Dependence of the phonon spectrum of InP on hydrostatic pressure

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The first- and second-order Raman spectra of InP have been measured in a diamond anvil cell as a function of hydrostatic pressure up to the phase transition (100 kbar). The Grüneisen parameters of the LO and TO phonons at Γ , and also those of several optical and acoustical phonons corresponding to critical points at the edge of the zone, have been measured. Particular emphasis is placed in the determination of the dependence of the dynamical charge as a function of lattice constant: a nonlinear decrease with decreasing lattice constant is found. The results are interpreted in terms of the bond orbital theory and of a pseudopotential calculation of the dynamical charge as a function of lattice constant.

I. INTRODUCTION

The development of the diamond anvil cell in conjunction with the ruby fluorescence manometer¹ have made possible light-scattering measurements under very high hydrostatic pressure.² The diamond and zinc-blende-type semiconductors are, because of their simplicity and the extensive knowledge of their vibronic properties, particularly appropriate for such investigations. The small sample volumes available, however, limit the measurements to laser frequencies below the lowest direct absorption edge E_0 . Work of this type has so far been reported for Si, GaP,² ZnS, ZnSe, and ZnTe.³ In cases in which Raman measurements with conventional visible or near infrared lasers are not possible inside the diamond anvil cell because of the strong absorption coefficient at low pressures, they may be possible at higher pressures as the sample becomes transparent or nearly transparent (indirect or forbidden transitions) to the exciting laser. The investigation of the pressure dependence of the phonon spectra thus becomes possible by measuring at zero pressure outside the cell and at high pressures in the cell. This situation obtains in most group-IV and -III-V semiconductors where the E_0 gap has a large and positive pressure coefficient. As an illustration of this method GaAs has been recently investigated.⁴ In this paper we present analogous data for InP, a material with a direct gap E_0 very similar to that of GaAs (1.43 eV for GaAs and 1.35 eV for InP at room temperature). The behavior of these gaps under pressure is also similar: they become transparent to the near-ir lines of conventional Ar lasers at pressures of $\simeq 20$ (GaAs) and 30 kbar (InP). Measurements of the complete first- and second-order Raman spectra thus become possible up

to the phase transitions at 100 kbar for InP and 180 kbar for GaAs.⁵ Hence the Grüneisen parameters of the LO and TO phonons at the Γ point (first-order spectrum) and those of a number of optical and acoustical phonons at the edge of the zone can be determined, the latter based on a critical point assignment of the observed second-order spectra. Of particular interest is the determination of the *negative* Grüneisen parameters of the TA phonons.

From the observed pressure dependence of the $LO(\Gamma)$ and $TO(\Gamma)$ modes the dependence of the dynamical charge (Born's transverse effective charge e_T^*) on lattice constant can be obtained. Like in all other zinc-blende-type materials measured, the LO-TO splitting decreases with increasing pressure. The dynamical charge obtained from this splitting also decreases with increasing pressure, a fact which reflects an increase in covalency upon compression. We discuss this observed decrease in e_T^* in terms of the semiempirical bond orbital model⁶ and of the microscopic theory of the dynamical charge.⁷

II. EXPERIMENT

The Raman measurements were performed in the diamond anvil cell described by Syassen and Holzapfel⁸ with a scattering configuration similar to that of Ref. 2. The pressure was measured with the ruby fluorescence technique.¹ Both Kr⁺- and Ar⁺-ion lasers were used in the measurements of the secondorder spectra; the exciting lines were chosen to be close to the direct gap E_0 at the pressure under consideration.⁹ The spectra were taken with a SPEX double-plus-third monochromator system and an RCA 31034 photomultiplier in the photon counting

4869

mode. The cell was optically aligned at pressures above 30 kbar with the 7993-Å line of the Ar⁺-ion laser. At that pressure the InP sample, approximately 40 μ m thick, becomes transparent to this wavelength. Once the sample is aligned the first-order Raman lines can be seen even at lower pressures, all the way down to atmospheric, while the second-order bands remain observable only in the region of transparency and under near resonant conditions (laser frequency $\hbar \omega = E_0$). All measurements were performed at room temperature.

III. RESULTS

A pair of representative first-order spectra, obtained at 33.4 and at 84.4 kbar, respectively, are shown in Fig. 1. The corresponding peak positions are plotted in Fig. 2 as a function of pressure (top horizontal scale) and of relative lattice compression $-\Delta a/a_0$ (bottom). The compression was related to the pressure with Murnaghan's equation¹⁰

$$p = (B_0/B_0')[(a_0/a)^{3B_0'} - 1] , \qquad (1)$$

where B_0 is the bulk modulus $[B_0 = 7.25 \times 10^{11} \text{ dyn/cm}^2 \text{ (Ref. 11)}]$ and B'_0 is its derivative with respect to pressure. No measurements of B'_0 seem to appear in the literature. In view of the near constancy of this parameter for a given family of materials^{12,13} we take in Eq. (1) for B'_0 the value reported¹³ for GaAs $(B'_0 = 4.67)$. The horizontal scale of Fig. 2 has been chosen to be linear in $\Delta a/a_0$ (not in *p*). With this choice the observed ω_{LO} and ω_{TO} frequen-



FIG. 1. First-order Stokes spectra of the LO and TO phonons of InP at room temperature and for two different pressures (84.4 and 33.4 kbar).



FIG. 2. Frequencies of the LO and TO modes of Fig. 1 as a function of lattice constant (linear lower scale) and pressure (upper scale). The solid line is a least-squares fit.

cies fall on straight lines within experimental error

$$\omega_{\rm LO} = 344.5 + (1280 \pm 15)(-\Delta a/a_0) ,$$

$$\omega_{\rm TO} = 303.3 + (1380 \pm 15)(-\Delta a/a_0) ,$$
 (2)

given in cm⁻¹, for InP. When plotted on a linear pressure scale the data of Fig. 2 show a slight sub-linearity

$$\omega_{\rm LO} = 344.5 + (0.54 \pm 0.01)p - (0.001 \pm 0.0001)p^2 ,$$
(3)

$$\omega_{\rm TO} = 303.3 + (0.58 \pm 0.01)p - (0.001 \pm 0.0001)p^2 ,$$

with p in kbar and the ω 's in cm⁻¹. A similar effect is observed for Si, GaP,² and GaAs.⁴ In GaAs, however, the variation of ω_{LO} and ω_{TO} is also slightly sublinear⁴ in $-\Delta a/a_0$:

$$\omega_{\rm LO} = 291.8 + 1.07 \times 10^{3} (-\Delta a/a_{0}) -2.84 \times 10^{3} (-\Delta a/a_{0})^{2} ,$$

$$\omega_{\rm TO} = 268.3 + 1.12 \times 10^{3} (-\Delta a/a_{0}) -2.28 \times 10^{3} (-\Delta a/a_{0})^{2}$$
(4)

for GaAs, in cm⁻¹. Nevertheless we should point out that some nonlinear component may appear in Eqs.

(2) if the measured B'_0 of InP were used in the evaluation of Eq. (1) instead of that of GaAs. This nonlinearity is expected to be smaller than that of Eq. (4).

Figures 1 and 2 show a decrease in the $\omega_{LO}-\omega_{TO}$ splitting with increasing pressure. This decrease is characteristic of most zinc-blende-type materials measured [GaP,² GaAs,⁴ ZnS,³ ZnSe, ZnTe,^{3,14} SiC (Ref. 13)] and will be related in Sec. IV to a decrease in ionicity with increasing pressure. For AlSb, a marginal increase in $\omega_{LO}-\omega_{TO}$ with increasing pressure (only up to 8 kbar) has been reported.¹⁵ Measurements on this material with the diamond anvil cell should be performed in order to clarify this matter. The dependence of $\omega_{LO}-\omega_{TO}$ on $(-\Delta a/a_0)$ and on p as measured for InP is shown in Fig. 3. Although this dependence is nearly linear, it can be fitted slightly better by the quadratic expressions

$$\omega_{\rm LO} - \omega_{\rm TO} = 41.2 - 3.3 \times 10^{-2} p - 1.7 \times 10^{-4} p^2$$

= 41.2 + 65 (\Delta a/a_0) - 1.8 \times 10^3 (\Delta a/a_0)^2 ,
(5)



FIG. 3. Splitting of the LO and TO modes of Fig. 2 as a function of lattice constant and pressure. The solid line represents a quadratic least-squares fit to the experimental points.



FIG. 4. Second-order spectra of InP at room temperature and for two different pressures in the region of LO and TO overtones and combinations.

in cm^{-1} and p in kbar.

A number of sharp structures are also observed in the second-order spectra of InP. They correspond mainly to overtones of the acoustic phonons and to overtones and combinations of the optical phonons at points of high density of states close to the Brillouinzone boundary (see Sec. IV).¹⁶ We show in Fig. 4 the second-order spectra observed for two different pressures in the region of TO and LO overtones and combinations. The measurements at 84.4 kbar were



FIG. 5. Dependence of the frequency of the features observed in the second-order spectrum of InP as a function of lattice parameter and pressure. The assignment of the features in terms of critical points is also given.

TABLE I. Mode Grüneisen parameters obtained for a number of critical points of tetrahedral semiconductors. The data given are those considered to be the most accurate available. For InP they stem from the present work, for GaAs from Ref. 4, the rest from Refs. 2, 15, 36, and 37.

	LO	то	LO-TO	TO(<i>L</i>)	TO(<i>X</i>)	$\frac{\text{TA}(W_1, W_2)}{\text{IA}(\epsilon_1, \epsilon_2)}$	TA(X)	TA(<i>L</i>)
	0.98 + 0.04	0.98 + 0.04	0	14+025	20+04		04+09	
Si	1.02 ± 0.02	1.02 ± 0.04	ů 0	1.4 ± 0.25 1 3 + 0 2	15+01	-0.2 ± 0.1	-1.4 ± 0.2	-1.3 ± 0.3
Ge	1.02 ± 0.02 1.12 ± 0.02	1.02 ± 0.02 1.12 ± 0.02	õ	0.9 ± 0.1				
GaP	0.95 ± 0.02	1.09 ± 0.02	0.14 ± 0.04	1.5 ± 0.05	1.31 ± 0.05	0	-0.72 ± 0.03	-0.81 ± 0.07
GaAs	1.23 ± 0.02	1.39 ± 0.02	0.16 ± 0.04	1.48 ± 0.15	1.73 ± 0.07	-0.37 ± 0.15	-1.62 ± 0.05	-1.72 ± 0.15
GaSb	1.21 ± 0.02	1.23 ± 0.02				• • •		
InP	1.24 ± 0.02	1.44 ± 0.02	0.20 ± 0.05	1.42 ± 0.1	1.42 ± 0.1	-0.27 ± 0.1	-2.08 ± 0.1	-2.00 ± 0.1
AISb	1.27 ± 0.05	1.23 ± 0.05		• • •				
ZnS	0.95 ± 0.1	1.85 ± 0.2	0.9 ± 0.2	1.0 ± 0.2	1.0 ± 0.2		-1.55 ± 0.2	-1.0 ± 0.2
ZnSe	0.9 ± 0.1	1.4 ± 0.1	0.5 ± 0.1	1.6 ± 0.3	1.6 ± 0.3		-1.30 ± 0.2	-1.5 ± 0.2
ZnTe	1.2 ± 0.1	1.7 ± 0.1	0.5 ± 0.1		1.8 ± 0.4		-1.55 ± 0.2	-1.5 ± 0.2

performed under extreme resonant conditions $(\hbar \omega = 1.92 \text{ eV}, \text{ gap } \hbar \omega_0 = 1.93 \text{ eV}, \text{ see following paper}^9)$. As a result the observed 2LO peak is produced mainly by phonons near Γ .¹⁷ Correspondingly, a LO(Γ) + TO(Γ) combination peak, not seen under less resonant conditions of the 33.3-kbar run, is observed also at 84.4 kbar.

Not shown in Fig. 4 are the structures associated with the TA bands which we have also investigated. They are basically the same as those reported in Ref. 17. Their wave numbers at zero pressure are 178 (a shoulder), 135 (a strong peak), and 107 cm⁻¹ (a peak). The dependence of the wave numbers of these peaks and shoulders on $-\Delta a/a_0$ (linear scale) and on p is given in Fig. 5. The mode Grüneisen parameters obtained from Figs. 2 and 5 are shown in Table I in comparison with similar data for other materials of the family.

IV. DISCUSSION

The Grüneisen parameters obtained for the TO(Γ) and LO(Γ) modes fit well into the systematics of the materials in Table I. Their weighted average $\frac{1}{3}(2\gamma_{TO(\Gamma)} + \gamma_{LO(\Gamma)}) = 1.37$ is somewhat higher than the values reported for its isoelectronic group-IV material, Ge. A number of phenomenological model theories for the dependence of the phonon frequencies on lattice constant have appeared in the literature (see Table I of Ref. 18). They do, however, usually take the Grüneisen parameter of the Γ phonons as an input in their calculation. A recent microscopic calculation based on the pseudopotential band structure yields for the optical phonons of Si at Γ a Grüneisen parameter of 1.8.¹⁹ Although no microscopic calculations have been performed for InP, on the basis of the results for silicon we can see that the "average" Grüneisen parameter found in the present work for the $TO(\Gamma)$ and $LO(\Gamma)$ modes is well understood from a microscopic point of view.

We now switch to the question of the dependence on lattice constant of the $\omega_{LO}(\Gamma)$ - $\omega_{TO}(\Gamma)$ splitting as shown in Fig. 3. This splitting is best related to microscopic theory through Born's transverse dynamical charge $e_T^{*,20}$

$$e_T^{*2} = (VM/4\pi)\epsilon_{\infty}(\omega_{\rm LO}^2 - \omega_{\rm TO}^2) \quad , \tag{6}$$

(in atomic units), where V is the volume of the unit cell, M is the reduced mass $(1/M = 1/M_{In} + 1/M_P)$, and ϵ_{∞} is the infrared dielectric constant for frequencies well above $\omega_{LO}(\Gamma)$ and below the electronic absorption edge.

In evaluating e_T^* as a function of lattice constant from Fig. 3 with Eq. (6) we encounter the difficulty that the volume dependence of ϵ_{∞} is not known experimentally. Data do exist, however, for GaAs and Ge (see Table III in Ref. 21). In view of the theory given also in Ref. 21 for the volume dependence of ϵ_{∞} we believe the corresponding coefficients for GaAs and InP should be nearly the same. We thus accordingly take²² $d \ln \epsilon_{\infty}/d \ln a = 3$ and obtain from Fig. 3 with Eq. (6) the dependence of e_T^* on lattice constant shown by the crosses in Fig. 6. The results are rather similar to those found for GaAs,⁴ which we reproduce for the sake of comparison in Fig. 7. The experimental data of Figs. 6 and 7 can be fitted with the quadratic forms

$$e_T^*(InP) = 2.54 + 4.5(\Delta a/a) - 88(\Delta a/a)^2 ,$$

$$e_T^*(GaAs) = 2.18 + 4.4(\Delta a/a) - 88(\Delta a/a)^2 .$$
(7)



FIG. 6. Born's effective dynamical charge as a function of lattice constant and pressure calculated from the data of Fig. 3 with Eq. (6) (crosses). The squares represent the results of the full pseudopotential calculation performed with Eq. (10) while the dashed lines were obtained with Eqs. (8) and (9) under the assumption that $V_2 \propto a^{-2}$. The calculated charges were slightly renormalized to bring them into agreement with experiment for $\Delta a = 0$.

As shown in Eqs. (7) the dependence of e_T^* on lattice constant is nearly the same for GaAs as for InP.

A number of attempts at calculating the e_T^* of tetrahedral semiconductors have been recently performed. They fall into two categories. One of them is based on semiempirical models of the tetrahedral bond, such as the bond orbital model.⁶ Within this model we find⁶

$$e_T^* = -\Delta Z + 7.6\alpha_P - 3.6\alpha_P^3$$
, (8)

where ΔZ is one-half the difference in core charges between the anion and the cation ($\Delta Z = 1$ for a III-V compound) and α_P is the polarity or ionicity parameter defined by Harrison and Ciraci⁶ ($\alpha_P = 0.50$ for GaAs, $\alpha_P = 0.58$ for InP). The "experimental" points in Figs. 6 and 7 can be used in conjunction with Eq. (8) to obtain the dependence of α_P on lattice constant, a property so far unknown. We obtain in this manner the results of Fig. 8. It is, however, maybe somewhat more instructive to adopt an opposite point of view, i.e., to estimate the dependence of α_P on lat-



FIG. 7. Same as Fig. 6 but for GaAs. The experimental points are from Ref. 4.

tice constant using reasonable assumptions and available information, to replace it into Eq. (8) and to compare the obtained dependence of e_T^* on $\Delta a/a$ with the experimental results. The polarity α_P can be written²²

$$\alpha_P = V_3 / (V_2^2 + V_3^2)^{1/2} , \qquad (9)$$



FIG. 8. Dependence on lattice constant of the polarity α_P of InP and GaAs as obtained with Eq. (8) from the data of Figs. 6 and 7.

where V_2 represents a "covalent" energy gap and V_3 is an ionic contribution to the gap which is similar to those designated as E_h and C by Van Vechten.²³ At this point we choose to neglect the minor difference between the points of view of Harrison and of Van Vechten (for a discussion see Ref. 22). The parameter V_2 is known²² to vary with lattice constant like a^{-2} (the equivalent parameter E_h in Van Vechten's treatment varies like $a^{-2.5}$). We do not know with certainty the variation of V_3 (or C) with a, but according to some indications in the literature^{21,24} it should be rather small. We thus assume V_3 to be independent of *a*. With this assumption and $V_2 \propto a^{-2}$ we obtain the dashed lines of Figs. 6 and 7. These lines agree with the experimental data reasonably well at low pressures. None of them, however, represents the nonlinearity observed at higher pressures.

Another possible approach is to use the microscopic pseudopotential expression for e_T^* [see Eq. (4.6) of Ref. 7 and Appendix A]:

$$e_T^* = -\Delta Z + \frac{2}{N} \sum_{\vec{G} \neq 0} \sum_{nn'\vec{k}} \frac{\theta_{n\vec{k}}(1 - \theta_{n'\vec{k}})}{(E_{n\vec{k}} - E_{n'\vec{k}})^2} \langle n\vec{k} | p_x | n'\vec{k} \rangle \langle n'\vec{k} | e^{i\vec{G}\cdot\vec{\tau}} | n\vec{k} \rangle G_x[i\upsilon_s(G)\sin\vec{G}\cdot\vec{\tau} - \upsilon_A(G)\cos\vec{G}\cdot\vec{\tau}]$$

$$\tag{10}$$

In this approach e_T^* is expressed in terms of the Bloch states $|n\vec{k}\rangle$ and energies $E_{n\vec{k}}$ of the crystal which are obtained from a pseudopotential-energyband calculation. In Eq. (10), $\Delta Z = \frac{1}{2}(5-3) = 1$ for III-V compounds, N is the number of unit cells, the \vec{G} 's are the reciprocal-lattice vectors, and \vec{p} is the momentum operator. Furthermore, $\theta_{n\vec{k}} = 1$ if n is one of the four valence bands and $\theta_{n\vec{k}} = 0$ otherwise. The crystal potential, which enters Eq. (1) explicitly as well as implicitly via the Bloch states, is in a plane wave basis $\langle \vec{k} + \vec{G} | v | \vec{k} + \vec{G}' \rangle = v(\vec{G} - \vec{G}')$ with

$$v(\vec{G}) = v_s(G) \cos\vec{G} \cdot \vec{\tau} + i v_a(G) \sin\vec{G} \cdot \vec{\tau} \quad (11)$$

Here $\vec{\tau} = (\frac{1}{8}a)(1, 1, 1)$ with a the lattice constant and

$$v_s(G) = v_{ln}(G) + v_P(G) ,$$

$$v_a(G) = v_{ln}(G) - v_P(G)$$
(12)

are the symmetric and asymmetric pseudopotential form factors expressed in terms of the atomic form factors. For zero pressure, we used the empirical pseudopotential form factors given by Heine and Cohen.²⁵ As customary, only form factors for $|G| \leq (2\pi/a_0)\sqrt{11}$ are taken $(a_0$ denotes the equilibrium lattice constant). About 60 plane waves were included in the band calculation and 10 special \overline{k} points²⁶ to perform the \vec{k} summation in Eq. (1). This gives $e_T^* = 1.81$ for InP (expt: $e_T^* = 2.55$). The effect of pressure on e_T^* arises from the change in lattice constant. This affects the pseudopotential form factors in two ways: (i) The form factors $v_{s,a}(\vec{q})$ are needed at different wave vectors $|\vec{q}|$ compared to zero pressure, namely, at $|\vec{q}| = (2\pi/a)(\sqrt{3}, \sqrt{4}, \sqrt{8})$ $\sqrt{11}$), where $a = a_0(1 - \Delta a/a_0)$ is the lattice constant under pressure. We obtained the form factors at the shifted wave vectors by interpolating the Cohen-Heine values with a cubic spline; (ii) the form factors v_{ln} and v_{P} are screened ionic pseudopotentials, e.g.,

$$v_{\mathrm{In, crystal}}(\vec{q}) = \frac{1}{\Omega_0 \epsilon(\vec{q})} \int d^3 r \, v_{\mathrm{In, ion}}(\vec{r}) e^{-i\vec{q}\cdot\vec{r}} , \quad (13)$$

and depend on the lattice constant via the atomic volume $\Omega_0 = \frac{1}{8}a^3$. The change of the dielectric function with pressure influences e_T^* only negligibly, mainly because $\epsilon(\vec{q})$ is needed only at momenta $q \ge (2\pi/a)\sqrt{3}$, where $\epsilon(\vec{q})$ is already close to unity. In addition we adopt a rigid-ion approximation where $v_{ion}(\vec{q})$ does not depend on the lattice constant.

The results of these calculations are shown in Fig. 6 for InP and Fig. 7 for GaAs (squares). The calculation yields a somewhat stronger pressure dependence of e_T^* than observed experimentally. As will be shown in the following paper⁹ the same type of pseudopotential calculation also yields a pressure dependence of the lowest gap E_0 larger than observed experimentally. This can be understood qualitatively from Eq. (10). Since e_T^* is inversely proportional to the band gaps, an overestimation of deformation potentials will be connected with an analog overestimation of the volume dependence of e_T^* . We find the E_0 gap to depend rather sensitively on the form factor $v_s(11)$. The dependence of the form factor on a is largely determined by the second zero of the pseudopotential which-according to Cohen and Heine²⁵-occurs at $q = (2.23)2\pi/a_0$ for v_{In} and at q = 2.14 a.u. for $v_{\rm P}$. A 5% shift of the second $v_{\rm In}$ zero to smaller q values brings the deformation potential in agreement with the measurement (see Paper II). Correspondingly, the decrease of e_T^* with pressure becomes smaller by a factor of 2, also in better agreement with experiment.

Both types of calculations presented above, the numerical as well as the bond orbital model of Eq. (8), predict the sign and the order of magnitude of the effect observed experimentally. They can be regarded as satisfactory in view of the crudeness of the assumptions involved and to superseed the macroscopic lattice dynamical approach of Humphreys and Maradudin.²⁷ It will be shown in Appendix A that the numerical theory just described can be approximated by a simple algebraic function of the pseudopotential form factors [Eq. (A7)]. This expression yields the

same trend of decreasing e_T^* with increasing pressure as the numerical calculations.

We now discuss the data of Fig. 5. The highest mode in this figure extrapolates to 792 cm⁻¹ = $2LO(\Gamma)$ at zero pressure. As already pointed out, the measurements under pressure were performed at near resonance conditions for which the 2LO overtone is due to phonons with $k \simeq 0$ (Γ phonons).¹⁶ It is thus not surprising to find for this peak a Grüneisen parameter $\gamma = 1.2 \pm 0.05$, equal to that obtained for the LO phonon in first order (Fig. 2. $\gamma = 1.24 \pm 0.02$). We should point out that for measurements performed²⁸ at a *fixed* laser frequency and low pressures on GaP one has found a Grüneisen parameter about 20% smaller for $2LO(\Gamma)$ than for LO(Γ). This was attributed in Ref. 28 to a change in the degree of resonance with pressure: $\omega - \omega_0$ increased with increasing pressure. The fact that in the present measurements, where the degree of resonance is kept nearly constant by changing the laser frequencies, nearly the same γ is found for LO(Γ) as for $2LO(\Gamma)$ confirms the conjecture of Ref. 28. Corresponding to the resonant 2LO (Γ) overtone mode, a resonant $LO(\Gamma) + TO(\Gamma)$ mode is also observed. Since this structure is weaker than the $2LO(\Gamma)$, it is only seen under strongly resonant conditions (84.4 kbar in Fig. 4, but not 33.3 kbar). The corresponding Grüneisen parameter, $\gamma = 1.3 \pm 0.6$, agrees well with that of the average of the first-order TO and LO modes ($\gamma = 1.34 \pm 0.03$).

An inspection of the neutron data of Ref. 29, the calculations of Ref. 30, and the infrared work of Ref. 31 suggests that the additional TO + LO overtone mode seen in Figs. 4 and 5 is due to phonons extending over most of the surface of the Brillouin zone: these overtone modes are nearly degenerate at X, L, and K. We designate the mode at LO(X,L) + TO(X,L). Although its Grüneisen parameter ($\gamma = 1.35 \pm 0.05$) is to be regarded as an average over the *surface* of the Brillouin zone, the measured spectra do not reveal any lifting of the X-L-K degeneracy at high pressures. We must thus conclude that the corresponding γ 's are nearly constant over the surface of the Brillouin zone.

The remaining modes of Fig. 5 show negative Grüneisen parameters. The mode at 190 cm⁻¹ for p = 0 can only be a combination of two split TA modes (the TA modes split along all directions except Γ and Γ -X. Its shape, position, and Grüneisen parameter enable us, in comparison with similar structure observed² at 300 cm⁻¹ for GaP, to assign the mode to TA(Σ) + IA₂(Σ) combinations and/or TA₁(W) + TA₂(W) combinations (the symbol I instead of T indicates that this mode is mixed longitudinal transverse). The remaining two modes, at 135 and 114 cm⁻¹ for p = 0, are assigned to 2TA overtones at X and L, respectively. The L overtones are likely to be degenerate over most of the hexagonal Brillouinzone faces,³ while the X overtones probably also extend over a wide area around the center of the square faces. The γ 's of these 2TA modes are, as usual for the tetrahedral semiconductors (see Table I), negative, and their magnitudes are large.

It has been suggested³ that there is a relationship between the negative γ 's of these TA modes and the pressure at which the phase transition (to an NaCl phase in the case⁵ of InP) takes place. Although this phase transition occurs at pressures far below those required to drive the TA modes to zero frequency, the negative γ indicates a "soft-mode" behavior which may be related to whatever mechanism is responsible for the phase transition. It has actually been suggested in Ref. 3 that $\gamma_{TA(X)}$ is a linear function of the transition pressure. Data obtained since, including the present ones, indicate that this law is not as accurately fulfilled as proposed in Ref. 3 (see Fig. 9). The measurement of $\gamma_{TA(X)}$ for a number of other tetrahedral semiconductors (Ge, GaSb, InAs, AlSb, CdTe) would be highly desirable in order to clarify the relationship, if any, between the TA "soft modes" and the phase transition under pressure.



FIG. 9. Grüneisen parameter $\gamma_{TA(X)}$ plotted vs the pressure of the phase transition for a number of zinc-blend-type semiconductors. With the exception of InP (present data) and GaAs (Ref. 4) the data stem from Ref. 3.

We now address ourselves to the theoretical interpretation of the large, negative γ 's of the TA modes. A number of macroscopic model calculations based on shell models or valence force parameters (see Refs. 2, 32, and 33) yield negative values $(\gamma_{TA(X)} \simeq -0.4)$ for this parameter but of a magnitude considerably smaller than observed. This discrepancy is not surprising since most of these calculations fail to yield the very flat TA bands and give for TA(X) frequencies about twice as high as observed experimentally. These frequencies can be lowered to agree with the experimental ones by introducing adiabatically moving bond charges.³⁴ The bond charges Z_b are related to the static dielectric constant ϵ_{∞} through $Z_b \simeq 2/\epsilon_{\infty}$.³⁵ Thus, while ϵ_{∞} decreases with increasing pressure, Z_b increases and drives the TA modes further down therefore increasing the magnitude of the negative γ_{TA} . A recent microscopic calculation for Si, based on the pseudopotential band structure, yields $\gamma_{TA(X)} = -2.4$, in reasonable agreement with the results reported here for InP.¹⁹

APPENDIX A: DYNAMICAL EFFECTIVE CHARGES

The transverse dynamical effective charges of the ions in a semiconductor or insulator can be defined as follows: a small displacement in direction λ of a whole sublattice (which we label by an index α) with respect to the rest of the crystal will induce a certain macroscopic dipole moment $P_{\mu}(\alpha)$ in the μ direction in the crystal. This is analogous to the piezoelectric polarization but requires an "optical" displacement of the ions rather than a macroscopic deformation of the crystal. Furthermore, the macroscopic electric field in the crystal is kept zero. This boundary condition is also used in piezoelectricity and serves to separate the surface depolarization effects from the intrinsic bulk dipole moment. The transverse or Born dynamical effective charge of ions of type α , $e_{T\lambda\mu}^*(\alpha)$, is defined as the dipole polarization $P_{\mu}(\alpha)$ per unit displacement of sublattice α in λ direction for a fixed electric field. For cubic materials symmetry gives $e_{T\lambda\mu}^*(\alpha) = e_T^*(\alpha)\delta_{\lambda\mu}$. Let us restrict ourselves to cubic crystals with two sublattices. For Si the point-group symmetry gives $e_T^*(1) = e_T^*(2)$. This

symmetry is not sufficient, however, to guarantee $e_T^* = 0$ in Si, or, more generally, $e_T^*(1) = -e_T^*(2)$ in binary compounds. This is a consequence of translational symmetry and charge neutrality: If one moves both sublattices by the same amount a polarization proportional to $e_T^*(1) + e_T^*(2)$ is induced. Since a rigid displacement of the whole crystal produces no net dipole moment, one must have

$$e_T^*(1) + e_T^*(2) = 0$$
 . (A1)

This property has been called the "acoustical" sum rule.^{38,39} e_T^* can be expressed in terms of linear response functions.⁷ By definition we have

$$e_{T\lambda\lambda}^{*}(\alpha) = Z_{\alpha} - \int d^{3}r \, r_{\lambda} \delta n_{\lambda}(r, \alpha) \quad , \qquad (A2)$$

where $\delta n_{\lambda}(r, \alpha)$ is the first-order change in electron density upon a unit shift of the sublattice with ions of type α with respect to the other in the λ direction and keeping the macroscopic field zero. We denote by $\delta V_{\lambda}(r, \alpha)$ the corresponding first-order change in the potential. The effect of the electric boundary condition can be understood by Fourier analysis of the total electric potential induced by the shift of sublattice α . The induced macroscopic field is constant over a unit cell and has therefore no Fourier components $G \neq 0$. The boundary condition of zero macroscopic electric field therefore leaves all $G \neq 0$ components of the induced potential unaltered while the G = 0 component is kept zero, $\delta V_{\lambda}(G, \alpha) = 0$ if G = 0. In terms of the electric polarizability $\chi(r,r')$, one has

$$\delta n_{\lambda}(r) = \int d^3r' \,\chi(r,r') \,\delta V_{\lambda}(r') \quad (A3)$$

In the rigid-ion model one has⁷

$$e_{T}^{*}(\alpha) = Z_{\alpha} - \sum_{\vec{G}\neq 0} \chi_{\mu}^{(1)}(0, \vec{G}) [\upsilon_{\alpha}(G)G_{\mu}e^{-iG\cdot\vec{\tau}_{\alpha}}] ,$$

$$\chi_{\mu}^{(1)}(0, \vec{G}) = \frac{\partial \chi(\vec{q}, \vec{q} + \vec{G})}{\partial q_{\mu}} \bigg|_{\vec{q}=0} .$$
(A4)

Here $Z_{\alpha} = 3$ and 5 for $\alpha = \text{In}$ and P, respectively. $v_{\alpha}(G)$ is the screened pseudopotential form factor for ions of type α and $\vec{\tau}_{\alpha} = \pm (\frac{1}{8}a)(1,1,1)$. In the Hartree approximation, $\chi(q,q+G)$ is given by the expression

$$\chi(\vec{q},\vec{q}+\vec{G}) = \frac{2}{N} \sum_{nn'\vec{k}} \frac{\theta_{n\vec{k}}(1-\theta_{n'\vec{k}})}{E_{n\vec{k}}-E_{n'\vec{k}+\vec{q}}} \langle n\vec{k} | e^{-i\vec{q}\cdot\vec{r}} | n'\vec{k}+\vec{q} \rangle \langle n'\vec{k}+\vec{q} | e^{i(\vec{q}+\vec{G})\cdot\vec{r}} | n\vec{k} \rangle .$$
(A5)

Here $|nk\rangle$ and $E_{n\overline{k}}$ are the valence and conduction Bloch states and energies of the perfect crystal which are obtained from a pseudopotential energy-band calculation. The remaining symbols are the same as in Eq. (10) in the main text. In the form of Eq. (A4), the acoustical sum rule is not automatically satisfied; i.e., if x is calculated in some approximation and used in Eq. (A4), the translational invariance condition (A1) might be violated. This results from the fact that linear response functions like Eq. (A5) are defined with respect to a fixed origin rather than with respect to the actual ion positions. One can show, however, that the acoustical sum rule is a selfconsistency requirement in Eq. (A4).^{7,40} It is fulfilled if the *same* pseudopotential is used on the right-hand side of Eq. (A4) as for the energy bands and wave functions in Eq. (A5).

It is illustrative to calculate e_T^* with a simple model for the Bloch states required in Eq. (A4). We adopt the band-structure model of Heine and Jones,⁴¹ where only the form factors at $G = (2\pi/a)\sqrt{3}$ and

,

 $G = (2\pi/a)\sqrt{8}$, which are labeled $v_{\alpha}(3)$ and $v_{\alpha}(8)$, are considered as nonzero. The bands and wave functions are calculated by perturbation theory assuming that the pseudopotential is small with respect to the kinetic energy. Since v (3) is actually of the same order as the kinetic energy, the perturbation treatment should give only qualitative results.

In the long-wavelength limit, one obtains⁴²

$$\lim_{q \to 0} \chi(\vec{q}, \vec{q} + \vec{G}) = \begin{cases} (2\vec{q} \cdot \vec{G}/E_g G^2), \quad \vec{G} = \{220\} \\ 16\vec{q} \cdot \vec{G}e^{i\vec{G} \cdot \vec{\tau}} \frac{V_S \cos\vec{G} \cdot \vec{\tau} - iV_A \sin\vec{G} \cdot \vec{\tau}}{E_g E_x G^2}, \quad \vec{G} = \{111\} \end{cases}$$
(A6)

In Eq. (A6), E_g represents the average energy gap which is in this model

$$E_{g} = v_{\text{In}}(8) + v_{\text{P}}(8) + (1/E_{x})[v_{\text{In}}^{2}(3) + v_{\text{P}}^{2}(3)] , \quad (A7)$$

and $E_{x} = \frac{1}{2}(2\pi/a)^{2}$. This gives for e_{T}^{*} ,
 $e_{T}^{*}(\alpha) = Z_{\alpha} - (8/E_{g})[v_{\alpha}(8) + v_{\alpha}^{2}(3)/E_{x}]$
 $= -\Delta Z - (8/E_{g})[v_{\alpha}(8) + 2v_{s}(3)v_{\alpha}(3)/E_{x}] .$
(A8)

We can now check whether the acoustical sum rule is fulfilled. Since $Z_{In} + Z_P = 8$, then

$$\sum_{\alpha} e_T^*(\alpha) = \sum_{\alpha} Z_{\alpha} - 8 = 0 \quad . \tag{A9}$$

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In Si, one has $Z_1 = Z_2 = 4$ and Eq. (A7) correctly gives $e_T^* = 0$. It is interesting to note that the translational invariance condition (A1) restricts the possible analytical forms for e_T^* . Once we infer from Eq. (A5) that $\chi \propto E_g^{-1}$, and use for E_g the perturbation expression of Eq. (A7), the acoustical sum rule alone already leads to the form of Eq. (A8).

The dependence of e_T^* on lattice constant results from the corresponding dependence of the factors as discussed in the main text. With Eq. (A8) we find a dependence somewhat larger than that obtained with the numerical calculation but the dependence found with Eq. (A8) is very sensitive to the exact value of $v_a(8)$ and its derivative. However, the trend of decreasing e_T^* with pressure is also found.

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