Lattice dynamics of zinc chalcogenides under compression: Phonon dispersion, mode Grüneisen, and thermal expansion

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A comprehensive phenomenological calculation is reported to understand the temperature- and pressure-dependent phonon properties in ZnS, ZnSe, and ZnTe. Using the pressure dependence of optical data established recently by Weinstein, we have constructed an 11-parameter rigid-ion model, which in the pressure $p \rightarrow 0$ limit goes over to the fitting of neutron scattering results of phonon dispersions. Model calculations for the lattice dynamics, frequency spectrum, mode gammas, Grüneisen constant, and the linear thermal-expansion coefficient are shown to be in good agreement with the experiments. The present results not only compare well with the low-temperature experimental data, but also predict accurately the temperature region for which the Grüneisen constant $[\bar{\gamma}(T)]$ and the linear thermal-expansion coefficient $[\alpha(T)]$ will be negative. We believe that the variation of α_{min} and γ_{TO} is not simply related to the ionicity but also to the physical fact that ionicity is affected by the bond charge and the bond length in zinc-blende-type crystals.

I. INTRODUCTION

The use of lasers in the excitation of Raman scattering has provided us an opportunity for measuring the pressure-dependent phonon properties in ionic and partially ionic solids.[1-4] It is worth mentioning that in some cases, especially with the low pressure (< 20 kbar), it becomes difficult to measure with relative accuracy the shifts of critical-point phonon energies. However, with the introduction of diamond anvil cell[5] (where a pressure up to several hundred kbar can be produced and measured with ~ 3% of accuracy), the interest in the Raman studies has significantly increased in recent years.[5-9] Quite recently, Weinstein[9] has reported the effect of high pressure on the lattice vibrations in zinc chalcogenides and we have performed similar experiments due to impurity vibrations in zinc sulfide.[10] Some ultrasonic measurements for the pressure-dependent lattice[11] and elastic stiffness constants[12] have also been published in the literature. From the earlier work of Novikova,[13] a

peculiar behavior of the negative thermal-expansion coefficient $[\alpha(T)]$ has been observed in several zinc-blende-type crystals. Smith et al.[14] and Collins et al.[15] have provided confirmation of this physical fact and have reported additional low-temperature results for $\alpha(T)$ in elemental and compound semiconductors. Despite the renewed experimental interest in recent years,[14-16] reliable theoretical calculations for the pressure-dependent phonon properties in zinc-blende-type crystals are either sparse[17] or incomplete.[18,19]

Two possible approaches can be used to understand the pressure-dependent properties in solids: (a) *microscopic analysis* which starts with an ionic potential screened by the electron gas and thus derives the structural properties[20-22] and (b) *macroscopic analysis* which uses a phenomenological model in terms of general interatomic forces and consequently explains the physical features of the systems.[17] In the former case, there does not exist a complete description and indeed all the microscopic theories are either limited to metals or elemental

semiconductors. Again, the vibrational properties of imperfect solids have not yet been treated through *ab initio* calculations and all the avaliable results by the Green's-function method use the macroscopic theories.[23,24]

At zero absolute temperature and vanishing external pressure (i.e., $p \rightarrow 0$), a great majority of semiconducting crystals can be considered as a system of coupled harmonic oscillators.[25] The atoms exhibit zero-point vibrations about their equilibrium positions and all the excited states of the crystal can be determined by harmonic forces. If the temperature is increased or the pressure is applied, the atoms get shifted from their original rest positions and the anharmonic forces are to be taken into account. All this is well understood and thoroughly treated in standard monographs.[26] Rather than considering in detail the anharmonic parameters (the majority of which being usually unknown), the standard treatment of *slightly* anharmonic crystals consists of the well-known *quasiharmonic* approximation. The system is regarded as a harmonic one, even at a temperature higher than zero or at nonvanishing pressure. The corresponding renormalized eigenfrequencies observed in experiments (with finite linewidths) are supposed to be originating from *effective* forces which are treated as perfectly harmonic. Quasiharmonic approximation thus will be applied throughout this paper.

Setting aside a good deal of theoretical work in ionic solids,[27−29] adequate attention has not been given to the phonon-assisted pressure-dependent properties in partially ionic zinc-blende-type crystals. The only macroscopic calculation for ZnTe, reported by Vetelino *et al.*,[17] uses a four-parameter rigid-ion-model (RIM4). However, in the absence of neutron scattering data (ZnTe), the RIM4 has largely underestimated the *lattice softening effect* for the transverse-acoustic modes. Furthermore, the authors (of Ref. 17) have neglected the pressure-dependent effects on the lattice and elastic constants. These are, presumably, some of the factors that have caused large discrepancies in the calculations[17] of thermal expansion and Grüneisen constant [especially in the low-tempertures region (c.f. Sec. IV)].

In a series of subsequent studies, an elaborate version of RIM11 has provided a very good description for the various phonon-assisted properties in numerous perfect and/or imperfect zinc-blende-type crystals.[30−34] The unique set of phenomenological parameters calculated by the least-squares-fitting method has provided us an additional check on the internal coherence and consequently on the reliability of phonons. However, there may arise some questions regarding the quality and the simplicity of the model. These include: (i) How good the RIM11 would be for explaining the pressure-dependent properties; (ii) Will the agreement between theory and experiments, if achieved specially for $\gamma(T)$ and $\alpha(T)$ in the low temperatures be a complete success?; (iii) Do the anharmonic effects become important at intermediate temperatures?; (iv) Is the effect of bond charge (bond ionicity or covalency) related with the bond length an important parameter for deciding the pressure-dependent phonon-assisted properties? The present paper is intended to provide some simple explanations to these general questions. In the framework of RIM11 (Ref. 30) and considering appropriate compression-variation effects of lattice constant,[11] elastic constant,[12] and phonon energies,[9] we have undertaken a comprehensive study of the phonon-assisted properties in zinc chalcogenides. Except for the high-temperature region, we find that the present phenomenological treatment in the harmonic approximation provides very good agreement to the Grüneisen constant, Grüneisen parameters, and linear thermal expansion in all the systems studied here.

The paper is organized into six sections. The relevant theoretical background for the pressure-dependent phonon properties is outlined in Sec. II. The problems encountered for using a more reliable lattice-dynamical scheme are pointed out, considering all the existing theoretical and experimental aspects (cf. Sec. III). The RIM11 has been preferred not only because of its simplicity but also because it provides us a systematic and consistent way for evaluating the pressure derivatives of the model parameters. Numerical computations are made and the results of numerous pressure-dependent properties have been compared with the available experimental and theoretical data in Sec. IV. The results with some criticisms are discussed in Sec. V, with concluding remarks presented in Sec. VI.

II. Theoretical Background

One of the most intriguing properties observed in the tetrahedrally coordinated (e.g., diamond − zinc-blende)[13−16] solids is their negative thermal-expansion coefficient at low temperatures (generally with $T \leq 0.07\Theta_0$), where Θ_0 is the limiting value of the Debye characteristic temperature as $T \rightarrow 0$.

On the basis of the dynamical theory of crystal lattices, Barron[35] has developed the general theory for the temperature dependence of the Grüneisen constant. In the *quasiharmonic approximation* the

individual Grüneisen parameters can be determined fairly accurately in terms of either the volume dependence

$$\gamma_i(\vec{q}) = -\frac{\partial \ln \nu_i(\vec{q})}{\partial \ln V} , \qquad (1a)$$

or the pressure dependence

$$\gamma_i(\vec{q}) = \frac{1}{X_T} \frac{1}{\nu_i(\vec{q})} \left[\frac{\partial \nu_i(\vec{q})}{\partial p} \right] , \qquad (1b)$$

of the phonon frequencies $\omega_i(\vec{q})[\equiv 2\pi\nu_i(\vec{q})]$. Here $X_T[\equiv -(1/V)(\partial V/\partial p)_T)]$ is known as the isothermal compressibility.

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

$$\overline{\gamma}(T) = \frac{3\alpha(T)V}{C_v(T)X_T} , \qquad (2)$$

where $C_v(T)$ is the specific heat at constant volume. Again, $\alpha(T)$ can be obtained theoretically from the relation

$$\overline{\gamma}(T) = \sum_{\vec{q}i} C_i(\vec{q},T)\gamma_i(\vec{q}) \Big/ \sum_{\vec{q}i} C_i(\vec{q},T) , \qquad (3)$$

where the weight factors $C_i(\vec{q},T)$ are given by the Einstein specific heat of the mode $(\vec{q}i)$. If the mode Grüneisen parameters are known for the wave vectors throughout the Brillouin zone, the temperature dependence of the Grüneisen constant

and the linear thermal expansion can easily be calculated.

In a phenomenological lattice-dynamical treatment the phonon branches in the $\vec{q}$ space can be determined by solving the usual secular equation[30]

$$| D_{\alpha\beta}^{SC}(\vec{q}|\kappa\kappa') - \omega^2(\vec{q})\delta_{\kappa\kappa'}\delta_{\alpha\beta}| = 0 , \qquad (4)$$

where κ or $\kappa' = 1,2$ denotes the type of atoms in a unit cell and α or $\beta = x,y,z$. In the RIM picture the dynamical matrix D^{SC} is comprised of the short-range $\{D^S\}$ and the long-range $\{D^C\}$ Coulomb forces. The elements of the short-range interaction matrix depend on the two (A,B) first-neighbor and eight $(C_\kappa, D_\kappa, E_\kappa,$ and F_κ with $\kappa = 1,2)$ second-neighbor force constants while the long-range Coulomb interaction matrix depends on the effective charge Z and the lattice constant a_0.

III. Lattice Dynamics

A. Choice of the model

In the harmonic approximation, the existing neutron data of phonon dispersions have provided us a very good account of the interatomic forces in zinc-blende-type crystals.[30] The lattice dynamics and related properties have been reported in recent years using RIM's,[30] shell models[36] (SM's), valence force-field models[37] (VFFM's), and overlap valence-shell models (OVSM's).[32] So far as the correct prediction of the eigenvectors is concerned, none of the

TABLE I. Calculated model parameters (10^5dyn cm^{-1}) for the lattice dynamics of ZnS, ZnSe, and ZnTe. The lattice parameter a_0 is in Å. Here we have considered the atom with lighter mass to be at the origin in describing the model parameters with the notation of Kunc (Ref. 30). The parameters C_1, D_1, E_1, and F_1 will change to C_2, D_2, E_2, and F_2 for ZnS if the heavier atom Zn is considered to be at the origin.

Model parameter	ZnS 1 atm	ZnS 150 kbar	ZnSe 1 atm	ZnSe 137 kbar	ZnTe 1 atm	ZnTe 95 kbar
a_0	2.70465	2.5794	2.8338	2.6994	3.05185	2.9208
A	−0.2863	−0.4043	−0.2706	−0.4175	−0.223	−0.3348
B	−0.2492	−0.330	−0.260	−0.390	−0.235	−0.345
C_1	−0.0429	−0.070	−0.0302	−0.0463	−0.0186	−0.0378
C_2	−0.0239	−0.0364	−0.0304	−0.0572	−0.033	−0.0498
D_1	−0.0262	−0.0728	−0.0310	−0.0863	−0.038	−0.0722
D_2	−0.0506	−0.0696	−0.0246	−0.0266	−0.009	−0.021
E_1	−0.0121	−0.0290	+0.054	+0.096	+0.054	+0.080
E_2	+0.0546	+0.0840	−0.032	−0.033	−0.062	−0.063
F_1	−0.0491	−0.0630	+0.096	+0.165	+0.071	+0.124
F_2	+0.0965	+0.172	−0.0883	−0.113	−0.082	−0.115
Z	0.909	0.8572	0.769	0.70	0.766	0.6321
M_1	32.064	32.064	65.38	65.38	65.38	65.38
M_2	65.38	65.38	78.96	78.96	127.61	127.61

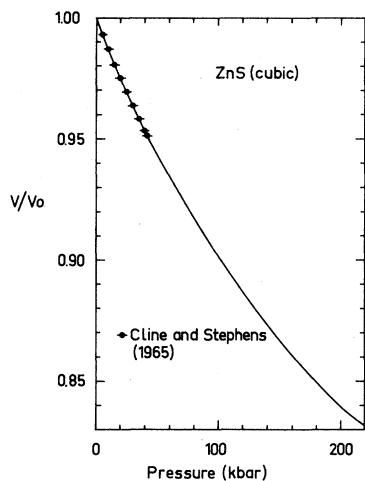(Note: M_1 and M_2 values are grouped with brace "a.u." for each column pair.)

FIG. 1. Volume-pressure relationship for ZnS. The curve represents the calculations [using Eq. (5)] with the parameter values given in Table I. The experimental data (●) due to Cline and Stephens (Ref. 11) are also shown.
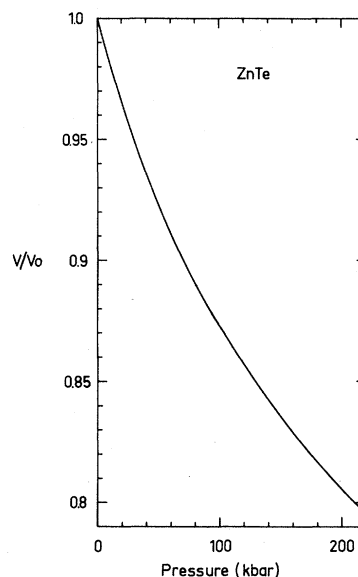

FIG. 3. Same key as of Fig. 1 for ZnTe.

schemes can be judged through any of the available experiments in zinc chalcogenides. However, in other zinc-blende-type crystals the analysis of optical data in terms of SM and its various ramifications has suggested that an OVSM10 is better than the most commonly used SM14.[38,39] Kunc and Bilz[38] have also pointed out that the SM14 (Ref. 36) is not suitable for its nonlinear extension for under-
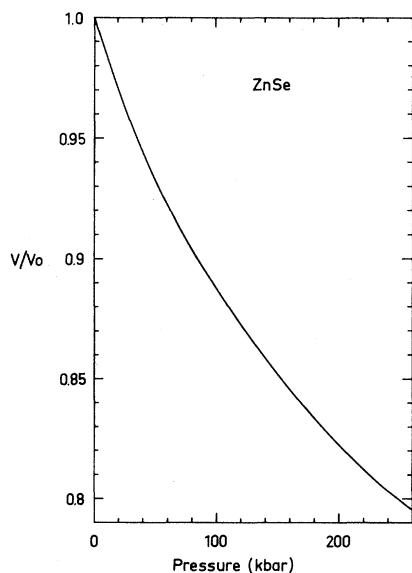
FIG. 2. Same key as of Fig. 1 for ZnSe.

standing the phonon-assisted Raman scattering spectra. Furthermore, it is fair to mention that the SM14 fitted neutron data fails to explain the two simultaneously observed impurity modes by a single defect in gallium phosphide.

Although, it was very much desired to extend the OVSM10 (Ref. 38) to the $p \neq 0$ case either by adding anharmonic parameters or at least in the quasiharmonic approximation, unfortunately, there are currently too many ambiguities, both conceptual and experimental, which make the task impossible. First of all, it is not clear whether the assumption in the OVSM10 scheme (viz., $R = S = T$) will still be true for the $p \neq 0$ case and/or the anharmonic terms which are significant for the p dependence will modify the core-core interactions only (leaving the shell-shell and the core-shell interactions unaltered). On the other hand, it seems plausible that the effect of pressure will change the local core-shell interactions (parameters k_1,k_2) and the redistribution of the valence charge may modify the shell charges (parameters Y_1,Y_2). Unfortunately, even with appropriate assumptions and reasonable speculations, the pressure-dependent model parameters cannot be determined in the above scheme. This is partly due to the insufficient Raman data of phonon dispersions and partly because of the incomplete experimental knowledge for the pressure derivatives of the dielectric constants in zinc chalcogenides.

In view of the existing situation, we feel that a

TABLE II. The values of the elastic constants C_{11}, C_{12}, and C_{44} (10^{11} dyn/cm²) and their respective pressure derivatives C'_{11}, C'_{12}, and C'_{44} for ZnS, ZnSe, and ZnTe. The bulk modulus B_0(10^{11} dyn/cm²) and its pressure derivative B'_0 is also reported.

Quantity	ZnS[a]	ZnSe[b]	ZnTe[b]
C_{11}	10.32	8.59	7.11
C_{12}	6.53	5.06	4.07
C_{44}	4.61	4.06	3.13
C'_{11}	3.98[c]	4.44	4.81
C'_{12}	4.69[c]	4.93	5.12
C'_{44}	0.45[c]	0.43	0.45
B_0	7.80[c]	6.24	5.08
B'_0	4.45[c]	4.77	5.04

[a] Reference 44.
[b] Reference 12.
[c] Calculated from the standard expressions given by Thurston (Ref. 42).

partial attempt based on the available experimental data[9–13] will be adequate rather than speculation. If the correct description of dielectric properties is deliberately given up, the use of the RIM in the pressure-dependent phonon-assisted properties may

not be completely inadequate. It will be shown that with the RIM11, one may get practically identical phonon dispersions in zinc chalcogenides if compared with those obtained from the more complicated schemes.[36–39] Another important point in the choice of RIM is that we can get all the model parameters and their pressure derivatives in a very systematic and consistent way[31] (cf. Sec. III B). Furthermore, if we insist on the trends of various parameters, namely the relations with the point defects, we find RIM11 to be the only one which has been systematized into a uniform and homogeneous scheme.[32–34] We are therefore choosing this model for our study as a first attempt to the pressure-dependent lattice dynamics of zinc chalcogenides.

B. Model parameters and their pressure derivatives

With a successive least-squares-fitting procedure,[31] all the RIM11 parameters can be calculated using experimental values of energies (at Γ, X, L, and K points), the elastic constants (C_{11}, C_{12}, C_{44}), and the lattice parameter (a_0). The unique set of neutron-fitted[37,40](1 atm) model parameters in ZnS, ZnSe,[30] and ZnTe (Ref. 31) have already been calculated.
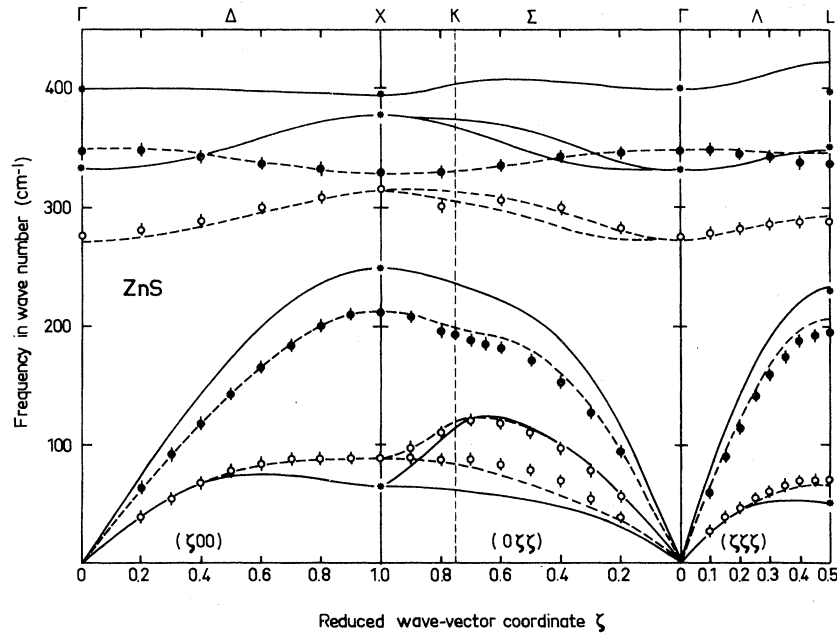

FIG. 4. RIM11 calculations for the phonon dispersions along high-symmetry directions for ZnS. The dotted curves represent the inelastic neutron scattering (Ref. 37) (● ⓓ 1 atm) fit whereas the full curves show the calculations for 150 kbar. Weinstein's data (Ref. 9) through Raman scattering measurements have also been denoted by (*).
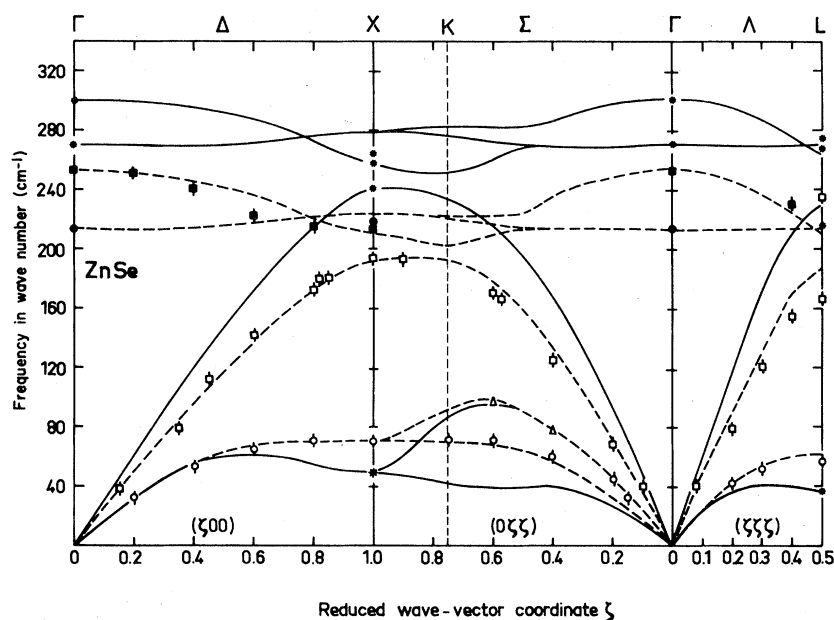
FIG. 5. Same key as of Fig. 4 for ZnSe (1 atm and 137 kbar). Experimental points are from Refs. 40 and 9.

This will help us in establishing the new set of values for the existing pressure-dependent Raman data[9] (see Table I).

In order to get the pressure derivatives of the model parameters, we require the compression-dependent physical quantities (e.g., critical-point en-

ergies, lattice and elastic constant, etc.). With Raman spectroscopy,[9] the effect of pressure on the critical-point phonon energies is known for ZnS (150 kbar), ZnSe (137 kbar), and ZnTe (95 kbar). Some ultrasonic measurements have also provided us information for the pressure derivatives of lattice
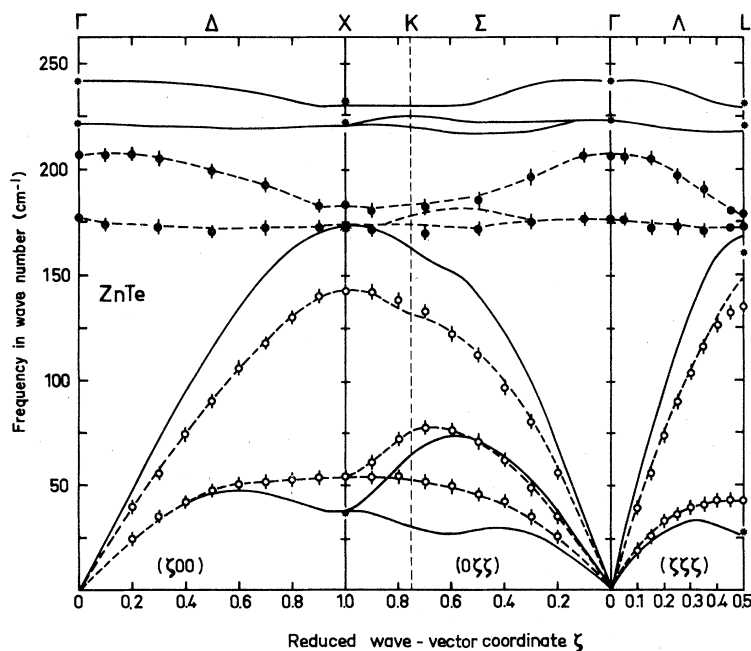
FIG. 6. Same key as of Fig. 4 for ZnTe (1 atm and 95 kbar). Experimental points are form Refs. 37 and 9.

FIG. 7. Calculated one-phonon density of state for ZnS.

(ZnS) (Ref. 11) and elastic stiffness[12] (ZnSe, ZnTe) constants. To fill the need for the missing data, however, we have followed some reliable theoretical methods[41,42]

An extrapolation formula (of Murnaghan),[41] valid for pressure up to several hundred kbar, can be used to calculate the change in lattice constant: At any desired pressure p, the volume ratio in cubic crytals (in terms of bulk modulus B_0 and its pressure derivative B_0') can be expressed as

$$\frac{V}{V_0} = \left[1 + p\frac{B_0'}{B_0} \right]^{-1/B_0'} \tag{5}$$

It is worth mentioning that in several papers[43] a
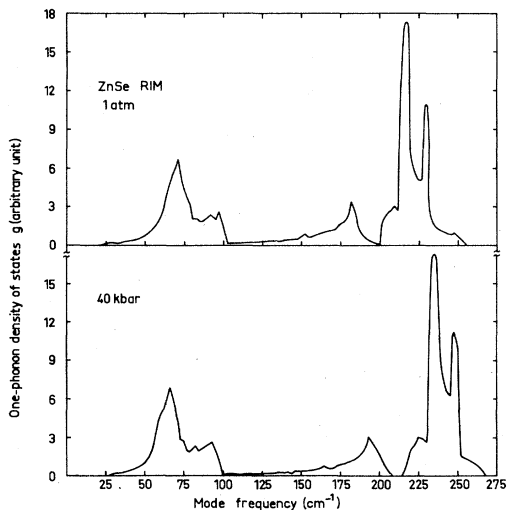
FIG. 8. Same key as of Fig. 7 for ZnSe.
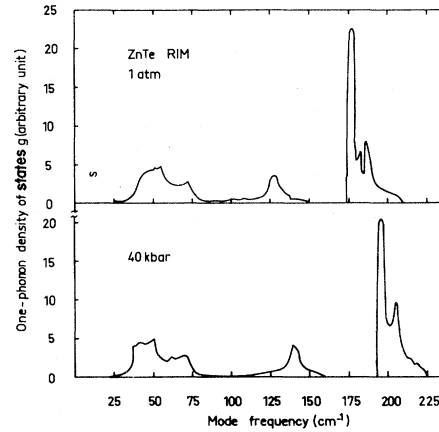
FIG. 9. Same key as of Fig. 7 for ZnTe.

slightly varied form of the *equation of state* [Eq. (5)] has been considered and the original contribution of Murnaghan[41] is either underestimated or completely neglected. However, we recognize the earlier work and report here the variation of the volume ratio (V/V_0) with pressure for ZnS, ZnSe, and ZnTe (cf. Figs. 1 − 3). For a comparable case ZnS, the agreement with the experimental data of
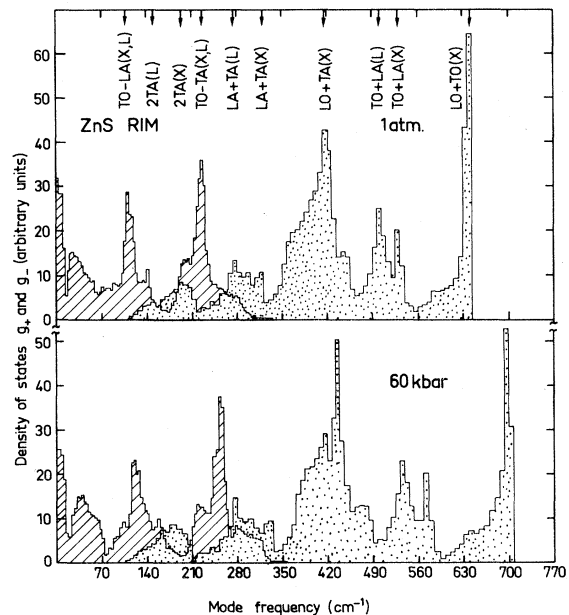
FIG. 10. Calculated two-phonon (▨ subtractive and ▨ additive) density of states for ZnS. The tentative assignments for the additive and subtractive peaks (shown by arrows) are made using the characteristic temperature dependence (as of Ref. 45) and the polarization selection rules (Ref. 46).
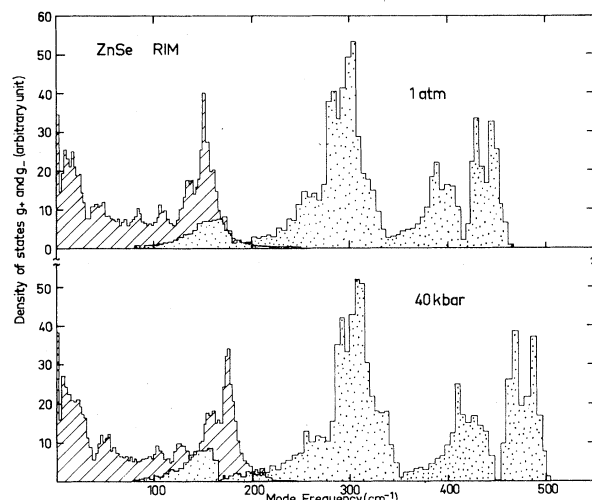
FIG . 11. Calculated two-phonon (▨ subtractive and ▨ additive) density of states for ZnSe.

Cline and Stephens[11] is excellent (see Fig. 1). This provides us confidence to believe that the pressure derivatives of the crystal volume for ZnSe and ZnTe will be equally reliable. In the framework of Thurston,[42] the pressure derivatives of the elastic constants are also obtained for ZnS (see Table II). The experimental results of elastic constants (1 atm) due to Berlincourt et al.,[44] have been incorporated in the actual numerical calculations.

If the compression-related effects are assumed to be linear for the elastic constants and for the crystal volume, the new set of RIM11 parameters for the Raman scattering data of Weinstein[9] can easily be calculated (see Table I and Figs. 4 — 6). In order to
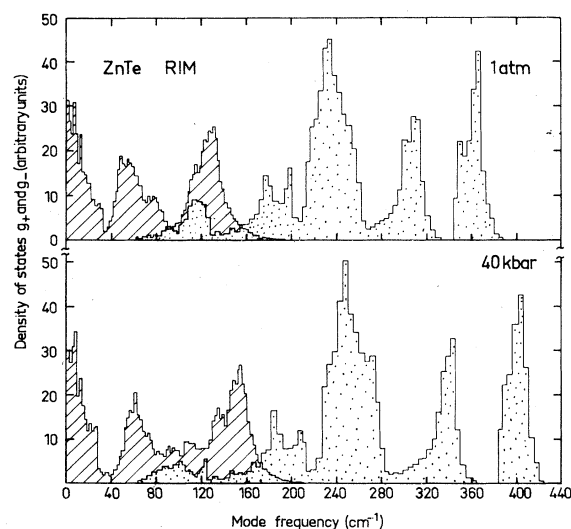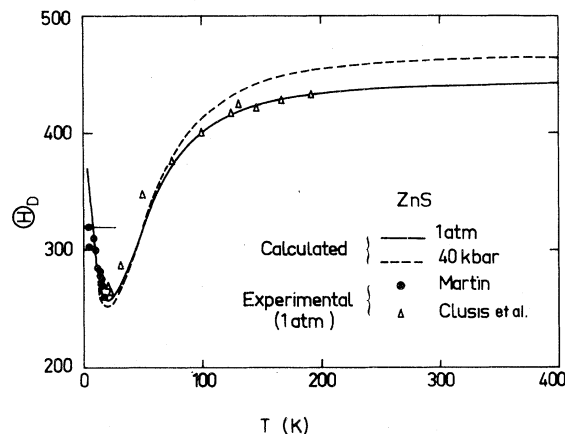

FIG. 12. Same key as of Fig. 11 for ZnTe.

FIG. 13. Calculated variation of Θ_D versus temperature for ZnS. Experimental points (●△) are taken from Refs. 47 and 48.

use the significance of the two set of parameters and moreover to calculate the phonon properties at any desired pressure p, we consider

$$\alpha_i(p) = \alpha_i(\text{neutron}) + p\frac{\partial \alpha_i}{\partial p} \quad , \qquad (6)$$

where α_i are the eleven RIM parameters.

IV. NUMERICAL COMPUTATIONS AND RESULTS

A. Phonons

The involved model parameters at any desired pressure p can be calculated using Eq. (6) and Table I. This enables us to compute the phonon-assisted pressure-dependent properties in zinc chalcogenides. A glance at Figs. 4 — 6 reveals that the calculated phonon dispersions along high-symmetry directions are in satisfactory agreement both with the neutron results [37,40] as well as with other phenomenological[36] data. In Figs. 7 — 12 we have displayed our results for the one- and two-phonon density of states in ZnS, ZnSe, and ZnTe. A tentative analysis of the two-phonon density of states (e.g., in ZnS, cf. Fig. 10) designates several features in the second-order Raman scattering spectra.[9] The assignments of the additive and subtractive peaks are consistent with their characteristic temperature dependence[45] and the polarization selection rules.[46] It is again remarkable to note that the pressure-dependent one- and two-phonon density of states maintains the general shape and exhibits accurately the shifts of the participating phonons in the additive and the subtractive processes.

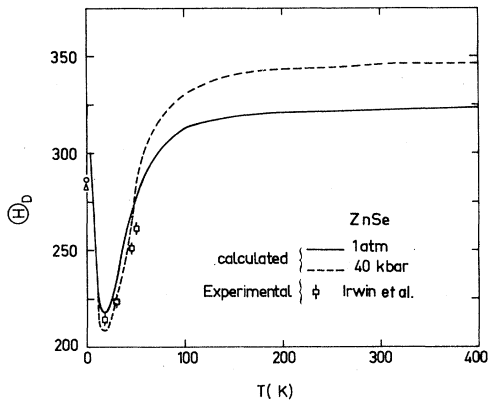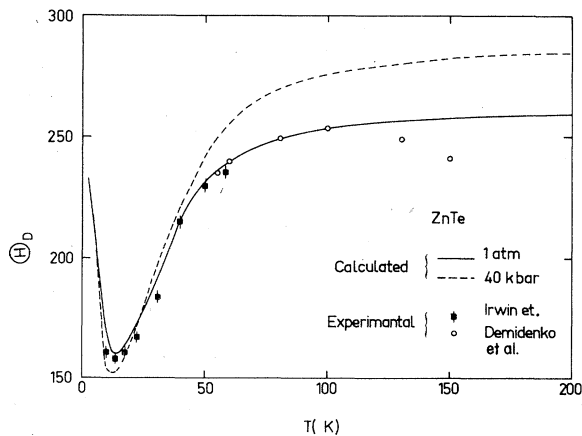A fair agreement between the calculated and the

FIG. 14. Same key as of Fig. 13 for ZnSe. Experimental [○△⌷] points are taken from Ref. 49.

FIG. 16. Calculated Grüneisen parameters along high-symmetry directions for ZnS.

experimental Θ_D-T curves (1 atm)[47−50] not only provides us the accuracy of the RIM11 parameters but also a confidence for predicting the results of 40 kbar (cf. Figs. 13−15). It can be noted that the pressure-dependent results at *low* and *high* temperatures exhibit a small *decrease* and *increase* in their Θ_D values (see Figs. 13−15). This behavior, in the pressure-dependent Θ_D-T curves, seems to be plausible and can be attributed to the negative and positive shifts of the low- and high-energy phonons, respectively.

B. Mode Grüneisen and thermal expansion

By incorporating the pressure derivatives of the phonon energies, the individual Grüneisen parameters [$\gamma_i(\vec{q})$] have been calculated for the wave vectors throughout the Brillouin zone. In Figs. 16−18, we have displayed our results of $\gamma_i(\vec{q})$ along high-symmetry ([$\zeta00$], [$0\zeta\zeta$], and [$\zeta\zeta\zeta$]) directions for

ZnS, ZnSe, and ZnTe, respectively. The values of the mode gammas at certain critical points have also been compared with the existing experimental[9] and theoretical data[17] (cf. Table III). One may note that in all the systems the agreement of our calculations with the optical results of Weinstein,[9] is generally very good. However, it is worth mentioning that the results of Vetelino et al.,[17] (ZnTe) for the mode gammas (especially for the TA modes) are very much different not only from ours but from the optical data too.[9]

dependence of $\overline{\gamma}(T)$ and $\alpha(T)$ once again provide a reasonable comparison with the recent low-temperature measurements of Smith et al.[14] (ZnS and ZnSe) and of Collins et al.[15] (ZnTe) (cf. Figs. 19 and 20). It is remarkable to note that in ZnSe, the low-temperature $\alpha(T)$ data of Novikova[13] are at variance not only with the present theoretical calculations but also with the experimental results of Smith et al.[14] (see Fig. 20). Considering the simplicity of the RIM11, the accurate prediction of the

FIG. 15. Same key as of Fig. 13 for ZnTe. Experimental [■○] points are taken from Refs. 49 and 50.

FIG. 17. Same key as of Fig. 16 for ZnSe.
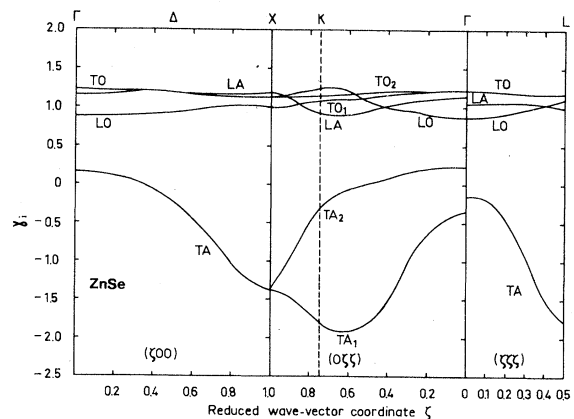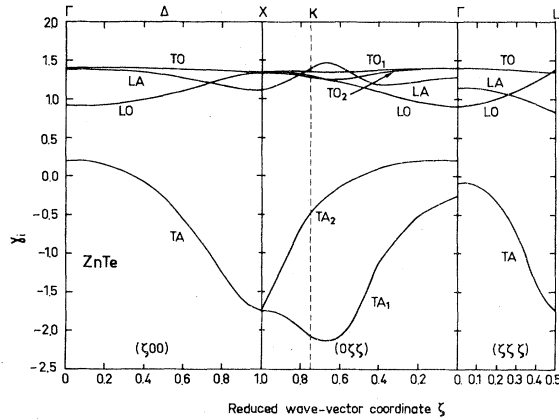
FIG. 18. Same key as of Fig. 16 for ZnTe.

temperature region, where the coefficient of thermal expansion will be negative, is satisfactory. Again, our calculations corroborate the same observed trend for the minimum values of $\alpha(T)$ and $\overline{\gamma}(T)$ in ZnS, ZnSe, and ZnTe, respectively.

V. COMMENTS AND DISCUSSION

Using Barron's[35] theoretical treatment, Blackman[51] has suggested the possibility of negative thermal expansion in solids. In a simplified ionic model with Coulomb interaction and repulsion term of the type $(-C/r^n)$, Blackman[51] has calculated the

three-mode γ's for the vibrations whose propagation velocities are determined by the elastic constants C_{11}, C_{44}, and $\frac{1}{2}(C_{11} - C_{12})$. For ZnS (with $n = 6$), the quoted values for the mode gammas are 1.24, -0.766, and -5.09, respectively. It may be noted that the negative values are associated with the transverse vibrations, and even more negative values of the mode gamma can be obtained for a stronger repulsion. In the lattice-dynamical description, which arises from the wave-vector dependence of the mode gammas, it is evident that both $\overline{\gamma}(T)$ and $\alpha(T)$ are closely related to the frequency spectrum of the solid [cf. Eq. (3)]. At low temperatures, where the acoustic vibrations are dominant, the average Grüneisen constant and/or $\alpha(T)$ can become negative if the pressure (or volume) derivatives of TA phonon energies are also negative (as found in several zinc-blende-type crystals).

Setting aside the case of Si, one may note (see Table IV) that the temperature at which α attains its minimum value is of the same order of magnitude, both for the covalent (Ge) and for the ionic (CuCl) crystals. At first it appears that the value of α_{min} can not be correlated with the bond ionicity (or covalency). However, for the same-row systems (e.g., Ge-GaAs-ZnSe and Sn-InSb-CdTe) where the bond lengths are practically constant, [52] we find that α_{min} decreases with the increase of the ionicity (or decrease of the covalency). As the short-range forces also decrease with the increase of the ionicity,[53] we

TABLE III. Comparison of the calculated mode Grüneisen parameters with the existing theoretical (ZnTe) and optical data for ZnS, ZnSe, and ZnTe.

Mode	ZnS Expt.[a]	ZnS Calc.[b]	ZnSe Expt.[a]	ZnSe Calc.[b]	ZnTe Expt.[a]	ZnTe Ref.[e]	ZnTe Calc.[b]
TO(Γ)	1.85 ± 0.2	1.31	1.4 ± 0.1	1.22	1.7 ± 0.1	1.52	1.4
			$1.65 \pm .1^d$		1.55 ± 0.1^c		
LO(Γ)	0.95 ± 0.1	0.88	0.9 ± 0.1	0.88	1.2 ± 0.1	0.76	0.91
			1.1 ± 0.1		1.0 ± 0.1^c		
TO(X)	1.0 ± 0.2	1.12	1.6 ± 0.2	1.13	1.8 ± 0.4	1.6	1.35
LO(X)	1.1 ± 0.2	1.22	0.9 ± 0.2	1.0	1.7 ± 0.3	1.33	1.34
TO(L)	1.0 ± 0.1	1.12	1.6 ± 0.3	1.18		1.70	1.35
LO(L)	1.1 ± 0.2	1.34	0.9 ± 0.2	1.1	1.8 ± 0.3	1.33	1.37
LA(X)		1.07	1.1 ± 0.2	1.19		1.33	1.103
TA(X)	-1.2 ± 0.2	-1.25	-1.3 ± 0.2	-1.37	-1.55 ± 0.2	-0.2	-1.72
			-1.1^d		-1.6^d		
LA(L)		0.79	1.1 ± 0.2	0.98		0.9	0.83
TA(L)	-1.5 ± 0.2	-1.1	-1.5 ± 0.2	-1.78	-1.0 ± 0.2	-0.16	-1.74
TA($\sim K2$)	-0.3 ± 0.1	-0.3	-0.4 ± 0.1	-0.35	-0.4 ± 0.1	-0.10	-0.45

[a]Reference 9.
[b]Present study.
[c]Reference 2.
[d]Reference 1.
[e]Reference 17 (approximately determined from their Fig. 2).
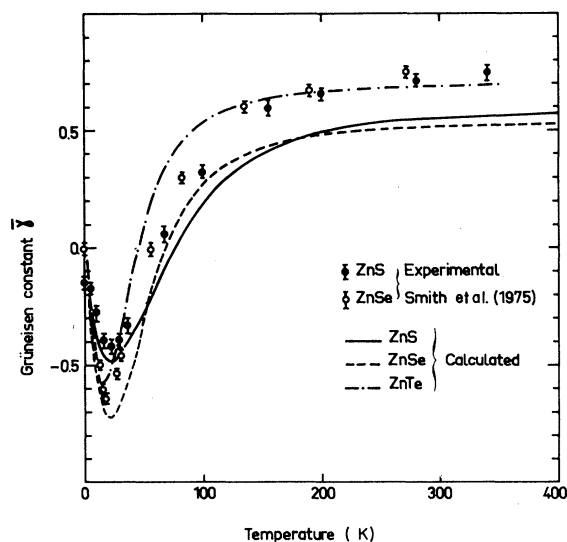
FIG. 19. Variation of Grüneisen constant $\overline{\gamma}$ with temperature for ZnS, ZnSe, and ZnTe. Experimental data [♦ ¢] are taken from Ref. 14.
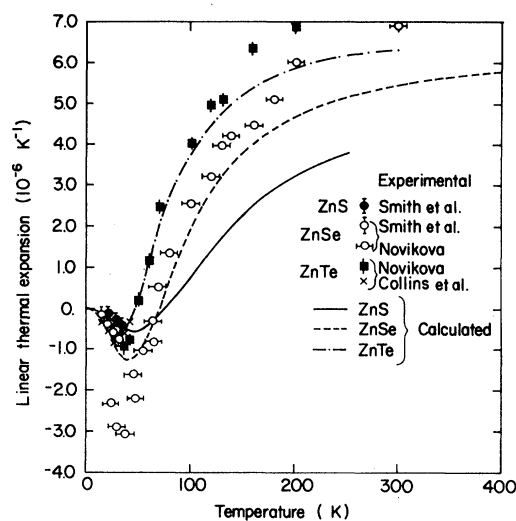

FIG. 20. Variation of linear thermal expansion coefficient (α) with temperature for ZnS, ZnSe, and ZnTe. Experimental data are taken from Refs. 13 — 15.

TABLE IV. To understand the correlation of minimum values of $\alpha(10^6\ \mathrm{deg}^{-1})$ and γ_{TO} $(\vec{q} \cong 0)$ with the ionicity scale, the existing experimental results are given for several diamond and zinc-blende-type crystals.

System	Ionicity scale[f] Coulson	Phillips	Temp. (K)	$\alpha_{min}(10^6\ \mathrm{deg}^{-1})$	$\gamma_{TO}(\vec{q} \cong 0)^e$
IV-IV					
C	0	0			0.98
Si	0	0	~80	-0.77^b	1.02
Ge	0	0	28	$-0.06^a, -0.4^b$	1.12
Sn	0	0	~24	0.9^b	
III-V					
GaSb	0.36	0.261	30	-1.0^b	1.23
GaAs	0.37	0.31	30	$-0.17^a, -0.5^b$	1.39
InSb	0.37	0.321	~30	-1.6^b	
GaP	0.37	0.374			1.09
InP	0.37	0.421			1.44
AlSb	0.36	0.426	~38	-1.02^b	1.23
II-VI					
ZnTe	0.66	0.546	28	-0.68^c	1.70
ZnS	0.61	0.623	28	-0.32^a	1.85
ZnSe	0.64	0.630	32	-0.69^a	1.40
CdTe	0.61	0.675	28	$-3.05^a, -3.3^b$	
I-VII					
CuCl	0.85	0.746	32	-0.33^d	

[a]Reference 14.
[b]Reference 13.
[c]Reference 15.
[d]Reference 16.
[e]Reference 8.
[f]Reference 52.

believe that the variation of α_{min} depends on the nature of the forces within the crystals.

In diatomic solids, it has been speculated that the value of $\gamma_{TO}(\bar{q} \approx 0)$ can either be related with the *coordination number*[54] or with the *ionic character*.[1−3] Except for a few cases of highly ionic solids, the above criteria do not hold well for covalent or partially ionic crystals (see Tables III and IV). However, in the later systems if the bond lengths are roughly the same [e.g., in Ge(1.12)-GaAs(1.3)-ZnSe(1.4) or approximately in Si(0.98)-GaP(1.09)-ZnS(1.25)], it is significant to note that the value of γ_{TO} (within parentheses) decreases with the decrease of the ionicity (or increase of the covalency). In zinc-blende-type crystals, we thus believe that the *bond length* plays an important role in deciding the variation of γ_{TO} with the ionicity (or the covalency).

It is also fair to mention that the calculated phonon dispersions under compression do not show the flatness of the transverse-acoustic branches (cf. Figs. 4−6). With pressure, the increase of all the short-range forces is believed to be quite reasonable (see Table I). However, the decrease of a_0 and Z (the parameters associated with the ionicity or the effective charge) can presumably shift the *bond charge* towards the cation site.[52] Whether the bending of TA branches is an artifact of the RIM11 or the peculiarity in zinc chalcogenides may be understood in terms of a bond-charge model.[55]

Despite the reasonable description of low-temperature results of $\bar{\gamma}(T)$ and $\alpha(T)$, the calculated values on the other hand deviate from the existing experimental data in the high temperatures. This may be attributed partly to the neglect of the anharmonic forces in the simplified RIM and partly to the diversity in the existing experimental pressure-dependent shifts of optical phonons.[1−9] Therefore, more theoretical and experimental efforts are necessary to understand the high-temperature results of the Grüneisen constant and linear thermal expansion in zinc-blende-type crystals.

VI. CONCLUDING REMARKS

In terms of a simplified RIM11 and using appropriate approximations to include pressure-dependent effects on the lattice parameter and elastic constants, we are able to study the lattice

dynamics and related properties in zinc-chalcogenides. The calculated results have been compared and discussed with the existing experimental and theoretical data. In contrast to the earlier attempts based on the elastic continuum model[18] and the RIM4,[17] we have been successful in calculating the characteristic deep minimum in the low-temperature $\bar{\gamma}(T)$ or $\alpha(T)$ behavior.[14,15] However, the effects of anharmonicity are essential to be included to gain better insight into physical processes at high temperature.

In a recent study,[34] we have pointed our the significance of the *bond charge* and the *bond length* for explaining the trends of force perturbations caused by the vibrations of various isolated and paired impurities in elemental and compound semiconductors. From the present study, one may also note that the variations of α_{min} and γ_{TO} are not simply related to the ionicity (or the covalency) but to the way ionicity is affected by the bond charge and the bond length. In highly ionic solids most of the vibrational properties are decided by their *ionicity*, but we feel however that in covalent and partially ionic crystals, the bond length and the redistribution of electronic charge density that modify the covalency (or the ionicity) of the bond (or the strength of the bond) are the important factors. Finally, the analysis of the phonon-assisted pressure-dependent Raman scattering spectra due to point defects in ZnS, in terms of Green's-function theory, using present phonon values under compression has been successfully performed and the results will be published in a subsequent paper.[10]

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[1]S. S. Mitra, C. Postmus, and J. R. Ferraro, Phys. Rev. Lett. 18, 455 (1967); Inorg. Nucl. Chem. Lett. 4, 55 (1958); Phys. Rev. 186, 942 (1969).

[2]O. Brafman and S. S. Mitra, in *Proceedings of the Second International Conference on Light Scattering in Solids,* edited by M. Balkanski (Flammarion, Paris, 1971), p. 284.

[3]C. J. Buchenauer, F. Cerdeira, and M. Cardona, in *Proceedings of the Second International Conference on Light Scattering in Solids,* Ref. 2, p. 280.

[4]B. A. Weinstein, J. B. Renucci, and M. Cardona, Solid State Commun. 12, 473 (1973).

[5]G. J. Piermarini and S. Block, Rev. Sci. Instrum. 46, 33 (1975).

[6]B. A Weinstein and G. J. Piermarini, Phys. Rev. B 12, 1172 (1975).

[7]B. A. Weistein, Solid State Commun. 20, 999 (1976).

[8]R. Trommer, H. Müller, M. Cardona, and P. Vogl, Phys. Rev. 21, 4869 (1980).

[9]B. A. Weinstein, Solid State Commun. 24, 595 (1977); and in *Proceedings of the Sixth High Pressure Science and Technology-AIRAPT Conferemce,* edited by K. D. Timmerhaus and M. S. Barker (New York, Plenum, 1979), Vol. I, p. 141.

[10]M. Zigone, M. Vandevyver, and D.N. Talwar, Phys. Rev. B (in press).

[11]C. F. Cline and D. R. Stephens, J. Appl. Phys. 36, 2869 (1965).

[12]B. H. Lee, J. Appl. Phys. 41, 2988 (1970).

[13]S. I. Novikova, Fiz. Tverd. Tela 2, 2341 (1960) [Sov. Phys.—Solid State 2, 2087 (1961)]; 3, 178 (1961) [3, 129 (1961)]; 5, 2138 (1963) [5, 1558 (1964)]; 1, 1841 (1959) [1, 1687 (1960)].

[14]T. F. Smith and G. K. White, J. Phys. C 8, 2031 (1975).

[15]J. G. Collins, G. K. White, J. A. Birch, and T. F. Smith, J. Phys. C 13, 1649 (1980).

[16]T. H. K. Barron, J. A. Birch, and G. K. White, J Phys. C 10, 1617 (1977).

[17]J. F. Vetelino, S. S. Mitra, and K. V. Namjoshi, Phys. Rev. B 2, 967 (1970).

[18]D. Gerlich, J. Phys. Chem. Solids 35, 1026 (1974).

[19]T. Soma and K. Kudo, J. Phys. Soc. Jpn. 48, 115 (1980).

[20]I. Ishida, J. Phys. Soc. Jpn. 39, 1282 (1975).

[21]D. J. Chadi and R. M. Martin, Solid State Commun. 19, 643 (1976).

[22]R. Zeyeher, Phys. Rev. Lett. 35, 174 (1975).

[23]D. N. Talwar and Bal K. Agrawal, Phys. Rev. B 12, 1432 (1975).

[24]M. Vandevyver and P. Plumelle, Phys. Rev. B 17, 675 (1978).

[25]A. A. Maradudin, E. W. Montrol, C. H. Weiss, and I. P. Ipatova, *Solid State Physics* (Academic, New York, 1971), Suppl. 3, 2nd edition.

[26]G. Leibfried and W. Ludwig, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1961), Vol. 12, p. 276.

[27]Sudhir Bijanki and R. J. Hardy, J. Appl. Phys. 49, 215 (1978).

[28]J. F. Vetelino, L. G. Roy, and S. S. Mitra, J. Phys. Chem. Solids 35, 47 (1974).

[29]G. R. Barsch and B. N. N. Achar, AIP Conference meeting, Chicago Illinois (1979).

[30]K. Kunc, Ann. Phys. (Paris) 8, 319 (1973–74).

[31]P. Plumelle and M. Vandevyver, Phys. Status Solidi B73, 271 (1976).

[32]P. Plumelle, D. N. Talwar, M. Vandevyver, K. Kunc, and M. Zigone, Phys. Rev. B 20, 4199 (1979).

[33]D. N. Talwar, M. Vandevyver, and M. Zigone, J. Phys. C 13, 3775 (1980); Phys. Rev. B 23, 1743 (1981).

[34]M. Vandevyver and D. N. Talwar, Phys. Rev. B 21, 3405 (1980).

[35]T. H. K. Barron, Ann. Phys. (N.Y.) 1, 77 (1957).

[36]For complete references of SM14 lattice-dynamical calculations in zinc-blende-type crystals, please see S. Hoshino, Y. Fujii, J. Harada, and J. D. Axe, J. Phys. Soc. Jpn. 41, 965 (1976).

[37]N. Vagelatos, D. Wehe, and J. S. King, J. Chem. Phys. 60, 3613 (1974).

[38]K. Kunc and H. Bilz, Solid State Commun. 19, 1027 (1976); and in *Proceedings of the Conference on Neutron Scattering, Gatlinburg, 1976,* edited by R. M. Moon (ORNL, Oak Ridge, Tennessee, 1976), p. 195.

[39]P. Borcherds and K. Kunc, J. Phys. C 11, 4145 (1978).

[40]B. Hennion, F. Moussa, G. Pepy, and K. Kunc, Phys. Lett. 36A, 376 (1971).

[41]F. D. Murnaghan, Proc. Nat. Acad. Sci. U.S.A. 30, 244 (1944).

[42]R. N. Thurston, J. Acoust. Soc. Am. 37, 348 (1965); 41, 1093 (1967).

[43]M. A. Cook and L. A. Rogers, J. Appl. Phys. 34, 2330 (1963).

[44]D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. 129, 1009 (1963).

[45]J. N. Hodgson, *Optical Absorption and Dispersion in Solids* (Chapman and Hall, London, 1970), p. 40.

[46]J. L. Birman, Phys. Rev. 131, 1489 (1963).

[47]D. L. Martin, Philos. Mag. 46, 751 (1955)

[48]K. Clusis and P. Marteck, Z. Phys. Chem. 134, 193 (1928).

[49]J. C. Irwin and J. LaCombe, J. Appl. Phys. 45, 567 (1974).

[50]A. F. Demidenko and A. K. Maltsen, Inorg. Mater. (U.S.S.R.) 5, 158 (1969).

[51]M. Blackman, Proc Phys. Soc. London, Sec. B 70, 827 (1957); Philos. Mag. 3, 831 (1958).

[52]J. C. Phillips, in *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

[53]M. Vandevyver, D. N. Talwar, P. Plumelle, K. Kunc, and M. Zigone, Phys. Status Solidi B 99, 727 (1980).

[54]A. Beinenstock, Philos. Mag. 9, 755 (1964).

[55]W. Weber, Phys. Rev. B 15, 4789 (1977); K. C. Rustagi and W. Weber, Solid State Commun. 18, 673 (1976).