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Lattice dynamical theory of thermal expansion and mode Grüneisen parameters in cubic BP

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Lattice dynamical theory of thermal expansion and mode Grüneisen parameters in cubic boron monophosphide is reported in the *quasiharmonic* approximation within the framework of a second-neighbor rigid-ion model. In this scheme, we optimized the involved force constants by using nonlinear least-squares procedures with constrained parameters and weighting of the available data on critical-point phonons and elastic and lattice constants. Theoretical results of the phonon dispersion curves along high-symmetry directions (both at ambient and 89 kbar pressures), mode Grüneisen parameters, and thermal expansion coefficient $\{\alpha(T)\}$ are compared and discussed with the existing experimental and *ab initio* calculations. Consistent with x-ray data, our calcualtion for the variation of $\alpha(T)$ with temperature in BP is found to be remarkably similar to that of β-SiC, and unlike most other III-V-compounds, it does not attain negative values at lower temperatures. [S0163-1829(97)03118-4]

I. INTRODUCTION

Technological interest in boron monophosphide (BP) has been stimulated in recent years by its potential use in optoelectronic and microelectronics devices working in extreme conditions.[1–5] The material BP exhibits both physical and chemical properties that differ significantly from the general trends of the III-V family. The factors that make BP attractive for device applications include its wide band gap, strong covalent bonding, high melting point, high Debye temperature, high thermoelectric power, high thermal conductivity, and strong mechanical strength with Knoop hardness of $4700\,\mathrm{kp\,mm}^{-2}$. Despite all these important features, very little experimental information was known, until recently, about its electronic and vibrational characteristics. The primary reason for this was the extreme difficulty of preparing sufficiently large BP crystals, which was due to its high melting point ($>3000\,°\mathrm{C}$) and high decomposition pressures ($\sim 10^5$ atm at $2500\,°\mathrm{C}$). The material-handling processes were equally complicated due to the refractory hardness and brittleness of BP.

The progress made in crystal growth techniques in recent years has, however, expedited the experimental studies. This has resulted in a considerable amount of data on the elastic,[6] vibrational,[7] structural,[8] and thermal properties[9,10] of cubic BP. Earlier, Suzuki *et al.*[11] reported high-pressure *in situ* x-ray diffraction studies using a diamond anvil cell, which resulted in experimental values for the volume compression, isothermal bulk modulus B_T $(=267\,\mathrm{GPa})$, and its pressure derivative B_T' $(=3.15)$. Elastic constant measurements[6] by Brillouin scattering have, however, suggested different values for the bulk modulus B_T $(=173\,\mathrm{GPa})$. In the absence of neutron scattering data of phonon dispersions, Raman scattering spectroscopy is regarded as a powerful tool for studying solid-state excitations in the energy range 0–0.4 eV. Pressure can cause large changes in the energies and interactions of these excitations within a given solid phase, and/or it can cause transitions to new phases having quite different excitation spectra. The effects of compression on the entire phonon dispersions in semiconductors has been studied through a combination of *one*- and *two*-phonon Raman measurements. In BP, however, Sanjurjo *et al.*[7] have reported vibrational properties (both at ambient and high pressures up to 89 kbar) by using *first*-order Raman scattering spectroscopy and derived valuable data for long-wavelength optical phonons $\{{}^{\omega}\mathrm{LO}(\Gamma),{}^{\omega}\mathrm{TO}(\Gamma)\}$ and mode Grüneisen $\{{}^{\gamma}\mathrm{LO}(\Gamma),{}^{\gamma}\mathrm{TO}(\Gamma)\}$ parameters. The *second*-order Raman spectrum, which arises from the scattering by two phonons with opposite wave vectors, predominantly near the Brillouin zone boundaries, was not attempted. Earlier, Slack and Bartram[10] measured the thermal expansion coefficient $\alpha(T)$ as a function of temperature using x-ray technique and suggested that at low temperatures the variation of $\alpha(T)$ in BP is different from most other III-V compounds, but is remarkably similar to that of β-SiC. Our recent study in β-SiC (Ref. 12) for the variation of $\alpha(T)$ with temperature has exhibited a behavior much like that of the variation of the specific heat with temperature. Moreover, we found that unlike most other tetrahedrally coordinated materials, $\alpha(T)$ in β-SiC does not attain a negative value at lower temperatures.

In spite of numerous experimental efforts, the amount of theoretical understanding for the electronic properties has been limited to a handful of studies[13–18] and, in particular, the knowledge of the vibrational and thermal properties of BP are rather scarce.[19] By using the norm-conserving pseudopotentials and plane wave expansions within density functional theory, Alves and Kunc[19] reported calculations for the phonon frequencies and Grüneisen parameters γ's at critical points in BP. To the best of our knowledge, there exists no theoretical study in BP that deals with the variation of the thermal expansion coefficient $\alpha(T)$ or Grüneisen parameter $\gamma(T)$ with temperature. Such a model calculation is of practical importance as we need this information to determinine the match or mismatch of dimensions in semiconductor materials and substrates cycled over large temperature ranges.

Two theoretical methodologies have been commonly used in the literature to treat the temperature- or pressure-dependent phonon properties in semiconductors. The first method relies on the phenomenological lattice dynamical models,[20] and the other technique uses the microscopic theory of lattice dynamics based on the electronic properties of solids.[21] In the latter approach, the total energy is generally evaluated for the atomic configuration in static equilibrium and for the configuration distorted by a given eigenvector. By using the ''frozen-phonon'' method, one can calculate the phonon frequencies, eigenvectors, and Grüneisen parameters γ's for different modes of vibrations at high-symmetry points in the Brillouin zone. Unfortunately, the microscopic approach, except for Si,[21] has not been used to study the variation of $\alpha(T)$ or $\gamma(T)$ with temperature in compound semiconductors. On the other hand, we have recently treated the pressure-dependent phonon properties in several compound semiconductors including β-SiC (Ref. 12) by using a phenomenological lattice dynamical scheme based on a second-neighbor rigid-ion model.[22] Theoretical values of $\alpha(T)$ are found to be in good agreement with the experimental data.

In this paper, we have reaffirmed the reliability of our rigid-ion model and reported the results of a comprehensive lattice dynamical study for the variation of $\alpha(T)$ with temperature in BP. Based upon the previous successes of such calculations for related materials,[20] we believe that our results present an attempt to supply the missing information about the phonon dispersions, density of phonon states, and mode Grüneisen parameters. Comparing theoretical and experimental data[10] for the thermal expansion coefficient of BP and β-SiC with other III-V compounds has allowed us to attain some useful insight into the different relative strengths of the bond-bending and bond-stretching forces that affect the phonon-mode behavior and consequently the vibrational properties.

In Sec. II, we give a brief account of the lattice dynamical theory for the thermal expansion in solids. For BP, we present our results of the phonon dispersions, mode Grüneisen parameters, and linear thermal expansion coefficient in Sec III, and compare them with the existing experimental and theoretical data. The results with some criticism are discussed in Sec. IV with concluding remarks presented in Sec. V.

II. THEORETICAL BACKGROUND

A. Thermal expansion and Grüneisen constant

One of the most intriguing properties observed[23] in tetrahedrally bonded solids is the negative thermal expansion coefficient $\alpha(T)$ at low temperatures (i.e., $T \leqslant 0.07\Theta_0$), where Θ_0 is the limiting value of the Debye characteristics temperature as $T \to 0$. For the nth mode in a crystal under compression, the Grüneisen parameter γ_n is a dimensionless quantity relating the volume dilation to the consequent fractional change in the phonon frequency. As the phonon frequency of the excited lattice modes ω_n goes to zero in the low-temperature limit $(T \to 0)$, the variation of the individual frequencies with volume, $\gamma_n = -d \ln\omega_n / d \ln V$, can be related to the volume dependences of the corresponding elastic constants c_n through the relationship[23]

$$\gamma_n = -\frac{1}{6} - \frac{1}{2}\frac{d \ln c_n}{d \ln V}. \tag{1}$$

The zero-temperature limit γ_0^{el} of the average $\gamma = \Sigma C_n \gamma_n / \Sigma C_n$, in which the individual γ_n are weighted by the heat capacity C_n contribution of the mode, should be equal to the value of γ_0^{th} determined from the experimental data of α as $T \to 0$:

$$\gamma^{\mathrm{th}} = \frac{3\alpha B_T V}{C_V}, \tag{2}$$

where V and C_V are the crystal volume and the specific heat at constant volume, respectively.

Earlier, the elastic continuum models and their various ramifications were used in the literature to account for the temperature dependence of γ in solids.[23] While such approaches provided fair descriptions of $\gamma(T)$ in metals and ionic compounds, they failed, however, to reproduce the observed deep minima in $\gamma(T)$ near $T \sim 0.05\Theta_0$, which seems to be a characteristic of the tetrahedrally bonded materials. For most solids, the continuum models also yielded reasonable values of γ_∞ (the high-temperature limit) for which all the lattice modes are excited and contribute with equal weighting. The agreement in these calculations is, however, spurious[24,25] and depends upon the fortuitous cancellation of the temperature-dependent contributions that arise from the wave vector dependence of γ_n and the excitation of optical modes, both of which are neglected in the elastic continuum models. Here we have adopted an alternative method for studying the temperature dependence of Grüneisen constant $\gamma(T)$ or $\alpha(T)$ in BP. This technique is based on a comprehensive description of the realistic lattice dynamical models and is quite different from the one offered by the continuum approximation.

In the *quasiharmonic* approximation, we treat the lattice vibrations as harmonic, but with assumed volume- and pressure-dependent frequencies. In this approximation the Helmholtz free energy of a crystal at given volume V and temperature T is given by[12]

$$\Phi(V,T) = \Phi_0(V) + \Phi_{\mathrm{vib}}(V,T), \tag{3}$$

where the $T=0$ internal energy $\Phi_0(V)$ is temperature independent. The vibrational contribution to Φ is given by

$$\Phi_{\mathrm{vib}}(V,T) = \frac{1}{2}\sum_{n\mathbf{q}} \hbar\omega_n(\mathbf{q}) + k_B T \sum_{n\mathbf{q}} \ln[1 - \exp\{-\hbar\omega_n(\mathbf{q})/k_B T\}]. \tag{4}$$

From the equilibrium condition $\partial\Phi/\partial V|_T = 0$, we obtain that at zero pressure the volume is given by

$$V(T) = V_0 + \frac{1}{2B_T}\sum_{n\mathbf{q}} \hbar\omega_n(\mathbf{q})\gamma_n(\mathbf{q})\coth[\hbar\omega_n(\mathbf{q})/2k_B T], \tag{5}$$

where the Grüneisen parameter of the $n,\mathbf{q}$ mode is

$$\gamma_n(\mathbf{q}) = -\left.\frac{\partial \ln\omega_n(\mathbf{q})}{\partial \ln V}\right|_{V_0} = \frac{1}{\chi_T}\frac{1}{\omega_n(\mathbf{q})}\frac{\partial\omega_n(\mathbf{q})}{\partial p}. \tag{6}$$

The term

$$\chi_T\left\{=\frac{1}{B_T}=-\frac{1}{V}\frac{\partial V}{\partial p}\bigg|_T\right\}$$

in Eq. (6) is the isothermal compressibility. The entropy of the vibrating lattice S_{vib} follows from the free energy described as $S_{\mathrm{vib}}=-\partial\Phi_{\mathrm{vib}}/\partial T|_V$. Its knowledge allows one to calculate the internal energy of the crystal by using the relation $U_{\mathrm{vib}}=\Phi_{\mathrm{vib}}+S_{\mathrm{vib}}T$. Apart from extremely low temperatures, the internal energy of the lattice also defines the heat capacity at constant volume of the crystal by $C_V(T)=-\partial U_{\mathrm{vib}}/\partial T|_V$. From Eq. (4) one can obtain $C_V(T)$ by using

$$C_V(T)=\sum_{n\mathbf{q}} k_B\left[\frac{\hbar\omega_n(\mathbf{q})}{k_BT}\right]^2\frac{\exp\{\hbar\omega_n(\mathbf{q})/k_BT\}}{[\exp\{\hbar\omega_n(\mathbf{q})/k_BT\}-1]^2}. \tag{7}$$

In terms of the linear thermal expansion coefficient $\alpha(T)$, the well-known thermodynamical relation for the average Grüneisen constant is defined as

$$\alpha(T)=\frac{1}{3B_TV}\sum_{n\mathbf{q}}\gamma_n(\mathbf{q})C_{Vn}(\mathbf{q},T), \tag{8}$$

where $C_{Vn}(\mathbf{q},T)$ are the contributions of the modes $\omega_n(\mathbf{q})$ to the specific heat. Once the mode Grüneisen parameters are known [cf. Eq. (6)] for the wave vectors throughout the Brillouin-zone, the temperature dependence of $\gamma(T)$ or $\alpha(T)$ can easily be calculated.

B. Lattice dynamics

In most IV-IV, III-V, II-VI, and I-VII zinc-blende-type materials, the existing neutron scattering data of phonon dispersions have provided us with a good description of interatomic forces using lattice dynamical schemes in the harmonic approximations.[22] More recently, the use of lasers in the excitation of Raman scattering and the introduction of diamond anvil cell have provided opportunities for measuring the pressure-dependent phonon properties in elemental and compound (e.g., group IV, III-V, and II-VI) semiconductors up to their phase transition pressure p_t.[23] Whenever phase transitions occur, Raman scattering reveals them as discontinuities in the frequency and/or the intensity of the phonon peaks. From the critical-point analysis of the pressure-dependent first- and second-order Raman spectra, one can obtain information about the variation of acoustical and optical phonons and consequently the mode Grüneisen parameters at high-symmetry points in the Brillouin zone. To extract knowledge of the interatomic binding forces in semiconductors under compression and to relate that information to charge-transfer effects and structural instabilities, the Raman data have provided us a good testing ground for theoretical studies. Consequently, the lattice dynamics and related phonon properties in zinc-blende-type crystals have been extensively studied in terms of rigid-ion models (RIM's),[26] shell models (SM's), valence force field models (VFFM's), and overlap valence shell models (OVSM's).[22]

In BP, although there exist no neutron scattering data of phonon dispersions, the values of optical phonons at the Γ critical point are known only from first-order Raman scattering spectroscopy[7] both at ambient- and high-pressure conditions. The pressure variations of acoustical phonons at X and L critical points are not available from Raman studies. As mentioned before (cf. Sec. I), the phonon frequencies and Grüneisen parameters at high-symmetry points Γ, X, and L are obtained *ab initio* using a density functional theory.[19] From the existing information about critical point phonons, elastic, Grüneisen, and lattice constants in BP, we have constructed a second-neighbor RIM for describing its lattice dynamical properties both at ambient- and high-pressure (89 kbar) conditions. The rigid-ion model incorporates long-range Coulomb forces in terms of an effective charge (Z_{eff}) and short-range [nearest-neighbor (A,B) and next-nearest-neighbor $(C_i,D_i,E_i,F_i$, with $i=1,2)$] forces up to and including second nearest neighbors.

We have optimized the two sets (ambient pressure and 89 kbar; see Table II below) of the RIM parameters by using a nonlinear least-squares method with constrained parameters and weighting, to the existing information about phonon modes, elastic constants, Grüneisen constants, and lattice constants (see Table I). The optimization process follows closely the procedure developed earlier in which similar ideas were applied for treating the pressure-dependent phonon properties of β-SiC.[12] In calculating the model parameters at 89 kbar, the compression-related effects are assumed to be linear for the elastic constants, critical-point phonon

TABLE I. Relevant data for BP used in optimizing the 11 rigid-ion model parameters both at ambient and 89 kbar pressures.

Relevant data used in the lattice dynamics of BP		
Phonon mode	Frequency (cm^{-1})	
LO(Γ)	828.9[a]	
TO(Γ)	799.0[a]	808[b]
LO(X)		800[b]
LA(X)		527[b]
TO(X)		701[b]
TA(X)		306[b]
LO(L)		764[b]
LA(L)		506[b]
Elastic constants	(10^{11} dyn/cm^2)	
C_{11}	31.50[c]	
C_{12}	10.0[c]	
C_{44}	16.0[c]	
Bulk modulus	(GPa)	
B_T	173[c] 267[d]	
B_T'	3.15[d]	
Lattice constant	(Å)	
a_0	4.538[c] (1 atm) 4.4669[e] (89 kbar)	

[a] Sanjurjo *et al.* (Ref. 7).

[b] Alves and Kunc (Ref. 19).

[c] Wettling and Windscheiff (Ref. 6).

[d] Suzuki *et al.* (Ref. 11).

[e] Calculated from Fig. 1(b) by using the Murnaghan equation of state [Eq. (9)] with the values of isothermal bulk modulus and its pressure derivative from (c) and (b), respectively.

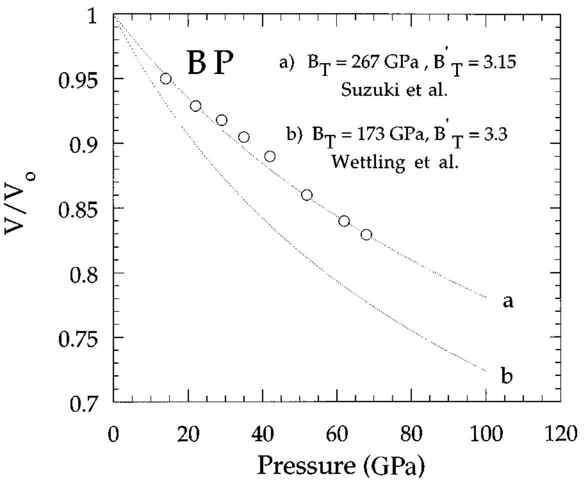

FIG. 1. Variation of volume ratio as a function of pressure for the cubic boron monophosphide. The curves (a) (solid line) and (b) (dotted line) represent, respectively, the calculations using Eq. (9) with the values of B_T and B_T' given by Suzuki *et al.* (Ref. 11), and Wettling *et al.* (Ref. 6). The open circles represent the *in situ* x-ray diffraction data from Ref. 11.

frequencies, and the crystal volume. The volume ratio (V/V_0) [or the lattice constant ratio (a/a_0)] in BP was calculated from the two sets of experimental values known for B_T and B_T' by using the well-known Murnaghan equation of state[27]

$$\frac{V}{V_0}=\left[1+p\,\frac{B_T'}{B_T}\right]^{-1/B_T'}, \tag{9}$$

valid for pressures up to several hundred kbar (see Fig. 1). As the total energy calculations provided results of B_T and B_T' close to those of Wettling and Windscheif,[6] we estimated the lattice constant at 89 kbar for BP from Fig. 1(b).

III. NUMERICAL COMPUTATIONS AND RESULTS: PHONONS, MODE GRÜNEISEN AND THERMAL EXPANSION

In order to assess the significance of the two sets of optimized RIM parameters (cf. Table II) and to treat the phonon properties of BP at any desired pressure p, we have considered a linear interpolation scheme

$$\mathrm{Par}_i(p)=\mathrm{Par}_i(\mathrm{ambient})+p\,\frac{\partial\ \mathrm{Par}_j}{\partial p}, \tag{10}$$

where Par_i $(i=1-11)$ are the 11 RIM parameters. The results of our theoretical calculations of phonon dispersions along high-symmetry directions and the corresponding one-phonon density of states [both at 1 atm pressure (solid lines) and 89 kbar (dotted lines)] are displayed in Figs. 2(a) (upper panel) and 2(b) (lower panel), respectively. In Table III, we have compared the calculated phonon frequencies at critical points with the Raman scattering data as well as with those derived from *ab initio* calculations. The phonon frequencies from our study show, in general, good agreement with the existing data. In the case of BP, both the linear expansion coefficient and mode Grüneisen parameters along high-symmetry directions are computed by performing the numerical derivatives of the frequencies. The results for the $\gamma_n(\mathbf{q})$ and $\alpha(T)$ are compared in Tables III and IV, respectively, with the available theoretical and experimental results.

TABLE II. Optimized set of rigid-ion model parameters (10^5 dyn/cm) for the lattice dynamics of BP at 1 atm and 89 kbar pressures.

Model parameters[a]	1 atm	89 kbar
A	-0.7757	-0.8656
B	-0.6000	-0.6700
C_1	$-0.057\,92$	-0.0623
C_2	-0.0888	-0.1000
D_1	-0.0639	$-0.083\,34$
D_2	-0.045	-0.09
E_1	0.105	0.136
E_2	-0.078	-0.0674
F_1	0.231	0.2710
F_2	-0.263	-0.2850
Z_{eff}	0.431 66	0.403 13

[a] In the notations of Ref. 22.

Similar to most III-V compounds, we find that in BP an increase in pressure causes increase in the short-range forces and hence an increase in the vibrational frequencies of the longitudinal and transverse optical (LO, TO), and longitudi-

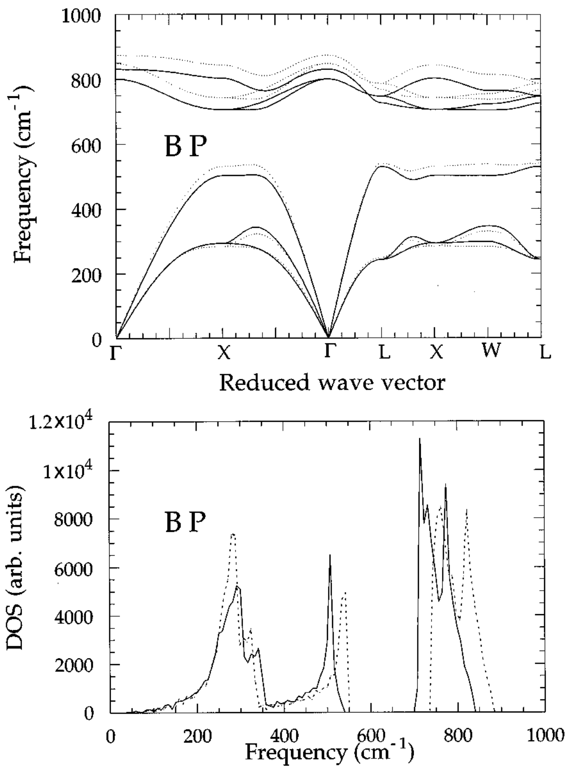

FIG. 2. (a) Rigid-ion model calculations for the phonon dispersions along high-symmetry directions for BP based on the set of parameters of Table II. The solid curves show the calculations at ambient pressure, whereas the dotted lines show the calculations at 89 kbar. (b) Calculated one-phonon density of states at ambient (solid lines) and 89 kbar pressures (dotted lines).

TABLE III. Comparison of the calculated critical-point phonon frequencies (cm^{-1}) and the Grüneisen parameters at critical points for BP with the existing experimental Ref. 7 and theoretical data Ref. 19.

	Phonon frequency (cm^{-1}) (1 atm)			Grüneisen parameter		
Modes	This work	a	b	This work	a	b
LO(Γ)	830.00	828.9		1.03	1.12	
TO(Γ)	800.00	799.0	808	1.16	1.30	1.14
LO(X)	803.24		800	0.99		0.90
TO(X)	706.66		701	1.01		1.54
LA(X)	502.24		527	1.11		0.94
TA(X)	293.61		306	-0.64		-0.27
LO(L)	727.18		764	1.13		1.03
TO(L)	747.15			1.04		
LA(L)	529.26		506	0.82		1.00
TA(L)	243.19			0.12		

[a] Sanjurjo *et al.* (Ref. 7).
[b] Alves and Kunc (Ref. 19).

nal acoustic (LA) modes throughout the Brillouin zone (cf. Fig. 2). From Table III, it is also clear that in BP the TO(Γ) mode shifts faster with pressure than the LO(Γ) so that the splitting $[\omega_{\mathrm{LO}(\Gamma)}-\omega_{\mathrm{TO}(\Gamma)}]$ decreases with pressure. This LO-TO splitting, related directly to the effective charge Z_{eff}, is an intuitively expected result since as the interatomic distance shortens with pressure it causes stiffening in the short-range forces (see Table II) and results in less transfer of charge for the compressed crystal causing thereby a decrease in Z_{eff}. Although the transverse acoustic (TA) modes at the X critical point soften with pressure (i.e, $\gamma_{\mathrm{TA}(X)}<0$), the effect of p on the mode γ's is seen to be much weaker $\{\gamma_{\mathrm{TA}(X)}=-0.64\}$ compared to the available data for several elemental [group IV: Si (-1.4), Ge (-1.53)] and compound [III-V: GaAs (-1.62); II-VI: ZnS (-1.2), ZnSe (-1.3), and ZnTe (-1.55)] semiconductors.[23] In fact, the available data for these materials show that $\gamma_{\mathrm{TA}(L)}$ exhibit similar negative values with a notable exception of diamond where γ_{TA}'s are positive. This means that in diamond the effective force constants for the transverse acoustic modes are not weakened with pressure and, therefore, the linear thermal expansion coefficient will not attain a negative value at lower temperatures. Although in BP our calculations revealed a small positive value of γ for the TA branch near the L critical point (cf. Table III), one should be careful not to generalize this result to other similar materials until more experimental data is collected.

TABLE IV. Experimental/or recommended values of the linear thermal expansion coefficients $\alpha(T)$ (10^{-6} K^{-1}) for GaAs, β-SiC, and BP.

	Linear thermal expansion coefficient (10^{-6} K^{-1})	
System	Experimental[a]/recommended	Lattice dynamical[c]
GaAs	0.001 at 5 K[b]	0.0021 at 5 K
	0.0027 at 10 K[b]	0.0042 at 10 K
	-0.016 at 15 K[b]	-0.027 at 15 K
	-0.065 at 20 K[c]	-0.086 at 20 K
	-0.126 at 25 K[b]	-0.139 at 25 K
	-0.168 at 30 K[b]	-0.179 at 30 K
β-SiC	0.27 at 100 K	0.26 at 100 K
	2.77, 3.50[b] at 300 K	2.47 at 300 K
	5.64 at 1600 K	5.16 at 1600 K
BP	1.77 at 200 K	1.63 at 200 K
	2.94 at 300 K	3.00 at 300 K
	3.65 at 400 K	3.81 at 400 K
	4.21 at 500 K	4.40 at 500 K
	4.65 at 600 K	4.73 at 600 K
	5.17 at 800 K	5.11 at 800 K
	5.42 at 1000 K	5.31 at 1000 K
	5.54 at 1200 K	5.42 at 1200 K

[a] Slack and Bartram (Ref. 10).
[b] Barron, Collins, and White (Ref. 31).
[c] Present calculation.

In Fig. 3, we have reported the linear thermal expansion coefficient $\alpha(T)$ in BP and compared our results with the existing experimental data.[10] In Table IV, we have also gathered experimental and theoretical values of $\alpha(T)$ at different temperatures for GaAs, β-SiC, and BP. A perusal of Table IV reveals that, in general, our lattice dynamical calculations provide a very good description of $\alpha(T)$ at all temperatures. In particular, the theory predicts very well the occurrence of low-temperature negative thermal expansion behavior in GaAs and the absence of negative $\alpha(T)$ in β-SiC and BP. In concurrence with the experimental observation, the theory also provides remarkably similar trends for the variation of $\alpha(T)$ in BP and β-SiC.

IV. COMMENTS AND DISCUSSION

The anomalous behavior of the thermal expansion coefficient in tetrahedral solids can be elucidated in terms of the balance between the weighted γ_i for the acoustic shear and compressional modes, the former having a tendency towards negative values, whereas the latter are positive. The temperature dependence of $\alpha(T)$ may be determined by the degree to

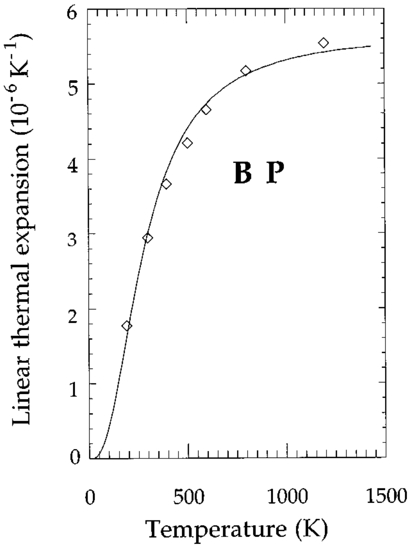

FIG. 3. Comparison of the calculated (solid lines) variation of linear thermal expansion coefficient $\alpha(T)$ as a function of temperature with the experimental data [open diamond (Ref. 10)].

which different phonons are excited and change sign as the relative thermal populations of the modes vary. In this context, Blackman[28] studied the mode γ's in four fold-coordinated solids by considering a simple ionic model in which the interaction between the ions was represented by the sum of the Coulomb potential acting on all neighbors and the inverse nth power law repulsive potential $(-C/r^n)$ between the nearest neighbors. For ZnS with $n=6$, the three mode γ's for the vibrations whose propagation velocities are determined by the elastic constants c_{11} $(=10.32\times10^{11}$ dyn/cm$^2)$, c_{44} $(=4.61\times10^{11}$ dyn/cm$^2)$, and $c'[=\frac{1}{2}(c_{11}-c_{12})=1.895\times10^{11}$ dyn/cm$^2]$ are found to be 1.24, -0.766, and -5.09, respectively. It may be noted that the negative values of the mode γ's are associated with the transverse acoustic vibrations related to the smaller values of the shear modulus. In GaAs, β-SiC, and BP the experimental values of c' are 3.345×10^{11}, 10.6×10^{11}, and 10.75×10^{11} dyn/cm^2, respectively. Clearly, in the strongly bonded materials BP and β-SiC, one expects that the stiffening in the shear modulus by angular forces will resist the bond bending. This resistance is believed to reduce the possibility for the TA modes to soften under pressure. On the other hand, in weakly bonded partially ionic tetrahedrally coordinated solids, the nonuniformity of the charge distribution along the bonds causes weakening in the angular forces which result in the mode Grüneisen parameters for the lowest shear modes to become increasingly negative.

In the lattice dynamical description of thermal expansion, which arises from the wave vector dependence of mode γ's, it is clear [cf. Eqs. (7) and (8)] that $\alpha(T)$ is closely related to the frequency spectrum of the solid. At low temperatures, since the acoustic vibrations are dominant, the average Grüneisen constant or $\alpha(T)$ can become negative if the pressure (or volume) derivatives of the TA phonons at critical points are also negative (e.g., in GaAs; cf. Table IV). This lattice softening effect for the TA phonons has been detected in several pressure-dependent Raman studies in tetrahedrally coordinated solids including GaAs. Although such lattice softening effect has not been observed experimentally in BP, our calculations have suggested negative mode γ's for the TA branch near the X zone boundary with γ_{TA} values being relatively weak. On the other hand, the calculated mode γ's for the TA branch near the L critical point are found to be slightly positive. The reason for the difference is that the directional partially covalent bonding in BP and β-SiC is much stronger than in GaAs.

Bond charge models represent the concentration of electron density in covalent bonds by point charges midway between the bonded atoms, in addition to the ion charges. Ishida[29] has applied such a model to calculate $\gamma(\mathbf{q})$ and $\gamma(T)$ for germanium with the bond charge and its volume dependence as adjustable parameters. To study the lattice dynamics of III-V compound semiconductors at $p=0$, Rustagi and Weber[30] extended the bond charge model (BCM) of elemental semiconductors by adding an additional parameter which measures the shift of the bond charge from the center towards the group-V ion. There is no reason why this model could not be employed to treat the pressure-dependent phonon properties in III-V compounds. This has not yet been attempted. However, we predict, on the basis of our present calculation, that for BP under pressure the bond charge should move adiabatically towards the center of the bond, which leads to an increase in the covalency of the bond.

V. CONCLUSIONS

In the absence of neutron scattering data for phonon dispersions, we have constructed rigid-ion models at ambient and 89 kbar pressures to study the lattice dynamics and related properties of BP. The involved force constants were optimized by using a nonlinear least-squares procedure with constrained parameters and weighting to the available data on critical-point phonons and elastic and lattice constants (cf. Table I). Results for the complete phonon dispersion curves, density of states, mode Grüneisen parameters, and thermal expansion coefficient are compared and discussed with the existing experimental and theoretical data. Considering the simplicity of our rigid ion model, an accurate prediction of the variation of $\alpha(T)$ with temperature in BP, β-SiC, and GaAs is satisfactory.

In compound semiconductors, as the tetrahedral bond becomes less covalent, the angular forces are weakened and the shear stiffness is reduced, causing transverse acoustic (TA) modes to soften under compression. This softening in the TA branches and their substantial weighting at low temperatures lead to the observed anomalous negative behavior of $\gamma(T)$ and $\alpha(T)$ in several fourfold-coordinated materials. In fact, pressure-dependent second-order Raman measurements[23] have made it possible to explicitly support this conjecture. However, to the best of our knowledge there exist no second-order Raman scattering experiments in BP concerning the pressure dependence of the acoustical and optical phonons. Such data are very much needed especially when the rigid-ion model used in the present study does not predict negative $\alpha(T)$ at low temperatures for BP and β-SiC. It is also worth mentioning that the TA modes depend upon the electronic polarizability, which is neglected in the rigid-ion model scheme.

Again, there are serious gaps in the temperature-dependent experimental data for $\alpha(T)$ in BP and β-SiC. With the advent of the high-sensitivity dilatometers for use at liquid helium temperatures and the accurate diffractometer furnaces for high-temperature applications, the collection of such data should be possible. The behavior of Grüneisen parameter around $T=0.05\Theta_0$ and above Θ_0 (Debye temperature) is of great interest, but requires corresponding specific heat and elastic constant data of high accuracy, which are not yet available. Finally, the effect of high pressure on anharmonicity in general, and thermal expansion in particular, presents challenging avenues for further research. The high-pressure and high-temperature measurements are difficult, but the experimental data in this area would be of great interest in understanding and verifying theoretical models.

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