1.39	−0.24
InSb	0.389	1.83	−0.24
InP	0.338	1.01	−0.26

and the equilibrium condition

$$B_1+B_2=-1.261Z[Z+8f(r)]\ , \tag{8}$$

where the abbreviation ∇ stands for

$$\nabla=\frac{-7.539.12Z[Z+8f(r)]+A_1-B_1}{-3.141Z[Z+8f(r)]+A_1+2B_1+21.765Zaf'(r)} \tag{9}$$

The values of the *vdW* coefficients (c_{ij},d_{ij}) due to dipole-dipole and dipole-quadrupole interactions required for these calculations have been evaluated by us using the Slater-Kirkwood variational (SKV) approach[16,17] and reported in Table I. The value of other input data listed in Table II have been used to compute the values of the model parameters $(b,\rho,f(r))$ reported in Table III. Their values have been used to compute the following for III-V semiconductors.

In order to obtain the structural phase-transition pressures, we have minimized the lattice energy given by Eqs. (3) and (4) for the equilibrium interionic spacings (r) and (r') corresponding to *ZB* and *RS* phases. The values of $r(r')$ together with the cohesive energies U_{B3} and U_{B1} and their differences $\Delta U(=U_{B3}-U_{B1})$ are listed in Table IV. The corresponding Gibbs free energy differences $\Delta G(=G_{B1}-G_{B3})$ have been obtained at different pressures (P) from Eqs. (1) and (2) using the method prescribed by Cohen and Gondon[19] and Jog *et al.*[14] These differences (ΔG) have been plotted against the pressure (P) as shown in Figs. 1 and 2 [(a) to (c)] for III-V semiconductors (GaAs, GaSb, GaP, InAs, InSb, and InP). The pressure at which ΔG approaches zero corresponds to the phase-transition pressures (P_t) as indicated by the arrows in these figures. The phase-transition pressure (P_t) obtained from Figs. 1 and 2 are listed in Table V and compared with their experimental values.[20-23]

Besides, the values of the relative volume changes $[\Delta V(P_t)/V(0)]$ associated with various compressions have been obtained and plotted to depict the phase diagrams in Figs. 1(d)–1(f) and 2(d)–2(f) for III-V semiconductors. The values of the combinations of the elastic stiffness constants C_{11}, C_{44}, $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$, and $\frac{1}{2}(C_{11}-C_{12})$ have been calculated from Eqs. (5)–(7) and plotted against the pressures (P) as shown in Figs. 3 and 4.

In order to test the modified Born-stability criterion,[7,23] we have calculated the dimensionless ratios (C_{44}/B_t) and $(C_{11}-C_{12})/2B_t$ of shear to bulk (B_t) moduli corresponding to the phase-transition pressures (P_t) for III-V semiconductors, and reported them in Table VI.

IV. DISCUSSION AND CONCLUSION

It is seen from Table IV that our TBP model has correctly predicted the relative stability of competitive structures as the values of $\Delta U(=U_{B1}-U_{B3})$ are positive (which is a required criterion[24]) in all the cases. Also, the values of equilibrium interionic separations (r) obtained by us from the minimization technique are closer to their experimental data.[18]

A look at Figs. 1 and 2 and Table V shows that there is a reasonably good agreement between the experimental and our theoretical results obtained from three-body potential approach.[14] Also, these agreements are comparable with those obtained by Chelikowsky[5] and Zhang and Cohen[6] from the first-principle pseudopotential total energy method. The success achieved in the present investigation can be ascribed to the inclusion of the charge transfer (or three-body) effects as envisaged earlier by Chelikowsky.[5]

The phase diagrams depicted in Figs. 1(d)–1(f) and 2(d)–2(f) have followed the trends similar to those revealed by experimental observations.[2] It is seen from these figures that the phase transitions from zinc blende to rocksalt structure are accompanied by the volume collapse in III-V semiconductors. The values of these volume collapses $[\Delta V(P_t)/V(0)]$ at the phase-transition pressures (P_t) listed in Table V are found to agree almost

TABLE IV. Cohesive properties and relative stability of III-V semiconductors.

Solids	Equilibrium separation (10^{-1} nm)[a] $r(B3)$	 $r'(B1)$	Cohesive energy U_{B3}	(kJ/mol) U_{B1}	ΔU(kJ/mol) $(U_{B1}-U_{B3})$
GaAs	2.777(2.447)	3.028	6555	6459	96
GaSb	3.041(2.650)	3.265	6056	6023	33
GaP	2.692(2.360)	2.917	6757	6660	97
InAs	3.058(2.615)	3.148	5957	5833	124
InSb	3.200(2.806)	3.441	5735	5729	6
InP	2.884(2.537)	3.132	6396	6329	67

[a] The values enclosed within parentheses correspond to their experimental values as reported by Singh (Ref. 18).

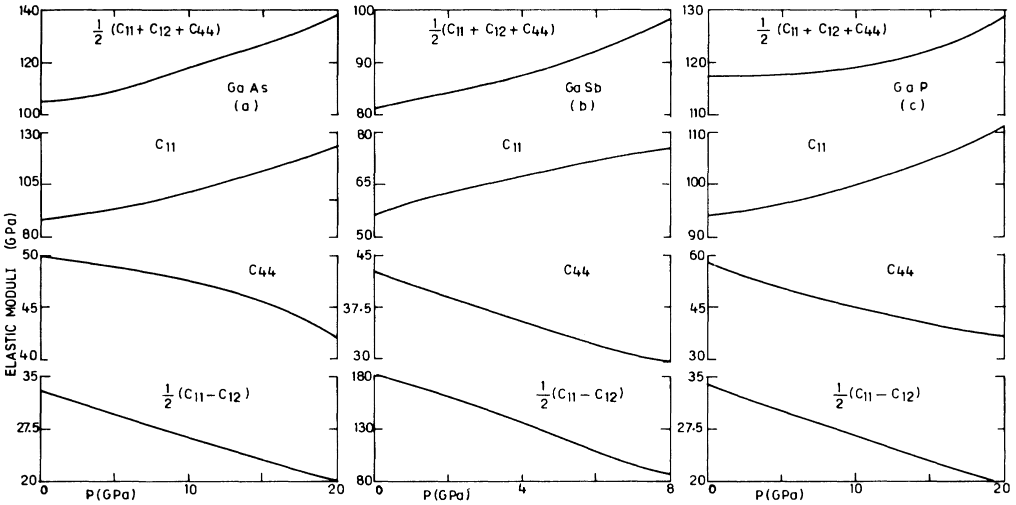

FIG. 3. The variation of the combinations of the second-order elastic constants for GaAs, GaSb, and GaP, respectively, shown in (a), (b), and (c).

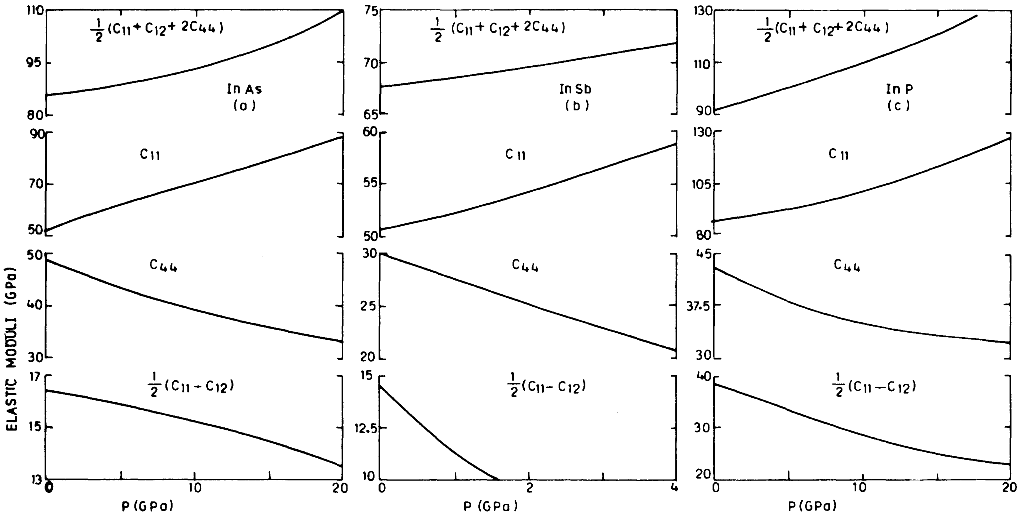

FIG. 4. The variation of the combinations of the second-order elastic constants for InAs, InSb, and InP, respectively, shown in (a), (b), and (c).

TABLE V. Phase-transition pressure (P_t) (GPa) and transition pressure volume collapse [$\Delta V(P_t)/V(0)$] for III-V semiconductors.

	P_t				$\Delta V(P_t)/V(0)$	
Solids	Expt.	Present theor.	Other theor.[i,j]	Expt.[j,f]	Present theor.	Other theor.[j]
GaAs	16–19[a–d]	17.0	26.7(16.0)		14	17
GaSb	6.2–8.4[a–c]	4.0	43.6(–)(–)		18	
GaP	22.0[a]	17.1	10.1(21.7)		14	16
InAs	7–8.4[c,f–h]	8.0	9.3(8.4)	19(17)	24	17
InSb	2.25[a]	1.0	11.7(–)(–)		19	
InP	10.5–11[e,h]	11.0	14.1(12.8)	19(–)	15	17

[a] Reference 7.
[b] Reference 10.
[c] Reference 20.
[d] Reference 3.
[e] Reference 21.
[f] Reference 2.
[g] Reference 22.
[h] Reference 9.
[i] Reference 5.
[j] Reference 6.

TABLE VI. Dimensionless ratios of shear to bulk moduli at the phase-transition pressure (p_t) for III-V semiconductors.

Solids	$(C_{11}-C_{12})/2B_t$	C_{44}/B_t
GaAs	0.29	0.58
GaSb	0.26	0.68
GaP	0.26	0.49
InAs	0.28	0.62
InSb	0.26	0.70
InP	0.29	0.48

well with their available experimental[2,6] and other theoretical[6] results.

In order to study the high-pressure elastic behavior of these semiconductors, we have calculated the pressure variations of the combinations of the second-order elastic constants C_{11}, C_{44}, $\frac{1}{2}(C_1+C_{12}+2C_{44})$, and $\frac{1}{2}(C_{11}-C_{12})$ and depicted them in Figs. 3 and 4. It is noted that both the shear moduli $\frac{1}{2}(C_{11}-C_{12})$ and C_{44} decrease linearly with the increase of pressure but neither of them tend to zero at the phase-transition pressures. This feature is in accordance with the first-order character of the transition and is similar to that observed by Miller *et al.* in the cases of HgTe (Ref. 7) and HgSe.[8] On the contrary, the values of C_{11} and $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ increase linearly with pressure and this feature resembles that observed in HgTe (Ref. 7) and HgSe.[8] The pressure induced decreases in C_{44} and $\frac{1}{2}(C_{11}-C_{12})$ show that the resistance of III-V semiconductors to any shear reduces as the phase transition is approached in them.

It is obvious from Table VI that the present values of the ratios of shear to bulk moduli, C_{44}/B_t and $(C_{11}-C_{12})/2B_t$, at the phase-transition pressure (P_t), have their values, respectively, around 0.5 and 0.2, which are identical to those obtained by others[7–9,23] and required to satisfy the modified Born-stability criterion[7,23] in several zinc blende structure semiconductors.

It is thus obvious from the overall achievements that the present three-body force model potential is adequately suitable for describing the relative stability, the phase-transition, and the high-pressure elastic properties of III-V compound semiconductors. This model has promise for such successful descriptions in the cases of II-VI compound semiconductors.

ACKNOWLEDGMENT

The authors are thankful to the Madhya Pradesh Council of Science and Technology (MAPCOST) for financial support.

---

[1] S. Schilling and R. N. Shelton, *Physics of Solids Under Pressure* (North-Holland, New York, 1981); A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. **30**, 2277 (1963).

[2] Y. K. Vohra, S. T. Weir, and A. L. Ruoff, Phys. Rev. B **31**, 7344 (1985).

[3] A. L. Ruoff and M. A. Baublitz, J. Appl. Phys. **53**, 6179 (1982).

[4] S. Froyen and M. L. Cohen, Phys. Rev. B **28**, 3258 (1983).

[5] J. R. Chelikowsky, Phys. Rev. B **35**, 1174 (1987).

[6] S. B. Zhang and M. L. Cohen, Phys. Rev. B **35**, 7604 (1987).

[7] A. J. Miller, G. A. Saunders, and Y. K. Yogurtcu, Philos. Mag. A **43**, 1447 (1981); J. Phys. Chem. Solids **42**, 49 (1981).

[8] P. J. Ford, A. J. Miller, G. A. Saunders, Y. K. Yogurtcu, J. R. Furdyna, and M. Jaczynski, J. Phys. C **15**, 657 (1982).

[9] D. S. Rimai and D. J. Sladek, Solid State Commun. **30**, 591 (1979).

[10] S. C. Yu, I. L. Spain, and E. F. Skelton, Solid State Commun. **25**, 49 (1978).

[11] C. Hrionak, Phase Transitions **8**, 1 (1986).

[12] R. M. Martin, Phys. Rev. B **1**, 4005 (1970).

[13] R. K. Singh, K. N. Jog, and S. P. Sanyal, Phys. Rev. B **31**, 6047 (1985).

[14] K. N. Jog, R. K. Singh, and S. P. Sanyal, Phys. Rev. B **35**, 5235 (1987).

[15] R. K. Singh, Phys. Rep. (Netherlands) **85**, 259 (1982).

[16] R. K. Singh and Sadhna Singh, Phys. Status Solidi B **140**, 407 (1987).

[17] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1937).

[18] R. K. Singh and R. D. Singh, Phys. Status Solidi B **114**, 235 (1982).

[19] A. J. Cohen and M. L. Gordon, Phys. Rev. B **14**, 4593 (1976).

[20] B. A. Weinstein (unpublished).

[21] S. Minomura and H. G. Drickamer, J. Phys. Chem. Solids **23**, 451 (1962).

[22] I. L. Spain, J. Z. Hu, C. S. Menoni, and D. Block, J. Phys. (Paris), Colloq. **8**, C-407 (1984).

[23] H. H. Demarest, R. Ota, and O. L. Anderson, in *High Pressure Research Applications in Geophysics,* edited by M. H. Manghnani and S. I. Akimoto (Academic, New York, 1977), p. 281.

[24] M. J. L. Sangster, U. Schroder, and R. M. Atwood, J. Phys. C **11**, 1523 (1978).